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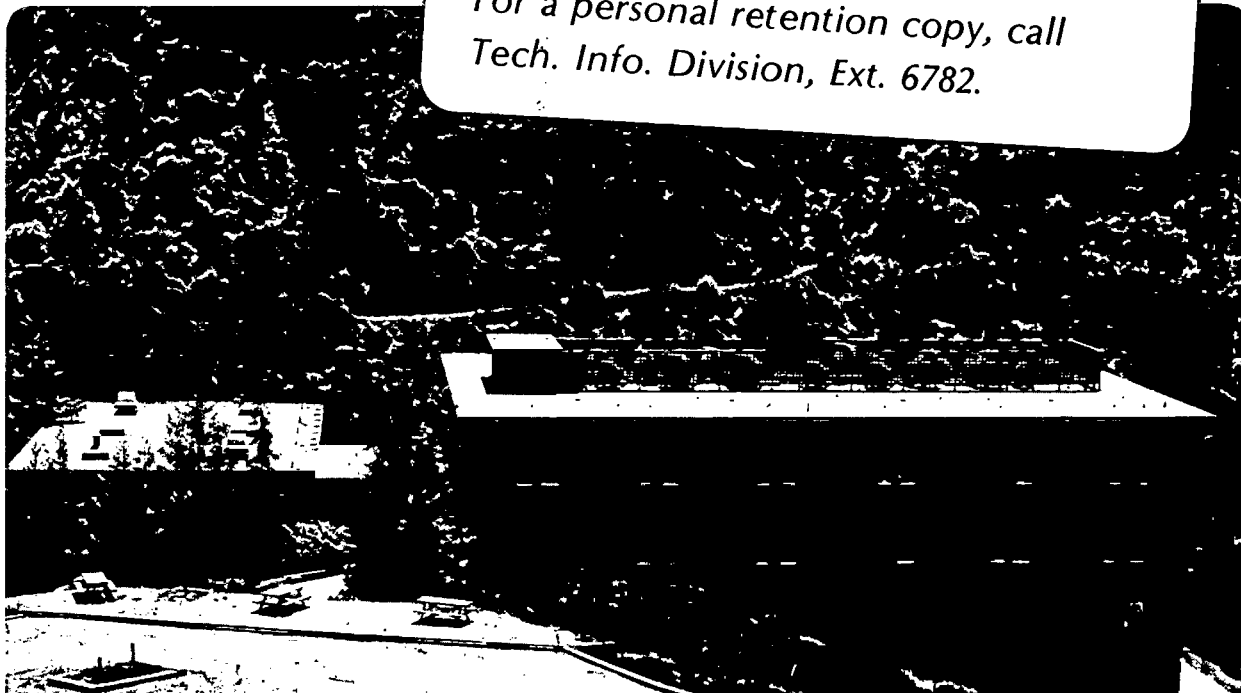## UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

# REACTION MECHANISMS IN THE FORMATION OF PZT SOLID SOLUTIONS

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# REACTION MECHANISMS IN THE FORMATION OF PZT SOLID SOLUTIONS

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## ABSTRACT

The solid-state reactions occurring in the $PbO-TiO_2-ZrO_2$ system were investigated using constant heating rates up to $1000°C$. DTA, dilatometric length changes, and X-ray diffraction analysis were used for characterization.  PbO and $TiO_2$ reacted exothermally to form the product $PbTiO_3$ with a large volume expansion between 450 and $600°C$.  Formation of $PbZrO_3$ from PbO and $ZrO_2$ occurred endothermally with a large volume expansion between $700-800°C$.  The expansion was due to reaction topology, differential molar volumes of products and reactants and the pellet microstructure.  In the formation of PZT from ternary powder mixtures, PT formed between 450 and $600°C$ followed by PZT formation above $700°C$ with no measurable amounts of $PbZrO_3$ formed as determined by XRD analysis.  The analysis of the mechanisms indicate that the overall kinetics of homogeneous PZT solid

solution formation are determined by either the ionic transport within the perovskite lattice or the phase boundary reactions leading to perovskite formation and not by the diffusion of Ti across PbO which is relatively rapid.

