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

### II. Relation between Ordering and Properties<sup>2</sup>

By

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Dedicated to Prof. Dr. Dr. h.c. Dr. E.h. P. GÖRLICH on the occasion of his 75th birthday

The ordering of the trivalent and pentavalent cations in 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 varied by suitable heat treatments. The degree as well as the kind of order strongly affects the character of the FE  $\rightarrow$  PE phase transition. A spatially homogeneous disorder leads to a diffuse phase transition whereas a hybrid crystal with a nonhomogeneous disorder shows a sequence of two FE  $\rightarrow$  PE transitions.

Die Anordnung der trivalenten und pentavalenten Kationen in den Perovskiten  $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  und  $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$  kann durch geeignete Temperung geändert werden. Sowohl der Grad als auch die Art der Ordnung beeinflusst den Charakter des FE  $\rightarrow$  PE-Phasenübergangs wesentlich. Eine räumlich homogene Fehlordnung führt zu einem diffusen Phasenübergang, während ein Hybridkristall mit einer nichthomogenen Fehlordnung eine Folge von zwei FE  $\rightarrow$  PE-Übergängen zeigt.

### 1. Introduction

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 PSN and PST, respectively) were investigated in Part I of this paper. In this part the relation between characteristic ordering parameters and the physical properties will be discussed, with special attention to the ferroelectric  $\rightarrow$  paraelectric phase transition.

PSN and PST are ferroelectric (FE) at room temperature but exhibit a structural displacive transition to the paraelectric (PE) phase at higher temperatures. In PST this transition takes place at 26 °C [1] and in PSN at 90 °C [1 to 3]. Several investigations were devoted to the transition in PSN. All authors [1 to 3] reported that the FE  $\rightarrow$  PE transition is a diffuse phase transition (DPT). In such a DPT the transition is smeared out over a certain temperature interval and the transition temperature is not really sharply defined. It appears that DPT's frequently occur in materials with more than one kind of ion on equivalent positions (solid solutions for example) and most theoretical models concerning this subject assume that the chemical disorder in such systems is responsible for the DPT. All these models lead implicitly to the conclusion that the diffuseness of the transition decreases with a decrease of the disorder, which is indeed observed experimentally in several material systems [4, 5]. For a more detailed description of theoretical models concerning DPT's the reader is referred to the original papers [4, 6 to 9].

The FE  $\rightarrow$  PE transition in PST is hardly investigated. It has been shown [5] that

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both the transition temperature and the diffuseness of the DPT is dependent on the degree of chemical long-range order. In this paper we shall discuss the relation between the chemical ordering and the diffuseness of the FE  $\rightarrow$  PE transition in Section 3. Some remarks should be made on the two kinds of chemical order that may occur. Generally the degree of order is expressed by the value of the long-range order parameter  $\Omega$ . In the case of PSN and PST this long-range order parameter is defined as  $2n - 1$ ,  $n$  is the occupation number of the  $\text{Sc}^{3+}$  ions at the 4b position in the ordered Fm3m structure and it gives a measure for the fraction of  $\text{Sc}^{3+}$  ions (or  $\text{Nb}^{5+}/\text{Ta}^{5+}$  ions) on the "right" position. The use of a long-range order parameter is limited to materials with a spatially homogeneous order. On a scale of some unit cells the order may fluctuate somewhat but measured over larger areas the order should be constant. In most cases such a homogeneous order is obtained only in materials that have reached an equilibrium situation with respect to the order at the preparation temperature.

