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Order-Disorder Reactions in the Ferroelectric Perovskites

$\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ and $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$

I. Kinetics of the Ordering Process

By

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The perovskites $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ and $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ can be obtained in a disordered state by means of a synthesis at high temperature (1250 to 1500 °C). Ordering of the trivalent and pentavalent ions occurs during annealing at lower temperatures. The kinetics of this ordering process are investigated by means of X-ray diffraction, dielectric polarisation, and DSC measurements. The ordering process proceeds via a nucleation-growth process and the average diameter of the ordered domains as a function of the annealing time is determined by X-ray line broadening. Disordering experiments are carried out on $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ and an order-disorder transition temperature of 1210 °C is yielded.

Die Perovskite $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ und $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ lassen sich durch Synthese bei hohen Temperaturen (1250 bis 1500 °C) in einem Fehlordnungszustand erhalten. Ein Ordnungsvorgang der trivalenten und pentavalenten Ionen tritt während der Temperung bei tiefen Temperaturen auf. Die Kinetik dieses Ordnungsprozesses wird mittels Röntgenbeugung, dielektrischer Polarisierung und DSC-Messungen untersucht. Der Ordnungsprozeß verläuft über einen Keimbildungsprozeß und der mittlere Durchmesser der geordneten Domänen als Funktion der Temperungsdauer wird durch die Röntgenlinienverbreiterung bestimmt. Fehlordnungsexperimente werden an $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ durchgeführt und eine Übergangstemperatur von 1210 °C für den Ordnungs-Fehlordnungübergang erhalten.

1. Introduction

In this paper we report on investigations concerning the kinetics of the ordering of the trivalent and pentavalent ions in the ferroelectric compounds $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ and $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (hereafter referred to as PSN and PST, respectively). Although many investigations with respect to the formation, properties, and phase transitions in PSN and PST have been reported in literature [1 to 5], the ordering and the relation between ordering and properties have hardly been studied up to now. It has been shown in [15] that ordering profoundly influences the material properties and therefore a thorough study seems worthwhile in order to elucidate the relation between ordering and properties.

Both PST and PSN have a perovskite structure ABO_3 . This structure may be described as a cubic closest packing of AO_3 layers (in this case $\text{A} = \text{Pb}^{2+}$). The small B cations occupy octahedral sites between the layers. In the case of PSN and PST two cations, Sc^{3+} and $\text{Ta}^{5+}/\text{Nb}^{5+}$, are present in the sublattice formed by the B positions and an ordered structure is possible [6]. This so-called 1:1 ordering is visualized in Fig. 1 and leads to a doubled unit cell and therefore the ordering can be detected by means of X-ray diffraction.

The fact whether $\text{Pb}(\text{B}', \text{B}'')\text{O}_3$ perovskites are ordered or not is determined by temperature, size difference between the B cations, and charge difference between the B cations. This can be seen from Table 1.

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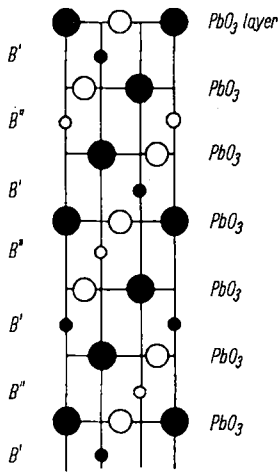


Fig. 1. The ordered $\text{Pb}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$ perovskite structure. The figure represents the (110) plane of the hexagonal cell for a cubic closest packing of PbO_3 layers

In materials like $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ the ordered structure is stable up to high temperatures as a result of the large charge difference between the Mg^{2+} and W^{6+} ions. Decreasing this charge difference results in a less stable ordered structure and the size difference between the two B cations becomes very important. This is evident from the fact that $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ has a disordered structure at about 900 °C, whereas $\text{Pb}(\text{Ho}_{1/2}\text{Nb}_{1/2})\text{O}_3$ has an ordered structure at the same temperature (Table 1, [6, 8]). In PSN and PST both charge and size differences are intermediate and therefore it may be expected that the degree of order can be varied by means of suitable heat treatments at non-extreme temperatures.

