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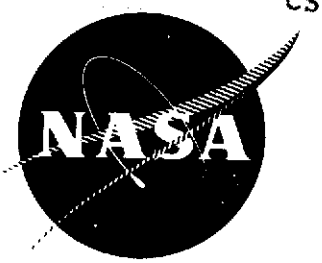


# ALKALI OXIDE-TANTALUM OXIDE AND ALKALI OXIDE-NIOBIUM OXIDE IONIC CONDUCTORS

by

R. S. Roth, H. S. Parker, W. S. Brower and D. Minor

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16. Abstract

A search was made for new cationic conducting phases in alkali-tantalate and niobate systems. The phase equilibrium diagrams were constructed for the six binary systems $Nb_2O_5$-$LiNbO_3$, $Nb_2O_5$-$NaNbO_3$, $Nb_2O_5$-$KNbO_3$, $Ta_2O_5$-$NaTaO_3$, $Ta_2O_5$-$LiTaO_3$ and $Ta_2O_5$-$KTaO_3$. Various other binary and ternary systems were also examined. Pellets of nineteen phases were evaulated (by the sponsoring agency) by dielectric loss measurements. Attempts were made to grow large crystals of eight different phases. The system $Ta_2O_5$-$KTaO_3$ contains at least three phases which showed peaks in dielectric loss vs. temperature. All three contain structures related to the tungsten bronzes with alkali ions in non-stoichiometric crystallographic positions.

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TABLE OF CONTENTS

SUMMARY . . . . . 2

INTRODUCTION . . . . . 3

DISCUSSION OF RESULTS

The System $Nb_2O_5$-$LiNbO_3$ . . . . . 4

The System $Ta_2O_5$-$LiTaO_3$ . . . . . 4

The System $Nb_2O_5$-$NaNbO_3$ . . . . . 5

The System $Ta_2O_5$-$NaTaO_3$ . . . . . 6

The System $Nb_2O_5$-$KNbO_3$ . . . . . 6

The System $Ta_2O_5$-$KTaO_3$ . . . . . 7

Other Systems . . . . . 8

Polycrystalline Specimen Preparation . . . . . 9

Crystal Growth . . . . . 10

$Nb_2O_5$-$KNbO_3$ . . . . . 11

$12K_2O$:$88Nb_2O_5$ . . . . . 11

$17.5K_2O$:$82.5Nb_2O_5$ . . . . . 12

$Ta_2O_5$:$KTaO_3$ . . . . . 12

$Ta_2O_5$:$LiTaO_3$ System . . . . . 12

$Nb_2O_5$-$NaNbO_3$ System . . . . . 13

$Ta_2O_5$-$NaTaO_3$ System . . . . . 13

Structural Mechanisms of Non-Stoichiometry in Alkali-Niobates and Tantales . . . . . 13

HTB . . . . . 14

TTB . . . . . 15

GTB . . . . . 15

TTBs . . . . . 16

Other Phases . . . . . 17

SUMMARY OF RESULTS . . . . . 18

FUTURE WORK . . . . . 19

REFERENCES . . . . . 20

FIGURE CAPTIONS . . . . . 22

TABLES OF EXPERIMENTAL DATA . . . . . 34

DISTRIBUTION LIST . . . . . 53

SUMMARY

This report summarizes work carried out between October 1972 and October 1973 under an agreement with the National Aeronautics and Space Administration, Lewis Research Center (Interagency Order C-29933-C) to study the phase equilibria of alkali oxide-tantalum and niobium oxide systems and synthesis of phases which might have interesting ionic conductivity.

The phase equilibrium relations of six systems were investigated in detail. These consisted of lithium, sodium and potassium tantalate, and niobate with the corresponding tantalum and niobium oxide. In addition, various other binary and ternary systems involving alkali oxides were examined in lesser detail. In all, thirteen phases were found to contain structures of sufficient interest to warrant further investigation. Nineteen phases were prepared as solid pellets and transmitted to LeRC for evaluation by dielectric loss measurement. Attempts were made to grow eight different phases as large single crystals, and two were submitted to LeRC for evaluation.

In terms of ionic conductivity, the most interesting phases from a structural point of view are those containing large tunnels only partially occupied by alkali ions. The potassium tantalate system contained four such phases, designated GTB, TTBs, HTB, and TTB (see table 6 for meaning of these initials). In all cases, the TB refers to a tungsten bronze type structure. Those phases which exhibit a maximum in the dielectric loss vs. temperature curves proved to be high temperature phases which are generally metastable at room temperature and do not have favorable melting characteristics for crystal growth directly from the melt.

In the coming year efforts will be expanded to include rubidium systems as well as antimonates and mixed tantalum-tungstates, in an effort to isolate an ionic conducting phase with favorable crystal growth possiblities.

## INTRODUCTION

In the search for new ionic conductors, compounds in oxide systems need to be examined for structure types where packing of the complex ions of the skeletal structure has the potential to produce loosely bound alkali ions.

The compounds of alkali oxides with tantalum oxide and with niobium oxide represent a class of such materials. The program summarized in this report involved the investigation of the phase diagrams to determine the phases which are actually contained in these systems and to define selected phases of potential interest as solid ionic conductors. Subsequent to this determination specimens were prepared of single phase polycrystalline ceramic pellets for screening measurements and, finally, attempts were made to grow single crystals of those materials which appeared most interesting and feasible. All the phases encountered were identified by single crystal x-ray diffraction patterns and/or identity with previously reported structures. For fast ion transport, it is probably advantageous to have an alkali ion in a "non-stoichiometric" crystallographic position. For commerical utilization of ionic conductivity, it is necessary to limit systems to those which will contain little or no electronic conductivity and, therefore, do not contain an element which is easily reduced during the synthesis. The $Ta^{+5}$ ion is apparently very difficult to reduce [1], and thus is ideally suitable as a host lattice for alkali "super-ionic-conductivity". Some preliminary work on alkali tantalate and niobate systems has been previously summarized by the present authors [2]. A complete detailed analysis of these systems is presently being prepared for publication and will be submitted to the Journal of Solid State Chemistry in the near future [3, 4, 5, 6].

## DISCUSSION OF RESULTS

### The System $Nb_2O_5$-$LiNbO_3$

A phase equilibrium diagram for the system $Li_2O$-$Nb_2O_5$ was published by Reisman and Holtzberg [7]. However, this diagram does not show the compound $LiNb_3O_8$ which is known to occur in this system [8, 9, 10], nor does it show the solid solution of $Nb_2O_5$ in $LiNbO_3$ [11] which has been found to be important in the production of large optical quality crystals. A phase equilibrium diagram indicating these corrections was previously published [2]; and this diagram is reproduced here, essentially unchanged, in figure 1. The experiments performed in this laboratory to check this diagram are listed in table 1. The unit cell dimensions of the phases will be given in the summary table of x-ray data near the end of this report (Table 12).

The $Nb_2O_5$-$LiNbO_3$ system contains only two intermediate phases, the compound $LiNb_3O_8$ and another phase which occurs at a very narrow compositional range near $Li_2O$:$14Nb_2O_5$. This phase was reported independently by the present authors [2] and by Norin and Nolander [12] to have the N-$Nb_2O_5$ structure. Only this phase and $LiNbO_3$ itself may be considered to have any interesting non-stoichiometric properties.

A detailed analysis of the work performed in this system, including x-ray diffraction patterns, will be published in the near future [3].

### The System $Ta_2O_5$-$LiTaO_3$

No phase equilibrium diagram for this system had been published prior to our preliminary work reported in reference [2]. The final phase diagram is shown in figure 2 and the experimental data from which it was constructed are listed in table 2. The present diagram differs from that given in [2] only in the first 5 mole percent $Li_2O$ content and near the melting point of $LiTa_3O_8$.

Lithium oxide has been found to stabilize the low temperature polymorph of $Ta_2O_5$ (L-$Ta_2O_5$); and, therefore, non-stoichiometric solid solutions appear on both sides of this system. There is only one intermediate compound, $LiTa_3O_8$, but it is trimorphic and apparently has no appre-

ciable non-stoichiometric region within the binary phase diagram. The low temperature form of $LiTa_3O_8$ is isostructural with $LiNb_3O_8$, the intermediate form is isostructural with the mineral wodginite, and the high temperature form is similar in structure to $LiTa_6O_{15}F$ and $LiNb_6O_{15}F$ [13].

The unit cell dimensions will be listed in the summary table of x-ray data near the end of the report (Table 12) and a detailed analysis of the work performed in this system, including x-ray diffraction patterns, will be published in the near future [3].

## The System $Nb_2O_5$-$NaNbO_3$

This system has been studied by several different groups and phase equilibrium diagrams were published by Reisman, Holtzberg and Banks [14], and by Shafer and Roy [15]. The former group reported a 1:4 and a 1:14 compound whereas the second reference shows 1:4, 1:7, and 1:10 compounds. These type of ratios represent mole ratio of alkali oxide to niobium (or tantalum) oxide. Sten Andersson [16] has shown that the high $Nb_2O_5$ content phase occurs at the 1:13 ratio ($NaNb_{13}O_{33}$) from crystal structure analyses [17] and found the other phase to occur at the 1:3 ratio ($NaNb_3O_8$). He found the compounds $Na_2Nb_4O_{11}$ and $NaNb_6O_{15}(OH)$ only in hydrothermal experiments at 500-700°C and 2000 atm. In a crystal structure analysis of Andersson's $NaNb_3O_8$ crystals, D. C. Craig and N. C. Stephenson decided that the composition of the crystal they examined was most likely $Na_{13}Nb_{35}O_{94}$ [18].

The phase equilibrium diagram which we have determined for this system is given in figure 3 and the experimental data from which it was determined are listed in table 3. We confirm the 1:13 compound but do not find any other between this and the "$NaNb_3O_8$" phase. The latter is apparently a non-stoichiometric solid solution with a tetragonal tungsten bronze-type substructure and an orthorhombic superstructure (TTBs). In addition $Na_2Nb_4O_{11}$ was found in equilibrium at low temperatures (below about 1000°C) and specimens near the 1:6 ratio was found to react with atmospheric moisture at temperatures between about 700-900°C to form $NaNb_6O_{15}(OH)$ without the necessity for hydrothermal techniques.

The unit cell dimensions of these phases will be listed in the summary table of x-ray data near the end of the report and a detailed analysis of the work performed in this system, including x-ray diffraction patterns, will be published in the near future [4].

## The System $Ta_2O_5$-$NaTaO_3$

The phase equilibrium diagram for this system had not been reported prior to our preliminary paper [2] although Reisman [19] had made a subsolidus study up to 1300°C. The diagram given in figure 4 is similar to that of [2] but has been reevaluated for the melting relations of the distorted tetragonal tungsten bronze-like phase (TTBs) between about 20 and 25 mole % $Na_2O$. This is the only non-stoichiometric phase in the system although apparently a very small amount of $Na_2O$ may be incorporated in L-$Ta_2O_5$, increasing the phase transition temperature. The only other phase in the system is $Na_2Ta_4O_{11}$ which has a hexagonal structure similar to the monoclinic $Na_2Nb_4O_{11}$.

The experimental data from which figure 4 has been constructed are listed in table 4. The unit cell dimensions of these phases will be listed in the summary table of x-ray data near the end of this report. A detailed analysis of the work performed in this system, including x-ray diffraction patterns, will be published in the near future [4].

## The System $Nb_2O_5$-$KNbO_3$

A phase equilibrium diagram for this system was previously reported by Reisman and Holtzberg [20]. Additional information on compound formation, crystal growth, and unit cell dimensions has been published by Guerchais [21], Whiston and Smith [22], and Nassau *et al* [23]. The phase equilibrium diagram determined in the present study is shown in figure 5 and the experimental data from which it was constructed are listed in table 5.

The system was found to contain six intermediate phases. The unit cell dimensions of each phase are listed in the summary table near the end of this report. From these dimensions it is apparent that at least three of these phases have non-stoichiometric-type structures. These are designated in the phase diagram as GTB, TTBs, and TTB and occur at

about 11.5, 16-20, and 35 mole % $K_2O$ respectively. The former has a structure similar to that reported by Gatehouse for a rubidium niobate phase [24] and herein referred to as a Gatehouse tungsten bronze (GTB). The other two have a distorted tetragonal tungsten bronze structure (TTBs) and an undistorted 'bronze' structure (TTB) respectively.

The unit cell dimensions of the 2:3 phase indicate a layer of niobia octahedra with all the potash possibly located in planes. The hydrated form of this phase reveals different x-ray diffraction intensity distributions depending on the hydration direction and rate. This phenomena may possibly indicate different distributions of $K^+$ ions which depend on the hydration. Ionic conductivity of this phase in a direction parallel to the cleavage, that is, parallel to the $K^+$ and/or $H_2O$ motion should be investigated more carefully.

A detailed analysis of the work performed in this system, including x-ray diffraction patterns, will be published in the near future [5].

## The System $Ta_2O_5$-$KTaO_3$

The phase equilibrium diagram published for the system $K_2O$-$Ta_2O_5$ by Reisman *et al* contained only two compounds between $Ta_2O_5$ and $KTaO_3$ [25]. The preliminary diagram published by the present authors [2] indicates nine equilibrium phases in this region and two other metastable phases. The present diagram, figure 6, differs from the previous only in the estimated width of the non-stoichiometric phases. The experimental data from which this diagram was constructed are listed in table 6.

The system was found to contain four stable non-stoichiometric regions in addition to five stable, apparently stoichiometric, phases. The phases with non-stoichiometric type structures include a Gatehouse tungsten bronze (GTB) at about 11.5 mole % $K_2O$, an orthorhombic distorted tetragonal tungsten bronze with superstructure (TTBs) between about 15-20 mole % $K_2O$, a hexagonal tungsten bronze (HTB) at about 21.75 mole % $K_2O$, existing over a very narrow temperature region below the solidus, and an undistorted tetragonal tungsten bronze with no superstructure at $\sim$34 mole % $K_2O$. Figures 7, 8, 9, and 10 show the results of measuring the dielectric loss (epsilon) versus temperature at a number of frequencies

for these four non-stoichiometric phases. The GTB and HTB phases show excellent ionic mobility. Unfortunately, single crystals of these phases have not yet been grown. The difficulty is due mainly to the very narrow primary phase field. An attempt must be made to find a system with wider primary phase regions for these structures, possibly in systems with $Rb_2O$, which can then be ion exchanged.

Other Systems

In the course of this study, a considerable number of specimens were investigated with compositions not included in the six systems described previously. The ternary systems involving these six systems with $MoO_3$ were all examined briefly for the purposes of growth of small crystals [2]. The compositions of the crystal growth preparations will be detailed at a later date [3, 4, 5, 6].

Several of these six binary systems were also examined in conjunction with $WO_3$, especially the psuedo-binary joins $NaTaO_3$-$WO_3$ and $KTaO_3$-$WO_3$. The $NaTaO_3$-$WO_3$ system proved to be completely non-binary and contained mostly solid solutions of sodium tungstates in the sodium tantalate type phases. However, the $KTaO_3$-$WO_3$ system is apparently a psuedo-binary system below the solidus and contains at least five phases. The compositions of the phases are about 25, 50, 50, 70, and 90 mole % $WO_3$. The ternary system $KTaO_3$-$WO_3$-$K_2WO_4$ has been found to be a promising flux system for crystal growth of both the pyrochlore and hexagonal tungsten bronze (HTB) type phases. Further work on this ternary will be conducted in the next year.

Some compositions in the $Li_2O$-$Ta_2O_5$-$WO_3$ system were prepared and examined for the purpose of introducing non-stoichiometry into the H-$LiTa_3O_8$ structure. Other compositions in the system $Li_2O$-$Ta_2O_5$-$TiO_2$ were also prepared for the same purpose. The $WO_3$ gave single phase non-stoichiometric solid solutions but showed no ionic mobility (table 7). The $TiO_2$ specimens did not exhibit solid solution.

A study of the $Li_2O$-$TiO_2$ system or rather of the $Li_2TiO_3$-$TiO_2$ system revealed only one high temperature intermediate phase. This phase has the ramsdellite structure; but, unfortunately, melts incongruently with the peritectic very close in composition and temperature to the eutectic.

Thus, single phase crystals could not be pulled from the melt. Experiments in the $Li_2O$-$TiO_2$-$MoO_3$ ternary also did not reveal any ideal flux compositions for crystal growth of this phase. The ramsdellite lithium titanate did not exhibit appreciable ionic mobility (table 7). Other experiments with $K_2O$-$Li_2O$-$TiO_2$ and $K_2O$-MgO-$TiO_2$ revealed a new structure type [26] which also failed the ionic mobility screening tests.

The only experiments performed under this contract which did not involve mixed oxides were conducted in the system NaF-$AlF_3$-$Na_2GeF_6$ in an attempt to produce Ge doped $NaAlF_4$. These experiments were not successful and no $NaAlF_4$ was obtained.

A few compositions involving the systems $NaSbO_3$-$Sb_2O_4$ and $KSbO_3$-$Sb_2O_4$ have been prepared in order to survey possible compound formation in these systems, because Aurivillius [27] has reported $K^+$ ions to occur in large tunnels in some potassium antimonates. In addition, several specimens were examined in the ternary systems $KSbO_3$-$Sb_2O_4$-$SiO_2$ and $KSbO_3$-$Sb_2O_4$-$Al_2O_3$ in an attempt to explain the published data of Spiegelberg [28] who reported a primitive cubic "polymorph" of $KSbO_3$ prepared in a porcelain crucible. These experiments were successful in demonstrating that a small amount of both $Si^{+4}$ and $Al^{+3}$ promote the formation of this cubic polymorph. These and similar antimonate systems will be examined in greater detail in the coming year.

Polycrystalline Specimen Preparation

The sections of this report dealing with the phase equilibrium relationships in alkali niobate and tantalate systems have described several phases which, from structual considerations alone, would appear to be worthy of screening for their potential as fast ion conductors. Accordingly, polycrystalline specimens were prepared and submitted to Lewis Research Center for dielectric and conductivity measurements.

The choice of composition and thermal treatment for use in pellet fabrication of a desired phase was made on the basis of the compositional and temperature stability limits of the phase as determined in the phase equilibrium studies. These limits are not always compatible with the sintering characteristics of the powders and, as a consequence, it was

not possible to prepare high density pellets of some of the phases of interest. Several alkali titanate pellets of interest were also prepared as an outgrowth of work under a previous contract. All compositions for use in pellet fabrication were given blending and calcining treatments similar to those utilized in the preparation of compositions for phase equilibrium studies. In the case of phases wherein alkali loss was anticipated during sintering or where a minimum temperature of stability necessitated rapid cooling of the pellets, the exact composition of the pellet was chosen to give as much latitude as possible in the sintering treatment. The appropriate 1:1 alkali niobate or tantalate was used as one constituent of the batch in these systems to avoid the use of carbonates.

Conventional ceramic dry pressing and sintering techniques were utilized for pellet preparation. Dry pressing was performed in steel dies at nominal pressures of the order of 10,000 to 18,000 psi. No organic binders or other additives were utilized except as noted. In general, several test heatings were necessary to determine a suitable time-temperature relationship for sintering. In some cases, excessive recrystallization during sintering, regardless of the schedule followed, prevented the formation of physically sound pellets. As discussed below, hot pressing was found useful in some cases.

The starting compositions after calcining, as well as the as-fired surface and interior of the sintered pellets, were characterized by x-ray diffraction techniques to insure that the final pellets were homogeneous and single phase.

Tables 8, 9, and 10 summarize the compositions, heat treatments and x-ray characterizations of the pellets submitted for evaluation. The results of screening tests conducted by LeRC are given in Table 7.

## Crystal Growth

The growth of large single crystals of the various non-stoichiometric phases found in the alkali niobate and tantalate systems is complicated by many factors: (1) some of the desired phases do not exist in equilibrium with the liquid, (2) incongruency, and (3) volatility of the alkali. For these reasons only a few of the compounds found in the phase equilibrium

studies were grown successfully. These were the congruently melting compounds and those incongruent compounds which existed in equilibrium with a liquid over a wide temperature range. In all crystal growth attempts the molten material was contained in either platinum or iridium crucibles which were heated inductively and the desired phase pulled either by the conventional Czochralski technique, or by an approximation to top seeded solution growth.

A number of the more interesting phases do not lend themselves to growth by the more conventional techniques and it will be necessary to explore various flux growth techniques in an effort to obtain crystals of a size suitable for physical property measurements.

The crystal growth experiments (table 11) are summarized as follows:

$Nb_2O_5$-$KNbO_3$

7:13 Phase (TTB)

Growth of the 7:13 phase was attempted from a melt composition of $36.5K_2O{:}63.5Nb_2O_5$. The first material to crystallize was the 4:9 phase, on continued pulling a small amount of 7:13 phase crystallized out on the side of the 4:9 phase as a polycrystalline mass. As the pull continued the remainder consisted of single phase 2:3. Several different melt compositions were tried and the results were essentially the same, in all cases the 4:9 phase crystallizes out and as more material is removed the composition of the crystallizing phase shifts to the 2:3 phase. Apparently the temperature-composition region over which the 7:13 exists in equilibrium is too small to successfully obtain crystals by the pulling technique.