Frequently such an equilibrium situation is not reached and this has been described for some PSN and PST materials in Part I of this paper. In these materials ordered domains are present in a disordered matrix and the long-range order is spatially non-homogeneous. It is not justified to characterize the degree of order in these materials by a long-range order parameter. In Part I of this paper the degree of order was characterized by the fraction  $x$  of ordered domains. In this paper we shall frequently use the notion hybrid for these compounds. Ubbelohde [10] used the notion hybrid crystal to describe a transitional state occurring during a continuous transition. This transitional state is characterized by the coexistence of two distinct but closely related structures in a small temperature interval around the transition. The structures cannot be treated independently in this temperature region and the Gibbs free energy expressions contain terms that reflect the fact that another structure is present. In this paper a hybrid crystal is defined as a crystal with coexistence of two distinct but closely related structures, separated by coherent (low energy) boundaries in one and the same parent crystal [11].

The aim of this paper is to report on investigations concerning the relation between chemical order and the FE  $\rightarrow$  PE transition in PSN and PST. The experimental details will be the subject of Section 2. In this section also a short review will be given of some important results on PST that were published elsewhere. The results will be discussed in Section 3 and it will be shown that the degree as well as the kind of order (homogeneous or nonhomogeneous) strongly affects the properties of the material.

## 2. Experimental

### 2.1 Materials with a spatially nonhomogeneous order parameter

Permittivity, polarization, and DSC measurements on the disordered material PSN 1 show that the FE  $\rightarrow$  PE transition is somewhat diffuse. The transition temperature is dependent on the method of measurement and takes place at about 100 to 109 °C. The permittivity curve is broadened (Fig. 1) and does not show Curie-Weiss behaviour in a temperature interval of about 150 K above the transition. In contrast with this a small heat effect of 90 J/mol was observed at a *sharply* defined temperature of 103 °C. The remanent polarization in a disordered material disappears rather gradually in a temperature interval 100 to 106 °C (Fig. 2).

In Part I of this paper it was shown that annealing at 940 °C of such a disordered PSN material leads to an isostructural ordering of the trivalent and pentavalent ions. The ordering proceeds via a nucleation growth process and a material with a non-homogeneous order parameter develops: ordered domains and disordered regions

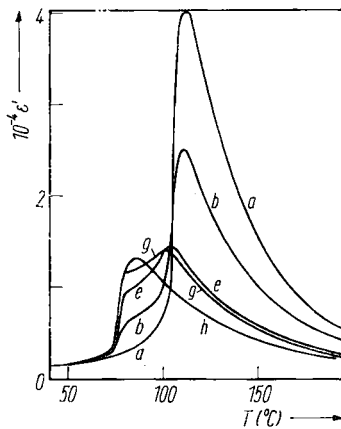


Fig. 1

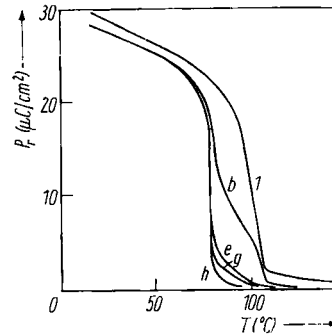


Fig. 2

Fig. 1. Dielectric constant as a function of temperature for several annealed PSN materials (10 kHz, heating curves). The notation of the materials is explained in Table 1. (a) PSN 1 and PSN 1a, (b) PSN 1b, (e) PSN 1e, (g) PSN 1g, (h) PSN 1h

Fig. 2. Remanent polarization as a function of temperature for several annealed PSN materials. The notation of the materials is explained in Table 1. (1) PSN 1, (b) PSN 1b, (e) PSN 1e, (g) PSN 1g, (h) PSN 1h

Table 1

Parameters describing the FE → PE transition in PSN materials that were annealed at 940 °C

No.	time (h)	$x$	$T_p$ (°C)	$T_{DSC}$ (°C)	$\Delta H$ (J/mol)	$T_0$ (°C)	$C_w$ ( $10^6$ °C)
1	0	0	95 to 106	103	90	173	1.91
1a	24	0.32		105	85	176	1.87
1b	48	0.52	80/105*	73/102*	70/50*	163	1.83
1c	96	0.59		76/103*	200/30*		
1d	192	0.68		74	165		
1e	408	0.75	79	75	210	137	1.75
1f	770	0.85	78	77	310	127	1.61
1g	1560	0.89	79	76	325	123	2.00
1h	3120	0.98	79	78	435	116	1.89

\*) Two transitions were observed.