Table 1

Ordered and disordered perovskite compounds

compound	diff. in charge of B ions	ionic radius of B' (Å)*	ionic radius of B'' (Å)	arrangement	ref.
$\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$	4	0.72	0.58	ordered	[7]
$\text{Pb}(\text{La}_{1/2}\text{Nb}_{1/2})\text{O}_3$	2	1.06	0.64	ordered	[6]
$\text{Pb}(\text{Ho}_{1/2}\text{Nb}_{1/2})\text{O}_3$	2	0.89	0.64	ordered	[8]
$\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$	2	0.73	0.64		this paper
$\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$	2	0.73	0.64		this paper
$\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$	2	0.65	0.64	disordered	[6]
$\text{Bb}(\text{Zr}_{1/2}\text{Ti}_{1/2})\text{O}_3$	0	0.72	0.61	disordered	[6]

*) Ionic radii of Shannon and Prewitt [16] were used.

In literature the kinetics of chemical ordering reactions are described by two models:

- (i) nucleation and growth model,
- (ii) continuous ordering model.

In a nucleation and growth process the disordered phase is metastable with respect to small fluctuations of the order parameter. A large fluctuation is required to start the ordering reaction and the disorder \rightarrow order transformation is initiated by the formation of a number of critical nuclei of the ordered phase, which then grow until the transformation is complete [9]. Characteristics for a nucleation growth process are:

- (i) the existence at the start of the transformation of an induction period during which the critical nuclei are formed;
- (ii) the coexistence of ordered and disordered regions side by side during the ordering process.

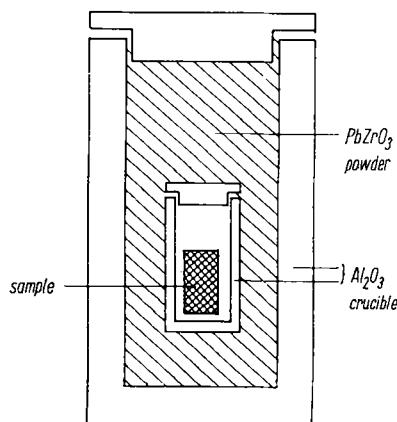
In a continuous ordering process the disordered phase is unstable with respect to small fluctuations of the order parameter and a nucleation step is not required [10, 11]. A spontaneous development of regions with increasing order occurs throughout the whole crystal. It is very important that during such an ordering process there should be regions in the crystal with an order parameter intermediate between complete order and complete disorder. Usually the continuous ordering is described with the same conceptual basis as spinodal decomposition. For a more detailed description of the continuous ordering mechanism the reader is referred to more specific literature [10 to 12].

In spite of the many papers on the subject of ordering and properties in perovskites [6, 13, 14] the *kinetics* of the chemical ordering have hardly been investigated. Most papers concerning this subject refer to binary alloys. Ordering processes that proceed via a nucleation growth process are well documented, good examples being the neo-structural ordering transformations in AuCu, Ni₂V, and Ni₂Cr [12]. One of the rare examples of an alloy with a continuous ordering reaction is AuZn [12].

In the work reported below, the kinetics of the ordering in PSN and PST were investigated by means of X-ray diffraction. The experimental details and results will be the subjects of Sections 2 and 3 and will be discussed in Section 4. In Part II of this paper we shall discuss the relation between the degree of order and the physical properties, paying special attention to the ferroelectric → paraelectric transition.

2. Preparation of the Materials and Experimental Methods

All ceramic materials were prepared by means of a mixed oxide method as described in [15]. To improve the sintering properties of the materials the oxides were weighed with an excess of PbO (2% in PSN, 8% in PST). This excess of PbO disappears during the sintering procedure. In the case of PSN the final sintering was performed in almost closed platinum capsules at 1250 °C during 8 h in oxygen and followed by slowly cooling (about 4 h) to room temperature. The loss of large quantities of PbO could be prevented by placing a few grams of PbZrO₃ powder in the bottom of the platinum capsule. In the case of PST the final sintering was performed in a similar way at 1500 °C. However, at this temperature the PbO losses were very high. Therefore, the pressed pellets were completely surrounded by PST powder and the sintering time was reduced to 4 h. The PST samples were air quenched after the sintering procedure. PSN and PST materials obtained in this way were disordered, as was determined by means of X-ray diffraction, and were used for the annealing experiments.