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## I. INTRODUCTION

The $PbZrO_3$-$PbTiO_3$ (PZ-PT) solid solution system exhibits many
desirable electrical properties such as pronounced
ferroelectric-piezoelectric behavior and high Curie temperatures.
Investigations have been conducted to control stoichiometry
and to study the effect of impurities and dopants on
the final properties and microstructure. It has been well
documented that the fabrication process determines to a
significant extent the electrical properties such as dielectric
constant, loss factor, coupling coefficients, etc. Using
available data, ceramic bodies in the PZT system can be sintered
to high densities by proper selection of a composition and
suitable control of ambient PbO vapor pressure. Phenomena
involved in the process of calcination, on the other hand, have
not yet been fully understood though their importance has been
noted. (1,2)

The reaction sequence through which PZT solid solutions are
formed by solid state reactions in a mixture of $PbO$-$TiO_2$-$ZrO_2$ has
been investigated by many workers but with differing conclusions.
Matsuo and Sasaki (3), Gesemann and Neels (4) and Harris (5) did
not observe formation of $PbZrO_3$ as an intermediate phase while
Ohno et.al.(6) reported that PZT solid solution was synthesized
after formation of both $PbTiO_3$ and $PbZrO_3$. Mori et.al.(7) re-
ported formation of PZ as an intermediate phase only when the

$ZrO_2$ content of the mixture exceeded 60 mole %. Similarly Yamaguchi et.al.(8) found that a ball milled oxide mixture showed no presence of PZ as an intermediate phase, while precipitation mixing resulted in PZ formation. None of the authors have provided a systematic discussion of the atomistic processes involved in the solid state reactions. Also, the thermodynamic heat effects associated with the formation of various compounds have not been clear. Whereas Speri (9) reported an endothermic heat effect associated with $PbTiO_3$ formation, others (5,7) observed an exothermic reaction. Moreover, the temperature and time range over which various reactions were observed differ considerably in various reports. The present study was undertaken to investigate the reaction sequence and the temperature range for each reaction step under constant heating rate conditions using DTA, dilatometry and X-ray diffraction analysis.

## II. EXPERIMENTAL PROCEDURES

Preparation of Powder Mixtures

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Lead monoxide used for the mixtures was reagent grade Massicot (PbO) with less than (0.5%) impurity content. Anatase ($TiO_2$) of 99.9% purity and reactor grade unstabilized baddeleyite (monoclinic) with hafnium content less than 0.2% were used. The volatile content as measured by weight loss up to $500^\circ C$ was less than 1% for all of the powders. Average particle size as

measured by Fisher subsieve sizer and specific surface area as measured by three point BET apparatus using nitrogen as an adsorbant were 0.7 micron and 1.5 $m^2/g$ for PbO, 0.6 micron and 10.7 $m^2/g$ for $TiO_2$, and 1.7 micron and 14.1 $m^2/g$ for $ZrO_2$. SEM photographs indicated that the $TiO_2$ and $ZrO_2$ powders were agglomerated with the crystallite size much smaller than the particle size. Five compositions chosen for the study are shown in Table I. Powders were mixed in stoichiometric ratios in a vibratory mill for two hours with $ZrO_2$ grinding media in isopropyl alcohol. The mixture slurries were dried at $80^{o}C$.

To study the effect of the crystal structure of $TiO_2$ on lead titanate formation, rutile was substituted for anatase. Rutile was obtained by quenching anatase heated at $1100^{o}C$ for 48 hours. To study the effect of monoclinic to cubic transformation of $ZrO_2$ on the reaction temperature, calcia-stabilized-zirconia (CSZ) was prepared (15 wt% CaO) and mixed with PbO.

Differential Thermal Analysis

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A multi-sample nickel block was used with cells 9.5 mm in diameter and 16.5 mm in depth. The sample reference temperature was assumed to be the same as the block temperature. DTA runs using Pt-Pt 10% Rh thermocouples were made up to $1000^{o}C$; some runs were terminated at intermediate temperatures by rapid cooling in order to identify the phases at those temperatures. Samples were

removed, crushed to -200 mesh in a mortar and subjected to
qualitative X-ray analysis.  A scanning rate of 1 degree/min was
used with Cu(Kα) radiation and a graphite monochromator.

Dilatometric Measurements

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A fused quartz tube and rod assembly with a LVDT attachment was
used for dilatometric measurements.   Samples 6.4 mm in diameter
and 19 mm in length were prepared by isostatically pressing the
powder mixtures in a latex rubber tube up to 2.1 x $10^8$ N/m$^2$.  A
thin platinum foil was then wrapped around the sample to avoid
any direct contact between sample and the fused quartz sample
holder.  Temperature was monitored by a chromel-alumel thermo-
couple placed close to the sample.  The following heating rates
were used:   3.2, 5.6, and 8.2$^o$C/min.  As with DTA, many dilato-
metric runs were terminated at temperatures below 1000$^o$C
in order to identify the phases present in the quenched
samples.