$12K_2O{:}88Nb_2O_5$ (GTB)

Attempts to pull the (GTB) bronze-like phase $12K_2O{:}88Nb_2O_5$ at a melt composition of $15K_2O{:}85Nb_2O_5$ resulted in a polycrystalline multiphase mass. This result was not unexpected as an inspection of the phase diagram indicates a very narrow compositonal range where this phase is in equilibrium with the melt. This situation makes it extremely difficult to grow large crystals of the 12:88 phase any place in the $K_2O$-$Nb_2O_5$

binary. Only by going to a flux system can one possibly expect to grow this phase.

$17.5K_2O:82.5Nb_2O_5$ (TTBs)

Attempts to grow the TTB phase from a melt composition of $20K_2O:80Nb_2O_5$ resulted in essentially single phase polycrystalline TTB with very fine grain size. This phase would be a likely candidate for top seeded solution growth (TSSG) or possibly the accelerated crucible rotation technique (ACR).

$Ta_2O_5:KTaO_3$

TTB Phase

As determined from phase equilibria studies, the TTB phase melts incongruently. For the crystal growth attempts, a melt composition of $45K_2O:55Ta_2O_5$ was chosen. With this composition and using a pull rate of 0.2 in/hr crystals of the desired phase were grown. The maximum diameter attained was the order of 1/8 in. diameter at the stated pull rate. The growth of larger crystals would necessitate much slower growth rates, as with top seeded solution growth.

$Ta_2O_5:LiTaO_3$ System

1:3

Single crystals of the 1:3 phase were grown both "on composition" and from compositions slightly rich in $Li_2O$. The "as-grown" crystals were light brown to colorless depending upon cooling rate. Subsequent annealing in air removed all traces of brown color. The reason for this change in color is not known.

5:95 Phase

The 5:95 phase or L-$Ta_2O_5$ has been grown in sizes up to as large as 2 cm long and 1.5 cm diameter. This is an incongruent melting compound and growth was by top seeded solution growth starting at a composition of $15Li_2O:85Ta_2O_5$. These are the first large crystals of L-$Ta_2O_5$ ever grown and are being used for a structure determination using neutron diffraction, in order to obtain a better knowledge of the mechanism of nonstoichiometry. The crystals are almost colorless when first grown but gradually turn yellow on exposure to light.

## $Nb_2O_5$-$NaNbO_3$ System

### 1:3 Phase

Single crystals of the 1:3 phase could be readily pulled from a melt of the stoichiometric composition, however, there was a problem with cracking which limited the size of usable crystals obtained. The cause of cracking was not investigated.

## $Ta_2O_5$-$NaTaO_3$ System

### 21:79 Phase (TTBs)

All attempts to grow crystals of the bronze-type phase by induction heating at ambient pressures were unsuccessful due to the rapid loss of $Na_2O$ from the melt.

## Structural Mechanisms of Non-stoichiometry in Alkali-Niobates and Tantalates

An abnormally large number of phases have been found in the six systems examined and discussed in this report. In addition to the end members, the $Li_2O$ systems contain two and three phases with $Nb_2O_5$ and $Ta_2O_5$ respectively whereas the $Na_2O$ systems contain two and four phases each and the $K_2O$ systems, six and nine phases each. The unit cell dimensions of each of these phases is listed in table 12 together with the pertinent crystallographic data where known.

The occurrence of the tungsten-bronze-type structures in these alkali niobate and tantalate binary systems is somewhat disconcerting, as the $A_xBO_3$ compositional range does not fall in these systems for any value other than x=1. It is quite evident, therefore, that it is impossible to have niobium and tantalum oxygen octahedra and pentagonal bipyramids form in a network structure in which only a non-stoichiometric amount of alkali ions compensate the framework for electrical neutrality. One possible hypothetical alternate of oxygen vacancies is both esthetically displeasing and structurally unsound. Furthermore, such structures have not been previously found to exist.

HTB

The most likely explanation, and one based on preliminary structural evidence of a similar phase, is that of interstitial niobium (or tantalum) ions. B. M. Gatehouse [24] has shown that niobium can occur interstitially in a rubidium hexagonal tungsten bronze structure in the 9-fold tricapped-prism interstitial vacancy common to all of the tungsten bronze-type structures. Gatehouse has suggested that the composition of this hexagonal bronze phase would be $RbNb_{3.4}O_9$ or 22.72 mole % $Rb_2O$. Some hypotheses can be made, on the basis of Gatehouse's work, concerning the mechanism of non-stoichiometry in the phases observed in this study.

In the system $Ta_2O_5$-$KTaO_3$, a phase having the hexagonal tungsten bronze structure has been observed to occur at about 21.75 mole % $K_2O$. By analogy to the $RbNb_{3.4}O_9$ phase, this can be considered to be $KTa_{3.4}O_9$. However, this formula would indicate 22.72 mole % $K_2O$ which is definitely not the case. The composition 21.75 mole % $K_2O$ would correspond to the formula $K_{0.95}Ta_{3.41}O_9$ and this non-stoichiometric phase must contain alkali vacancies as well as tantalum interstitials.

TTB

This same analogy may be used to explain the non-stoichiometry in the tetragonal tungsten bronze phases which occur with no sign of superstructure in both the $Ta_2O_5$-$KTaO_3$ and $Nb_2O_5$-$KNbO_3$ systems. The formula for one unit cell of the tetragonal tungsten bronze structure is $A_6B_{10}O_{30}$. If all the B ions have a valence of +5, then the formula for the ideal end member would be $K_6^{+1}B_{10.8}^{+5}O_{30}$ or 35.71 mole % $K_2O$. In the $Nb_2O_5$-$KNbO_3$ system this phase has been observed at ∿35 mole % $K_2O$ corresponding to the formula $K_{5.83}Nb_{10.83}O_{30}$. In the $Ta_2O_5$-$KTaO_3$ system, this phase has been observed at ∿33 1/3 mole % $K_2O$ corresponding to the formula $K_{5.45}Ta_{10.91}O_{30}$.

GTB

In his paper on rubidium niobates, Gatehouse discussed a new structure type containing 4-, 5-, 6-, and 7-sided tunnels which may be partially occupied by alkali ions. This phase has been called the Gatehouse tungsten bronze in the present paper and was observed to occur at about 11.5 mole % $K_2O$ in both the $Ta_2O_5$-$KTaO_3$ and $Nb_2O_5$-$KNbO_3$ systems. Gatehouse was unable to arrive at a correct composition for this phase, but in a personal communication confirmed the proposed structure:
". . . having recently obtained some magnificent lattice image photographs which completely confirm the basic structure--7-sided holes and all."
The basic formula for this structure is $A_8B_{54}O_{146}$. If all the B ions have a valence of +5 and the excess is supplied via interstitual $B^{+5}$ ions then the ideal end member composition would be $A_8^{+1}B_{54}^{+5} + 2.8O_{146}$. This ideal formula would correspond to 12.35 mole % alkali oxide. The formula for the observed 11.5 mole % composition would be $K_{7.4}B_{54} + 2.92O_{146}$ when B is either $Nb^{+5}$ or $Ta^{+5}$. The solid solution region probably goes down to at least a composition of $K_7B_{57}O_{146}$ (10.94 mole % $K_2O$) and possibly even slightly lower in $K^+$ content. It should be pointed out that this hypothesis involves $K^+$ ions in both the six and seven (or possible four) sided tunnels whereas Gatehouse explicitly stated that the seven- and four-sided tunnels appeared to be empty. It is obvious that the details of this structure need to be examined with more accurate data. Dr. Gatehouse has informed us that he is now refining three dimensional crystallographic data on his rubidium niobate, and NBS will attempt to do an accurate single crystal crystallographic study of the chemically well-characterized potassium niobate phase.

TTBs

The case of the TTBs phase, that is, the orthorhombic tetragonal tungsten bronze with superstructure indicating that one of the a tetragonal axes is tripled, is more complex then the other three. This phase occurs in all four systems of sodium and potassium with niobium and tantalum. In the $Nb_2O_5$-$NaNbO_3$ system, it occurs between about 22.5 to 27.5 mole % $Na_2O$ and between about 19.5 and 25.5 mole % $Na_2O$ in the $Ta_2O_5$-$NaTaO_3$ system.

However, in the $Nb_2O_5$-$KNbO_3$ and $Ta_2O_5$-$KTaO_3$ systems, this same structure type occurs between about 15 and 20 mole % $K_2O$. Although the absolute limits of these have not been accurately located, these rough limits of about 15 to 27.5 mole % alkali oxide must be explained.

D. C. Craig and N. C. Stephenson [18] have examined the crystal structure of a specimen of $NaNb_3O_8$ supplied by S. Andersson [16]. They concluded that the particular crystal examined had the composition $Na_{13}Nb_{35}O_{94}$ or 27.08 mole % $Na_2O$ rather than the 25 mole % $Na_2O$ suggested by Andersson. Stephenson reports that the tripled "tetragonal-tungsten-bronze" cell has a basic structure of $Na_6Nb_{34}O_{94}$ and that twelve excess positive charges must be accommodated by Na and/or Nb distributed in the eight 5-sided tunnels. He considers only the cases of $Nb^{+5} + 7Na^{+}$ and $2Nb^{+5} + 2Na^{+}$ and says that the former more nearly coincides with the experimental intensities. In this paper [18], Craig and Stephenson dismiss the possibility of $Nb^{+5}$ in the three sided tunnels as being ". . . incompatible with the directional properties of the bonding orbitals of niobium (V)." This statement is subject to considerable doubt and leaves open the actual position of the "interstitial" niobium. Apparently Craig and Stephenson did not consider the possibility that this phase might have a non-integral number of $Na^{+1}$ and $Nb^{+5}$ ions, that is, be a composition in the middle of a non-stoichiometric solid solution.

The basic-structure of the tripled tetragonal tungsten bronze (TTBs) unit cell is, therefore, $[A_6^{+1}B_{34}^{+5}O_{94}]^{-12}$ and contains a maximum of eight excess positions for alkali ions. The composition can, therefore, vary from a maximum alkali content of $A_{14}^{+1}B_{34.8}^{+5}O_{94}$ with 28.7 mole % alkali oxide to a minimum alkali content of $A_6^{+1}B_{36.4}^{+5}O_{94}$ with 14.15 mole % alkali oxide. It is noteworthy that the limits of the observed phases, 15 to 27.5 mole % alkali oxide, occur just within the theoretical minimum and maximum values of 14.15 to 28.7 mole % alkali oxide.

In the above four cases, therefore, the most likely structural mechanism for non-stoichiometry is that of transition metal interstitials plus alkali ion vacancies. However, other mechanisms can also be found in the six systems discussed in this report.

Other Phases

The N-$Nb_2O_5$ phase stabilized by $Li_2O$ can be considered to be $Li_2O{:}14Nb_2O_5$ or $Li_{18}(Li_{0.45}Nb_{31.55})O_{80}$ with $Li^+$ ions substituting for $Nb^{+5}$ and also present in interstitial four-sided channels. This non-stoichiometric phase is thus accounted for by a mechanism of alkali substitution plus alkali interstitials.

The high temperature form of $LiTa_3O_8$ or $Li_2Ta_6O_{16}$ is apparently isostructural with $LiTa_6O_{15}F$ and $Ta_4W_2O_{16}$. Either fluorine or tungsten ions can be utilized to generate a non-stoichiometric phase and the structural mechanism is thus alkali ion vacancies plus cation (or anion) substitution.

The low temperature form of $Ta_2O_5$ (L-$Ta_2O_5$) is stabilized by the addition of $Li_2O$. This structure is apparently intrinsically non-stoichiometric with the formula $Ta_{22}O_{55}$ and five oxygen "vacancies" [25]. The $Li^+$ ions either substitute for $Ta^{+5}$ creating more anion vacancies or more likely occur interstitially filling some of the anion "vacancies" already present or a mechanism of cation substitution plus anion interstitials.

It should be remembered that all of the mechanisms discussed in this section are hypothetical and must be checked by careful single crystal x-ray diffraction or even neutron diffraction studies. Until such studies can be made, our understanding of the structural mechanisms by which nature compensates a non-stoichiometric phase for electrical neutrality will remain poorly understood.

SUMMARY OF RESULTS

1. The phase equilibria of various alkali tantalates have been studied up to and including liquidus temperatures and phase equilibrium diagrams have been constructed most consistent with the experimental data in the systems:

   $Ta_2O_5$-$LiTaO_3$
   $Ta_2O_5$-$NaTaO_3$
   $Ta_2O_5$-$KTaO_3$

2. The phase equilibria of various alkali niobates have been studied up to and including liquidus temperatures and phase equilibrium diagrams have been constructed most consistent with the experimental data in the systems:

   $Nb_2O_5$-$LiNbO_3$
   $Nb_2O_5$-$NaNbO_3$
   $Nb_2O_5$-$KNbO_3$

3. Pellets of nineteen phases were transmitted to the sponsoring agency for evaluation and the following three compositions were found to show peaks in the dielectric loss vs. temperature, indicating some ionic mobility.

   $11K_2O:89Ta_2O_5$ - Gatehouse tungsten bronze structure (GTB)
   $21.75K_2O:78.25Ta_2O_5$ - Hexagonal tungsten bronze structure (HTB)
   $34K_2O:66Ta_2O_5$ - Tetragonal tungsten bronze structure (TTB)

4. Attempts were made to grow large crystals of eight different phases and two crystals were transmitted to the sponsor for evaluation.

FUTURE WORK

1. The most interesting phases in the $K_2O$-$Ta_2O_5$ system (GTB and HTB) did not have phase equilibria relations favorable for crystal growth from the melt. Preliminary examination of the $Rb_2O$-$Nb_2O_5$ and $Rb_2O$-$Ta_2O_5$ systems suggests that these systems may be more favorable for melt growth of the GTB and HTB type phases. The phase equilibria in these systems will be examined in more detail and attempts made to grow crystals which might then be ion exchanged.

2. Small crystals of the hexagonal tungsten bronze phase in the system $KTaO_3$-$WO_3$ have been successfully grown from a potassium tungsten oxide flux. Attempts will be made to grow larger single crystals of this phase for dielectric loss and/or ionic conductivity measurements.

3. A cubic phase of $KSbO_3$, similar to the high pressure polymorph previously demonstrated to exhibit ionic mobility, has been successfully synthesized by the addition of a small amount of either $SiO_2$ or $Al_2O_3$. The phase equilibria of the $Sb_2O_4$-$NaSbO_3$ and $Sb_2O_4$-$KSbO_3$ systems will be studied and the effects will be studied of various impurities on the stabilization of the cubic modifications of $KSbO_3$ and $NaSbO_3$. Attempts will be made to prepare single crystals of these cubic phases and/or other interesting alkali antimonates.

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[5] R. S. Roth, H. S. Parker, W. S. Brower and J. L. Waring (to be submitted to J. Solid State Chem.)

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## FIGURE CAPTIONS

Figure 1 Phase equilibrium diagram for the system $Nb_2O_5$-$LiNbO_3$ redrawn to conform with accepted published data.

o - liquidus [7]

◒ - transition [7]

● - solidus and solid solution boundary [7,11]

X - present work

Figure 2 Phase equilibrium diagram of the system $Ta_2O_5$-$LiTaO_3$, mostly from reference [2].

o - completely melted

- - partially melted

● - no melting

Figure 3 Phase equilibrium diagram of the system $Nb_2O_5$-$NaNbO_3$

X - liquidus values from reference [4]

o - completely melted

◒ - partially melted

● - no melting

dotted line - a phase resulting from reaction with atmospheric moisture

Figure 4 Phase equilibrium diagram for the system $Ta_2O_5$-$NaTaO_3$

o - completely melted

◒ - partially melted

● - no melting

X - quenched specimen

Figure 5 Phase equilibrium diagram for the system $Nb_2O_5$-$KNbO_3$

X - liquidus values from reference [20]

o - completely melted

◒ - partially melted

● - no melting

Figure 6 Phase equilibrium diagram for the system $Ta_2O_5$-$KTaO_3$

● - solidus and liquidus values from reference [25]

o - completely melted

◒ - partially melted

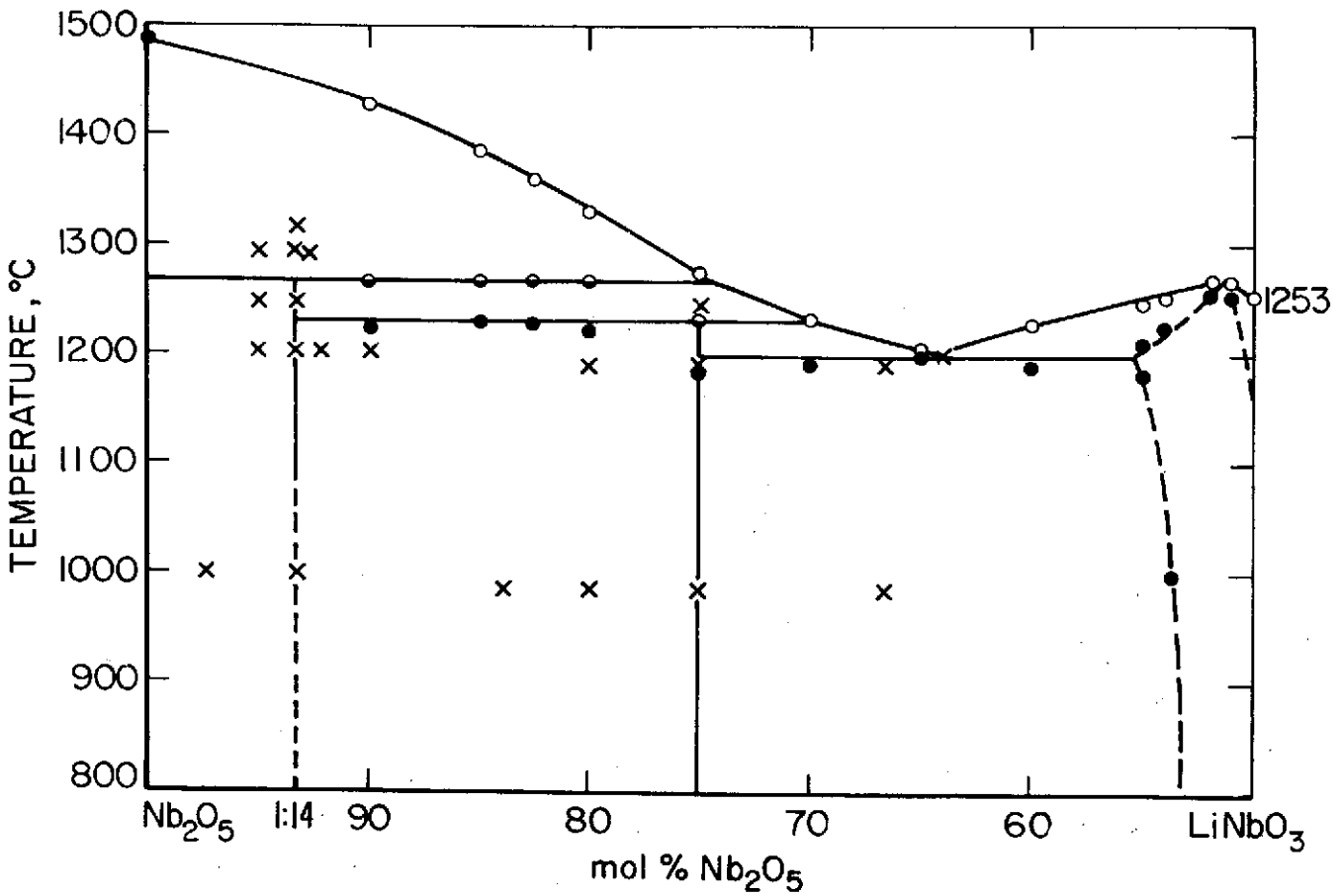
X - no melting

Figure 7 Dielectric loss (epsilon-2) versus reciprocal temperature (theta = $10^3$ x degrees Kelvin$^{-1}$) for a specimen of $11K_2O{:}89Ta_2O_5$ (sample No. 27) having the structure of the Gatehouse Tungsten Bronze (GTB).

Figure 8 Dielectric loss (epsilon-2) versus reciprocal temperature (theta = $10^3$ x degrees Kelvin$^{-1}$) for a specimen of $16.67K_2O{:}83.33Ta_2O_5$ (sample No. 23) having the structure of a Tetragonal Tungsten Bronze modified by superstructure to a tripled cell with orthorhombic (TTBs).

Figure 9 Dielectric loss (epsilon-2) versus reciprocal temperature (theta = $10^3$ x degrees Kelvin$^{-1}$) for a specimen of $21.75K_2O{:}78.25Ta_2O_5$ (sample No. 39) having the structure of a Hexagonal Tungsten Bronze (HTB).