The annealing experiments were carried out in a capsule as shown in Fig. 2, which is especially designed to prevent PbO losses. In such a capsule the materials did not show weight losses during the long heat treatments at 940 (PSN) nor at 1000 nor

Fig. 2. Annealing capsule especially designed to prevent PbO losses at high temperatures

1050 °C (PST). It will be shown in Section 3 that these heat treatments result in an ordering of the Sc^{3+} and the pentavalent ions. Characteristics of the materials are:

(i) *Homogeneity*: All materials used in our experiments were homogeneous. Second phases could not be detected with X-ray diffraction or scanning electron microscopy. As has been shown in [15] a very sensitive indication for the presence of inhomogeneities is a strong yellow (sometimes local) coloration of the samples. Such indications were not observed.

(ii) *PbO deficiency*: The PbO deficiency of the samples was determined from a chemical analysis performed by means of X-ray fluorescence or from the observed weight losses during the synthesis. For PSN this deficiency varies from 0.7 to 1.0% and for PST values ranging from 1.0 to 1.5% were observed. In most cases the annealed materials showed a somewhat higher PbO content, which proves the usefulness of the capsule shown in Fig. 2.

(iii) *Grain size*: Average grain sizes were determined for polished and thermally etched samples by means of the linear intercept method [17]. Grain sizes of about 12 and 20 μm were determined for PSN and PST materials, respectively.

(iv) *Density*: The PSN ceramics all showed a density better than 97% of the theoretical density. The PST materials have a somewhat lower relative density which varies from 89 to 94%.

Discs with a diameter of 6 mm and a thickness of about 0.5 mm were made from the sintered and annealed specimens. Gold electrodes were evaporated on the discs to enable dielectric measurements to be made.

X-ray powder diffraction patterns at room temperature were determined with a Philips diffractometer using $\text{CuK}\alpha$ radiation. X-ray intensities were obtained by standard counting methods. A Rohde and Schwartz bridge, type VKB, BN 3520 was used to measure the capacity and loss tangent of the samples at 10 kHz (applied voltage ≤ 40 V/cm). EP hysteresis loops were obtained at a frequency of 0.05 Hz by means of a modified Sawyer-Tower circuit.

Remanent polarization as a function of temperature was determined from these hysteresis loops. Heating and cooling rates for all electrical measurements were 1 to 2 K/min. Transition heats were determined with Dupont type 990 DSC (differential scanning calorimetry) equipment, using ceramic discs. A heating rate of 5 or 10 K/min was used in all experiments.

3. Experimental Results

3.1 PST

X-ray diffraction patterns at room temperature show that the disordered starting material PST 1 has a cubic symmetry with cell parameter $a_0 = 4.074(1)$ Å, which is in accordance with earlier results [1]. Although the X-ray diffraction pattern does not show clear superstructural lines pointing to a 1:1 ordering it should be remarked that a slightly increased background can be observed around the 2θ values where the superstructural lines might be expected. This may point to some kind of short-range ordering.

After annealing at 1000 or 1050 °C the material still shows a cubic symmetry and the subcell parameter a_0 does not change significantly. However, in the X-ray diffraction patterns a development of superstructural lines due to the onset of the 1:1 ordering can be observed. The intensity of the superstructural lines increases with an increase of the annealing time and can be used as a measure for the degree of ordering. For PST the large superstructural reflections (111) and (131) were measured and compared with the fundamental reflections (200) and (222), respectively. For a completely ordered

material and neglecting the Pb deficiency it can be calculated that $I_{111}/I_{200} = 1.33$ and $I_{131}/I_{222} = 0.59$.²⁾ Assuming that the quantity of ordered material is linearly related to the measured I_{111}/I_{200} or I_{131}/I_{222} ratio the fractional conversion degree x for the disorder \rightarrow order reaction was calculated. The results are given in Table 2 and Fig. 3. It can be seen that the rate of ordering is high at 1050 °C. After six days annealing the material is almost completely ordered. A somewhat lower rate of ordering is more convenient for kinetic studies, especially in the earlier stages of the process (short annealing times). Therefore, in most annealing experiments a temperature of 1000 °C was chosen. It can be seen from Table 2 that the values of x_{111} and x_{131} are almost equal. This result excludes a wrong interpretation due to a preferred orientation of the samples in the X-ray diffractometer. Fig. 3 shows that the ordering process starts without a notable induction period.