## III.   RESULTS AND DISCUSSION

The DTA thermograms for compositions V, IV and II are shown in
Fig. 1.  The curves for compositions I and III were similar to
that for II.  The PT formation starts at about 450$^o$C and is
exothermic in nature.  X-ray diffraction analysis of quenched
samples indicated that formation of PT was complete at about 600$^o$

C even at rapid heating rates. When rutile was used instead of anatase, the reaction was also exothermic and ranged from 450 to 650°C indicating no significant effect of the $TiO_2$ crystal structure on the nature of the reaction. As seen in Fig. 1, formation of PZ is endothermic and begins at about 700°C. Patterns with $ZrO_2$ supplied by two different manufacturers gave similar results. The DTA trace of the ternary composition II shows an exothermic peak starting at about 450°C and an endothermic peak starting at about 725°C. The pattern is essentially a composite of the two binary mixtures.

It is known that a phase transformation in one of the reactants can alter the kinetics and thermodynamics of solid-state reactions (Hedval effect). To determine if the monoclinic to cubic transformation of $ZrO_2$ usually observed at about 1000°C has any effect on the formation of PZ, cubic CSZ was substituted for baddeleyite. The DTA pattern up to 900°C of the PbO + CSZ mixture was similar to that of the PbO + $ZrO_2$ mixture, and an XRD pattern indicated the formation of a $PbZrO_3$-$CaZrO_3$ solid solution. To check if the formation of a PZ surface layer of crystallites on monoclinic $ZrO_2$ catalyzes the martensitic transformation to cubic $ZrO_2$, a mixture of 10 mole % PbO with baddeleyite was subjected to DTA and XRD. The DTA pattern did not show any peak in addition to that for PZ formation. It can be concluded that up to 900°C the structural transformation of $ZrO_2$ is not promoted by PZ formation and that the substitution of CSZ for monoclinic $ZrO_2$

has no detectable effect on the PZ formation. The observed endo-
thermic heat effect must thus be associated solely with the
chemical reaction between $ZrO_2$ and PbO.

From the thermodynamic principle of successive entropy states,
reversible reactions are characterized by an endothermic heat
effect while irreversible reactions exhibit an exothermic effect
on increase in temperature. Therefore, the endothermic formation
of PZ suggests reversibility of reaction at an as yet undeter-
mined equilibrium temperature below $700^\circ C$. Exothermic
synthesis of lead titanate on the other hand points out to
irreversibility of the reaction.

It has been reported (10) that in the formation of PT, PbO is
transported to the $TiO_2$ particles where the reaction proceeds at
the interface. If vapor pressure data (11) for PbO are extra-
polated to $500^\circ C$, calculations show that the vapor pressure
will be $1.5 \times 10^{-9}$ atm. This value suggests that at the
lower temperatures the reaction starts at the contact points and
that surface diffusion of PbO probably plays the major transport
role.

The thermal expansion curves for mixtures V, IV and II obtained
at a heating rate of $8.2^\circ C/min$ are shown in Figure 2. Curves for
heating rates of 3.2 and $5.6^\circ C/min$ were essentially the same. A
P+T mixture shows normal volume expansion up to about $450^\circ C$, fol-

lowed by a sharp volume increase up to about 600°C and rapid

shrinkage with further heating. This temperature range

corresponds to the exothermic peak on the DTA curve. The expan-

sion behavior of the P+Z mixture also shows a large volume expan-

sion beginning at about 700°C followed by shrinkage at tempera-

tures above 800°C. This temperature range corresponds to the

endothermic peak on the DTA curve and was associated with the

formation of PZ. The curve for the ternary mixture is

essentially a composite of the curves for the binary mixtures.

Changes in ($ZrO_2$ / $TiO_2$) ratio in the ternary compositions only

changed the extent of expansion during each of the two reactions.


Theoretical calculations of volume changes due to the solid state

reactions can be made. Since PbO is the mobile species, it can

be assumed that PT forms as a 'shell' on the particles of $TiO_2$.

Based on X-ray density values, molar volumes of PT and anatase

are 37.8 and 20.8 $cm^3$, respectively. Therefore, if a dense sphe-

rical single particle of $TiO_2$ is completely converted to a dense

particle of PT, the radius of the resulting PT particle will be

22% larger than the parent anatase particle. If primarily the

$TiO_2$ particles form a skeletal structure in the original PbO+$TiO_2$

mixture with PbO packed into the interstices, the large radial

expansion of $TiO_2$ particles can be expected to be translated into

an overall expansion of the pellet. The actual amount of pellet

expansion may in addition be affected by the external load and

ability of the particulate matrix to accomodate rearrangement. A

similar analysis applied to the formation of PZ indicates a radial expansion of 25% on complete conversion of a dense spherical particle of baddeleyite to $PbZrO_3$. The smaller expansion observed experimentally than for PT formation may be due to a lesser effective skeletal structure becasue of the smaller $ZrO_2$ molar volume than for $TiO_2$.