Figure 10 Dielectric loss (epsilon-2) versus reciprocal temperature (theta = $10^3$ x degrees Kelvin$^{-1}$) for a specimen of $34K_2O{:}66Ta_2O_5$ (sample No. 28) having the structure of a Tetragonal Tungsten Bronze with no superstructure (TTB).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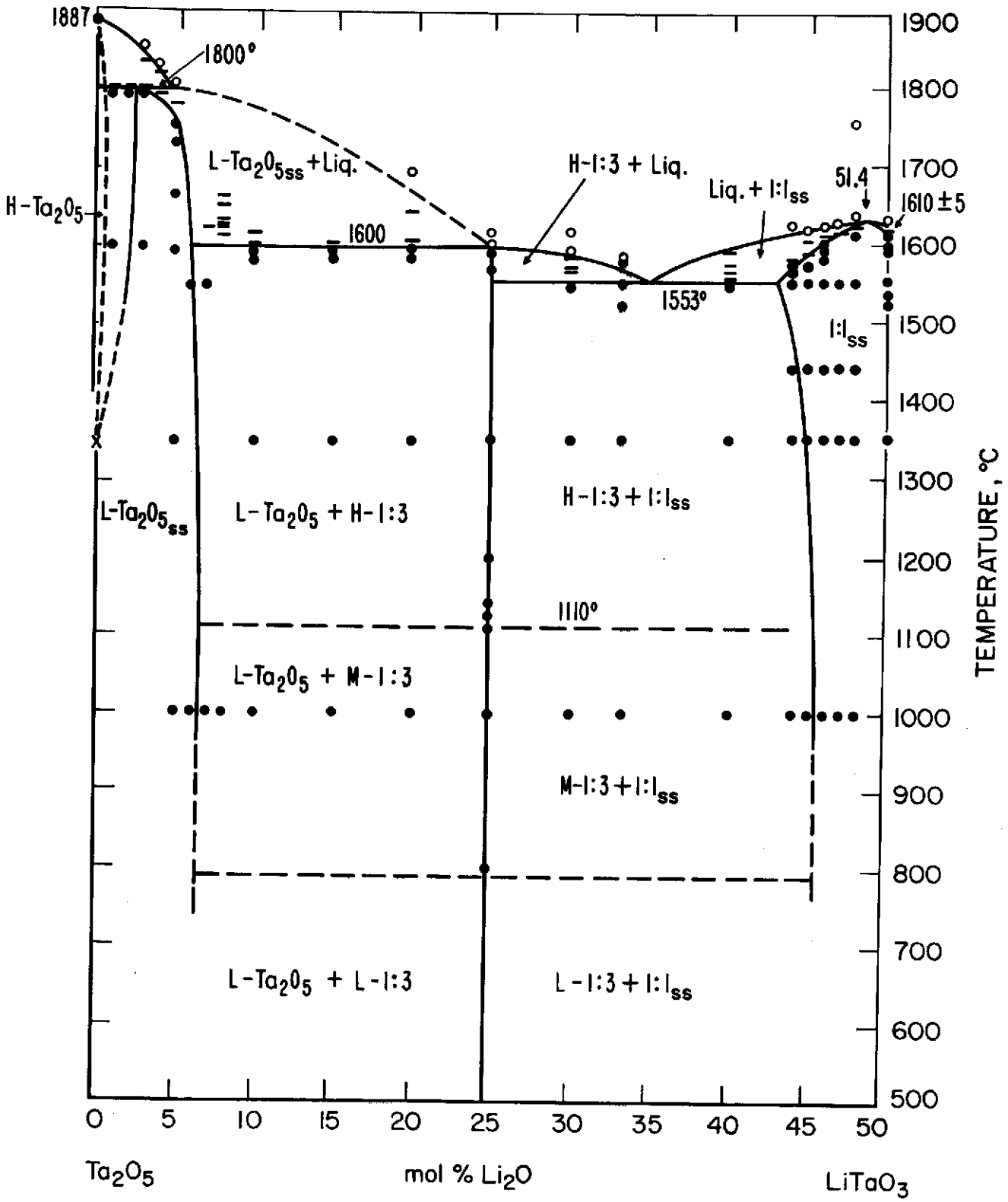
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H-Ta2O5
1600
H-1:3 + Liq.
Liq.+ 1:1ss
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1610±5
1553°
1:1ss
L-Ta2O5ss
L-Ta2O5 + H-1:3
H-1:3+1:1ss
1110°
L-Ta2O5 + M-1:3
M-1:3+1:1ss
L-Ta2O5 + L-1:3
L-1:3+1:1ss
1900
1800
1700
1600
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600
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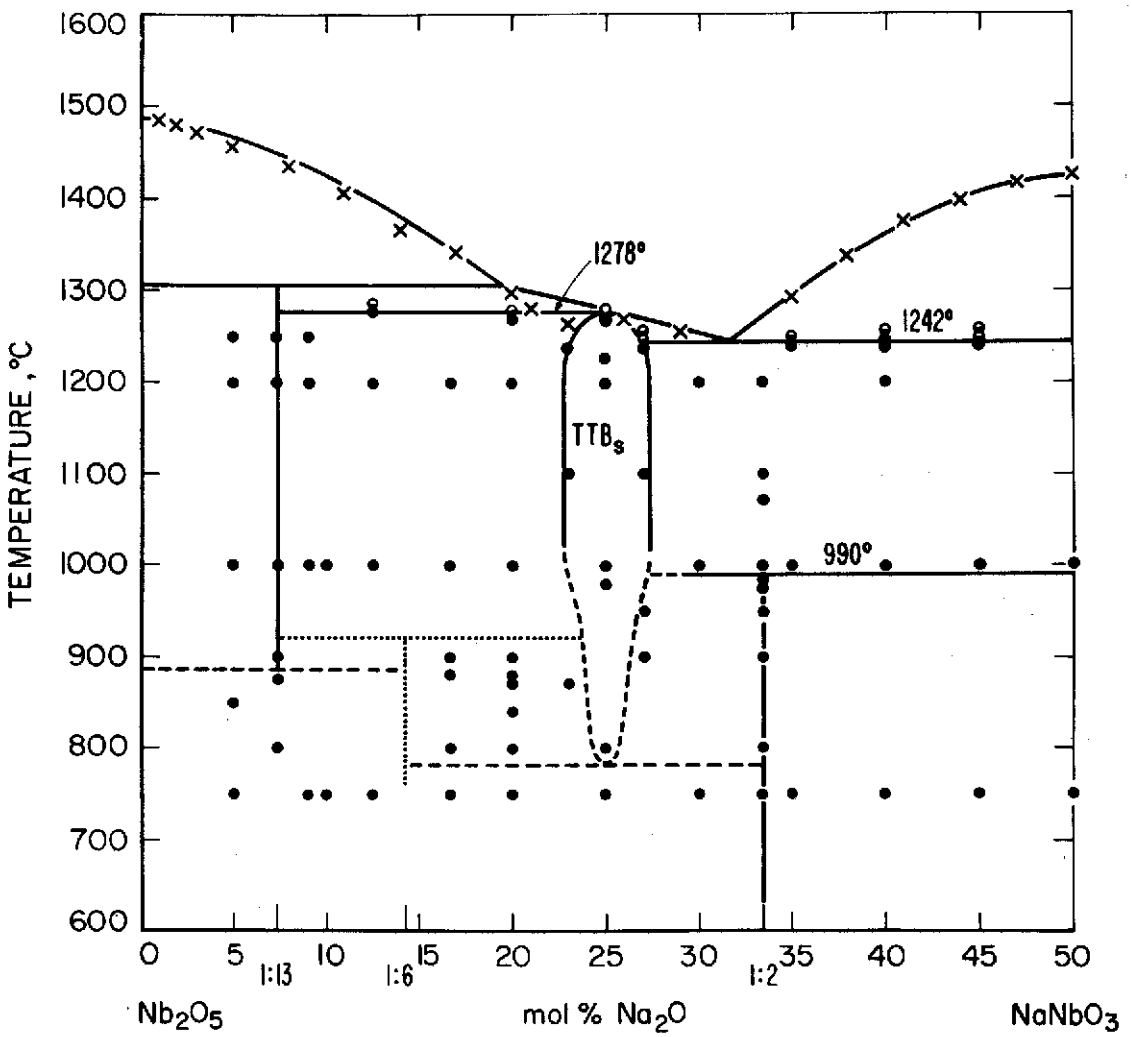
50
Ta2O5
mol % Li2O
LiTaO3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5
10
15
20
25
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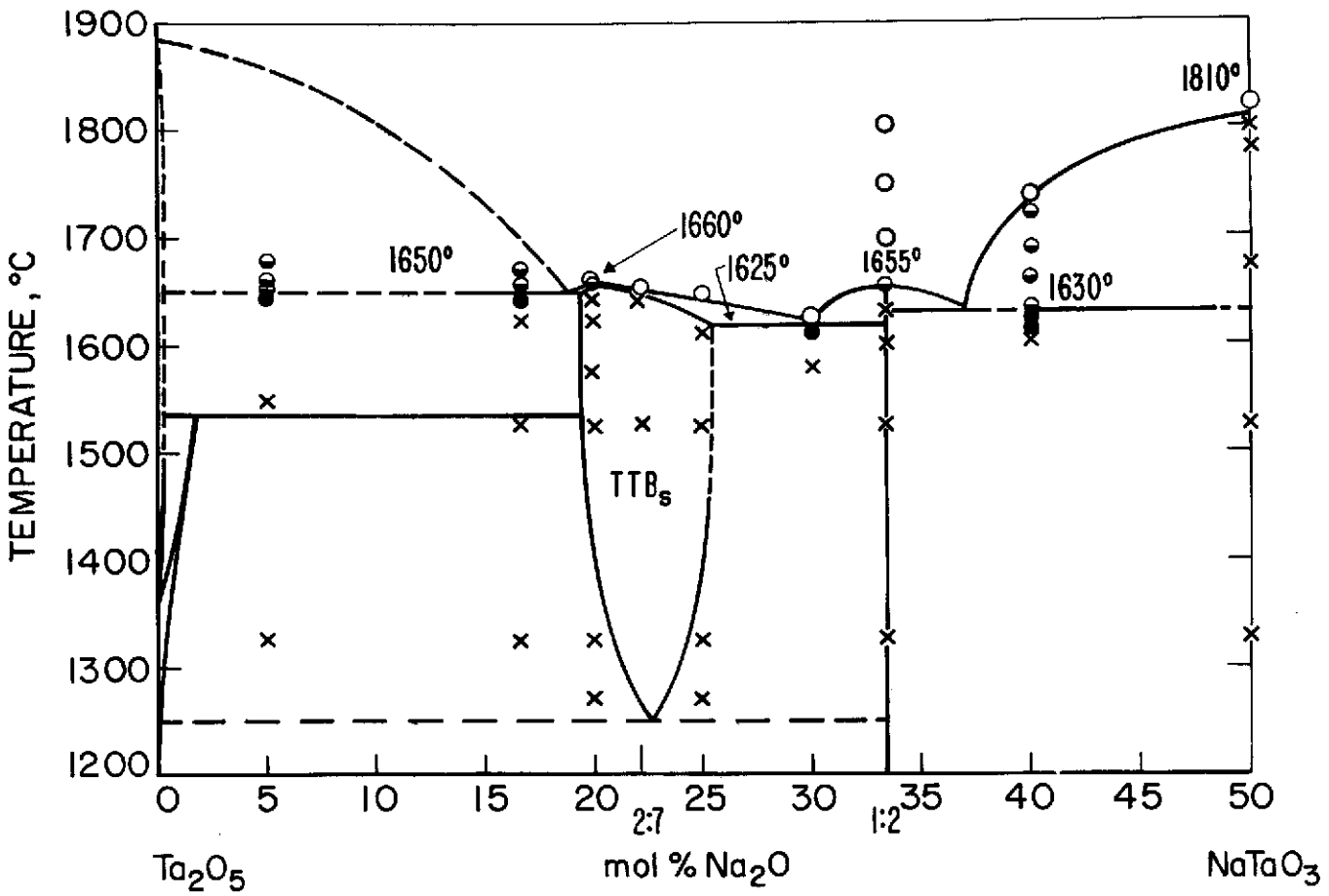
1:6
1:2
Nb$_2$O$_5$
mol % Na$_2$O
NaNbO$_3$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5
10
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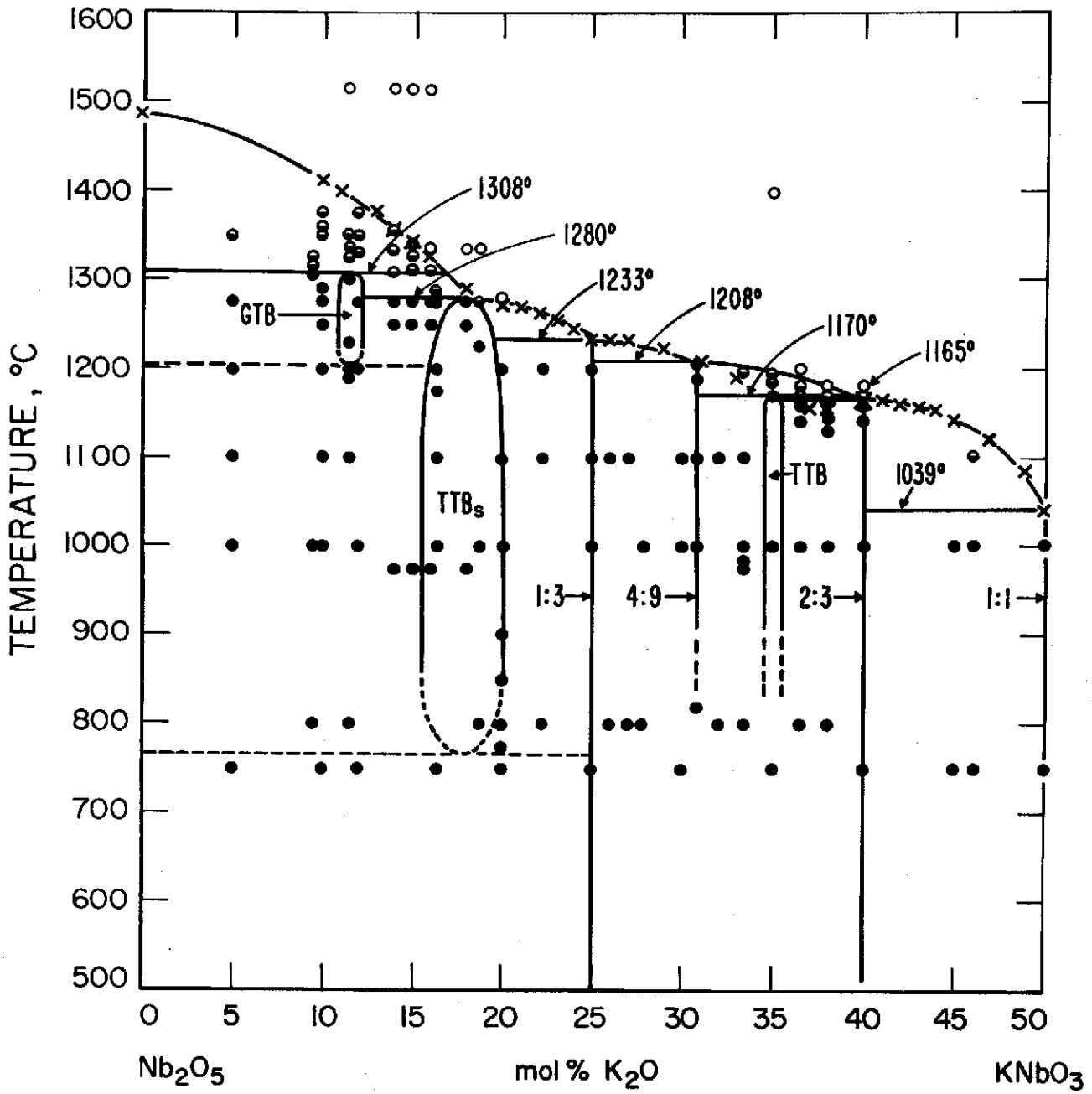
1:2
$Ta_2O_5$
mol % $Na_2O$
$NaTaO_3$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TTBs
TTB
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4:9
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25
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35
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45
50
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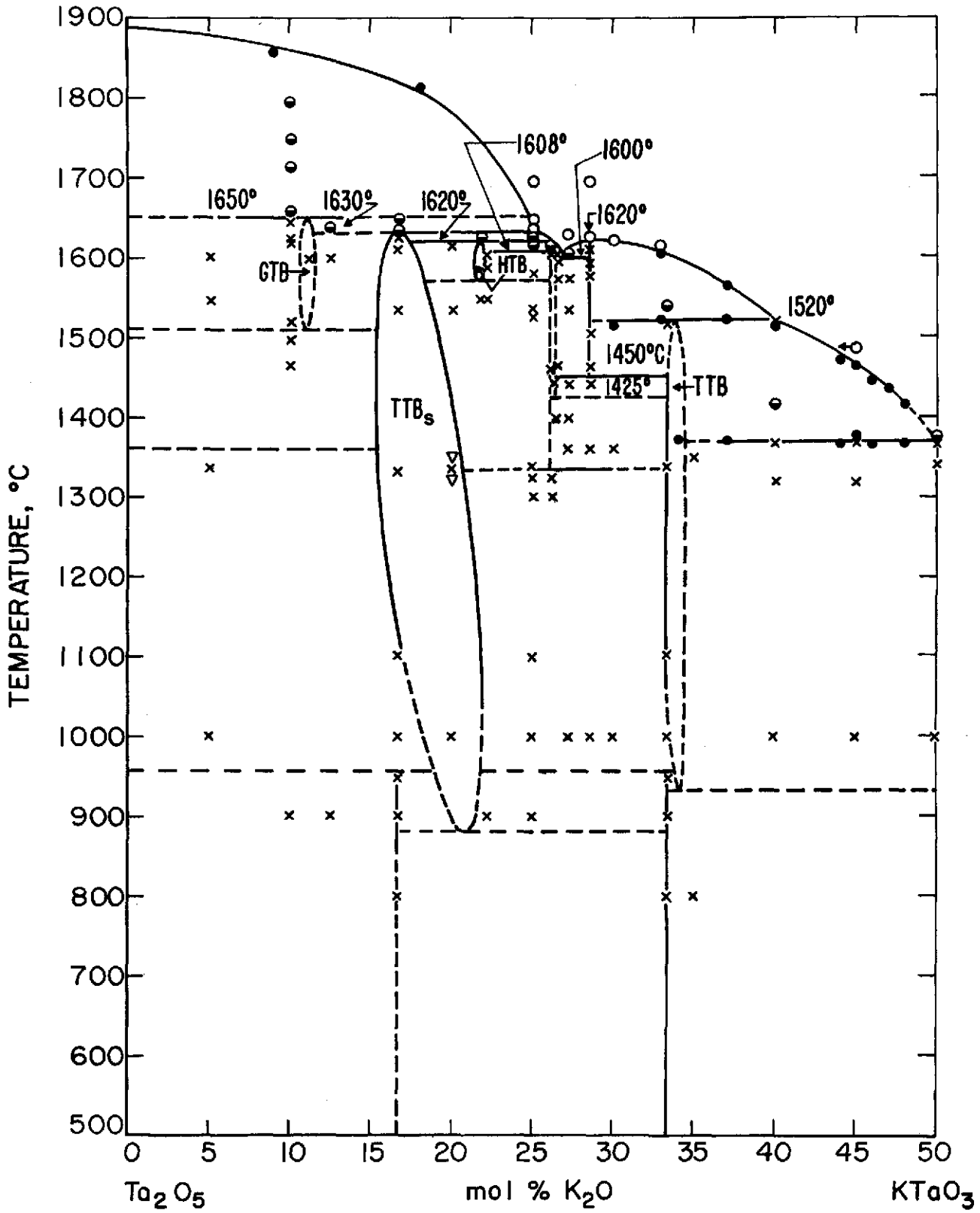
mol % K2O
KNbO3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TTB
TTB$_s$
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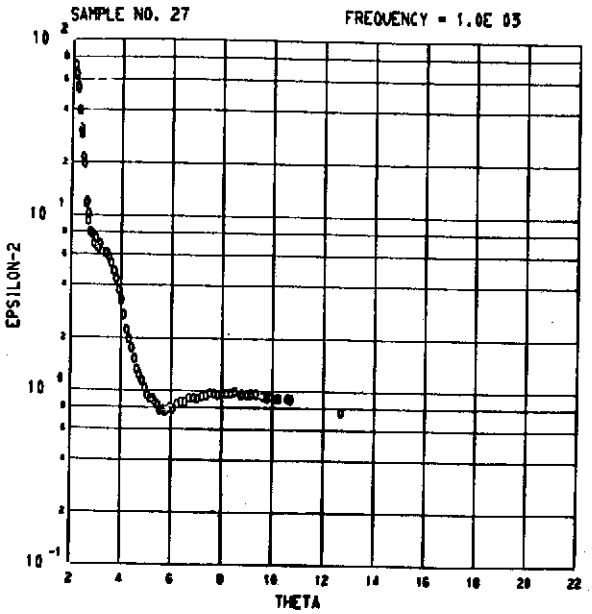
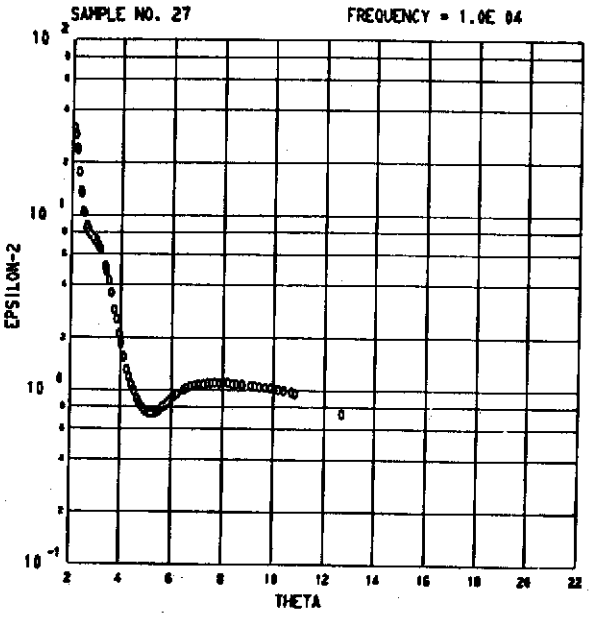
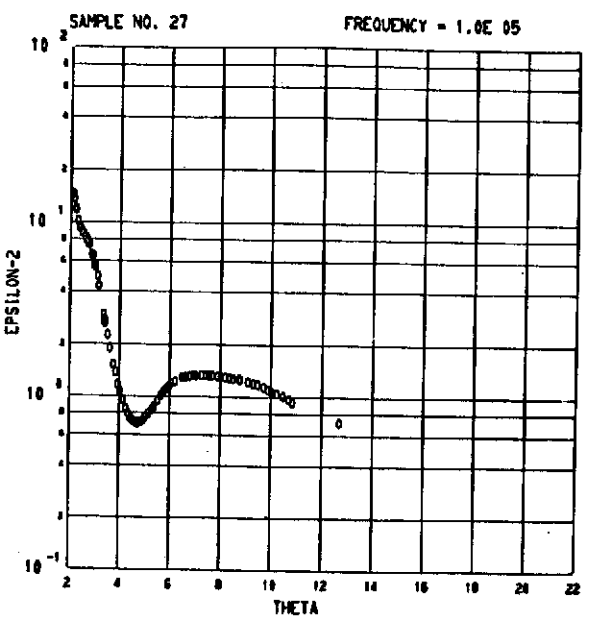
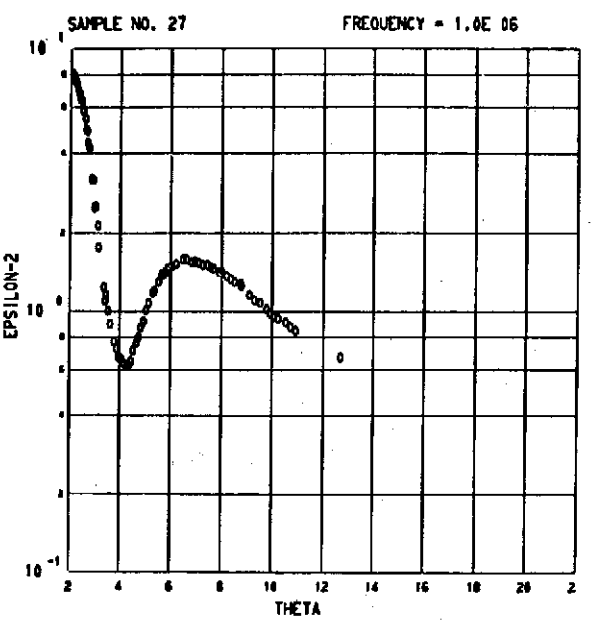
$Ta_2O_5$
mol % $K_2O$
$KTaO_3$