Especially in the early stages of the ordering process the superstructural reflections are broadened compared to the fundamental reflections as can be seen from Fig. 4. It is remarkable that most of the broadening occurs around the foot of the reflection. This broadening is not caused by the residual disorder itself. In [15] it has been shown that sintering at high temperatures ($1250\text{ °C} < T < 1500\text{ °C}$) leads to material with an order parameter $\Omega < 1$, but the superstructural lines are almost unbroadened. In our opinion the broadening is due to the fact that in the beginning ordering occurs in small domains. For an estimation of domain sizes as a function of the annealing time X-ray line broadening measurements have been performed [18]. The integral breadths of the (111) and (131) reflections were determined and compared to the unbroadened (200) and (222) fundamental reflections, respectively. Corrections were carried out according to Jones' method [18]. The results obtained from the (111) and (131) reflections agree rather well and the mean value is given in Table 2. It can be concluded

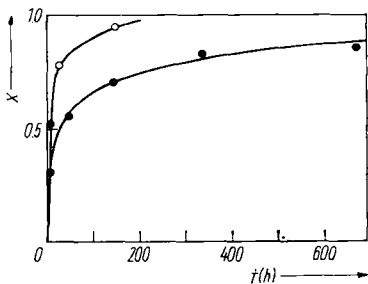


Fig. 3

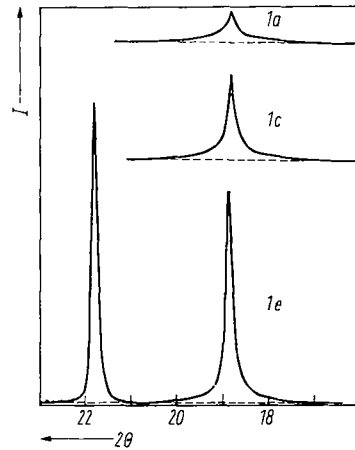


Fig. 4

Fig. 3. Fractional conversion degree x for the disorder \rightarrow order transformation in PST as a function of the annealing time at 1000 (●) and 1050 °C (○)

Fig. 4. (111) superstructural reflection for several annealed PST materials. The notation of the materials is explained in Table 2. For sample PST 1e the fundamental reflection (200) is also given

²⁾ The intensity of the fundamental reflections is dependent on the Pb deficiency. For a Pb deficiency of 1% the value of I_{111}/I_{200} increases to 1.40 and the difference with the ideal value of 1.33 is only small. Moreover all samples show about the same small Pb deficiency.

Table 2

Fractional conversion degree and size of the ordered domains for the disorder \rightarrow order transition in PST at 1000 °C

material	time (h)	x_{111}	x_{131}	\bar{D} (Å)
PST 1	0	0	0	0
PST 1a	3	0.32		190
PST 1b	6	0.49	0.54	300
PST 1c	48	0.53	0.57	290
PST 1d	144	0.67	0.73	330
PST 1e	336	0.80	0.85	530
PST 1f	672	0.82	0.88	520
PST 1g	1500	0.88	0.90	800

x_{111} fractional completion for the disorder \rightarrow order transformation calculated from the I_{111}/I_{200} ratio.

x_{131} idem from the I_{131}/I_{222} ratio.

D domain size in Å. The mean of the values calculated from the broadening of the (111) and the (131) reflections is given.

that the average domain size increases slowly with an increase of the annealing time. The fact that most of the broadening is observed around the foot of the superstructural reflections will be discussed in Section 3.

3.2 PSN

X-ray diffraction patterns at room temperature of the starting material PSN 1 do not show any indications for a 1:1 ordering. A rhombohedral symmetry is observed with cell parameters $a_0 = 4.080(1)$ Å and $\alpha = 89.89(1)^\circ$. In the literature all authors assume a tetragonal symmetry [2 to 4]. However, in our diffraction patterns we did not observe the splitting of the (200) and (400) reflections, required for tetragonal symmetry, whereas the 111 and 222 reflections show a very small but clearly visible splitting. This proves that PSN has a rhombohedral and not a tetragonal symmetry at room temperature.