The time is the annealing time at 940 °C in h,

$x$  fractional conversion degree for the disorder-order transformation determined by means of X-ray diffraction (see Part I of this paper),

$T_p$  temperature at which the remanent polarization disappears,

$T_{DSC}$  temperature at which a heat effect is observed by means of DSC measurements,

$\Delta H$  magnitude of the heat effect,

$T_0$  extrapolated Curie temperature,

$C_w$  Curie-Weiss constant.

separated by coherent boundaries coexist during the ordering process and a hybrid crystal is formed. The results of DSC measurements on these materials are given in Table 1. Together with the appearance of ordered domains a heat effect develops at about 76 °C in the DSC curves. With an increase of the fraction of ordered material the magnitude of the heat effect at 76 °C increases, whereas the original heat effect at 103 °C disappears.

Similar effects were obtained from electrical measurements. In Fig. 1 the permittivity curves of some annealed PSN materials are given. It appears that an anomaly develops in the permittivity curve at about 80 °C as a result of the annealing procedure. This anomaly becomes more important with an increase of the fraction of ordered material. At the same time the original maximum in the permittivity curve gradually disappears (Fig. 1). All materials, annealed or not, show deviations from the classical Curie-Weiss behaviour in a certain temperature interval above the transition. Only at high temperatures a Curie-Weiss behaviour is observed and the Curie-Weiss parameters are given in Table 1. In all cases the extrapolated Curie temperature  $T_0$  is higher than the temperature where the dielectric constant is at maximum, but  $T_0$  decreases with an increase of the amount of ordered material indicating that the behaviour becomes more classical with increasing order.

Remanent polarization was obtained from EP hysteresis loops at several temperatures. The results are shown in Fig. 2. It can be seen that the temperature  $T_p$  (temperature at which the remanent polarization disappears) shifts from about 105 to 78 °C as a result of the annealing procedure. At temperatures  $T < T_p$  some remanent polarization is retained.

The results of the measurements on hybrid PSN materials can be summarized as follows: A disordered material shows a somewhat diffuse FE  $\rightarrow$  PE transition at 100 to 109 °C. After annealing of the disordered material the original transition gradually disappears and it seems that a new transition develops at about 78 °C. Attention must be paid to the fact that only these two transition temperatures were observed. Transition temperatures between 78 and 105 °C were not observed.

The same effects were observed in PST materials. As has been shown in [5] the disordered material PST 1 has a diffuse FE  $\rightarrow$  PE transition somewhere between  $-6$  and  $+13$  °C.

The strongly broadened maximum in the permittivity curve occurs at about  $+13$  °C (Fig. 3), whereas the remanent polarization disappears at  $-6$  °C. A small heat effect  $\Delta H$  (34 J/mol) is observed at  $-5$  °C by means of DSC measurements. In Part I of this paper it has been pointed out that annealing at 1000 °C of this disordered material results in the creation of ordered domains in a disordered matrix. At the

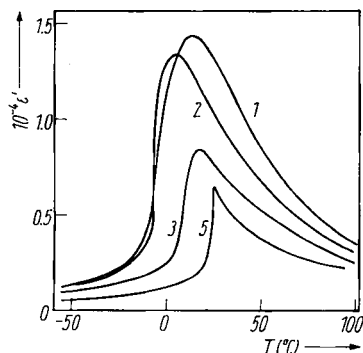


Fig. 3. Dielectric constant as a function of temperature for several PST materials with a homogeneous order parameter (10 kHz, heating curves). The notation of the materials is explained in Table 3, (1) PST 1, (2) PST 2, (3) PST 3, (5) PST 5

same time the heat effect at  $-5\text{ }^{\circ}\text{C}$  disappears and a new heat effect at about  $32\text{ }^{\circ}\text{C}$  develops. This latter heat effect increases with an increase of the amount of ordered material as can be seen from Table 2.