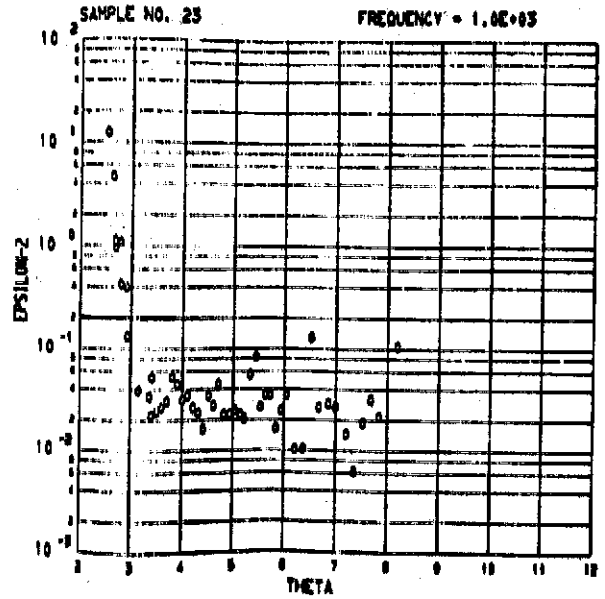


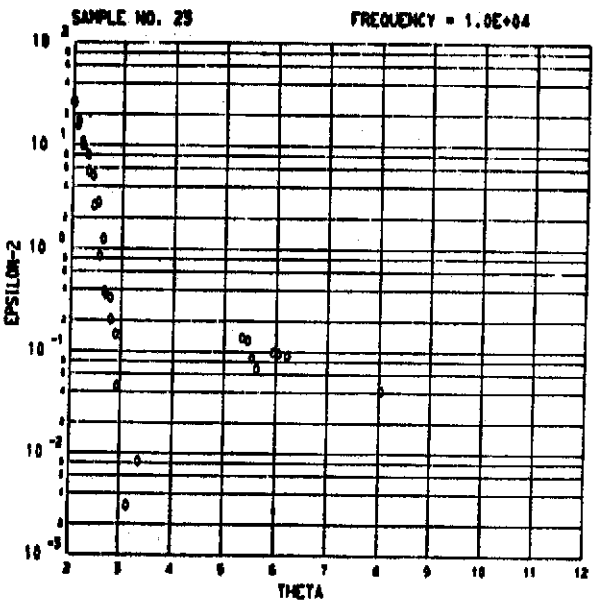



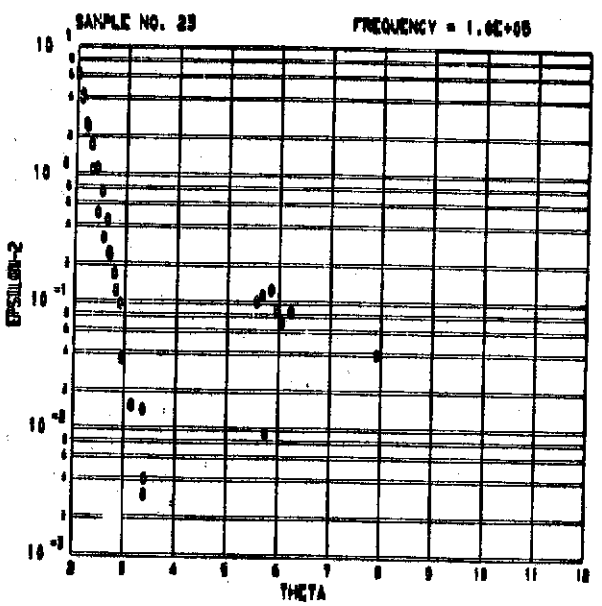



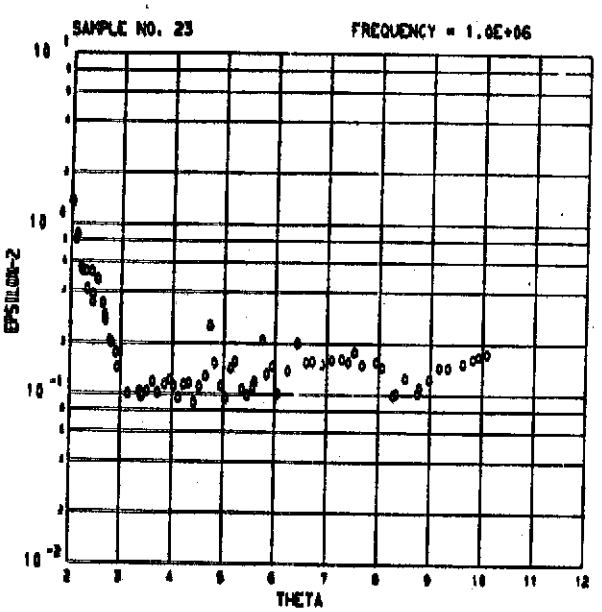




DIELECTRIC LOSS (EPSILON-2) VERSUS RECIPROCAL TEMPERATURE (THETA = $10^3$ x DEGREES KELVIN$^{-1}$) FOR A SPECIMEN OF $11K_2O{:}89Ta_2O_5$ (SAMPLE No. 27) HAVING THE STRUCTURE OF THE GATEHOUSE TUNGSTEN BRONZE (GTB).

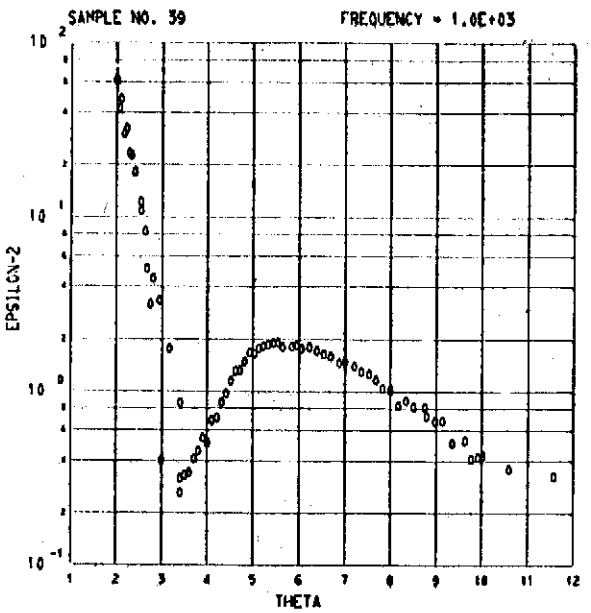


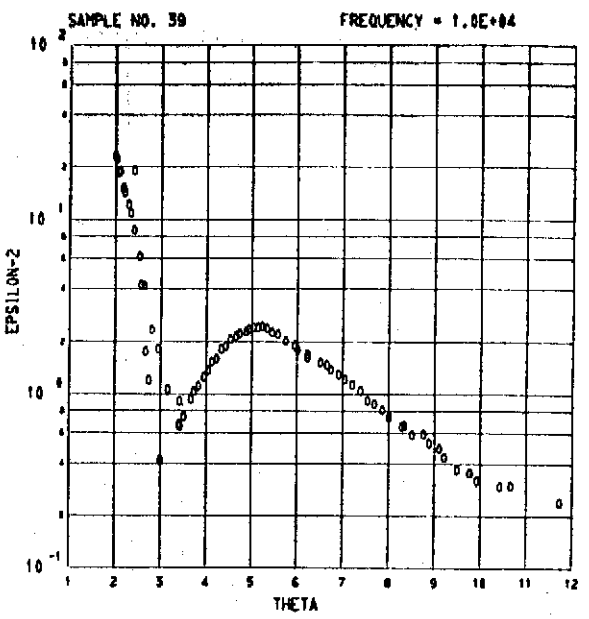



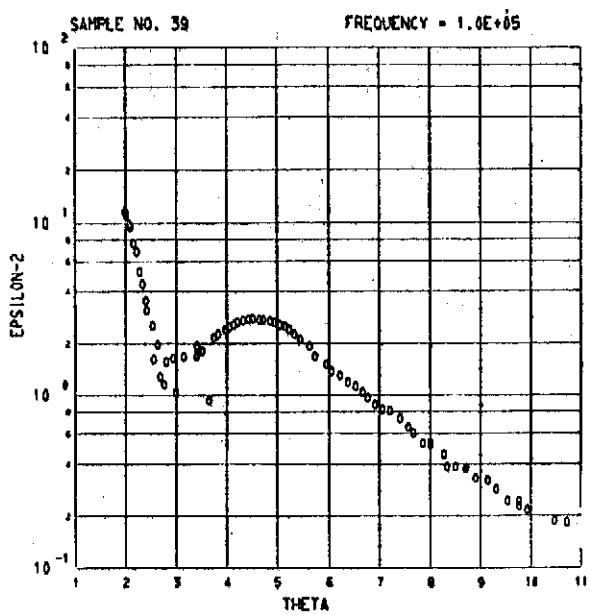



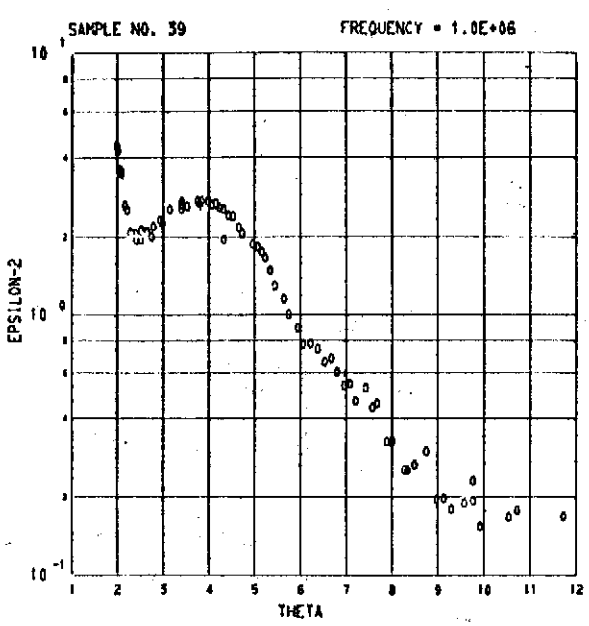




Dielectric loss (epsilon-2) versus reciprocal temperature (theta = $10^3$ x degrees Kelvin$^{-1}$) for a specimen of $16.67K_2O:83.33Ta_2O_5$ (sample No. 23) having the structure of a Tetragonal Tungsten Bronze Modified by superstructure to a tripled cell with orthorhombic symmetry (TTBs)

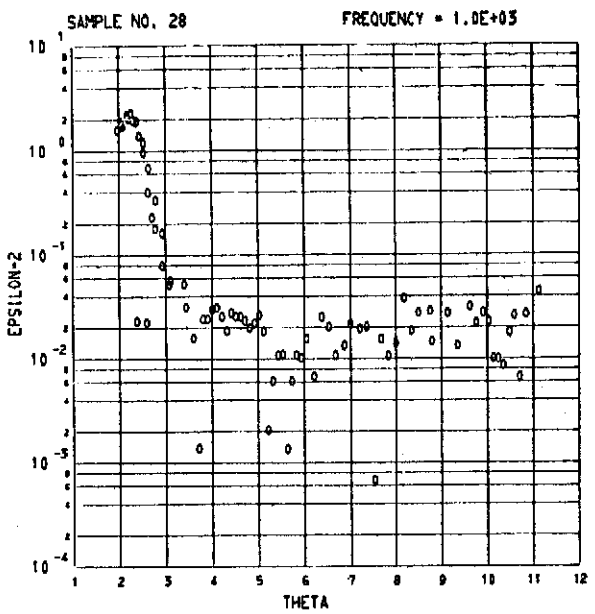


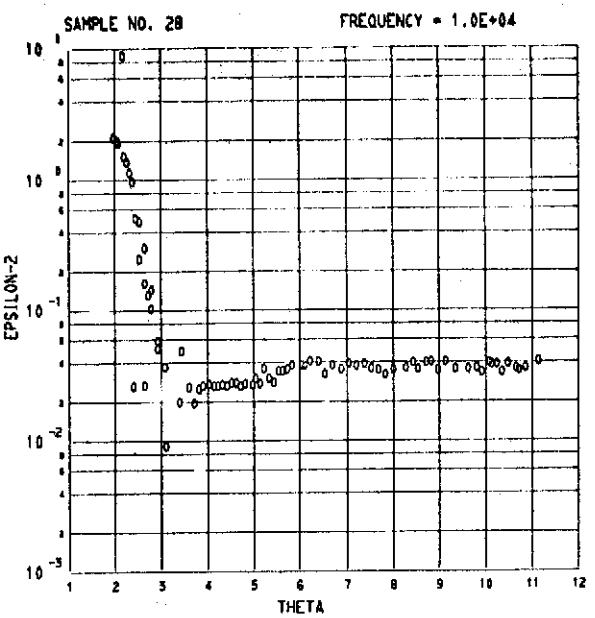



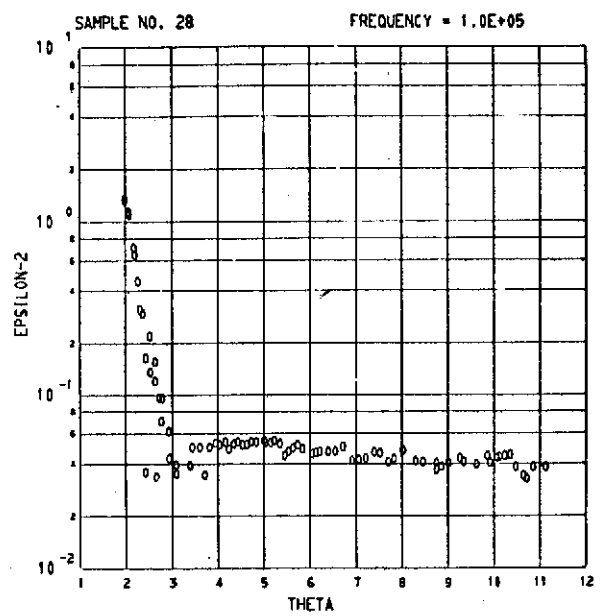



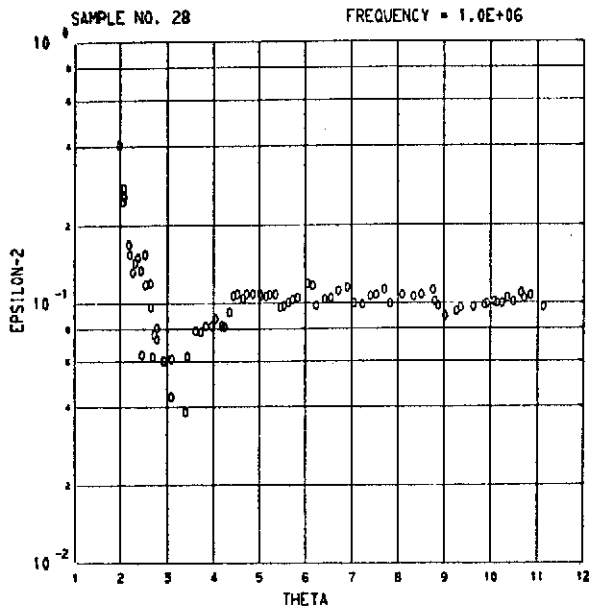




Dielectric loss (epsilon-2) versus reciprocal temperature (theta = $10^3$ x degrees Kelvin$^{-1}$) for a specimen of $21.75K_2O{:}78.25Ta_2O_5$ (sample No. 39) having the structure of a Hexagonal Tungsten Bronze (HTB).




