



ORDERING AND DIFFUSE PHASE TRANSITIONS IN $Pb(Sc_{0.5}Ta_{0.5})O_3$ CERAMICS

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The ordering of the Sc^{3+} and Ta^{5+} ions in $Pb(Sc_{0.5}Ta_{0.5})O_3$ can be varied by proper heat treatments (1000-1500°C). The ferroelectric \rightarrow paraelectric transition is strongly influenced by this ordering. With decreasing orderparameter Ω the phase transition becomes more diffuse and a number of properties show strong changes.

1. Introduction

$PbSc_{0.5}Ta_{0.5}O_3$ (PST) has a perovskite structure ABO_3 . The A-position is occupied by Pb^{2+} ions and the octahedral B-position by Ta^{5+} and Sc^{3+} ions. The arrangement of Ta^{5+} and Sc^{3+} can be disordered or ordered in which latter case a so-called 1:1 ordering [1] is formed. This 1:1 ordering leads to a doubled unit cell and the development of this type of ordering can be detected by the presence of superstructural lines in the X-ray diffraction pattern.

PST is ferroelectric (FE) at low temperatures and at 26°C a transition to the high temperature paraelectric (PE) phase takes place [2]. Many phase transitions in macroscopic homogeneous materials are characterised by the fact that the transition temperature is not really sharply defined. In these so-called diffuse phase transitions (DPT's) [3,5], the transition is smeared out over a certain temperature interval. Although the problem of DPT's is far from being solved, the fact that most pronounced examples of DPT behaviour are observed in FE solid solutions indicates that the chemical disorder in such systems influences the phase transition.

In this paper we show that in PST materials the diffuseness of the phase transition is strongly correlated with the degree of ordering of the Sc^{3+} and Ta^{5+} ions.

2. Preparation of the Materials

All ceramic materials were prepared by means of a mixed oxide method starting with the pure (> 99.8%) oxides PbO , Sc_2O_3 and Ta_2O_5 . The raw materials were dried (PbO and Ta_2O_5 at 200°C Sc_2O_3 at 800°C) and weighed according to the batching formula $Pb_{1.08}Sc_{0.5}Ta_{0.5}O_{3.08}$. The excess of PbO in this formula is necessary for improving the sintering properties of the material. In all cases the excess of PbO disappears during the sintering procedure. After mixing, the oxides were pre-fired at 850°C during 16 hours and at 1000°C for 2 hours. After each firing step the powders were ball milled under isopropanol. After isostatic pressing at 4000 atm, the materials were sintered in almost closed platinum capsules in a controlled O_2 and PbO atmosphere in the following way:

- PST1 and PST2: sintering temperatures 1500°C

and 1450°C, sintering time 4 hours. To prevent the loss of large quantities of PbO , the pellets were completely surrounded by PST powder.

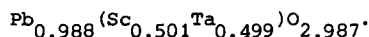
- PST3: sintering temperature 1300°C, sintering time 8 hours. If the material is completely surrounded by PST powder, the excess of PbO is not completely removed at this temperature. Therefore only a few grams of $PbZrO_3$ powder were placed at the bottom of the platinum capsule in order to maintain a fixed PbO atmosphere.

- PST4 and PST5: after the same sintering procedure as given for PST3, the materials were given an additional long heat treatment at 1050°C in a capsule especially designed to prevent PbO losses.

A complete summary of the sintering conditions is given in table I. From the sintered specimens discs were made with a diameter of 6 mm and a thickness of 0.5 mm.

3. Characterisation of the Materials

- Composition. Chemical analysis of PST1, performed by means of X-ray fluorescence, gives the following formula for this material:



PbO deficiencies for the other materials were calculated from the observed weight losses during the (total) synthesis and are smaller than 1.7%.

- Homogeneity. Second phases were not observed with X-ray diffraction and scanning electron microscopy. Large scale compositional fluctuations will generally result in a broadening of the X-ray diffraction lines. However, the half widths of the 222 reflection lines ($\bar{D} \approx 0.18^\circ$) are comparable with the half width of the unbroadened reflection lines of Si. A very sensitive indication for the homogeneity in the case of PST materials is the color of the sample. Pb deficiencies larger than about 2 at% result in a strong yellow coloration of the samples and the formation of a pyrochlore phase as can be deduced with X-ray diffraction. None of the present PST materials showed such a (local) coloration. It can be concluded therefore that large scale compositional fluctuations are absent in the materials under investigation here.