Ordering experiments on PSN were carried out at 940 °C. It appears that the results are qualitatively similar to those obtained for PST (Section 3.1). Annealing leads to an ordering of the Sc^{3+} and Nb^{5+} ions, which is visualized by the formation of superstructural lines in the X-ray diffraction pattern. Especially in the early stages of the ordering process these superstructural lines are somewhat broadened. Contrary to PST, serious difficulties arise from the fact the superstructural lines are very small, which makes the results less reliable. Moreover a strong tendency for a preferred orientation of the samples in the X-ray diffractometer is observed. This makes it necessary to compare a superstructural reflection with a fundamental reflection from a parallel plane. Because of these problems only the (111) reflection was measured and compared with the (222) fundamental reflection. It appears that after a long annealing period the ratio I_{111}/I_{222} extrapolates to a value of 0.12.³⁾ This value can be considered as the equilibrium value at this annealing temperature, correspond-

³⁾ This value is somewhat higher than the theoretical value for complete order of 0.103. Probably this is due to the fact that both reflections were measured with the same receiving slits which may give the reflection at the higher diffraction angle an intensity which is relatively too low.

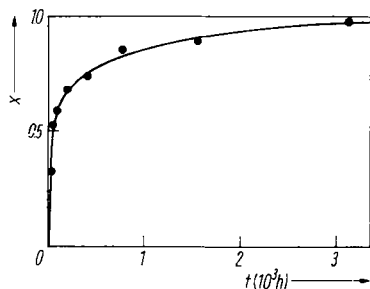


Fig. 5. Fractional conversion degree x for the disorder \rightarrow order transformation in PSN as a function of the annealing time at 940 °C

ng to a complete transformation to the ordered state. Assuming once more a linear relation between x and the ratio I_{111}/I_{222} an $x(t)$ plot can be constructed. The result is given in Fig. 5. Just as in the case of PST the ordering process starts without a notable induction period.

As in PST the superstructural lines in PSN are somewhat broadened. Very accurate measurements of this broadening were impossible because of the smallness of the superstructural reflections and therefore a domain size calculation as for PST was not performed. After one day annealing the (111) reflection has an integral breadth of about 0.35° (2θ) which gradually decreases to about 0.20° (2θ) after four months annealing. This has to be compared with the integral breadth of the unbroadened (200) reflection of 0.16° (2θ). These results indicate that, especially in the beginning, the ordering occurs in small domains.

4. Discussion

Although an induction period at the start of the transformation is not observed, in our opinion the experimental results can be explained by assuming that the ordering in PSN and PST proceeds via a nucleation growth process. The fact that during the ordering the superstructural lines in the X-ray diffraction patterns are broadened may point to a structure with coexistence of small ordered and disordered regions. Such a structure is a necessary transitional stage in a nucleation growth process. A strong indication in favour of the nucleation growth process is the observed change of physical properties.

An extensive discussion about the properties of PSN and PST materials will be given in Part II of this paper so that here we shall only refer to some important results. PSN is ferroelectric at room temperature [1 to 5]. It will be shown in Part II of this paper that in a disordered material a somewhat diffuse transition to the paraelectric phase occurs at about 105 °C. In an ordered material this transition takes place at about 75 °C. These transitions can be observed in the permittivity, DSC, and remanent polarization curves. If the ordering transformation proceeds by a nucleation growth process, then well-defined ordered and disordered regions will coexist and this process should be evidenced by a gradual disappearance of the transition at 105 °C and a gradual increase of the transition at 75 °C with no changes in positions (on the temperature scale) being observed. Suppose on the other hand, that the ordering proceeds via a continuous process. Then the transitional stages during the ordering process are characterized by the existence of regions with an order intermediate to complete disorder and complete order. It may be expected that in this case the transition at 105 °C gradually shifts to lower temperatures which is not observed experimentally. It has been found that the first effect occurs and this proves the correctness of the nucleation growth model.

The lack of an induction period at the start of the disorder \rightarrow order transition may have two explanations:

- (i) The nucleation step goes so rapidly that an induction period is not measured.
- (ii) At the start of the annealing experiments the critical nuclei have already formed.