DIELECTRIC LOSS (EPSILON-2) VERSUS RECIPROCAL TEMPERATURE (THETA = $10^3$ X DEGREES KELVIN$^{-1}$) FOR A SPECIMEN OF $34K_2O{:}66Ta_2O_5$ (SAMPLE NO. 28) HAVING THE STRUCTURE OF A TETRAGONAL TUNGSTEN BRONZE WITH NO SUPERSTRUCTURE (TTB)

TABLE 1: EXPERIMENTAL DATA FOR THE SYSTEM $Nb_2O_5$-$LiNbO_3$

| Composition Mole % [a] | | Initial Heat Treatment [b] | | Final Heat Treatment [c] | | Results of Physical Observation | Results of X-Ray Diffraction Analyses [d] |
|---|---|---|---|---|---|---|---|
| | | Temp. | Time | Temp. | Time | | |
| $Nb_2O_5$ | $Li_2O$ | °C | Hrs. | °C | Hrs. | | |
| 97.50 | 2.50 | 1000 | 96 | -- | -- | --- | H-$Nb_2O_5$ + 1:3 + N-$Nb_2O_5$ (tr) |
| 95.00 | 5.00 | 1000 | 63 | -- | -- | --- | ----- |
| | | | | 1202 | 20 | --- | N-$Nb_2O_5$+ H-$Nb_2O_5$ |
| | | | | 1249 | 19 | Not melted | " " |
| | | | | 1274 | 24 | Not visibly melted | ----- |
| | | | | 1294 | 22 | Not visibly melted | N-$Nb_2O_5$ + H-$Nb_2O_5$ |
| | | | | 1318 | 24 | Not visibly melted | ----- |
| | | | | 1336 | 23 | Some liquid present | ----- |
| 93.33 | 6.67 | 1000 | 63 | -- | -- | --- | H-$Nb_2O_5$ + 1:3 |
| | | | | 1202 | 20 | --- | N-$Nb_2O_5$ |
| | | | | 1249 | 19 | Not melted | N-$Nb_2O_5$ |
| | | | | 1274 | 24 | Not melted | ----- |
| | | | | 1294 | 22 | Not visibly melted | N-$Nb_2O_5$ [e] |
| | | | | 1318 | 24 | Partially melted | H-$Nb_2O_5$ + 1:3 + N-$Nb_2O_5$ |
| | | | | 1336 | 23 | Partially melted | ----- |
| 92.86 | 7.14 | 1000 | 60 | -- | -- | --- | ----- |
| | | | | 1294 | 22 | Not melted | N-$Nb_2O_5$ + H-$Nb_2O_5$ + 1:3 |
| 92.31 | 7.69 | 1000 | 63 | -- | -- | --- | ----- |
| | | | | 1202 | 20 | Not melted | N-$Nb_2O_5$ + 1:3 |
| | | | | 1248 | 18.75 | Partially melted | ----- |
| 90.00 | 10.00 | 1000 | 63 | -- | -- | --- | ----- |
| | | | | 1202 | 20 | Not melted | N-$Nb_2O_5$ + 1:3 |
| 83.33 | 16.67 | 985 | 64 | -- | -- | Not melted | ----- |
| | | | | 1244 | 20 | Partially melted | ----- |
| 80.00 | 20.00 | 985 | 65 | -- | -- | Not melted | 1:3 + H-$Nb_2O_5$ |
| | | | | 1190 | 96 | Not melted | 1:3 + N-$Nb_2O_5$ |
| | | | | 1224 | 25 | Not melted | ----- |
| 75.00 | 25.00 | 985 | 65 | -- | -- | Not melted | 1:3 |
| | | | | 1190 | 96 | Not melted | 1:3 |
| | | | | 1224 | 25 | Not melted | --- |
| | | | | 1244 | 20 | Partially melted | N-$Nb_2O_5$ + 1:3 + 1:1 |
| 70.00 | 30.00 | 1000 | 70.5 | -- | -- | Not melted | ----- |
| | | | | 1183 | 23 | Not melted | ----- |
| | | | | 1195 | 24 | No visible melting | ----- |
| | | | | 1203 | 25 | Some melting | ----- |
| | | | | 1207 | 23 | Some melting | ----- |
| | | | | 1215 | 24 | Some melting | ----- |
| 66.67 | 33.33 | 985 | 65 | -- | -- | --- | 1:1 + 1:3 |
| | | | | 1190 | 96 | Not melted | 1:1 + 1:3 |
| | | | | 1224 | 25 | Melted | ----- |
| 63.99 | 36.01 | 1000 | 70.5 | -- | -- | --- | ----- |
| | | | | 1183 | 23 | Not melted | ----- |
| | | | | 1195 | 24 | Partially melted | ----- |
| | | | | 1203 | 25 | Melted | 1:1 + 1:3 |
| | | | | 1207 | 23 | Melted | ----- |

[a] For ease and accuracy of weighing $Li_2O$ was added to $Nb_2O_5$ as $LiNbO_3$ not as the oxide end member.

[b] All specimens were initially calcined in Pt crucibles at the indicated temperature and time.

[c] All subsequent heat treatments were quenched in sealed Pt tubes from the indicated temperature.

[d] All phases identified are given in order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.
H-$Nb_2O_5$ - the high temperature form of $Nb_2O_5$
N-$Nb_2O_5$ - a metastable form of $Nb_2O_5$ apparently stabilized by $Li_2O$.
1:3 - $LiNb_3O_8$
1:1 - $LiNbO_3$ solid solution

[e] These experiments suggest that the N-$Nb_2O_5$ phase melts incongruently between 1294° and 1318° rather than at the 1268° value given by Reisman.

TABLE 2: EXPERIMENTAL DATA FOR THE SYSTEM $Ta_2O_5$-$LiTaO_3$

| Composition Mole % [a] | | Initial Heat Treatment [b] | | Final Heat Treatment [c] | | Results of Physical Observation | Results of X-Ray Diffraction Analyses [d] |
|---|---|---|---|---|---|---|---|
| | | Temp. | Time | Temp. | Time | | |
| $Ta_2O_5$ | $Li_2O$ | °C | Hrs. | °C | Hrs. | | |
| 99 | 1 | 1000 | 60 | -- | -- | ----- | ----- |
| | | | | 1600 | 19.00 | No melting | H-$Ta_2O_5$ + L-$Ta_2O_5$ ss |
| | | | | 1795 | 0.17 | No melting | " " |
| | | | | 1805 | 0.17 | Partially melted | ----- |
| 98 | 2 | 1000 | 60 | -- | -- | ----- | ----- |
| | | | | 1600 | 24.00 | No melting | L-$Ta_2O_5$ ss + H-$Ta_2O_5$ |
| | | | | 1795 | 0.17 | No melting | " " |
| | | | | 1806 | 0.25 | Partially melted | " " |
| 97 | 3 | 1000 | 60 | -- | -- | ----- | ----- |
| | | | | 1600 | 24.00 | No melting | L-$Ta_2O_5$ ss |
| | | | | 1795 | 0.17 | No melting | " |
| | | | | 1803 | 0.17 | Partially melted | ----- |
| | | | | 1842 | 0.03 | Partially melted | ----- |
| | | | | 1855 | 0.03 | Completely melted | ----- |
| 96 | 4 | 1000 | 60 | -- | -- | ----- | ----- |
| | | | | 1794 | 0.17 | Partially melted | ----- |
| | | | | 1820 | 0.33 | Partially melted | ----- |
| | | | | 1834 | 0.33 | Completely melted | ----- |
| 95 | 5 | 1000 | 10 | -- | -- | ----- | ----- |
| | | | | 1350 | 24.00 | No melting | L-$Ta_2O_5$ ss |
| | | | | 1594 | 16.00 | No melting | " |
| | | | | 1597 | 0.50 | No melting | ----- |
| | | | | 1667 | 0.17 | No melting | ----- |
| | | | | 1732 | 0.17 | No melting | ----- |
| | | | | 1757 | 0.17 | No melting | ----- |
| | | | | 1782 | 0.17 | Partially melted | L-$Ta_2O_5$ ss |
| | | | | 1809 | 0.17 | Completely melted | " |
| 94 | 6 | 1000 | 10 | -- | -- | ----- | L-$Ta_2O_5$ ss |
| | | | | 1550 | 16.00 | No melting | ----- |
| 93 | 7 | 1000 | 10 | -- | -- | ----- | L-$Ta_2O_5$ ss + M-1:3 |
| | | | | 1550 | 24.00 | No melting | " " |
| | | | | 1625 | 16.00 | Partially melted | L-$Ta_2O_5$ ss |
| 92 | 8 | 1000 | 10 | -- | -- | ----- | ----- |
| | | | | 1615 | 1.00 | Partially melted | ----- |
| | | | | 1625 | 0.75 | Partially melted | ----- |
| | | | | 1627 | 0.75 | Partially melted | ----- |
| | | | | 1635 | 0.50 | Partially melted | ----- |
| | | | | 1653 | 0.50 | Partially melted | ----- |
| | | | | 1663 | 1.00 | Partially melted | L-$Ta_2O_5$ ss + H-1:3 |
| 90 | 10 | 1000 | 10 | -- | -- | ----- | ----- |
| | | | | 1350 | 24.00 | No melting | L-$Ta_2O_5$ ss + H-1:3 |
| | | | | 1583 | 0.50 | No melting | ----- |
| | | | | 1590 | 16.00 | No melting | L-$Ta_2O_5$ ss + H-1:3 |
| | | | | 1593 | 0.50 | No melting | ----- |
| | | | | 1607 | 0.75 | Partially melted | L-$Ta_2O_5$ ss + H-1:3 + 1:1 |
| | | | | 1618 | 0.50 | Partially melted | ----- |
| 85 | 15 | 1000 | 10 | -- | -- | ----- | ----- |
| | | | | 1350 | 24.00 | No melting | ----- |
| | | | | 1583 | 0.50 | No melting | ----- |
| | | | | 1593 | 0.75 | No melting | ----- |
| | | | | 1605 | 0.50 | Partially melted | ----- |
| 80 | 20 | 1000 | 10 | -- | -- | ----- | M-1:3 + L-$Ta_2O_5$ ss |
| | | | | 1350 | 24.00 | No melting | H-1:3 + L-$Ta_2O_5$ ss |
| | | | | 1580 | 1.00 | No melting | " " |
| | | | | 1595 | 1.00 | No melting | ----- |
| | | | | 1609 | 0.50 | Partially melted | ----- |
| | | | | 1642 | 0.50 | Partially melted | ----- |
| | | | | 1646 | 0.50 | Partially melted | ----- |
| | | | | 1695 | 0.75 | Probably completely melted | ----- |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 75 | 25 | 800 | 307 | -- | -- | ----- | L-1:3 + H-1:3 |
| | | 1000 | 10 | -- | -- | ----- | H-1:3 |
| | | | | 1077 | 312.00 | No melting | " |
| | | | | 1110 | 42.00 | No melting | " |
| | | | | 1111 | 307.00 | No melting | H-1:3 |
| | | | | 1126 | 96.00 | No melting | " |
| | | | | 1130 | 16.00 | No melting | " |
| | | | | 1143 | 16.00 | No melting | " |
| | | | | 1144 | 115.00 | No melting | " |
| | | | | 1205 | 18.00 | No melting | " |
| | | | | 1265 | 18.00 | No melting | ----- |
| | | | | 1350 | 24.00 | No melting | H-1:3 |
| | | | | 1573 | 16.00 | No melting | " |
| | | | | 1592 | 1.00 | No melting | ----- |
| | | | | 1601 | 1.00 | Completely melted | ----- |
| | | | | 1616 | 1.50 | Completely melted | H-1:3 + L-$Ta_2O_5$ ss + 1:1 |
| | | 1000 | 10 | -- | -- | ----- | ----- |
| | | 1205 | 18 | -- | -- | ----- | ----- |
| | | | | 1130 | 16.00 | No melting | ----- |
| | | | | 1143 | 16.00 | No melting | ----- |
| | | | | 1144 | 115.00 | No melting | ----- |
| | | 1000 | 10 | -- | -- | ----- | ----- |
| | | 1250 | 30 | -- | -- | ----- | H-1:3 |
| | | | | 1077 | 312.00 | ----- | H-1:3 |
| | | | | 1111 | 307.00 | ----- | ----- |
| | | | | 1126 | 96.00 | ----- | ----- |
| 70 | 30 | 1000 | 10 | -- | -- | ----- | ----- |
| | | | | 1350 | 24.00 | No melting | ----- |
| | | | | 1545 | 0.50 | No melting | ----- |
| | | | | 1555 | 0.50 | Partially melted | ----- |
| | | | | 1566 | 1.00 | Partially melted | ----- |
| | | | | 1572 | 0.75 | Partially melted | ----- |
| | | | | 1587 | 0.50 | Partially melted | ----- |
| | | | | 1594 | 0.25 | Probably completely melted | ----- |
| | | | | 1616 | 0.75 | " | ----- |
| | | | | 1616 | 0.50 | " | H-1:3 + 1:1 ss |
| 66.67 | 33.33 | 1000 | 10 | -- | -- | ----- | H-1:3 + 1:1 ss |
| | | | | 1350 | 24.00 | No melting | H-1:3 + 1:1 ss |
| | | | | 1525 | 2.50 | No melting | ----- |
| | | | | 1551 | 2.50 | No melting | ----- |
| | | | | 1555 | 0.50 | Probably some melting | ----- |
| | | | | 1567 | 1.00 | Considerably melted | ----- |
| | | | | 1578 | 2.00 | Completely melted | ----- |
| | | | | 1581 | 0.25 | Completely melted | ----- |
| | | | | 1583 | 3.00 | Completely melted | H-1:3 + 1:1 ss |
| 60 | 40 | 1000 | 10 | -- | -- | ----- | ----- |
| | | | | 1350 | 24.00 | No melting | ----- |
| | | | | 1547 | 0.50 | No melting | ----- |
| | | | | 1555 | 0.50 | Partly melted | ----- |
| | | | | 1566 | 0.50 | Partly melted | ----- |
| | | | | 1572 | 0.50 | Partly melted | ----- |
| | | | | 1590 | 1.00 | Considerably melted | ----- |
| 56 | 44 | 1000 | 10 | -- | -- | ----- | ----- |
| | | | | 1348 | 66.00 | No melting | 1:1 ss + H-1:3 |
| | | | | 1440 | 70.00 | No melting | " |
| | | | | 1550 | 0.75 | No melting | ----- |
| | | | | 1565 | 0.50 | No melting | ----- |
| | | | | 1576 | 0.50 | No melting | ----- |
| | | | | 1581 | 0.50 | Partially melted | ----- |
| | | | | 1622 | 0.50 | Completely melted | ----- |
| 55 | 45 | 1000 | 10 | -- | -- | ----- | ----- |
| | | | | 1348 | 66.0 | No melting | 1:1 ss |
| | | | | 1350 | 24.00 | No melting | 1:1 ss + H-1:3 (tr) |
| | | | | 1440 | 70.00 | No melting | 1:1 ss |
| | | | | 1550 | 1.00 | No melting | ----- |
| | | | | 1572 | 0.75 | No melting | 1:1 ss |
| | | | | 1587 | 0.50 | Partially melted | ----- |
| | | | | 1606 | 0.50 | Partially melted | ----- |
| | | | | 1617 | 0.75 | Completely melted | ----- |
| 54 | 46 | 1000 | 10 | -- | -- | ----- | ----- |
| | | | | 1348 | 66.00 | No melting | 1:1 ss |
| | | | | 1440 | 70.00 | No melting | " |
| | | | | 1550 | 1.00 | No melting | ----- |
| | | | | 1581 | 0.50 | No melting | ----- |
| | | | | 1592 | 0.50 | No melting | ----- |
| | | | | 1605 | 0.50 | No melting | ----- |
| | | | | 1612 | 0.50 | Partially melted | ----- |
| | | | | 1624 | 0.50 | Completely melted | ----- |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 53 | 47 | 1000 | 10 | -- | -- | ----- | ----- |
| | | | | 1348 | 66.00 | No melting | 1:1 ss |
| | | | | 1440 | 70.00 | No melting | " |
| | | | | 1550 | 1.00 | No melting | ----- |
| | | | | 1612 | 0.50 | Just begun to melt | ----- |
| | | | | 1623 | 0.50 | Completely melted | ----- |
| 52 | 48 | 1000 | 10 | -- | -- | ----- | 1:1 ss |
| | | | | 1348 | 66.00 | No melting | " |
| | | | | 1440 | 70.00 | No melting | " |
| | | | | 1550 | 1.00 | No melting | ----- |
| | | | | 1612 | 0.75 | No melting | ----- |
| | | | | 1623 | 0.50 | Just begun to melt | ----- |
| | | | | 1637 | 0.33 | Completely melted | ----- |
| | | | | 1754 | 0.17 | Completely melted | ----- |
| 50 | 50 | Starting material | | -- | -- | Powder | 1:1 |
| | | | | 1348 | 19.00 | No melting | " |
| | | | | 1522 | 16.00 | No melting | " |
| | | | | 1538 | 2.50 | No melting | " |
| | | | | 1553 | 20.00 | No melting | ----- |
| | | | | 1592 | 1.00 | No melting | ----- |
| | | | | 1598 | 1.75 | No melting | ----- |
| | | | | 1607 | 1.00 | No melting | ----- |
| | | | | 1612 | 1.00 | No melting | ----- |
| | | | | 1616 | 1.00 | Partially melted | ----- |
| | | | | 1630 | 0.50 | Completely melted | ----- |
| | | | | 1633 | 1.00 | Completely melted | ----- |

a/ For ease and accuracy of weighing, $Li_2O$ was added to $Ta_2O_5$ as $LiTaO_3$ not as the oxide end member.

b/ All specimens were initially calcined in Pt crucibles at the indicated temperatures and time.

c/ Specimens were heated in both open and sealed Pt tubes and seemed to show no difference or discrepancy in results, as very little, if any, volatilization takes place even from the melt.

d/ All phases identified are given in order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.

H-$Ta_2O_5$ - The high temperature polymorph of $Ta_2O_5$.
L-$Ta_2O_5$ ss - A solid solution of the low temperature polymorph of $Ta_2O_5$ stabilized by $Li_2O$.
L-1:3 - The low temperature polymorph of $LiTa_3O_8$ isostructural with $LiNb_3O_8$.
M-1:3 - The medium temperature polymorph of $LiTa_3O_8$ isostructural with the mineral woodgenite.
H-1:3 - The high temperature polymorph of $LiTa_3O_8$ isostructural with $LiTa_6O_{15}F$ and $Ta_4W_2O_{16}$.
1:1 ss - A solid solution of $LiTaO_3$.