The reaction sequence for the formation of PZT solid solution has not been clear. Previous publications (3-8) have differed on whether the PT, which forms first, reacts directly with PbO and $ZrO_2$ without the formation of PZ as an identifiable intermediate product, or with PZ that forms from PbO and $ZrO_2$. Samples of ternary mixtures with $ZrO_2/TiO_2=65/35$ were subjected to XRD analysis after quenching from several temperatures (Fig. 3). Specimens quenched from 580$^{\circ}$C and 655$^{\circ}$C showed peaks for PT but no detectable peaks for PZ or PZT. At 715$^{\circ}$C features appeared in the pattern which can be interpreted as reflecting the initial formation of PZT solid solution. Formation of PZT solid solution is virtually complete by 785$^{\circ}$C. No peaks attributable to PZ alone were observed indicating that significant amounts of PZ were not formed. However, formation of small amounts of PZ can not be ruled out due to difficulty in interpretation of the X-ray patterns. Above the Curie temperatures, PT and PZ form a continuous solid solution of cubic structure. On cooling to room temperature, the solid solutions can exist in one of three structures: tetragonal, rhombohedral or othorhombic depending on the

Zr/Ti ratio (12). As a result, XRD patterns are complex involving overlaps and shifts of peaks due to solid solution formation. Nevertheless, the XRD analysis rules out the PZT formation based primarily on the initial formation of PT and PZ in large amounts followed by slow interdiffusion of $Ti^{4+}$ and $Zr^{4+}$ to form PZT. The DTA and thermal expansion data support the XRD data that PT is formed first and with increasing temperature $ZrO_2$ takes part in the reaction. The three reactants PbO, $ZrO_2$, and PT then form a reactive system in which the perovskite formation can proceed at two interfaces, $ZrO_2$/PbO and $ZrO_2$/PT, as schematically shown in Figure 4.

Assuming that oxygen does not diffuse over a long range and the charge balance in solid solution formation is achieved by proper interdiffusive fluxes of cations, following critical factors should be noted:

(i)     A $Ti^{4+}$ gradient exists in PbO from Ti saturated PT/PbO interface to its interface with the perovskite providing a driving force for $Ti^{4+}$ transport across PbO. The ratio Zr/Ti in the perovskite formed will be determined by the rapidity of such transport.

(ii)    The initially formed PT phase in contact with PbO and $ZrO_2$ continues to grow as PZT at the expense

of these reactants probably with a lower Zr/Ti

ratio.

(iii)    A net gradient of quadrivalent ions exists from

$ZrO_2$ to PbO in perovskite products forming at

both the original interfaces as long as the

reaction continues, as shown in Fig. 4.   A flux

of $Pb^{2+}$ exists in the opposite direction.


(iv)    Interdiffusion of $Ti^{4+}$ and $Zr^{4+}$ within and

between the PZT phases forming at the original

$PbO/ZrO_2$ and $PT/ZrO_2$ interfaces results in an

overall PZT of homogeneous composition.


As evident from PZT formation at the $PbO/ZrO_2$ interface, titanium

transport through PbO is relatively rapid and does not form the

rate limiting step in the overall formation of a homogeneous PZT

solid solution.   The rate limiting mechanism must therefore be

associated with the ionic transport across the perovskite or the

phase boundary reactions at the perovskite interfaces, as evident

from the nature of reaction sequences with the increasing

temperature.


In the above discussion, it was implicitly assumed that the

contact between the reactants at various interfaces was ideal.

Discrepancies in the reaction mechanisms observed by various

authors (3-8) may be attributed to the different experimental

conditions to the extent that processing operations like mixing,
particulate characteristics and the volume fractions of the
reactants determine ideality of an experimental set-up.

## IV. CONCLUSIONS

Formation of PT begins at about $450^{\circ}$C and finishes at about
$600^{\circ}$C, is exothermic in nature suggesting irreversibility, and
is accompanied by a large volume expansion. Since the vapor
pressure of PbO at these temperatures is low, mass transport of
PbO to the $TiO_2$ particle surfaces is believed to be due to
surface diffusion. Formation of PZ begins at about $700^{\circ}$C and is
almost complete at about $800^{\circ}$C also accompanied by a large volume
increase. The reaction is endothermic and hence theoretically
reversible at some undetermined equilibrium temperature below
$700^{\circ}$C.