- Grain Size. Average grain sizes, given in table I, were determined for polished and thermally etched (1150°C during 5 minutes in controlled PbO atmosphere) samples by means of the linear intercept method and by using the relation $\bar{D} = 1.56 \bar{G}$ [4]. It can be seen from table I that a decrease of the sintering temperature leads to a decrease of the average grain size. Furthermore the long annealing time at 1050°C leads to some grain growth.

- Ordering. The long range order parameter is defined as $\Omega = 2n-1$

n = occupation number of the Sc atoms at the 4b position.

The occupation number b is determined by X-ray diffraction techniques. A summary of the method is given in appendix I and the results are given in table I. Apparently a decrease in sintering

- ii In a certain temperature interval above the transition the permittivity does not show Curie Weiss behaviour.
- iii The values of $b\frac{1}{2}$ increase with decreasing order parameter Ω ($b\frac{1}{2}$ is defined as the width of the permittivity curve at $\frac{1}{2}$ of its maximum height).
- iiii Frequency dependence of the dielectric constant in the transition region of the highly disordered materials, which is similar to the frequency dependence as observed in other materials with a DPT [3,5].

A second notable feature in fig. 1 is the fact that in these materials a more diffused phase transition is accompanied by an increasing ϵ'_{max} DSC measurements.

All samples showed a latent heat effect at the temperature T_t (see table 1). An increase of the

Table I: Syntheses, Characterisation and Properties of PST Materials

Material	Heat treatment	Cooling rate °C/min	\bar{D} µm	ρ	PbO def. at%	Ω	T'_c °C	$b\frac{1}{2}$ °C	T_p °C	T_t °C	ΔH J/mol
PST1	4h 1500	100	20	0.89	1.2	0	13	41	-6	-5	34
PST2	4h 1450	50	4.2	0.96	1.3	0.52(8)	5	33	-6	-5	75
PST3	8h 1300	10	2.4	0.95	1.2	0.74(6)	17	27	5	7	235
PST4	8h 1300/113h 1050	3	4.4	0.96	1.6	0.82(6)	25	12	25	24	420
PST5	8h 1300/340h 1050	3	4.3	0.96	1.7	0.94(4)	25	13	25	24	420

Heat treatment: time is given in hours, temperature in °C

Cooling rate : the values are only rough estimates

\bar{D} : average grain size

ρ : density relative to the theoretical density

PbO def. : deficiency of PbO in the material given in at% Pb

Ω : long range order parameter. Standard deviations in parentheses

T'_c : temperature at which the dielectric constant is at maximum

$b\frac{1}{2}$: width of the permittivity curve at $\frac{1}{2}$ of its maximum height

T_p : temperature at which the remanent polarization disappears

T_t : temperature at which a latent heat is observed

ΔH : magnitude of the latent heat effect

temperature leads to an increase of the order parameter Ω . Moreover long time annealing at 1050°C leads to highly ordered PST materials.

4. Physical properties

Dielectric constants, EP hysteresis loops and thermal properties were measured using standard methods as described in [5]. A short summary is given in table I.
Dielectric Measurements.

The dielectric constant as a function of temperature is given in fig. 1 for several PST materials. It can be seen that the transition becomes less diffuse when the order parameter Ω is increased. This can also be concluded from the following:

- i The temperature at which the dielectric constant is at maximum (T'_c) does not coincide with the temperature where the dielectric loss is at maximum (T_b).

order parameter Ω corresponds with an increase of the latent heat and temperature T_t . The temperature T_t is not coincident with the temperature at which the dielectric constant is maximum ($T_t < T'_c$). The difference between T_t and T'_c increases with decreasing order parameter Ω .

EP Hysteresis Measurements.