TABLE 3: EXPERIMENTAL DATA FOR THE SYSTEM $Nb_2O_5$-$NaNbO_3$

| Composition Mole % [a] | | Initial Heat Treatment [b] | | Final Heat Treatment [c] | | Results of Physical Observation | Results of X-Ray Diffraction Analyses [d] |
|---|---|---|---|---|---|---|---|
| | | Temp. °C | Time Hrs. | Temp. °C | Time Hrs. | | |
| $Nb_2O_5$ | $Na_2O$ | | | | | | |
| 95 | 5 | 750 | 69 | -- | -- | ----- | H-$Nb_2O_5$ + 1:2 |
| | | 1000 | 69 | -- | -- | Not melted | 1:13 + H-$Nb_2O_5$ |
| | | | | 1200 | 21 | Not melted | " |
| | | | | 1250 | 21 | Not melted | ----- |
| 92.86 | 7.14 | 800 | 69 | -- | -- | ----- | H-$Nb_2O_5$ + 1:6 |
| | | | | 875 | 19.5 | Not melted | " |
| | | | | 900 | 140 | Not melted | 1:13 + H-$Nb_2O_5$ + 1:6 |
| | | | | 1200 | 21 | Not melted | 1:13 |
| | | 1000 | 164 | -- | -- | Not melted | " |
| | | | | 1250 | 67 | Not melted | " |
| | | 1225 | 64 | -- | -- | Not melted | ----- |
| | | | | 1000 | 234 | Not melted | 1:13 |
| 90.01 | 9.09 | 750 | 69 | -- | -- | ----- | H-$Nb_2O_5$ + 1:2 |
| | | 1000 | 69 | -- | -- | Not melted | 1:13 + TTBs + H-$Nb_2O_5$ |
| | | | | 1200 | 22 | Not melted | 1:13 + TTBs |
| | | | | 1250 | 21 | Not melted | " |
| 90 | 10 | 750 | 64 | -- | -- | ----- | H-$Nb_2O_5$ + 1:2 |
| | | 1000 | 69 | -- | -- | Not melted | 1:13 + TTBs |
| 87.5 | 12.5 | 750 | 69 | -- | -- | ----- | H-$Nb_2O_5$ + 1:2 |
| | | 1000 | 69 | -- | -- | Not melted | 1:13 + TTBs |
| | | | | 1200 | 22 | Not melted | " |
| | | | | 1278 | 72 | Partially melted | " |
| | | | | 1285 | 1 | Partially melted | " |
| | | 800 | 114 | -- | -- | ----- | ----- |
| | | 1225 | 8 | -- | -- | Not melted | 1:13 + TTBs |
| 83.33 | 16.67 | 750 | 64 | -- | -- | ----- | H-$Nb_2O_5$ + 1:2 |
| | | | | 800 | 113 | Not melted | 1:6 + H-$Nb_2O_5$ + TTBs |
| | | | | 880 | 20 | Not melted | TTBs + H-$Nb_2O_5$ + 1:6 |
| | | | | 900 | 18.5 | Not melted | " |
| | | 1000 | 69 | -- | -- | ----- | 1:13 + TTBs |
| | | | | 1200 | 22 | Not melted | " |
| 80 | 20 | 750 | 64 | -- | -- | ----- | H-$Nb_2O_5$ + 1:2 |
| | | | | 800 | 113 | Not melted | 1:6 + H-$Nb_2O_5$ + TTBs |
| | | | | 840 | 70 | Not melted | TTBs + 1:6 + H-$Nb_2O_5$ |
| | | | | 869 | 19 | Not melted | " |
| | | | | 880 | 20 | Not melted | " |
| | | | | 900 | 18.5 | Not melted | " |
| | | | | 1000 | 67 | Not melted | TTBs + 1:13 |
| | | 1000 | 69 | -- | -- | ----- | " |
| | | | | 1200 | 22 | Not melted | " |
| | | | | 1270 | 1 | Not melted | ----- |
| | | | | 1275 | 1.5 | Not melted | ----- |
| | | | | 1278 | 2.5 | Partially melted | ----- |
| 77 | 23 | 870 | 91 | -- | -- | ----- | TTBs + H-$Nb_2O_5$ + 1:2 |
| | | 1100 | 21 | -- | -- | ----- | TTBs + 1:13 |
| | | 1100 | 44 | -- | -- | ----- | TTBs |
| | | | | 1238 | 19 | ----- | " |
| 75 | 25 | 750 | 64 | -- | -- | ----- | H-$Nb_2O_5$ + 1:2 |
| | | | | 800 | 113 | Not melted | 1:6 + TTBs + 1:2 |
| | | | | 980 | 18.5 | Not melted | TTBs |
| | | | | 1000 | 20 | Not melted | " |
| | | 1000 | 69 | -- | -- | Not melted | " |
| | | | | 1200 | 21 | Not melted | " |
| | | | | 1270 | 1 | Not melted | ----- |
| | | | | 1275 | 1.5 | Not melted | ----- |
| | | | | 1278 | 2.5 | Completely melted | ----- |
| | | | | 1280 | 1 | Completely melted | ----- |
| | | 1200 | 21 | 800 | 115 | Not melted | TTBs |
| | | 900 | 62 | -- | -- | ----- | ----- |
| | | 1000 | 96 | -- | -- | Not melted | TTBs |
| | | | | 1225 | 1 | Not melted | " |
| | | | | 1225 | 5 | Not melted | " |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 72.92 | 27.08 | 900 | 19 | -- | -- | ----- | TTBs + 1:2 + H-$Nb_2O_5$ |
| | | 900 | 135 | -- | -- | ----- | TTBs + 1:2 |
| | | | | 950 | 91 | ----- | " |
| | | 1100 | 44 | -- | -- | Not melted | TTBs (+ 1:1 ?) [e] |
| | | | | 1238 | 19 | Not melted | ----- |
| | | | | 1249 | 3.5 | Partially melted | ----- |
| | | | | 1255 | 16.5 | Partially melted | ----- |
| 70 | 30 | 750 | 64 | -- | -- | ----- | 1:2 + 1:1 + H-$Nb_2O_5$ |
| | | 1000 | 69 | -- | -- | Not melted | 1:2 + TTBs (+1:1) [e] |
| | | | | 1000 | 20 | Not melted | " |
| | | | | 1200 | 22 | Not melted | TTBs (+1:1 ?) [e] |
| 66.67 | 33.33 | 800 | 62 | -- | -- | ----- | ----- |
| | | 900 | 93 | -- | -- | Not melted | ----- |
| | | | | 950 | 93 | Not melted | 1:2 |
| | | 800 | 62 | -- | -- | ----- | ----- |
| | | 1100 | 62 | -- | -- | Not melted | TTBs + 1:1 |
| | | | | 975 | 21 | Not melted | 1:2 |
| | | | | 985 | 22 | Not melted | 1:2 (+TTBs + 1:1) trace |
| | | 800 | 89 | -- | -- | ----- | 1:2 |
| | | | | 985 | 45 | Not melted | 1:2 (+1:1 + TTBs) trace |
| | | | | 1000 | 169 | Not melted | TTBs + 1:1 |
| | | | | 1073 | 67 | Not melted | " |
| | | | | 1200 | 21 | Not melted | " |
| 65 | 35 | 750 | 64 | -- | -- | ----- | 1:2 + 1:1 + H-$Nb_2O_5$ |
| | | | | 1241 | 19 | Not melted | ----- |
| | | | | 1254 | 19 | Partially melted | ----- |
| | | 1000 | 69 | -- | -- | Not melted | 1:2 + 1:1 |
| | | | | 1250 | 21 | Partially melted | TTBs + 1:1 (?) |
| 60 | 40 | 750 | 64 | -- | -- | ----- | 1:2 + 1:1 |
| | | | | 1241 | 19 | Not melted | 1:1 + TTBs |
| | | | | 1245 | 65 | Partially melted | ----- |
| | | | | 1254 | 19 | Partially melted | ----- |
| | | 1000 | 69 | -- | -- | Not melted | 1:2 + 1:1 (+TTBs) [e] |
| | | | | 1200 | 21 | Not melted | 1:1 + TTBs |
| | | | | 1250 | 21 | Partially melted | " |
| 55 | 45 | 750 | 64 | -- | -- | ----- | 1:1 + 1:2 |
| | | | | 1241 | 19 | Not melted | 1:1 + TTBs |
| | | | | 1245 | 65 | Partially melted | ----- |
| | | | | 1254 | 19 | Partially melted | ----- |
| | | 1000 | 69 | -- | -- | Not melted | 1:1 + 1:2 |
| 50 | 50 | 750 | 64 | -- | -- | ----- | 1:1 |
| | | 1000 | 69 | -- | -- | Not melted | 1:1 |

[a] For ease and accuracy of weighing $Na_2O$ was added to $Nb_2O_5$ as $NaNbO_3$ not as the oxide end member.

[b] All specimens were initially calcined in Pt crucibles at the indicated temperatures and time.

[c] All subsequent heat treatments were quenched in sealed Pt tubes from the indicated temperature.

[d] All phases identified are given in order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.

H-$Nb_2O_5$ - The high temperature form of $Nb_2O_5$

1:13 - $NaNb_{13}O_{33}$

1:6 - $NaNb_6O_{15}(OH)$. The presence of this phase indicates that the specimen has reacted with atmospheric moisture.

TTBs - A nonstoichiometric solid solution having an orthorhombic distortion of a tetragonal tungsten bronze-type lattice with superstructure indicating a tripled unit cell.

1:2 - $Na_2Nb_4O_{11}$

1:1 - $NaNbO_3$

[e] The presence of a small amount of either 1:1 or TTBs in equilibrium with a large amount of the other cannot be determined because of a complete overlap of all of the strongest peaks.

TABLE 4: EXPERIMENTAL DATA FOR THE SYSTEM $Ta_2O_5$-$NaTaO_3$

| Composition Mole % [a] | | Initial Heat Treatment [b] | | Final Heat Treatment [c] | | Results of Physical Observation | Results of X-Ray Diffraction Analyses [d] |
|---|---|---|---|---|---|---|---|
| | | Temp. °C | Time Hrs. | Temp. °C | Time Hrs. | | |
| $Ta_2O_5$ | $Na_2O$ | | | | | | |
| 95 | 5 | 1000 | 109 | -- | -- | ----- | L-$Ta_2O_5$ + 1:2 |
| | | | | 1328 | 16.00 | Not melted | ----- |
| | | | | 1549 | 16.00 | Not melted | H-$Ta_2O_5$ (tri.) + TTBs |
| | | | | 1648 | 0.08 | Not melted | ----- |
| | | | | 1653 | 0.08 | Partially melted | ----- |
| | | | | 1664 | 0.08 | Partially melted | ----- |
| | | | | 1679 | 0.08 | Partially melted | ----- |
| 83.33 | 16.67 | 1000 | 109 | -- | -- | ----- | ----- |
| | | | | 1328 | 16.00 | Not melted | TTBs + L-$Ta_2O_5$ |
| | | | | 1527 | 16.00 | Not melted | TTBs + L-$Ta_2O_5$ss |
| | | | | 1625 | 41.00 | Not melted | TTBs + H-$Ta_2O_5$ |
| | | | | 1643 | 0.08 | Not melted | ----- |
| | | | | 1658 | 0.08 | Partially melted | ----- |
| | | | | 1670 | 0.08 | Partially melted | ----- |
| 80 | 20 | 1000 | 109 | -- | -- | --- | 1:2 + L-$Ta_2O_5$ |
| | | | | 1195 | 552.00 | No melting | " |
| | | | | 1270 | 360.00 | No melting | TTBs + L-$Ta_2O_5$ |
| | | | | 1329 | 64.00 | No melting | " |
| | | | | 1527 | 16.00 | No melting | TTBs |
| | | | | 1577 | 19.00 | No melting | " |
| | | | | 1623 | 17.00 | No melting | " |
| | | | | 1643 | 0.16 | No melting | ----- |
| | | | | 1654 | 0.16 | Partially melted | ----- |
| | | | | 1660 | 0.08 | Completely melted | ----- |
| | | | | 1670 | 0.08 | Completely melted | ----- |
| | | 1527 | 16 | 1195 | 552.00 | No melting | TTBs + L-$Ta_2O_5$ |
| | | | | 1270 | 360.00 | No melting | " |
| 77.78 | 22.22 | 800 | 112 | -- | -- | ----- | ----- |
| | | | | 1350 | 48.00 | Not melted | TTBs |
| | | | | 1527 | 16.00 | Not melted | ----- |
| | | | | 1642 | 0.16 | Not melted | ----- |
| | | | | 1654 | 0.16 | Completely melted | ----- |
| 75 | 25 | 1000 | 109 | -- | -- | ----- | 1:2 + L-$Ta_2O_5$ |
| | | | | 1195 | 552.00 | Not melted | 1:2 + L-$Ta_2O_5$ + TTBs (tr) |
| | | | | 1270 | 360.00 | Not melted | TTBs + 1:2 |
| | | | | 1329 | 64.00 | Not melted | " |
| | | | | 1527 | 6.00 | Not melted | TTBs |
| | | | | 1613 | 17.00 | Not melted | " |
| | | | | 1643 | 0.25 | Completely melted | ----- |
| | | | | 1722 | 0.08 | Completely melted | ----- |
| | | 1527 | 6 | 1195 | 552.00 | Not melted | TTBs + 1:2 (tr) |
| | | | | 1270 | 360.00 | Not melted | " |
| | | 1722 | 0.08 | 1576 | 16.00 | Not melted | TTBs |
| 70 | 30 | 1000 | 109 | -- | -- | ----- | ----- |
| | | | | 1580 | 64.00 | Not melted | 1:2 + TTBs |
| | | | | 1612 | 0.08 | Not melted | ----- |
| | | | | 1627 | 0.08 | Completely melted | ----- |
| 66.67 | 33.33 | 1000 | 109 | -- | -- | Not melted | 1:2 |
| | | | | 1329 | 64.00 | Not melted | " |
| | | | | 1524 | 7.00 | Not melted | " |
| | | | | 1601 | 1.00 | Not melted | ----- |
| | | | | 1620 | 0.75 | Not melted | ----- |
| | | | | 1633 | 0.08 | Not melted | ----- |
| | | | | 1655 | 0.08 | Completely melted | ----- |
| | | | | 1698 | 0.08 | Completely melted | ----- |
| | | | | 1750 | 0.08 | Completely melted | ----- |
| | | | | 1805 | 0.08 | Completely melted | ----- |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 60 | 40 | 1000 | 109 | -- | -- | ----- | ----- |
| | | | | 1602 | 5.00 | Not melted | 1:2 + 1:1 |
| | | | | 1617 | 0.08 | Not melted | ----- |
| | | | | 1628 | 0.08 | Not melted | ----- |
| | | | | 1632 | 0.08 | Partly melted | ----- |
| | | | | 1664 | 0.08 | Partly melted | ----- |
| | | | | 1685 | 0.08 | Partly melted | ----- |
| | | | | 1690 | 0.08 | Partly melted | ----- |
| | | | | 1722 | 0.08 | Partially melted | ----- |
| | | | | 1737 | 0.08 | Completely melted | ----- |
| 50 | 50 | 600 | 4 | -- | -- | ----- | 1:1 |
| | | | | 1328 | 16.00 | Not melted | ----- |
| | | | | 1527 | 0.50 | Not melted | ----- |
| | | | | 1622 | 0.50 | Not melted | ----- |
| | | | | 1676 | 0.08 | Not melted | ----- |
| | | | | 1782 | 0.08 | Not melted | ----- |
| | | | | 1800 | 0.08 | Not melted | ----- |
| | | | | 1821 | 0.08 | Completely melted | ----- |

a/ For ease and accuracy of weighing $Na_2O$ was added to $Ta_2O_5$ as $NaTaO_3$ not as the oxide end member.

b/ All specimens were initially calcined in Pt crucibles at the indicated temperatures and time.

c/ All subsequent heat treatments below about 1650° were quenched in sealed Pt tubes from the indicated temperatures. Experiment above about 1650° were performed in an inductively heated Ir crucible using sealed 80/20 Pt/Rh tubes.

d/ All phases identified are given in order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.

L-$Ta_2O_5$ - The low temperature polymorph of $Ta_2O_5$
H-$Ta_2O_5$ - The high temperature polymorph of $Ta_2O_5$
ss - Solid solution
tri - Triclinic
tr - Trace
TTBs - A nonstoichiometric solid solution having an orthorhombic distortion of a tetragonal tungsten bronze-type lattice with superstructure indicating a tripled cell.
1:2 - $Na_2Ta_4O_{11}$
1:1 - $NaTaO_3$

TABLE 5: EXPERIMENTAL DATA FOR THE SYSTEM $Nb_2O_5$-$KNbO_3$

| Composition Mole % [a] | | Initial Heat Treatment [b] | | Final Heat Treatment [c] | | Results of Physical Observation | Results of X-Ray Diffraction Analyses [d] |
|---|---|---|---|---|---|---|---|
| | | Temp. °C | Time Hrs. | Temp. °C | Time Hrs. | | |
| $Nb_2O_5$ | $K_2O$ | | | | | | |
| 95 | 5 | 750 | 69 | -- | -- | ----- | H-$Nb_2O_5$ + 1:3 |
| | | 1000 | 69 | -- | -- | No melting | H-$Nb_2O_5$ + TTBs |
| | | | | 1100 | 114 | No melting | " |
| | | | | 1200 | 69 | No melting | " |
| | | | | 1275 | 20 | No melting | H-$Nb_2O_5$ + GTB |
| | | | | 1350 | 20 | Partially melted (?) | " |
| 90.54 | 9.46 | 800 | 62 | -- | -- | ----- | ----- |
| | | 1000 | 96 | -- | -- | No melting | H-$Nb_2O_5$ + TTBs |
| | | | | 1305 | 140 | No melting | GTB (+H-$Nb_2O_5$ ?) |
| | | | | 1315 | 46.5 | Partially melted | H-$Nb_2O_5$ + HTB + ? |
| | | | | 1325 | 17 | Partially melted | H-$Nb_2O_5$ + GTB + HTB + ? |
| 90 | 10 | 750 | 69 | -- | -- | ----- | H-$Nb_2O_5$ + 1:3 |
| | | 1000 | 69 | -- | -- | No melting | TTBs + H-$Nb_2O_5$ |
| | | | | 1100 | 23 | No melting | " |
| | | | | 1200 | 69 | No melting | " |
| | | | | 1250 | 40 | No melting | GTB + H-$Nb_2O_5$ (+TTBs ?) |
| | | | | 1275 | 20 | No melting | GTB + H-$Nb_2O_5$ (trace) |
| | | | | 1290 | 16 | No melting | " |
| | | | | 1350 | 20 | Partially melted | H-$Nb_2O_5$ + GTB + TTBs (?) + HTB (?) |
| | | | | 1360 | 20 | Partially melted | H-$Nb_2O_5$ + TTBs + ? |
| | | | | 1375 | 40 | Partially melted | H-$Nb_2O_5$ + HTB |
| 88.5 | 11.5 | 800 | 62 | -- | -- | ----- | ----- |
| | | 1000 | 96 | -- | -- | No melting | TTBs + H-$Nb_2O_5$ |
| | | | | 1200 | 66 | No melting | TTBs + H-$Nb_2O_5$ |
| | | | | 1300 | 18 | No melting | GTB |
| | | | | 1515 | 1 | Completely melted | ----- |
| | | 1300 | 18 | -- | -- | ----- | GTB |
| | | | | 1190 | 18 | No melting | ----- |
| | | | | 1200 | 18 | No melting | ----- |
| | | | | 1200 | 66 | No melting | GTB |
| | | | | 1210 | 71 | No melting | GTB |
| | | | | 1230 | 71 | No melting | GTB. |
| | | | | 1325 | 17 | Partially melted | TTBs + H-$Nb_2O_5$ + ? |
| | | | | 1335 | 70.5 | Partially melted | ----- |
| | | | | 1350 | 43 | Partially melted | ----- |
| | | 1515 | 1 | -- | -- | Melted | ----- |
| | | | | 1300 | 72 | Not melted | GTB |
| 88 | 12 | 750 | 69 | -- | -- | ----- | H-$Nb_2O_5$ + 1:3 + 1:1 |
| | | 1000 | 69 | -- | -- | No melting | TTBs + H-$Nb_2O_5$ |
| | | | | 1100 | 45 | No melting | " |
| | | | | 1200 | 69 | No melting | " |
| | | | | 1275 | 20 | No melting | GTB + TTBs |
| | | | | 1330 | 18 | Partially melted | GTB |
| | | | | 1335 | 71 | Partially melted | H-$Nb_2O_5$ + HTB + ? |
| | | | | 1350 | 20 | Partially melted | GTB + H-$Nb_2O_5$ (?) |
| | | | | 1360 | 20 | Partially melted | ----- |
| | | | | 1375 | 40 | Partially melted | H-$Nb_2O_5$ + HTB |
| 86 | 14 | 975 | 23 | -- | -- | ----- | H-$Nb_2O_5$ + TTBs + 1:3 |
| | | 1250 | 91 | -- | -- | Not melted | TTBs + GTB |
| | | | | 1275 | 19 | Not melted | ----- |
| | | | | 1310 | 19 | Partially melted (?) | GTB + TTBs |
| | | | | 1332 | 18 | Partially melted | TTBs + H-$Nb_2O_5$ + ? |
| | | | | 1335 | 120 | Partially melted | ----- |
| | | | | 1355 | 125 | Partially melted | ----- |
| | | | | 1515 | 1 | Completely melted | ----- |
| 85 | 15 | 975 | 23 | -- | -- | ----- | H-$Nb_2O_5$ + TTBs + 1:3 + 2:3 hyd. |
| | | 1250 | 91 | -- | -- | Not melted | TTBs + GTB |
| | | | | 1275 | 19 | Not melted | ----- |
| | | | | 1310 | 19 | Partially melted | GTB + TTBs |
| | | | | 1325 | 16 | Partially melted | ----- |
| | | | | 1335 | 19 | Partially melted | H-$Nb_2O_5$ + TTBs + ? |
| | | | | 1335 | 125 | Partially melted | ----- |
| | | | | 1515 | 1 | Completely melted | ----- |
| 84 | 16 | 975 | 23 | -- | -- | ----- | H-$Nb_2O_5$ + TTBs + 1:3 + 2:3 hyd. |
| | | 1250 | 91 | -- | -- | Not melted | TTBs + GTB (?) |
| | | | | 1275 | 19 | Not melted | ----- |
| | | | | 1310 | 19 | Partially melted | GTB + TTBs |
| | | | | 1335 | 19 | Completely melted | ----- |
| | | | | 1515 | 1 | Completely melted | ----- |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 83.66 | 16.34 | 750 | 69 | -- | -- | ----- | ----- |
| | | 1000 | 69 | -- | -- | Not melted | TTBs |
| | | | | 1100 | 114 | Not melted | " |
| | | | | 1176 | 24 | Not melted | " |
| | | | | 1200 | 69 | Not melted | " |
| | | | | 1275 | 21 | Not melted | " |
| | | | | 1279 | 1 | Not melted | ----- |
| | | | | 1285 | 1 | Partially melted | ----- |
| | | | | 1287 | 1 | Partially melted | ----- |
| 82 | 18 | 975 | 16 | -- | -- | ----- | H-$Nb_2O_5$ + TTBs + 1:3 + 2:3 hyd. |
| | | 1250 | 91 | -- | -- | Not melted | ----- |
| | | | | 1275 | 19 | Not melted | ----- |
| | | | | 1335 | 18 | Completely melted | ----- |
| 81.25 | 18.75 | 800 | 62 | -- | -- | ----- | ----- |
| | | 1000 | 96 | -- | -- | Not melted | TTBs |
| | | | | 1225 | 5 | Not melted | " |
| | | | | 1275 | 19 | Partially melted (?) | ----- |
| | | | | 1335 | 18 | Completely melted | TTBs + HTB |
| 80 | 20 | 750 | 69 | -- | -- | ----- | 1:3 + H-$Nb_2O_5$ |
| | | | | 1000 | 69 | Not melted | TTBs + 1:3 + 2:3 |
| | | | | 1100 | 114 | Not melted | TTBs |
| | | | | 1200 | 69 | Not melted | TTBs + 1:3 |
| | | | | 1275 | 21 | Partially melted | TTBs |
| | | | | 1279 | 1 | Completely melted | ----- |
| | | 900 | 24 | -- | -- | ----- | TTBs + 1:3 + H-$Nb_2O_5$ |
| | | 1000 | 59 | -- | -- | ----- | TTBs |
| | | | | 775 | 42 | ----- | " |
| | | | | 800 | 65 | ----- | " |
| | | | | 850 | 40 | ----- | " |
| | | (uncalcined) | | 775 | 42 | ----- | TTBs + 1:3 + H-$Nb_2O_5$ |
| | | | | 800 | 65 | ----- | " |
| | | | | 850 | 40 | ----- | " |
| 77.78 | 22.22 | 800 | 69 | -- | -- | ----- | ----- |
| | | | | 1100 | 45 | ----- | TTBs + 1:3 |
| | | | | 1200 | 69 | Not melted | " |
| 75 | 25 | 750 | 69 | -- | -- | ----- | 1:3 + 2:3 + H-$Nb_2O_5$ |
| | | 1000 | 69 | -- | -- | Not melted | 1:3 + TTB |
| | | | | 1100 | 114 | Not melted | " |
| | | | | 1200 | 69 | Not melted | 1:3 |
| 74 | 26 | 800 | 45 | -- | -- | ----- | ----- |
| | | | | 1000 | 45 | Not melted | 1:3 + 4:9 |
| 73 | 27 | 800 | 45 | -- | -- | ----- | ----- |
| | | | | 1100 | 45 | Not melted | 1:3 + 4:9 |
| 72.2 | 27.8 | 800 | 62 | -- | -- | ----- | ----- |
| | | 1000 | 96 | -- | -- | Not melted | 1:3 + 4:9 |
| 70 | 30 | 750 | 69 | -- | -- | ----- | 4:9 + 1:3 |
| | | 1000 | 69 | -- | -- | Not melted | " |
| | | | | 1100 | 114 | Not melted | ----- |
| 69.23 | 30.77 | 820 | 73 | -- | -- | ----- | ----- |
| | | 1000 | 79 | -- | -- | ----- | ----- |
| | | | | 1100 | 21 | Not melted | 4:9 |
| | | | | 1100 | 45 | Not melted | ----- |
| | | | | 1188 | 43 | Not melted | 4:9 |
| | | | | 1205 | 2 | Not melted | " |
| 68 | 32 | 800 | 45 | -- | -- | ----- | ----- |
| | | | | 1100 | 45 | Not melted | 4:9 + TTB |
| 66.67 | 33.33 | 800 | 89 | -- | -- | ----- | 1:3 + 2:3 |
| | | 1000 | 164 | -- | -- | Not melted | TTB + 4:9 |
| | | | | 975 | 21 | Not melted | TTB + 4:9 |
| | | | | 985 | 45 | Not melted | TTB + 4:9 |
| | | | | 1100 | 114 | Not melted | " |
| | | | | 1195 | 20 | Partially melted | 4:9 |
| 65 | 35 | 750 | 64 | -- | -- | ----- | ----- |
| | | 1000 | 69 | -- | -- | Not melted | TTB |
| | | | | 1100 | 21 | Not melted | TTB |
| | | | | 1195 | 18 | Partially melted | TTB |
| | | | | 1215 | 0.17 | Melted | ----- |
| | | 1398 | 1 | -- | -- | Melted | (?) |
| | | | | 1170 | 2 | Not melted | TTB |
| | | | | 1170 | 19 | Not melted | TTB |
| | | | | 1183 | 19 | Partially melted | TTB + 4:9 + 2:3 hyd. |
| | | | | 1189 | 2 | Partially melted | " |
| | | | | 1191 | 67 | Partially melted | 4:9 + 2:3 hyd. |
| | | 800 | 47 | -- | -- | ----- | ----- |
| | | 1000 | 70 | -- | -- | ----- | TTB |
| | | | | 1125 | 8 | Not melted | TTB |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 63.5 | 36.5 | 800 | 65 | -- | -- | ----- | ----- |
| | | 1000 | 45 | -- | -- | Not melted | TTB + 2:3 hyd. |
| | | | | 1143 | 2 | Not melted | " |
| | | | | 1158 | 1 | Not melted | " |
| | | | | 1165 | 1 | Not melted | ----- |
| | | | | 1170 | 2 | Partially melted | TTB |
| | | | | 1180 | 2 | Partially melted | (?) |
| | | | | 1200 | 0.5 | Melted | TTB |
| 62 | 38 | 800 | 65 | -- | -- | ----- | ----- |
| | | 1000 | 45 | -- | -- | Not melted | 2:3 hyd. + TTB |
| | | | | 1130 | 16 | Not melted | " |
| | | | | 1143 | 2 | Not melted | ----- |
| | | | | 1158 | 1 | Not melted | ----- |
| | | | | 1160 | 1 | Not melted | ----- |
| | | | | 1165 | 1 | Not melted | ----- |
| | | | | 1170 | 2 | Completely melted | ----- |
| | | | | 1180 | 2 | Completely melted | ----- |
| | | | | 1200 | 0.5 | Completely melted | 2:3 + TTB |
| 60 | 40 | 750 | 69 | -- | -- | ----- | 1:3 + 2:3 + 1:1 |
| | | 1000 | 69 | -- | -- | Not melted | 2:3 + 2:3 hyd. |
| | | | | 1000 | 20 | Not melted | 2:3 |
| | | | | 1143 | 2 | Not melted | ----- |
| | | | | 1158 | 1 | Not melted | ----- |
| | | | | 1165 | 1 | Completely melted | ----- |
| | | | | 1170 | 2 | Completely melted | ----- |
| | | | | 1172 | 2 | Completely melted | ----- |
| | | | | 1180 | 2 | Completely melted | ----- |
| 55 | 45 | 750 | 69 | -- | -- | ----- | 1:1 + 1:3 + 2:3 |
| | | 1000 | 69 | -- | -- | Not melted | 1:1 + 2:3 + 2:3 hyd. |
| 53.85 | 46.15 | 750 | 69 | -- | -- | ----- | 1:1 + 2:3 + 1:3 |
| | | 1000 | 69 | -- | -- | Not melted | 1:1 + 2:3 + 2:3 hyd. |
| | | | | 1000 | 20 | Not melted | " |
| | | | | 1100 | 23 | Partially melted | 1:1 + 2:3 |
| 50 | 50 | 750 | 69 | -- | -- | ----- | 1:1 |
| | | 1000 | 69 | -- | -- | Not melted | 1:1 |