The large volume increases during the formation of the binary
compounds can be attributed to (a) the relative specific molar
volumes of reactants $TiO_2$ and $ZrO_2$ and the products and (b) the
topology of reaction whereby the product layer is formed on the
surface of the reactants $TiO_2$ and $ZrO_2$, and (c) the particulate
packing is such that $TiO_2$ and $ZrO_2$ form a skeletal structure.

In the ternary mixture of PbO + $ZrO_2$ + $TiO_2$ the DTA and the dila-
tometric data are a composite of the data for the binary mixtures

of P+Z and P+T. In the formation of PZT solid solution, PT forms
first or most rapidly. The formation of PZT is believed to occur
by a coupled reactive exchange of 2 $Pb^{2+}$ and $Zr^{4+}$ at the $PT/ZrO_2$
and 2 $Pb^{2+}$ and $Ti^{4+}$ at the PbO/PT interfaces followed by counter-
diffusion of $Zr^{4+}$ and $Ti^{4+}$ within the perovskite lattice. Simi-
larly, the reaction at $PbO/ZrO_2$ contact points proceeds by the
exchange of $2Pb^{2+}$ and $Zr^{4+}$. This is followed by interdiffusion
of quadrivalent cations within the product where transport of Ti
across PbO to the PbO/PZT interface forms a source of Ti.
The diffusion of Ti across PbO was rapid enough that no sign-
ificant peaks of PZ were detected in X-ray diffraction analysis.
Thus, the rate determining step in the overall kinetics of homo-
geneous PZT solid solution formation appears to be the ionic
transport within the perovskite lattice or the phase boundary
reactions leading to perovskite formation at $PT/ZrO_2$ as well as
$PbO/ZrO_2$ interfaces. The DTA and dilatometry data support the
proposed mechanism on the basis that the positions of endothermic
and expansion peaks for binary P+Z and ternary P+Z+T mixtures are
the same.

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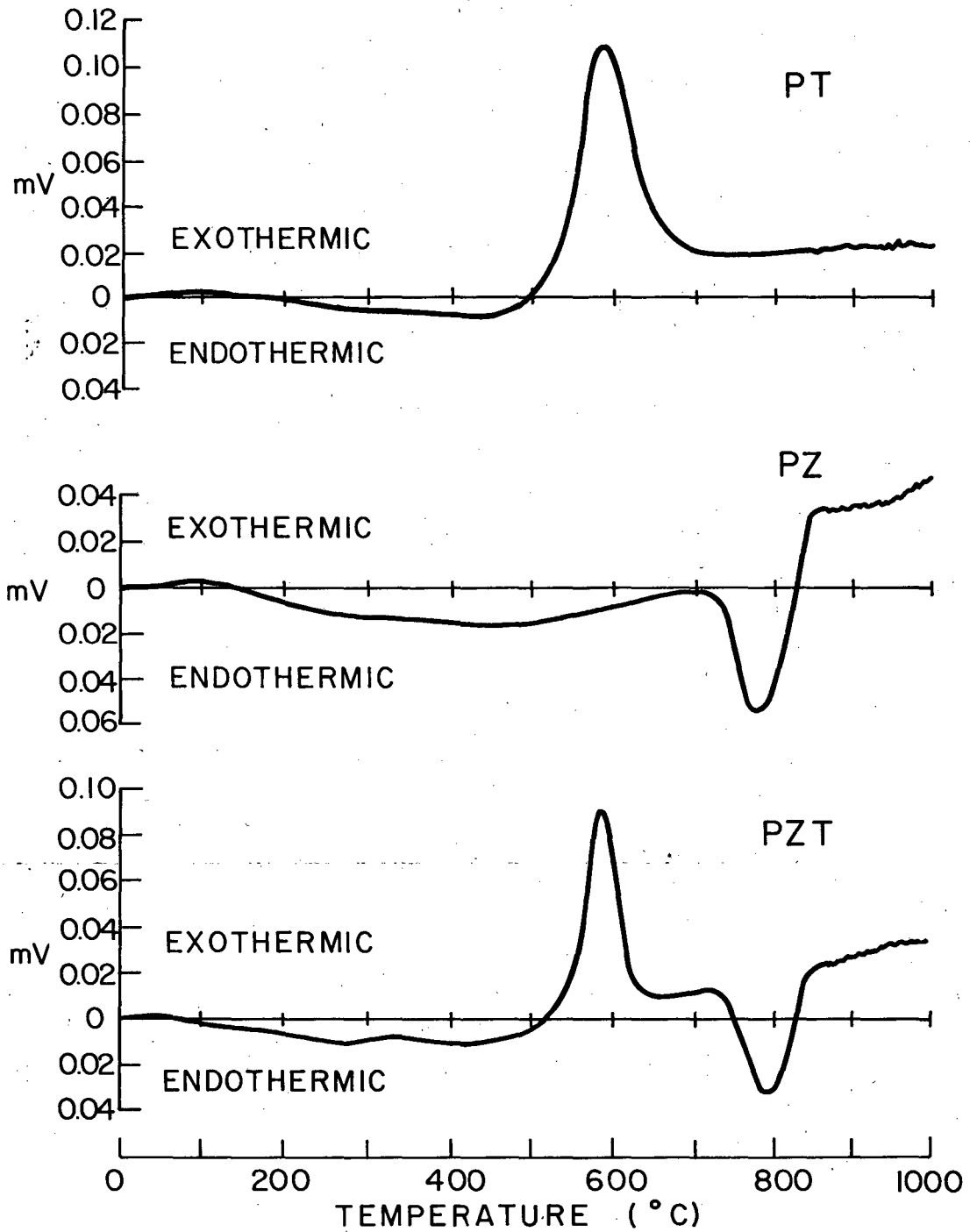12. E. Sawaguchi, J. Phy. Soc. Japan, 8, pp. 615 (1953).