Table 2

Parameters describing the FE  $\rightarrow$  PE transition in PST materials that were annealed at  $1000\text{ }^{\circ}\text{C}$

No.	time (h)	$x$	$T_{\text{DSC}}$ ( $^{\circ}\text{C}$ )	$\Delta H$ (J/mol)
1	0	0	-5	34
1b	6	0.52	-6	30
1c	48	0.55	-*)	-*)
1d	144	0.70	30**)	100**)
1e	336	0.83	31	250
1f	672	0.85	35	400

\*) No measurable heat effect.

\*\*\*) Exact values hard to determine because of the existence of strong premonitory effects.

The time is the annealing time at  $1000\text{ }^{\circ}\text{C}$  in h.

All other parameters are explained in Table 1.

## 2.2 Materials with a spatially homogeneous order parameter

Experimental results on these materials were previously reported in [5]. PST samples were prepared at high temperatures (see Table 3) and it is assumed that at these high temperatures an equilibrium situation with a spatially homogeneous order parameter has developed. Further justification is mainly abstracted from the fact that sintering of the material at  $1300\text{ }^{\circ}\text{C}$  yields an order parameter  $\Omega = 0.76(6)$  independent of the sintering time. Moreover the physical properties like transition temperature, broadening of the maximum in the permittivity curve, etc. are independent of the sintering time.

The experimental results were extensively discussed in [5] and here we shall only refer to the more important results as given in Table 3 and Fig. 3. It can be seen that in these materials a decrease of the long-range order parameter results in:

- (i) an increased broadening of the maximum in the permittivity curve,
- (ii) a shift of the FE  $\rightarrow$  PE transition to lower temperatures,
- (iii) a decrease of the observed heat effect at the transition.

The permittivity does not follow a Curie-Weiss law at temperatures  $T > T'_c$ . Only at high temperatures a Curie-Weiss behaviour is found. The Curie-Weiss parameters are given in Table 3. Just as in the case of PSN (Section 3.1) an increase of the order leads to a decreased value of the extrapolated Curie temperature  $T_0$ .

## 3. Discussion

### 3.1 Materials with a spatially nonhomogeneous order

In this section the physical properties of materials with a spatially nonhomogeneous order will be discussed. The experimental results on such hybrid materials can be explained by a model in which the ordered and disordered phases have different FE  $\rightarrow$  PE transition temperatures. Moreover the transition temperatures for the ordered and the disordered phases are independent of the amount of ordered material. The FE  $\rightarrow$  PE transition in disordered PSN for example occurs at about  $105\text{ }^{\circ}\text{C}$ ,

Table 3  
Parameters describing the FE  $\rightarrow$  PE transition in PST materials with a homogeneous long-range order parameter  $\Omega$

material	heat treatment $t$ (h)	$T$ ( $^{\circ}$ C)	$\Omega$	$T'_c$ ( $^{\circ}$ C)	$b_{3/4}$ ( $^{\circ}$ C)	$T_0$ ( $^{\circ}$ C)	$C_w$ ( $10^8$ $^{\circ}$ C)	$T_p$ ( $^{\circ}$ C)	$T_{DSC}$ ( $^{\circ}$ C)	$\Delta H$ (J/mol)
PST 1	4	1500	0	13	41	76	1.47	-6	-5	34
PST 2	4	1450	0.52	5	33			-6	-5	75
PST 3	8	1300	0.74	17	27	40	1.60	5	7	235
PST 5	8	1300	0.94	25	13	33	1.56	25	24	420
	340	1050								

$T'_c$  temperature at which the dielectric constant is maximum,  $b_{3/4}$  width of the permittivity curve at  $\frac{3}{4}$  of its maximum height. All other parameters are explained in Table 1.