a/ For ease and accuracy of weighing $K_2O$ was added to $Nb_2O_5$ as $KNbO_3$ not as the oxide end member.

b/ All specimens were initially calcined in Pt crucibles at the indicated temperatures and time.

c/ All subsequent heat treatments were quenched in sealed Pt tubes from the indicated temperatures.

d/ All phases identified were given in order of amount present at room temperature (greatest amount first). The phases were not necessarily those present at the temperature to which the specimen was heated.

H-$Nb_2O_5$ - The high temperature form of $Nb_2O_5$.

1:3 - $NaNb_3O_8$.

GTB - Gatehouse Tungsten Bronze - A nonstoichiometric solid solution having a large tetragonal unit cell with 7-sided tunnels first described by B. M. Gatehouse for a rubidium niobate of unknown composition.

TTBs - A nonstoichiometric solid solution having an orthorhombic distortion of a tetragonal tungsten bronze-type lattice with superstructure indicating a tripled cell.

4:9 - A compound having the apparent composition $4K_2O{:}9Nb_2O_5$ ($K_8Nb_{18}O_{49}$).

TTB - Tetragonal Tungsten Bronze - A nonstoichiometric solid solution having an undistorted tetragonal lattice with no superstructure.

2:3 - $K_4Nb_6O_{17}$.

2:3 hyd. - The hydrated form of $K_4Nb_6O_{17}$ in equilibrium with atmospheric moisture at room temperature.

1:1 - $KNbO_3$.

HTB - A phase resulting from a quenched liquid with an x-ray pattern resembling a hexagonal tungsten bronze.

? - An unknown phase which apparently results from quenching a liquid.

TABLE 6: EXPERIMENTAL DATA FOR THE SYSTEM $Ta_2O_5$-$KTaO_3$

| Composition Mole % [a] | | Initial Heat Treatment [b] | | Final Heat Treatment [c] | | Results of Physical Observation | Results of X-Ray Diffraction Analyses [d] |
|---|---|---|---|---|---|---|---|
| | | Temp. °C | Time Hrs. | Temp. °C | Time Hrs. | | |
| $Ta_2O_5$ | $K_2O$ | | | | | | |
| 95 | 5 | 1000 | 109 | -- | -- | ----- | L-$Ta_2O_5$ + 1:5 + TTBs |
| | | | | 1337 | 16 | No melting | L-$Ta_2O_5$ + TTBs |
| | | | | 1549 | 16 | No melting | H-$Ta_2O_5$ + GTB |
| | | | | 1602 | 16 | No melting | " |
| 90 | 10 | 900 | 168 | -- | -- | ----- | ----- |
| | | | | 1466 | 168 | No melting | TTBs + L-$Ta_2O_5$ + H-$Ta_2O_5$ |
| | | | | 1500 | 17 | No melting | TTBs + H-$Ta_2O_5$ + L-$Ta_2O_5$ |
| | | | | 1553 | 1.0 | No melting | ----- |
| | | | | 1609 | 17 | No melting | GTB + H-$Ta_2O_5$ (?) |
| | | | | 1715 | 1.5 | Partially melted | ----- |
| | | | | 1747 | 1.5 | Partially melted | HTB + H-$Ta_2O_5$ |
| | | | | 1795 | 1.5 | Partially melted | HTB + H-$Ta_2O_5$ + L-$Ta_2O_5$ |
| | | 1000 | 109 | 1521 | 44 | No melting | ----- |
| | | | | 1601 | 0.75 | No melting | ----- |
| | | | | 1619 | 64 | No melting | GTB + H-$Ta_2O_5$ |
| | | | | 1620 | 16 | No melting | GTB + H-$Ta_2O_5$ |
| | | 1609 | 17 | 1466 | 168 | No melting | GTB + TTBs |
| | | | | 1500 | 17 | No melting | ----- |
| | | | | 1521 | 44 | No melting | ----- |
| | | | | 1624 | 0.17 | No melting | ----- |
| | | | | 1647 | 0.17 | No melting | ----- |
| | | | | 1657 | 0.17 | Partially melted | ----- |
| 89 | 11 | 800 | 115 | -- | -- | ----- | 1:5 + L-$Ta_2O_5$ |
| | | | | 1600 | 12 | No melting | GTB |
| 87.5 | 12.5 | 900 | 216 | -- | -- | ----- | 1:5 + L-$Ta_2O_5$ |
| | | | | 1601 | 17 | No melting | GTB + TTBs |
| | | | | 1640 | 19 | Partially melted | GTB |
| 83.33 | 16.67 | 800 | 192 | -- | -- | ----- | L-$Ta_2O_5$ + 1:2 |
| | | 900 | 168 | -- | -- | ----- | 1:5 |
| | | | | 950 | 360 | No melting | 1:5 + TTBs (tr) |
| | | | | 1100 | 64 | No melting | 1:5 + TTBs + L-$Ta_2O_5$ |
| | | 1000 | 109 | -- | -- | ----- | TTBs + 1:5 + L-$Ta_2O_5$ |
| | | | | 1337 | 16 | ----- | TTBs |
| | | | | 1532 | 16 | ----- | TTBs |
| | | | | 1610 | 16 | ----- | TTBs |
| | | | | 1624 | 0.17 | Not melted | ----- |
| | | | | 1634 | 6.5 | Partially melted | GTB + HTB |
| | | | | 1635 | 0.17 | Partially melted | ----- |
| | | | | 1647 | 0.17 | Partially melted | ----- |
| 80 | 20 | 1000 | 109 | -- | -- | ----- | TTBs + 1:5 |
| | | | | 1337 | 16 | Not melted | TTBs |
| | | | | 1538 | 16 | Not melted | TTBs + 9L |
| | | | | 1614 | 16 | Not melted | HTB + TTBs |
| | | | | 1617 | 16 | Not melted | " |
| | | | | 1618 | 16 | Not melted | " |
| | | 1617 | 16 | 1325 | 168 | Not melted | TTBs |
| | | 1618 | 16 | 1350 | 144 | Not melted | " |
| 78.25 | 21.75 | 800 | 91 | 1600 | 6 | ----- | HTB |
| 77.78 | 22.22 | 900 | 168 | -- | -- | ----- | ----- |
| | | | | 1549 | 1.0 | Not melted | TTBs + 9L + HTB |
| | | | | 1571 | 1.0 | Not melted | ----- |
| | | | | 1575 | 10 | Not melted | ----- |
| | | | | 1581 | 19 | Not melted | HTB |
| | | | | 1602 | 6.5 | Not melted | HTB |
| | | | | 1607 | 0.5 | Not melted | ----- |
| | | | | 1620 | 16 | Partly melted (?) | HTB + 9L |
| | | | | 1632 | 19 | Partly melted | ----- |
| | | 1581 | 19 | 1549 | 19 | Not melted | HTB + TTBs |
| | | 1602 | 6.5 | 1549 | 1.0 | Not melted | ----- |
| | | | | 1571 | 1.0 | Not melted | HTB + TTBs |
| | | | | 1603 | 0.17 | Not melted | ----- |
| | | | | 1613 | 0.17 | Not melted | ----- |
| | | | | 1624 | 0.17 | Partly melted | ----- |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 75 | 25 | 900 | 168 | -- | -- | ----- | 1:2 + 1:5 + TTBs |
| | | | | 1304 | 96 | Not melted | TTBs + TTB |
| | | | | 1340 | 19 | Not melted | ----- |
| | | | | 1579 | 16 | Not melted | 9L + HTB |
| | | | | 1600 | 68 | Not melted | ----- |
| | | | | 1692 | 2 | Completely melted | 11L + HTB |
| | | 1000 | 109 | -- | -- | ----- | TTBs + TTB + 3L |
| | | | | 1100 | 64 | Not melted | TTBs + TTB |
| | | | | 1327 | 120 | Not melted | TTBs + TTB |
| | | | | 1340 | 19 | Not melted | 9L + TTBs |
| | | | | 1340 | 72 | Not melted | " |
| | | | | 1538 | 64 | Not melted | " |
| | | | | 1575 | 10 | Not melted | " |
| | | | | 1598 | 0.5 | Not melted | ----- |
| | | | | 1611 | 5.5 | Not melted | 9L + HTB |
| | | | | 1634 | 16 | Melted | HTB + H-1:3 |
| | | | | 1646 | 1.0 | Melted | " |
| | | 1340 | 72 | -- | -- | ----- | ----- |
| | | | | 1600 | 68 | Not melted | 9L + HTB |
| | | | | 1606 | 16 | Not melted | 9L + HTB |
| | | 1340 | 72 | | | | |
| | | 900 | 1.5 | 1610 | -- | Not melted | 9L + HTB |
| | | 1000 | 109 | | | | |
| | | 1538 | 64 | 1528 | 72 | Not melted | 9L + TTBs |
| | | 1600 | 68 | 1603 | 0.25 | Not melted | ----- |
| | | | | 1613 | 0.25 | Melted | ----- |
| | | | | 1624 | 0.25 | Melted | ----- |
| 73.85 e/ | 26.15 | 1462 | 69 | -- | -- | Not melted | 9L |
| | | | | 1304 | 96 | Not melted | 9L + TTB |
| | | | | 1327 | 120 | Not melted | 9L + TTB |
| | | | | 1603 | 0.17 | Not melted | ----- |
| | | | | 1613 | 0.17 | Partially melted | ----- |
| 73.67 e/ | 26.33 | 1443 | 89 | -- | -- | Not melted | 9L + 16L |
| 73.5 e/ | 26.5 | 1466 | 64 | -- | -- | ----- | 16L + 9L (tr) |
| | | | | 1400 | 48 | Not melted | 16L + 9L + 11L |
| | | | | 1574 | 0.5 | Not melted | ----- |
| | | | | 1574 | 16 | Not melted | 16L |
| | | | | 1586 | 16 | Not melted | ----- |
| | | | | 1594 | 4 | Not melted | ----- |
| | | | | 1603 | 0.17 | Not melted | ----- |
| 72.73 | 27.27 | 1000 | 68 | -- | -- | ----- | ----- |
| | | | | 1361 | 24 | Not melted | 9L + TTB |
| | | | | 1400 | 48 | Not melted | " |
| | | | | 1573 | 0.17 | Not melted | ----- |
| | | | | 1573 | 16 | Not melted | 11L + 16L |
| | | | | 1589 | 0.17 | Not melted | ----- |
| | | | | 1629 | 0.17 | Completely melted | ----- |
| | | | | 1632 | 0.08 | Completely melted | ----- |
| 71.43 | 28.57 | 1000 | 68 | -- | -- | ----- | TTBs + TTB + 1:2 + 1:5 + 3L |
| | | | | 1361 | 24 | Not melted | 9L + TTB |
| | | | | 1438 | 75 | Not melted | 16L + TTB |
| | | | | 1465 | 336 | Not melted | 11L |
| | | | | 1507 | 139 | Not melted | 11L |
| | | | | 1578 | 1.0 | Not melted | ----- |
| | | | | 1583 | 3.5 | Not melted | 11L + TTB |
| | | | | 1591 | 88 | Not melted | 11L |
| | | | | 1611 | 0.08 | Not melted | ----- |
| | | | | 1613 | 0.17 | Not melted | ----- |
| | | | | 1618 | 0.08 | Not melted | ----- |
| | | | | 1618 | 16 | Not melted | ----- |
| | | | | 1624 | 0.08 | Melted | ----- |
| | | | | 1626 | 1.5 | Melted | ----- |
| | | | | 1694 | 1.0 | Melted | 11L |
| | | 1575 | 10 | -- | -- | ----- | 11L + TTB |
| | | 1583 | 3.5 | 1438 | 75 | ----- | 11L + 16L + TTB |
| | | | | 1465 | 336 | ----- | 11L |
| | | | | 1507 | 137 | ----- | 11L |
| 70 | 30 | 1000 | 68 | -- | -- | ----- | ----- |
| | | | | 1361 | 24 | Not melted | TTB + 9L |
| | | | | 1622 | 1.0 | Melted | 11L + TTB (tr) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 66.67 | 33.33 | 800 | 192 | -- | -- | ----- | 1:2 + 1:1 + L-$Ta_2O_5$ |
| | | 900 | 168 | -- | -- | ----- | 1:2 |
| | | | | 950 | 360 | Not melted | " |
| | | | | 1100 | 64 | Not melted | TTB |
| | | 1000 | 109 | -- | -- | ----- | 1:2 + TTB + 3L |
| | | | | 798 | 163 | Not melted | " |
| | | | | 1340 | 19 | Not melted | TTB |
| | | | | 1340 | 72 | Not melted | " |
| | | | | 1515 | 64 | Not melted | TTB + 11L |
| | | | | 1538 | 20 | Partially melted | 11L + TTB |
| | | | | 1616 | 1.0 | Completely melted | 11L + TTB + 9L |
| 66 | 34 | 800 | 90 | 1400 | 10 | Not melted | TTB |
| 65 | 35 | 800 | 112 | -- | -- | ----- | 1:1 + 1:2 + L-$Ta_2O_5$ |
| | | | | 1350 | 66 | Not melted | TTB (+1:1 ?) |
| 60 | 40 | 1000 | 92 | -- | -- | ----- | TTB + 1:1 |
| | | | | 1318 | 64 | Not melted | TTB + 1:1 |
| | | | | 1368 | 0.5 | Not melted | ----- |
| | | | | 1412 | 16 | Partially melted | ----- |
| 55 | 45 | 1000 | 92 | -- | -- | ----- | 1:1 + TTB |
| | | | | 1318 | 64 | Not melted | " |
| | | | | 1368 | 0.5 | Not melted | ----- |
| | | | | 1480 | 18 | Completely melted | ----- |
| 50 | 50 | 600 | 4 | -- | -- | ----- | 1:1 |
| | | | | 1340 | 19 | Not melted | " |
| | | | | 1368 | 0.5 | Not melted | ----- |
| | | | | 1375 | 0.5 | Completely melted | ----- |

a/ For ease and accuracy of weighing $K_2O$ was added to $Ta_2O_5$ as $KtaO_3$ not as the oxide end member.

b/ All specimens were initially calcined in Pt crucibles at the indicated temperature and time.

c/ All subsequent heat treatments were quenched in sealed Pt tubes from the indicated temperatures.

d/ All phases identified are given in order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.

L-$Ta_2O_5$ - The low temperature polymorph of $Ta_2O_5$.
H-$Ta_2O_5$ - The high temperature polymorph of $Ta_2O_5$.
1:5 - $KTa_5O_{13}$ - An orthorhombic compound of undetermined structure.
GTB - Gatehouse Tungsten Bronze - A nonstoichiometric solid solution having a large tetragonal unit cell with 7-sided tunnels first described by B. M. Gatehouse for a rubidium niobate of unknown composition.
TTBs - A nonstoichiometric solid solution having an orthorhombic distortion of a tetragonal tungsten bronze-type lattice with superstructure indicating a tripled cell.
HTB - Hexagonal Tungsten Bronze - A nonstoichiometric solid solution with an x-ray pattern resembling a hexagonal tungsten bronze.
9-L - A hexagonal phase with a c-axis ∿ 9 x 4 Å.
16-L - A hexagonal phase with a c-axis ∿ 16 x 4 Å.
11-L - A hexagonal (rhombohedral) phase with a c-axis ∿ 11 x 4 Å.
3-L - An apparently metastable hexagonal phase with a c-axis ∿ 3 x 4 Å.
1:2 - $K_2Ta_4O_{11}$.
H-1:3 - A monoclinic phase which apparently results from quenching a liquid near the composition $K_2O{:}3Ta_2O_5$.
TTB - Tetragonal Tungsten Bronze - A nonstoichiometric solid solution having an undistorted tetragonal lattice with no superstructure.
1:1 - $KTaO_3$.

e/ Made from the 1000° calcines of the 75:25 and 72.73:27.27 mixtures.