For PST we have some evidence that this latter point is the case. As has been mentioned in Section 3 the X-ray diffraction patterns have a slightly increased background around 2θ values where the superstructural lines are expected. This may point to a certain number of very small nuclei that may have formed during an inadequate quenching of the starting materials.

For a nucleation growth process Avrami [19] derived a rate expression

$$x = 1 - e^{-kt^n}$$

with k rate constant, n time exponent. Our attempts to fit the experimental results with this so-called Avrami equation did not give reasonable results, for which we do not have an explanation.

The size of the ordered domains in PST was determined from the broadening of the superstructural lines in the X-ray diffraction pattern. It appears that the domain size increases with an increase of the annealing time (Table 2). However, it should be mentioned that the domain sizes in Table 2 represent average values. An indication about the distribution of the domain sizes can be obtained from the fact that in most samples not the whole reflection is broadened. All PST materials that were annealed for more than 3 h have superstructural lines in which most of the broadening occurs around the foot of the reflection. As becomes evident from Fig. 4 the half-widths of the superstructural reflections are almost unbroadened. A domain size calculation based on this halfwidth gives a diameter of 1000 Å after two days annealing at 1000 °C. If on the other hand, we make use of the integral breadth, a domain size of 290 Å is obtained (Table 2). This may point to a bimodal distribution of domain sizes. A substantial number of domains are much smaller than 290 Å and this results in a very broad Bragg reflection. On the other hand, domains being much larger than 290 Å give rise to an almost unbroadened superstructural reflection. A superposition of these two effects gives a sharp reflection with a broadened foot. The broadening of the foot is still visible in PST 1e and PST 1f, which proves that even in the later stages of the ordering process a certain amount of small domains is present. This may be an indication that small domains are still being formed in these stages and consequently that nucleation goes on for as long as disordered material is available. In the last stages of the ordering most of the material is transformed to the ordered state and the nucleation stops. However, the growth process proceeds and probably results in a decrease in the number of antiphase domain boundaries.

A question that arises is whether the equilibrium situation corresponds to a completely ordered state at the temperatures that have been used for the annealing experiments. For PST it has been shown [15] that long annealing at 1050 °C leads to a situation with a long-range order parameter $\Omega = 0.94(4)$. Therefore, it can be concluded that for PST the equilibrium situation equals an almost completely ordered state at 1000 or 1050 °C. In the case of PSN a determination of Ω was carried out for a material that was annealed at 940 °C during one month. The method is described in [15]. A long-range order parameter $\Omega = 0.9(2)$ was obtained. The large standard deviation is a result of the fact that the superstructural reflections are very small. However, just as in the case of PST the equilibrium situation is almost completely ordered.

5. Order-Disorder Transition Temperature

PSN is disordered at 1250 °C but can be ordered at 940 °C. This leads to the conclusion that the transition temperature for the order \rightarrow disorder transition is situated somewhere between 940 and 1250 °C. We tried to determine a more accurate transition temperature. Disordering experiments were preferred since in most cases a disordering reaction proceeds faster than an ordering reaction [9]. An ordered PSN sample was allowed to disorder at several temperatures > 940 °C during 24 and 72 h. In all cases the intensity of the (111) superstructural reflection did not change anymore at temperatures $T \geq 1050$ °C after 24 h and we assumed that an equilibrium situation was reached after 24 h. The results are given in Fig. 6. The transition temperature equals 1210 °C. Furthermore the $I_{111}/I_{222}(T)$ curve is a gradual one. A jump of the I_{111}/I_{222} ratio at the transition is not observed and probably the order \rightarrow disorder transition is of second order.⁴⁾

Disordering experiments on PST were not performed. It has been shown that the material is partly ordered at 1450 °C and disordered at 1500 °C [15]. Therefore, the temperature for the order-disorder transition must be located between 1450 and 1500 °C.

6. Stability of $\text{Pb}(\text{B}', \text{B}'')\text{O}_3$ Compounds

A remark should be made with respect to the difficulties we have met in preparing ceramic perovskite $\text{Pb}(\text{B}', \text{B}'')\text{O}_3$ compounds by a mixed oxide method. It appears that in these compounds a pyrochlore phase is competitive with the perovskite phase. Sometimes the formation of a pyrochlore phase was mentioned but mostly these difficulties were underestimated [7, 20 to 23].