Table I.  Experimental Compositions from $PbTiO_3$-$PbZrO_3$ System

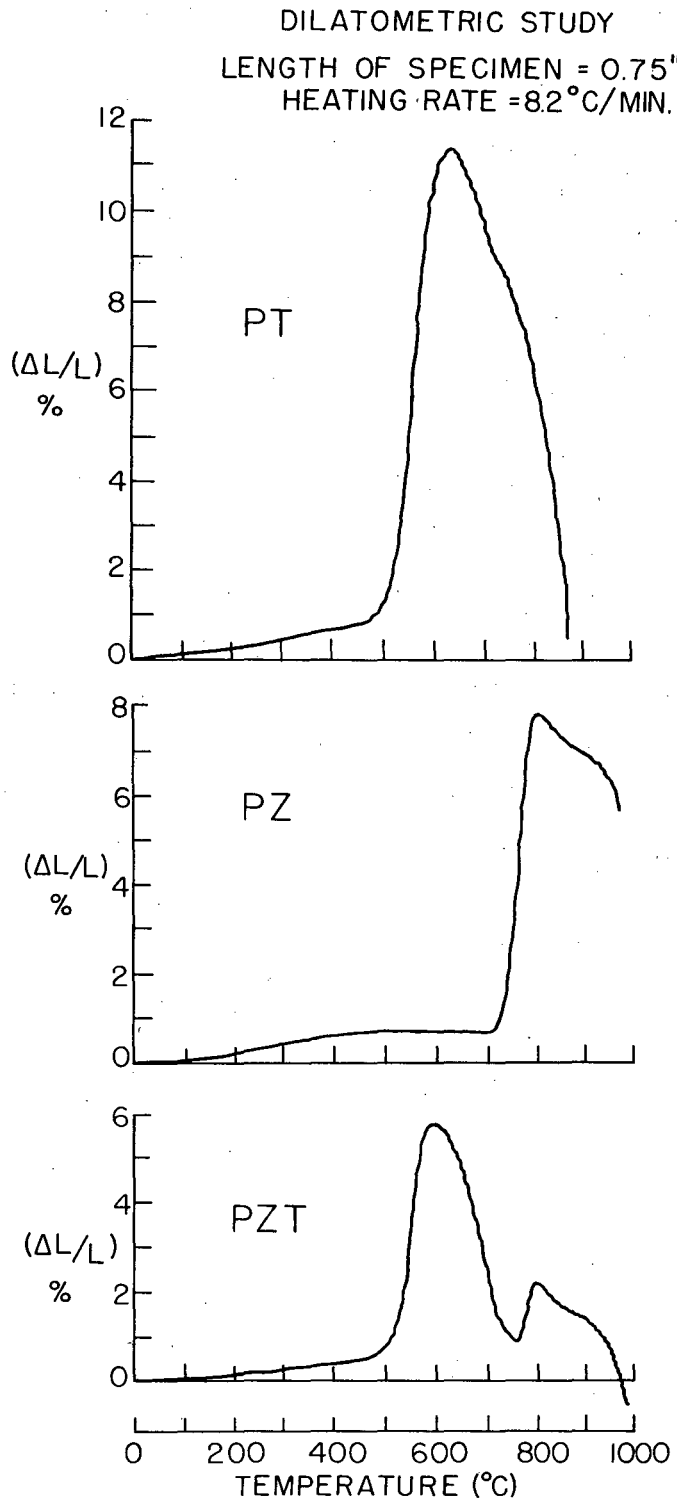| COMPOSITION | MOLAR RATIOS | | |
|:---:|:---:|:---:|:---:|
| | PbO | $TiO_2$ | $ZrO_2$ |
| I | 1.00 | 0.35 | 0.65 |
| II | 1.00 | 0.50 | 0.50 |
| III | 1.00 | 0.65 | 0.35 |
| IV | 1.00 | 0 | 1.00 |
| V | 1.00 | 1.00 | 0 |