whereas this transition in ordered PSN occurs at 78 °C. Annealing of the disordered material leads to the formation of a hybrid crystal in which ordered and disordered regions with different transition temperatures coexist. A very nice example for this behaviour is PSN 1b. In this material all measurements show a sequence of the two FE → PE transitions, one for the ordered material and the other for the disordered material. In most other materials only in the permittivity curves two transitions are clearly visible. The DSC curves do not reflect the FE → PE transition of the disordered material anymore for  $x > 0.6$ . Probably this is due to the smallness of the heat effect of this transition. In the  $P_r(T)$  curves the small remanent polarization at temperatures  $T > 78$  °C may be an indication for the FE → PE transition at 105 °C in the disordered material, but this result is not very clear.

As can be seen from Fig. 1 and Table I there is no evidence that an equilibrium situation with respect to the physical properties was obtained in PSN after very long annealing ( $t \geq 65$  d) at 940 °C. The magnitude of the heat effect is not yet constant and also the permittivity curve shows some significant changes. Assuming that the completely ordered material has a classical FE → PE transition at 78 °C an estimation of the annealing time necessary for reaching such a situation can be made. For a classical transition the extrapolated Curie temperature must be smaller than (or equals) the real transition temperature of 78 °C. In our PSN materials we observe  $T_0 \gg 78$  °C, but the difference decreases with an increase of the annealing time as can be seen from Table I. In Fig. 4 the value of  $T_0$  is plotted as a function of  $\lg t$  and a straight line is obtained. An extrapolation to  $T_0 = 78$  °C shows that the situation corresponding to this temperature is reached after 1000 d annealing at 940 °C. Although this value should not be taken too exactly it gives an indication that a truly classical transition and an equilibrium situation with respect to the physical properties is obtained only after extremely long annealing.

In the two-phase model discussed above, the permittivity curves in Fig. 1 can be regarded as a superposition of the permittivity curves for the ordered and for the disordered material. We tried to generate the permittivity curves in Fig. 1 by adding<sup>3)</sup> the permittivity curve of the disordered material and the permittivity curve of a fictitious material having a first-order transition at 80 °C. A good agreement with the experimental curves can be obtained for  $T < 80$  and  $> 110$  °C but at temperatures  $80$  °C  $< T < 110$  °C rather large deviations were observed. This may be an indication that especially in this temperature range the dielectric constant of the ordered phase is strongly influenced by the presence of a disordered phase in the same sample or vice versa (the ordered phase is PE whereas the disordered phase is FE at these temperatures).

PST materials with a spatially inhomogeneous order parameter were not investigated as extensively as PSN materials, but the results show that both compounds

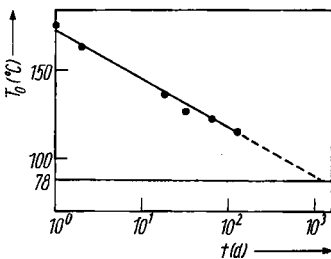


Fig. 4. Extrapolated Curie temperature as a function of the annealing time for PSN materials

<sup>3)</sup> The adding was carried out in three ways: arithmetic, reciprocal, and logarithmic. In all cases a minimum in the dielectric constant is observed between 80 and 110 °C (which does not exist in the experimental curves).

behave in a similar way. The disordered and ordered materials show heat effects at  $-6$  and at about  $32$  °C (Table 2), respectively.<sup>4)</sup> Heat effects at intermediate temperatures were not observed during the ordering process. Contrary to PSN, the DSC curves do not show a sequence of the two transitions in one and the same sample. This is due to the fact that the heat effect at the low-temperature transition has become unmeasurably small before the heat effect at the high-temperature transition is measurable, which may be an indication that the heat effect at the low-temperature transition is influenced by the presence of disordered material and vice versa. The fact that heat effects were observed only at the two temperatures  $-6$  and  $+32$  °C proves that during the ordering process only two states exist, an ordered and a disordered state. The transition temperature for the FE  $\rightarrow$  PE transition in the ordered phase is not influenced by the presence of disordered material in the same sample and vice versa.