In PSN, PST, and $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ a pyrochlore phase is formed during the first stages of the synthesis, but a careful preparation eventually yields pure perovskite phases. However, in some other compositions such as $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$, $\text{Pb}(\text{Fe}_{1/2}\text{Ta})\text{O}_3$, and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ this pyrochlore phase cannot be removed completely at temperatures ranging from 900 to 1300 °C. A Pb deficiency in these cases resulted in a strong increase of the pyrochlore phase whereas the amount of pyrochlore phase could be diminished somewhat by introducing an excess of PbO , but pure perovskites were not obtained. X-ray diffraction results are given in Table 3. The X-ray diffraction pattern of the composition $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ shows a mixture of a (pseudo)cubic pyrochlore, a (pseudo) cubic perovskite, and In_2O_3 . Apparently in this composition the

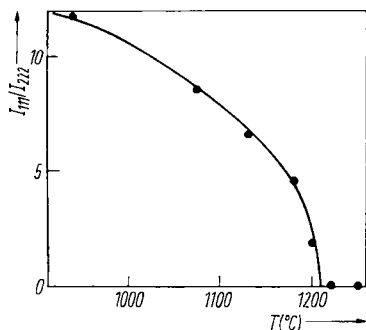


Fig. 6. The ratio I_{111}/I_{222} as a function of temperature for PSN

⁴⁾ The superstructural reflections are small and this makes accurate measurements impossible. A small jump in the I_{111}/I_{222} ratio may occur in the last stages of the disordering process, but will not be visible by means of X-ray diffraction.

Table 3

Cell parameters of pyrochlore and perovskite phases in several $\text{Pb}(B', B'')\text{O}_3$ compositions

material	pyrochlore a_0 (Å)	perovskite a_0 (Å)
$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	10.583(1)	4.043(1)
$\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$	10.567(5)	4.015(2)
$\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$	10.647(3)	4.111(1)

formation of the pyrochlore phase is coupled with a decomposition of the perovskite phase.

More interesting are the results for $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and $\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$. The X-ray diffraction patterns of these samples can be indexed completely by assuming a mixture of a cubic perovskite and a pseudocubic pyrochlore phase. No evidence for another phase was observed not even in samples containing a large amount of pyrochlore phase. This may point to a pyrochlore phase that has the same composition as the perovskite phase. Defect pyrochlore structures with a composition $\text{Pb}_2\text{B}_2\text{O}_6$ were investigated by Longo et al. [24]. This structure contains B cations in corner-shared octahedra as in perovskite, but the B–O–B angle is reduced to 135° . From electrostatic considerations the structure is unstable because it contains Pb–Pb neighbours. However, the defect pyrochlore structure can be stabilized by creating a Pb–Pb bond across a vacant oxygen site [24]. Probably the formation of perovskite structures in compositions $\text{Pb}(B', B'')\text{O}_3$ is hardly more favourable than the formation of an oxygen defect pyrochlore structure.

7. Conclusions

1. Annealing of the compounds PSN at 940°C and PST at 1000°C results in an ordering reaction of the Sc^{3+} ions and the pentavalent ions. At these temperatures the equilibrium value of the order parameter corresponds to $\Omega \geq 0.92$. Starting with a disordered material the kinetics of this ordering process were investigated by means of X-ray diffraction. The results are given in Fig. 3 and 5.

2. Both for PSN and PST the ordering process as represented in $x(t)$ curves starts without a notable induction period. However the X-ray diffraction experiments in combination with the development of some physical properties give evidence that the ordering proceeds via a nucleation growth process. In the first stages of the ordering process the ordered domains have an average diameter of 190 \AA . This diameter increases gradually with an increase of the annealing time.

3. The order–disorder transition in PSN is of second order and takes place at 1210°C . For PST the order–disorder transition temperature is situated between 1450 and 1500°C .

4. PSN has a rhombohedral symmetry with unit cell parameters $a_0 = 4.080(1)\text{ \AA}$ and $\alpha = 89.89(1)^\circ$ contrary to what has been reported in literature.

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