# FIGURE CAPTIONS

Fig. 1.     DTA plots for ($PbO + TiO_2$), ($PbO + ZrO_2$) and ($PbO +$ $0.5\ TiO_2 + 0.5\ ZrO_2$) mixtures at the constant heating rate of $10^0 C/min$ in air (V, IV, and II in Table 1).

Fig. 2.     Dilatometric expansion characteristics of ($PbO +$ $TiO_2$), ($PbO + ZrO_2$) and ($PbO + 0.5\ TiO_2 + 0.5\ ZrO_2$) mixtures at constant heating rate of $8.2^0 C/min$ (II, IV and V in Table 1).

Fig. 3.     Room temperature X-ray diffractometry patterns for Composition I ($PbO + 0.65\ ZrO_2 + 0.35\ TiO_2$) showing various phases.  Samples were heated to the shown temperatures at the constant rate of $5.6^0 C/min$ and quenched rapidly after reaching the shown temperature.

Fig. 4.     Schematic of reaction system after lead titanate formation is complete.  The dotted line is not a true interface since PZ-PT form a continuous solid solution above Curie temperatures.
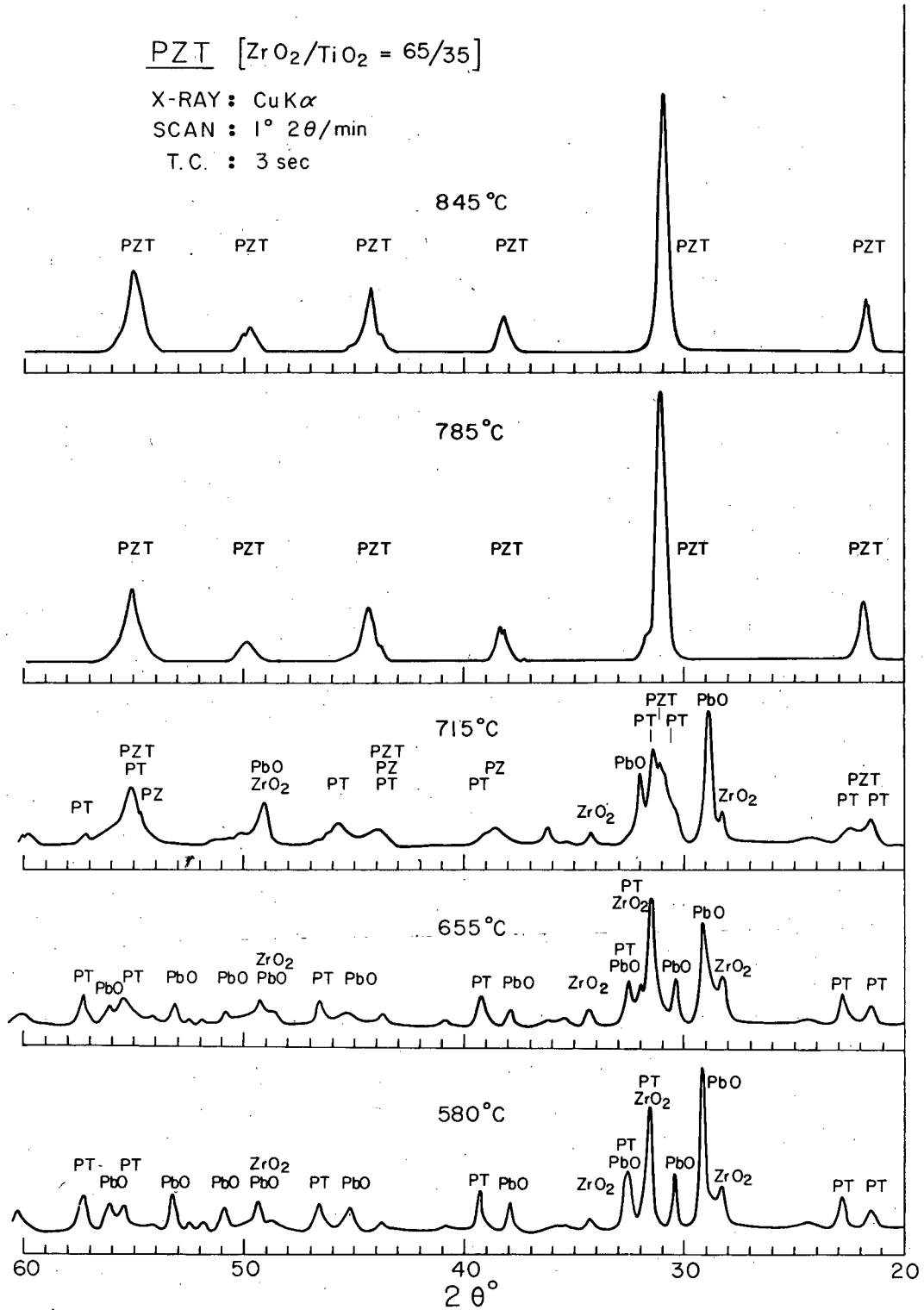
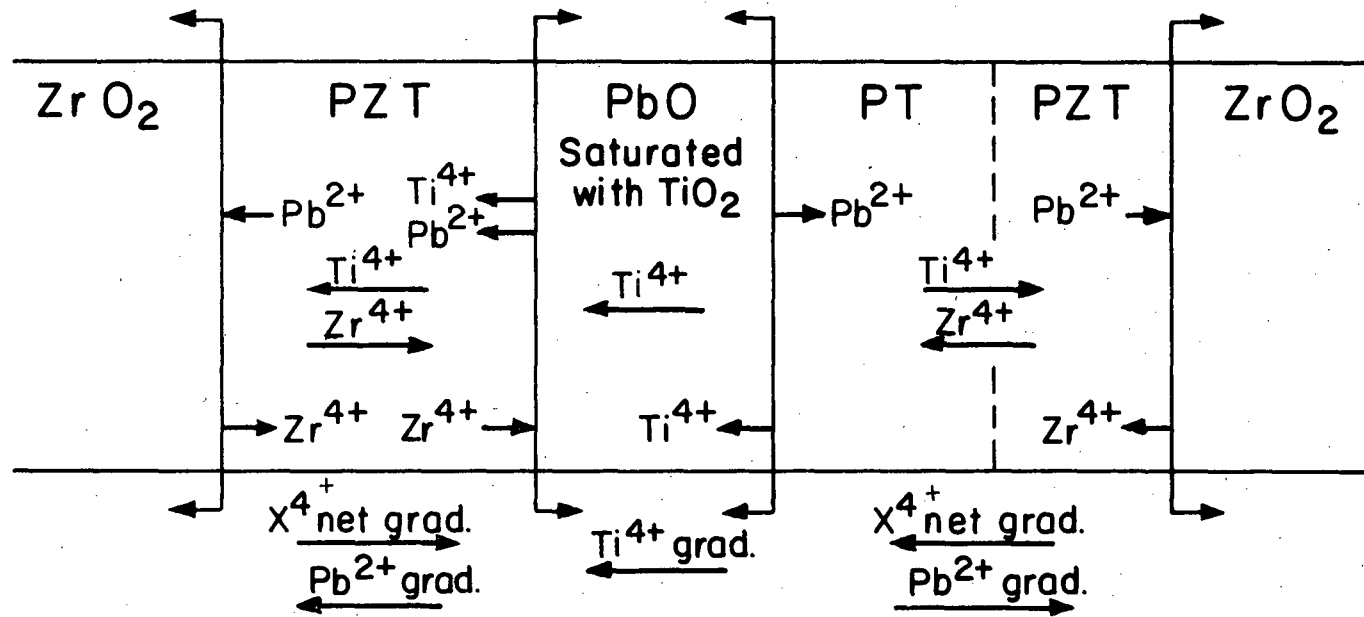DIFFERENTIAL THERMAL ANALYSIS (D.T.A.)

Fig. 1

XBL 756-6525

DILATOMETRIC STUDY

LENGTH OF SPECIMEN = 0.75"
HEATING RATE = 8.2°C/MIN.



Fig. 2

XBL 756-6424

Fig. 3

Fig. 4

XBL 807-5511