A very remarkable point is the fact that the FE  $\rightarrow$  PE transition in *ordered* PSN material takes place at a *lower* temperature than in disordered PSN. In contrast with this the *ordered* PST phase has a higher transition temperature than the disordered PST phase. We do not have an explanation for this different behaviour of PSN and PST.

### 3.2 Materials with a spatially homogeneous order

In this section the physical properties of PSN and PST materials with a spatially homogeneous (dis)order will be discussed. A homogeneous disorder in PST leads to a diffuse FE  $\rightarrow$  PE transition and the diffuseness of this transition increases with a decrease of the long-range order parameter. This result *seems* to fit very well in models that explain the DPT by assuming that the material is chemically heterogeneous on a microscale. Therefore, the results will be discussed successively in the framework of these models:

- (i) compositional fluctuation model,
- (ii) order fluctuation model,
- (iii) model of Burns and Reinecke.

It will be shown that the first two models cannot explain the DPT in our materials.

In the well-known compositional fluctuation model [6] the material is supposed to be heterogeneous on a scale of 100 to 1000 Å. Fluctuations in the Ta<sup>5+</sup> and Sc<sup>3+</sup> content in PST should give rise then to microregions with different transition temperatures. A superposition of all transitions in these so-called Kántzig regions results in a DPT.

In this model the diffuseness of the DPT is determined by:

- (i) the width  $\Delta y$  of the compositional fluctuations,
- (ii) the dependence of the transition temperature on the composition,  $dT_c/dy$ .

For a binary alloy  $A_y B_{1-y}$  it has been determined that the width of the compositional fluctuations is given by [12]

$$\overline{\Delta y^2} = \left( \frac{n}{y(1-y)} - \frac{2zn \Delta H}{kT} \right)^{-1},$$

where  $n$  is the number of atoms in the fluctuation,  $z$  the coordination number,  $\Delta H$  the enthalpy of interaction between A and B, and  $T$  the preparation temperature.

Taking for example a volume of  $100 \times 100 \times 100$  Å<sup>3</sup> ( $n \approx 16000$  unit cells) of PST ( $y = 0.5$ ) and neglecting in first approximation the interaction term ( $\Delta H = 0$ ),

<sup>4)</sup> In [5] it was shown that a PST material with  $\Omega = 0.94$  has a transition at  $25$  °C. After annealing at  $1000$  °C the transition temperature is somewhat higher ( $30$  to  $35$  °C). This could be a result of an increased value of  $\Omega$ .



it can be calculated that  $\Delta y = 0.004$ . In a completely disordered PST sample  $T'_c = +13$  °C, but deviations from the Curie-Weiss law were observed up to  $+165$  °C. If remanent ferroelectricity resulting from compositional fluctuations is responsible for these deviations, then it can be concluded that fluctuations with a transition temperature of  $T'_c + 150$  °C should occur. This gives  $dT'_c/dy = 150/0.4 = 375$  K/%. In the case of PST the interaction term is certainly not negligible because of the charge difference between the  $\text{Sc}^{3+}$  and  $\text{Ta}^{5+}$  cations. There is a strong tendency for ordering and  $\Delta H < 0$ . A negative value of  $\Delta H$  results in decreased compositional fluctuations and therefore  $dT'_c/dy \gg 375$  K/%. Such a large value is hard to imagine and in our opinion compositional fluctuations cannot explain the DPT in these materials.