At low temperatures all samples show square FE hysteresis loops. Increasing the temperature leads to a disappearance of the square loops at the temperature T_p . The materials PST1, PST2, PST4 and PST5 show double hysteresis loops in a small temperature interval above T_p ($T_p < T < T_p+10$), which change into so-called slim loops at still higher temperatures. The material PST3 does not show clear double hysteresis loops and the square loop changes into a slim loop at the temperature T_p . Remanent polarization as a function of temperature was obtained from these EP hysteresis loops and is shown

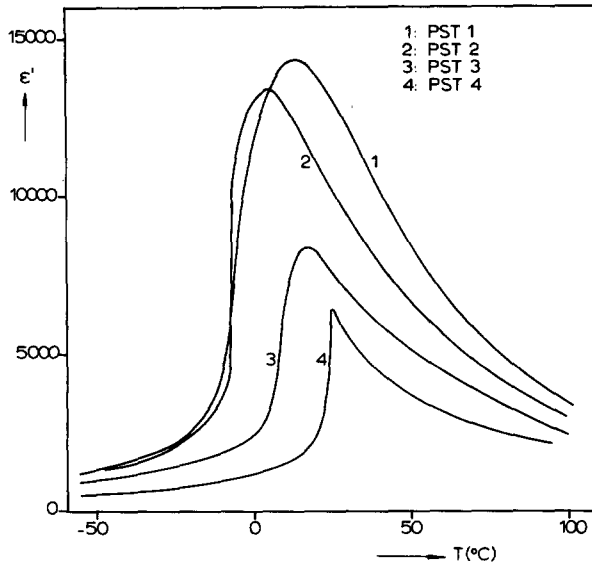


fig. 1: Dielectric constant as function of temperature for several PST materials (10 kHz, heating curves). The notation of the materials is explained in table I.

in fig. 2. It can be seen that at the temperature T_p all materials show a loss of overall polarization. The temperature T_p appears to be coincident with the temperature where a latent heat effect is observed (T_t , table I).

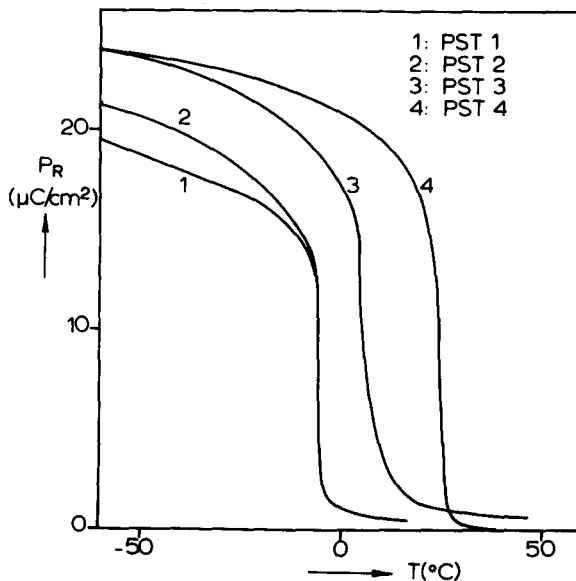


fig. 2: Remanent polarization as function of temperature for several PST materials.

5. Discussion

The most interesting point is the fact that a *decrease* of the long range order leads to an *increased* diffuseness of the phase transition and a strong change in a number of other properties. In the following it will be discussed whether secondary effects can be responsible for the observed effects.