TABLE 7

Summary of LeRC Measurements [a] of Dielectric Loss on Polycrystalline NBS Samples

| Composition | | Frequency, Hz [b] | | | | Resonance [c] |
|---|---|---|---|---|---|---|
| | | $10^3$ | $10^4$ | $10^5$ | $10^6$ | |
| $6Li_2O:17TiO_2$ | ε' | 54 | 30 | 22 | 19 | No Peaks |
| | ε" | 622 | 67 | 9.8 | 1.9 | |
| $K_{1.55}Li_{1.26}(LiTi)O_{16}$ | ε' | 796 | 418 | 225 | 132 | No Peaks |
| | ε" | 401 | 194 | 94 | 43 | |
| $K_{1.6}Mg_{0.8}Ti_{3.8}O_8$ | ε' | 80 | 74 | 71 | 70 | ΔE = 15.1 kcal/mole |
| | ε" | 4.0 | 3.1 | 1.4 | 0.9 | $\rho_{25} = 2.7 \times 10^9$ Ω-cm |
| $5Li_2O:95Ta_2O_5$ [d] | ε' | 64 | 59 | 57 | 58 | No Peaks |
| | ε" | 7 | 2 | 0.7 | 0.3 | |
| $5Li_2O:95Ta_2O_5$ | | --- | --- | --- | --- | No Peaks |
| $Li_{1.8}Ta_{5.8}W_{0.2}O_{16}$ | ε' | 19 | 18 | 18 | 18 | No Peaks |
| | ε" | 0.3 | 0.02 | < 0.002 | 0.05 | |
| $Na_2O:13Nb_2O_5$ | ε' | 20 | 19 | 19 | 19 | No Peaks |
| | ε" | 0.9 | 0.4 | 0.3 | 0.2 | |
| $NaNb_3O_8$ | | --- | --- | --- | --- | No Peaks |
| $Na_{10.8}Nb_{34}W_{1.8}O_{95.6}$ | | --- | --- | --- | --- | ΔE > 10<br>$\rho_{25} \approx 3 \times 10^7$ Ω-cm |
| $21Na_2O:79Ta_2O_5$ | ε' | 22 | 22 | 21 | 21 | No Peaks |
| | ε" | 0.3 | 0.2 | 0.1 | 0.2 | |
| $7K_2O:13Nb_2O_5$ | | --- | --- | --- | --- | Slight Peaks<br>ΔE = 5.6 to 6.8<br>$\rho_{25} \sim 1$ to $5 \times 10^4$ Ωcm |
| $11.5K_2O:88.5Nb_2O_5$ | ε' | 25 | --- | --- | --- | No Peaks |
| | ε" | 5.1 | --- | --- | --- | |
| $3K_2O:13Nb_2O_5$ | | --- | --- | --- | --- | No Peaks |
| $KNb_3O_8$ [e] | ε' | < 100 | < 100 | < 100 | < 100 | No Peaks, two orientations. |
| | ε" | < 2 | < 0.1 | < 0.1 | < 0.1 | |
| $K_4Nb_6O_{17}\cdot XH_2O$ [e] | ε' | 536 | 264 | 102 | 64 | No Peaks, two orientations. |
| | ε" | 854 | 64 | < 1 | < 1 | |
| $11K_2O:89Ta_2O_5$ | ε' | 52 | 43 | 38 | 36 | High Temp. ΔE = 10.3 kcal/mole<br>$\rho_{25} = 2 \times 10^8$ Ω-cm |
| | ε" | 6.1 | 4.7 | 2.6 | 1.1 | Low Temp. ΔE = 8 kcal/mole<br>$\rho_{25} = 1 \times 10^8$ Ω-cm |
| $K_2O:5Ta_2O_5$ | ε' | 18 | 18 | 18 | 18 | No Peaks |
| | ε" | 0.03 | 0.01 | 0.01 | 0.1 | |
| $K_2O:4Ta_2O_5$ | ε' | 22 | --- | 22 | --- | No Peaks |
| | ε" | 0.04 | --- | 0.1 | --- | |
| $21.75K_2O:78.25Ta_2O_5$ | | --- | --- | --- | --- | ΔE = 7.9 kcal/mole<br>$\rho_{25} = 1 \times 10^4$ Ω-cm |
| $34K_2O:66Ta_2O_5$ | | --- | --- | --- | --- | ΔE ≈ 20 to 25 kcal/mole<br>$\rho_{25} = 6 \times 10^{13}$ Ω-cm |
| $K_{0.51}Ta_{0.51}W_{0.49}O_3$ | | --- | --- | --- | --- | No Peaks. |

[a] Measurements made by H. E. Kautz, LeRC.

[b] at 25°C.

[c] Values of ΔE obtained from ε vs temperature measurements.

[d] hot pressed specimen.

[e] Single crystal specimens, supplied by K. Nassau, BTL.

TABLE 8

ALKALI TANTALATE PELLET FABRICATION

| Composition | Calcine | Forming | Sintering | X-Ray |
|---|---|---|---|---|
| 5 $Li_2O$:95 $Ta_2O_5$ | 1000°C - 144 hours | Hot pressed[a] 1200°C | Refire 1500°C 16.5 hours | Low $Ta_2O_5$, crystallinity improved by refiring |
| | | Hot pressed[a] 1300°C | Refire 700°C 18 hours | Low $Ta_2O_5$, crystallinity improved by refiring |
| $Li_2O$:3 $Ta_2O_5$ ($LiTa_3O_8$) | 1000°C - 23 hours 1050°C - 44 hours | 10,000 psi | 1300°C - 22 hours air quenched | Single phase, $LiTa_6O_{15}F$-type |
| "Substituted $LiTa_3O_8$" $Li_{1.8}Ta_{5.8}W_{0.2}O_{16}$ | 1000°C - 23 hours 1050°C - 44 hours | 10,000 psi | 1400°C - 23 hours air quenched | Single phase, $LiTa_6O_{15}F$-type |
| "Tetragonal Bronze" 21 $Na_2O$:79 $Ta_2O_5$ | 1000°C - 23 hours 1050°C - 44 hours | 10,000 psi | 1400°C - 17 hours air quenched | Single phase bronze |
| 11 $K_2O$:89 $Ta_2O_5$ | 800°C - 90 hours | 10,000 psi | 1600°C - 12 hours Removed at temperature and placed on chill block for rapid cooling | Single phase |
| $K_2O$:5 $Ta_2O_5$ | 800°C - 90 hours | 10,000 psi | 1500°C - 20 hours air quenched | Tetragonal bronze |
| $K_2O$:4 $Ta_2O_5$ | 800°C - 90 hours | 10,000 psi | 1400°C - 20 hours air quenched | Tetragonal bronze |
| 21.75 $K_2O$:78.25 $Ta_2O_5$ | 800°C - 91 hours | 10,000 psi | 1600°C - 6 hours Pellet sealed in platinum, welded closed. Removed at temperature and water-quenched | After removal of surface layer by grinding, single phase hexagonal bronze |
| 34 $K_2O$:66 $Ta_2O_5$ | 800°C - 90 hours | 10,000 psi | 1400°C - 10 hours Cooled at 120°C/hour | Single phase |
| $K_{.51}Ta_{.51}W_{.49}O_3$ (Pyrochlore) | 800°C - 34 hours | 10,000 psi | 950°C - 27 hours Removed at temperature and placed in quartz tube, evacuated to $p \leq 10^{-5}$ Torr and sealed to prevent hydration | X-ray of pellet impregnated with silicone resin to prevent hydration showed single phase pyrochlore |

[a] Hot pressing performed by the Haselden Co., San Jose, California.

TABLE 9

ALKALI NIOBATE PELLET FABRICATION

| Composition | Calcine | Forming | Sintering | X-Ray |
|---|---|---|---|---|
| $Li_2O$:14 $Nb_2O_5$ | 1000°C - 18 hours<br>1250°C - 68 hours | 10,000 psi | 1250°C - 12 hours<br>Cooled at 180°C/Hr. | Single phase N-$Nb_2O_5$ after surface grinding |
| $Na_2O$:13 $Nb_2O_5$ | 800°C - 114 hours | 10,000 psi | 1225°C - 8 hours<br>Cooled at 180°C/Hr. | Single phase except for one line of phase next highest in $Na_2O$ content. |
| $NaNb_3O_8$ | 800°C - 62 hours<br>1000°C - 96 hours | 18,000 psi | 1225°C - 1 hour<br>air quenched | Single phase 1:3 |
| $Na_{10.8}(NbO)_4(WO)_{1.8}Nb_{30}O_{90}$ | 800°C - 89 hours<br>1000°C - 70 hours | 18,000 psi | 1225°C - 3 hours<br>air quenched | Single phase, pattern similar to $NaNb_3O_8$ |
| 11.5 $K_2O$:88.5 $Nb_2O_5$ | 800°C - 62 hours<br>1000°C - 96 hours | 18,000 psi | 1300°C - 6.5 hours<br>air quenched.<br>Specimens poorly sintered. Excessive grain growth under all conditions.<br>Hot pressing in progress. | Gatehouse tungsten bronze |
| 3 $K_2O$:13 $Nb_2O_5$ | 800°C - 62 hours<br>1000°C - 96 hours | 18,000 psi | 1225°C - 1 hour<br>air quenched | Tetragonal tungsten bronze with super-structure. |
| 7 $K_2O$:13 $Nb_2O_5$ | 800°C - 47 hours<br>1000°C - 70 hours | 18,000 psi | 1225°C - 1 hour<br>air quenched | Tetragonal tungsten bronze without super-structure. |

TABLE 10

ALKALI TITANATE PELLET FABRICATION

| Composition | Calcine | Forming | Sintering | X-Ray |
|---|---|---|---|---|
| **Ramsdellite**<br>6 $Li_2O$:17 $TiO_2$<br>$[Li_{.8}(Li_{.3}Ti_{1.7})O_4]$ | 9 pbw $6Li_2O$:$17TiO_2$ calcined:<br>800°C - 2.5 Hr.<br>1050°C - 68.5 Hr.<br>1 pbw raw batch,<br>6 $Li_2CO_3$:17 $TiO_2$ | 10,000 psi | 1200°C - 17 hours air quenched. | Single phase Ramsdellite |
| $K_2O$:MgO:4 $TiO_2$<br>$[K_{1.6}(Mg_{.8}Ti_{3.2})O_8]$ | 800°C - 18 hours<br>1000°C - 24 hours | 10,000 psi<br>0.5 percent by weight stearic acid as binder. | 1200°C - 13 hours air quenched | Single phase, "Cmcm-phase" |

TABLE 11

Summary of Crystal Growth Experiments

| System | Phase | Melt Composition | Method | Comments |
|---|---|---|---|---|
| $K_2O$-$Nb_2O_5$ | 7:13 (TTB) | 36.5$K_2O$:63.5$Nb_2O_5$ | TSSG* | Yield: 4:9 → small amount 7:13 → 2:3 |
| | 17.5:82.5 (TTBs) | 17.5$K_2O$:82.5$Nb_2O_5$ | TSSG | Yield: polycrystalline multiphase |
| | 17.5:82.5 (TTBs) | 20.0$K_2O$:80.0$Nb_2O_5$ | TSSG | Yield: polycrystalline TTB |
| | 12.5:81.5 (GTB) | 15.0$K_2O$:85.0$Nb_2O_5$ | TSSG | Yield: $Nb_2O_5$ |
| $K_2O$-$Ta_2O_5$ | 1:2 (TTB) | 45$K_2O$:55$Ta_2O_5$ | TSSG | Yield: single phase |
| $Li_2O$-$Ta_2O_5$ | 1:3 | 25$Li_2O$:75$Ta_2O_5$ | Czochralski | Yield: single crystals |
| | 5:95 (L-$Ta_2O_5$) | 15$Li_2O$:85$Ta_2O_5$ | TSSG | Yield: single crystals |
| $Na_2O$-$Nb_2O_5$ | 1:3 (TTBs) | 25$Na_2O$:75$Nb_2O_5$ | Czochralski | Yield: single crystals |
| $Na_2O$-$Ta_2O_5$ | 21:79 (TTBs) | 25$Na_2O$:75$Ta_2O_5$ | Czochralski | Excessive vaporization of $Na_2O$ |

* Top seeded solution growth.

**TABLE 12**

**Crystallographic Data for Phases in the $Nb_2O_5$-Alkali Niobate and $Ta_2O_5$-Alkali Tantalate Systems**

| System | Designation | Composition Mol % | | Symmetry | Unit Cell Dimensions a Å | b Å | c Å | α | β | γ | Conditions Limiting Possible Reflections | Probable Space Groups |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Nb_2O_5$-$LiNbO_3$ | | $Nb_2O_5$ | $Li_2O$ | | | | | | | | | |
| | N-$Nb_2O_5$ | 93.33 | 6.67 | Monoclinic | 25.518 | 3.827 | 17.554 | --- | 124°59.1' | --- | hkℓ:h+k=2n | C2,Cm,C2/m |
| | 1:3 | 75 | 25 | Monoclinic | 7.457 | 5.035 | 15.264 | --- | 107°18.7' | --- | h0ℓ:ℓ=2n<br>0k0:k=2n | $P2_1/c$ |
| $Ta_2O_5$-$LiTaO_3$ | | $Ta_2O_5$ | $Li_2O$ | | | | | | | | | |
| | L-$Ta_2O_5$ss | 95 | 5 | Orthorhombic | 6.198 | 40.29 | 3.888 | --- | --- | --- | None | pm,pg [1] |
| | L-1:3 | 75 | 25 | Monoclinic | 7.41 | 5.10 | 15.12 | --- | 107°12' | --- | h0ℓ:ℓ=2n<br>0k0:k=2n | $P2_1/c$ |
| | M-1:3 | 75 | 25 | Monoclinic | 9.420 | 11.536 | 5.055 | --- | 91°32' | --- | hkℓ:h+k=2n<br>h0ℓ:ℓ=2n | Cc,C2/c |
| | H-1:3 | 75 | 25 | Orthorhombic | 16.716 | 8.941 | 3.840 | --- | --- | --- | 0kℓ:ℓ=2n | Pnma,$P2_1$ma,<br>Pm2a |
| $Nb_2O_5$-$NaNbO_3$ | | $Nb_2O_5$ | $Na_2O$ | | | | | | | | | |
| | 1:13 | 92.86 | 7.14 | Monoclinic | 22.40 | 3.834 | 15.37 | --- | 91°28.2' | --- | hkℓ:h+k=2n | C2,Cm,C2/m |
| | 1:6** | 80 | 20 | Orthorhombic | ∿14.7 | ∿10.2 | ∿3.9 | --- | --- | --- | hkℓ:h+k=2n | C222,Cm2m,<br>Cmm2,Cmmm |
| | TTBs | 75 | 25 | Orthorhombic | 12.364 | 36.992 | 3.955 | --- | --- | --- | 0kℓ:k=2n<br>h0ℓ:h=2n | Pbam,$Pba2_1$ |
| | 1:2 | 66.67 | 33.33 | Monoclinic | 10.840 | 6.162 | 12.745 | --- | 106°13.2' | --- | hkℓ:h+k=2n<br>h0ℓ:ℓ=2n | Cc,C2/c |
| $Ta_2O_5$-$NaTaO_3$ | | $Ta_2O_5$ | $Na_2O$ | | | | | | | | | |
| | TTBs | 80 | 20 | Orthorhombic | 12.397 | 37.34 | 3.903 | --- | --- | --- | h0ℓ:h=2n | Pnam,$P2_1$am,<br>Pma2 |
| | TTBs | 75 | 25 | Orthorhombic | 12.398 | 37.28 | 3.899 | --- | --- | --- | h0ℓ:h=2n | " " |
| | 1:2 | 66.67 | 33.33 | Hexagonal | 6.120 | --- | 36.629 | --- | --- | --- | hkℓ:-h+k+ℓ=3n<br>h0ℓ:ℓ=2n | R3c,$R\bar{3}c$ |
| $Nb_2O_5$-$KNbO_3$ | | $Nb_2O_5$ | $K_2O$ | | | | | | | | | |
| | GTB | 88.5 | 11.5 | Tetragonal | 27.518 | --- | 3.9687 | --- | --- | --- | h00:h=2n | $P42_12$,$P42_1m$ |
| | TTBs | 83.33 | 16.67 | Orthorhombic | 12.519 | 37.558 | 3.952 | --- | --- | --- | h0ℓ:h=2n | Pnam,$P2_1$am,<br>Pma2 |
| | TTBs | 80 | 20 | Orthorhombic | 12.545 | 37.636 | 3.957 | --- | --- | --- | " | " " |
| | HTB | Unknown* | | Hexagonal | 7.511 | --- | 3.889 | --- | --- | --- | None | P6/mmm |
| | 1:3 | 75 | 25 | Orthorhombic | 8.925 | 21.232 | 3.808 | --- | --- | --- | hkℓ:k+ℓ=2n<br>h0ℓ:h=2n | Amam,$A2_1$am,<br>Ama2 |
| | 4:9 | 69.23 | 30.77 | Triclinic | 13.353 | 13.915 | 15.022 | 82°11.8' | 69°42' | 89°4.3' | None | $P_1$,$P\bar{1}$ |
| | TTB | 65 | 35 | Tetragonal | 12.589 | --- | 3.981 | --- | --- | --- | h0ℓ:h=2n | Pnam,$P2_1$am,<br>Pma2 |
| | 2:3 | 60 | 40 | Orthorhombic | 7.822 | 33.019 | 6.481 | --- | --- | --- | h0ℓ:h+ℓ=2n<br>hk0:k=2n | Pmnb,$P2_1$nb |
| | 2:3 hyd. | 60 | 40 | Orthorhombic | 7.824 | 38.073 | 6.485 | --- | --- | --- | h00:h=2n<br>0k0:k=2n<br>00ℓ:ℓ=2n | $P2_12_12_1$ |
| $Ta_2O_5$-$KTaO_3$ | | $Ta_2O_5$ | $K_2O$ | | | | | | | | | |
| | GTB | 88.5 | 11.5 | Tetragonal | 27.55 | --- | 3.899 | --- | --- | --- | h00:h=2n | $P42_12$,<br>$P42_1m$ |
| | 1:5 | 83.33 | 16.67 | Orthorhombic | 5.654 | 10.713 | 16.80 | --- | --- | --- | h0ℓ:ℓ=2n<br>0kℓ:k=2n | Pbcm,$Pbc2_1$ |
| | TTBs | 80 | 20 | Orthorhombic | 12.547 | 37.641 | 3.922 | --- | --- | --- | h0ℓ:h=2n | Pnam,$P2_1$am,<br>Pma2 |
| | HTB | 78.25 | 21.75 | Hexagonal | 7.527 | --- | 3.901 | --- | --- | --- | None | P6/mmm |
| | 9L | 73.85 | 26.15 | Hexagonal | 7.55 | --- | 36.583 | --- | --- | --- | hhℓ:ℓ=2n | $P6_3mc$,$P\bar{6}2c$,<br>$P6_3/mmc$ |
| | 16L | 73.5 | 26.5 | Hexagonal | 7.542 | --- | 65.57 | --- | --- | --- | hhℓ:ℓ=2n | " " |
| | 11L | 71.43 | 28.57 | Hexagonal | 7.54 | --- | 43.512 | --- | --- | --- | hkℓ:-h+k+ℓ=3n | R3,$R\bar{3}$,R32,<br>R3m,$R\bar{3}$m |
| | 1:2 | 66.67 | 33.33 | Hexagonal | 6.283 | --- | 36.878 | --- | --- | --- | hkℓ:-h+k+ℓ=3n | " " |
| | TTB | 66 | 34 | Tetragonal | 12.569 | --- | 3.957 | --- | --- | --- | h0ℓ:h=2n | Pnam,$P2_1$am,<br>Pma2 |
| | 3L* | 75 | 25 | Hexagonal | 9.051 | --- | 12.284 | --- | --- | --- | h0ℓ:ℓ=2n | $P6_3cm$,$P\bar{6}c2$,<br>$P6_3/mcm$ |
| | H-1:3* | 75 | 25 | Monoclinic | 14.615 | 3.774 | 6.557 | --- | 98°30' | --- | None | P2,Pm,P2/m |

[1] Two dimensional plane groups.

* Metastable phase obtained from quenched liquid.

** Probably due to reaction with atmospheric moisture-$NaNb_6O_{16}(OH)$.