A modification of the compositional fluctuation model is given by Smith and Cross [13]. They explained the DPT in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  by assuming that chemical order fluctuations would give rise to a spread in transition temperatures. In this model one expects that the broadening and deviations from the classical behaviour (non-Curie-Weiss behaviour) are limited to a temperature interval between the transition temperature for the ordered phase and the transition temperature for the disordered phase. In Table 3 we see that chemical disordering leads to a gradual decrease of the transition temperature. However, the broadening of the permittivity curves is certainly not limited to a temperature interval below the transition temperature of the ordered phase: deviations from the Curie-Weiss law can still be observed more than 125 K above this transition temperature. Therefore, it can be concluded that order fluctuations can hardly explain the broadening of the permittivity curves in PST materials with a spatially homogeneous disorder.

Related to the compositional fluctuation model is the model proposed by Burns [4] and Reinecke and co-workers [8, 9]. In this model the DPT is explained by assuming that localized perturbations are coupled to the optic modes. This coupling leads to an enhancement of the dielectric constant and the formation of localized polarized regions far above the transition temperature. The transition is not associated with a soft phonon mode, which is indeed observed experimentally [4, 9]. In the view of Burns and Reinecke the localized perturbations are impurities, vacancies, local deviations from the stoichiometry in solid solutions, or localized structural perturbations. This model may be applied to PST. In the case of PST perturbations are formed by localized deviations from the long-range order. In this model it is logical that the diffuse character of the FE  $\rightarrow$  PE transition decreases with an increase of the order. Although this model seems to be promising for the explanation of DPT's, there are two very important features that must be checked in order to decide whether this model may be used for the DPT in PST:

- (i) the absence of a soft phonon mode,
- (ii) the existence of polarized regions far above the transition temperature.

Although the deviations from the Curie-Weiss law may be an indication that polarized regions exist far above the transition temperature, a more direct proof is necessary. Direct evidence for the existence of polar regions may be obtained from second harmonic generation (SHG) measurements [18]. However, preliminary SHG experiments on powdered samples failed because the experiments were irreproducible, which is probably caused by the fact that the SHG signal is weak.

### 3.3 Properties of highly ordered materials

The FE  $\rightarrow$  PE transition in the ordered phase of PSN is of first order. This follows from the fact that in materials with  $x \geq 0.8$  we have observed:

- (i) double EP hysteresis loops in the temperature interval 78 to 86 °C,
- (ii) a strong *latent* heat effect in the DSC measurements,

(iii) a thermal hysteresis in the permittivity curves for  $T < 85$  °C. The FE  $\rightarrow$  PE transition in ordered PST is of first order, too [5].

Whatever model may be used for the explanation of the DPT (see Section 3.2) it is justified to expect that a material without perturbations, order fluctuations, etc., in other words a completely ordered material, shows a classical, sharp transition. Both in PSN and PST long annealing did not give this result. In PST long annealing at 1050 °C leads to a highly ordered material ( $\Omega = 0.94$ ). It appears that both  $\Omega$  and the physical properties are independent of further heat treatments and it can be concluded that equilibrium is reached in this case. The FE  $\rightarrow$  PE transition is sharp but deviations from the Curie-Weiss law at  $T > T'_c$  were observed. For PSN the  $\epsilon'(T)$  curve is far from classical although the disorder  $\rightarrow$  order transformation is almost completed ( $x = 0.98$ ). However, this high value of  $x$  does not indicate that a situation with  $\Omega = 1$  has developed. A structural refinement of highly ordered materials (see Part I) shows that  $\Omega = 0.9(2)$ . The large standard deviation makes an accurate determination of  $\Omega$  impossible. Some residual disorder may be present and it has been shown that probably only an extremely long heat treatment at 940 °C will yield a completely ordered material with a classical FE  $\rightarrow$  PE transition. In our opinion the deviations from the classical behaviour are due to some kind of residual disorder in the samples. This residual disorder could be due to one of the following facts:

- (i) The equilibrium situation at the annealing temperature has  $\Omega \neq 1$ .
- (ii) The equilibrium situation at the annealing temperature is not yet reached.
- (iii) In the ordered material a certain amount of small antiphase domains is present.