- i Grain size effect. Theoretical models and experimental results [6,7] in related material systems show that an increase of the grain size leads to a sharper transition. However, as can be seen from table I, the PST materials with the larger grain size show the more pronounced DPT behaviour and the diffuseness of the transition decreases with decreasing grain size. This leads in our opinion to the conclusion that the observed broadening of the permittivity curves can not be attributed to grain size effects.
 - ii Inhomogeneity effect. As has been shown in chapter 3 no inhomogeneities were observed. All materials have the same small Pb deficiency. Therefore neither Pb deficiencies, nor large scale inhomogeneities can explain the broadened permittivity curves.
 - iii Mechanical stresses. These can arise during the cooling and during the mechanical processing of the materials. However, indications that large stresses had developed during the cooling period, such as microcracks, were not observed. To remove mechanical stresses, all samples were annealed during 2 hours at 800°C followed by slowly cooling. PbO losses were not observed and the degree of ordering did not change because of this heat treatment.
 - iiii Porosity effect. The material PST1 shows a rather high porosity and this fact alone may cause a broadened permittivity curve together with a low value of ϵ'_{max} . It can be seen however from table I that the value of ϵ'_{max} of PST1 is the highest one. Furthermore the other PST materials have equal porosities and it is clear that in these materials the diffuseness of the transition is not correlated with the porosity. Therefore a porosity effect does not play a significant role.
- Finally it should be remarked that all the above mentioned secondary effects can lead to a broadening of the $\epsilon'(T)$ curves, but as has been shown in literature such a broadening is accompanied by a strong decrease of ϵ'_{max} . In our PST materials however we observed just the opposite; that a *broadening* of the permittivity curves is accompanied by a strong increase of ϵ'_{max} . All these considerations lead in our opinion to the conclusion that in PST materials a *decrease* of the order leads to *more diffuse* phase transitions. In the well ordered materials PST4 and PST5 a more or less classical sharp FE \rightarrow PE transition was observed: the maxima in the $\epsilon'(T)$ and $\epsilon''(T)$ curves are sharply defined and the transition-temperatures as obtained by different techniques coincide ($T_p \approx T_t \approx T'_c \approx T_b$). The transition is first order, which can be deduced from:

- i double hysteresis loops were observed at $T_p < T < T_p + 10^\circ\text{C}$,

ii the occurrence of a sharp and strong latent heat effect,
 iii thermal hysteresis in the permittivity curve. If the long range order parameter decreases, the transition becomes diffuse and $T_p = T_t < T_b < T'_c$, which is a normal feature for materials with a DPT, as for example (Pb, La)(Zr, Ti)O₃ [5].

In a subsequent paper, studies concerning the kinetics of the ordering process will be presented. Moreover it will be shown that similar effects as described here for PST, can be observed in Pb(Sc_{1/2}Nb_{1/2})O₃.

6. Conclusions

-Heat treatments at temperatures between 1000°C and 1500°C result in homogeneous PST samples, with a long range order parameter Ω varying between 0 and 1 (dependent on heat treatment).

-A material with $\Omega = 0.82$ already shows an almost classical sharp first order transition. A decrease of the long range order parameter to zero leads to diffuse FE \rightarrow PE transitions and to an increase of ϵ'_{max} by a factor of three.

-All materials show a latent heat effect at a temperature T_c . The temperature T_c appears to be coincident with the temperature at which the remanent polarization disappears. Both the temperature T_c and the magnitude of the heat effect decrease with a decreasing order parameter Ω .

Appendix: Determination of Ω .

X-ray intensities were obtained by standard counting methods, using a Philips powder diffractometer with CuK α radiation. The calculations were carried out on a DEC 10 computer using a non-linear least squares computer program [8]. The program attempts to minimize the

value $\sum_i W_i (I_{obs,i} - I_{calc,i})^2$ where Σ is the summation over all measured peaks. The weight W of each peak is calculated according to the formula $W = \frac{1}{I_{obs} + 2B}$ in which B = background.

In each case the final refinement was carried out for the space group Fm3m, using 20-30 reflections. The refined parameters were:

- scale factor
- overall isotropic temperature factor. In all cases a value 1.2-1.4 (1) was obtained
- occupation numbers of Sc and Ta on the positions 4a and 4b. The results are converted to Ω values and given in table I. For PST1 a value $\Omega = 0$ is given because no superstructural lines were observed.
- Occupation number of Pb on the position 8c. In all cases values of 0.93 - 0.98 (3) were obtained. This is somewhat lower than has been expected in view of the chemical analysis. It is found however, that the Ω values are not influenced by the occupation number of Pb on the position 8c.
- Positional oxygen parameter on the position 24e (x00). In all cases a value $x = 0.24$ (1) has been observed, which is not significantly different from the value in the disordered Pm3m structure ($x = 0.25$). Ferroelectric shifts of the ions in PST4 and PST5 were too small to be detected.
- R-factors ranging from $R = 4.7 - 5.5\%$ were obtained.

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