The fact that the deviations from the classical behaviour are observed in spite of the fact that the materials are almost completely ordered leads to the conclusion that the introduction of a small amount of disorder in an ordered material strongly affects the physical properties and it seems that measurement of the deviations from Curie-Weiss behaviour offers a very sensitive tool for the detection of small amounts of disorder in FE materials.

### 3.4 Comparison with literature

It appears that our results on PSN are somewhat different from the results reported in literature [1 to 3]. As has been shown in Part I of this paper the symmetry of PSN is rhombohedral and not tetragonal. Moreover our disordered samples have a different FE  $\rightarrow$  PE transition temperature and the  $\epsilon'(T)$  curve is less broadened than has been reported in literature (Table 4).

Table 4

Curie temperature ( $T'_c$ ), maximum dielectric constant ( $\epsilon'_{\max}$ ), and  $b_{3/4}$  (see Table 3) for disordered PSN materials

authors	$T'_c$ (°C)	$\epsilon'_{\max}$	$b_{3/4}$ (°C)	reference
Smolenskii	90	2400	65	[1]
Molchanova et al.	90	21000	26	[2]
Kuchar and Valenta	90	25000	35	[3]
Stenger and Burggraaf	109	40000	18	this paper

Perhaps these differences are due to small differences in degree of order that result from different preparation techniques. Our materials were sintered at 1250 °C but in literature mostly a somewhat lower sintering temperature was used and sometimes the materials were hot pressed. All authors reported completely disordered samples, but the superstructural lines in the X-ray diffraction patterns are hardly visible for materials with a low degree of ordering. So the precise degree of disorder in the materials reported in literature is not determined but is in our opinion different from the disorder in our PSN 1 sample. This hypothesis is supported by the fact that our PSN samples were sintered at temperatures above the order-disorder transition temperature (1210 °C, see Part I of this paper) whereas many PSN samples that were used in literature were sintered below the order-disorder transition temperature.

### 3.5 Comparison with related materials

Finally a comparison with some other compounds should be made. It has been shown that disordered PST has a strong DPT behaviour. The diffuseness of the FE → PE transition in PSN 1 is less, but still clearly visible. On the basis of theoretical DPT models this result is not unexpected and it is in full agreement with the experimental observation that disordered  $\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$  and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  also show DPT behaviour [14,15]. Long heat treatments carried out by the present authors ( $\geq 1$  month at 900 and 950 °C) did not result in a significant change of the  $\epsilon'(T)$  curves of these materials, but an increased order was not observed by means of X-ray diffraction. Probably the degree of order did not change as a result of the heat treatments. On the other hand, the completely disordered compound  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  shows a classical, sharp second-order FE → PE transition [16, 17]. This is unexpected in view of the other results on disordered perovskite compounds. Any model that treats the DPT as a result of chemical disorder should have an explanation for the fact that the transition in  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  is sharp despite its high degree of chemical disorder.

## 4. Conclusions

1. The influence of chemical disorder on the FE → PE transition has been investigated in PSN and PST. Both in the case of PSN and in the case of PST the ordered phase shows a first-order FE → PE transition at 78 and 32 °C, respectively. The disordered phase has no clearly defined transition temperature. Dependent on the method of measurement this temperature varies for PST from -6 to +13 °C and for PSN from +100 to +109 °C.
2. A spatially homogeneous disorder leads to a diffuse FE → PE transition. In PST it has been shown that the degree of diffuseness is dependent on the value of the long-range order parameter. A decrease of  $\Omega$  leads to a more diffuse transition.
3. A hybrid material in which chemically ordered domains exist in a disordered matrix shows two successive FE → PE transitions. The transition temperatures are almost independent of the fraction of disordered material and represent the FE → PE transition of the disordered and ordered material, respectively.

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