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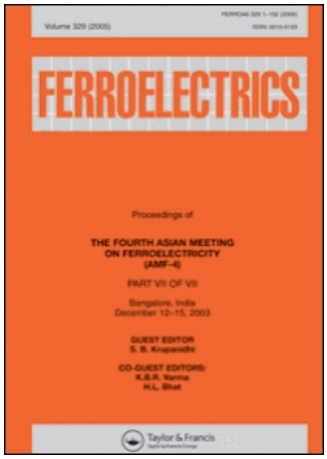

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The Nature of Different Behaviour of PSN and PST Relaxors

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Dielectric anomaly of disordered PSN appears at higher temperature than that of the ordered PSN, whereas in PST the situation is opposite. TEM studies of $Pb[Sc_{0.5}(Nb_{1-x}Ta_x)]O_3$ single crystals (x = 0, x = 1, x = 0.3) show that PSN crystals are grown in more disordered state than the PST crystals and the PSNT crystals are the mostly ordered: linear sizes of {111} ordered regions are 3–4 nm, 30–40 nm and 60–100 nm, respectively. The behaviour is associated with nonlinear and spatial correlation contribution to the random field distribution function.

Keywords: ferroelectric relaxors; $Pb(Sc_{0.5}Nb_{0.5})O_3$; $Pb(Sc_{0.5}Ta_{0.5})O_3$; $Pb(Sc_{0.5}Nb_{0.2}Ta_{0.3})O_3$

INTRODUCTION

Complex perovskites have attracted the interest from the mid fifties when Smolensky et al. discovered diffused phase transition in $A(B'B'')O_3$ compounds[1-4]. The diffuseness of the transition was related

to a heterogeneity of very small scale from the very beginning [4,5] but only the results of studies of Setter and Cross[6,7] and also Stenger and Burggraaf[8,9] pointed to an essential role of B-site ion distribution in the relaxor behaviour of $Pb(Sc_{0.5}Nb_{0.5})O_3$ (abbreviated to PSN) and $Pb(Sc_{0.5}Ta_{0.5})O_3$ (PST). Nanoscale B-site ordering was revealed later in TEM studies of PST relaxors[10-15]. Regions in which the Sc^{3+} and Ta^{5+} ions occupy alternate B-sites along the [111] direction were observed as giving rise to a F-centred superstructure doubling the basic perovskite unit cell. Randall and Bhalla[16] discussed various possibilities of B-cation order: random occupation, short coherent long-range order (nanoscale) and long coherent long-range order of B-site cations in correlation with relaxor or normal ferroelectric/antiferroelectric behaviour.

Various models have been proposed to explain the relaxor behaviour of complex perovskites. The first, of Smolensky[4], related the diffuseness of the transition to the chemical heterogeneity of the perovskites but could not explain strong frequency dispersion characteristic of the relaxors. The polar glass model[17] and the superparaelectric model proposed by Cross[18] described the dispersive behaviour of relaxors but could not explain the spontaneous transition from the relaxor state to the ferroelectric phase observed in PSN and PST[19-21]. Theory of the dielectric response of relaxor ferroelectrics, taking into account the dynamics of interacting clusters, was published by Vugmeister and Rabitz[22,23]. Glinchuk and Stephanovich[24] proposed a model of mixed ferroglass phase with the coexistence of both long- and short-range order to describe the dielectric behaviour of ferroelectric relaxors. Here we would like to discuss the behaviour of PSN, PST and $Pb(Sc_{0.3}Nb_{0.2}Ta_{0.3})$ (PSNT) crystals in correlation with the sizes of {111} ordered regions revealed by TEM.

RELAXOR BEHAVIOUR OF PSN AND PST

The ability of the B-site ions to be ordered in the $A(B'B'')O_3$ perovskite structure is determined by the difference between the valency of the B'' and B' ions and the difference between the ionic radii of B' and B''[8]. Moreover, the B-O bond strengths should affect the ordering and various approaches to involve the strength were proposed[21,25-27].

In the case of $Pb(B'_{0.5}B''_{0.5})O_3$ compounds, with B' trivalent and B'' pentavalent cations, strong elastic interaction determined by considerable difference ($r_{B'} - r_{B''}$) results in a stable long coherent long-range

structure (for instance $Pb(Ho_{0.5}Nb_{0.5})O_3$ and $Pb(Yb_{0.5}Nb_{0.5})O_3$ compounds), whereas small difference in the ionic radii favours the disordered structure (e.g. $Pb(Fe_{0.5}Nb_{0.5})O_3$).

PSN and PST are of special interest because the degree of structural order of the B-site cations can be varied by thermal treatment[6-9]. Ordered PSN and PST, with basic perovskite structure, are normal ferroelectrics, whereas the disordered materials, with short coherent ordering of B-site cations, exhibit relaxor behaviour and on cooling transform spontaneously into the ferroelectric state. The temperature of relaxor-ferroelectric phase transition coincides with the freezing temperature T_f obtained from fitting the dispersive dielectric anomaly to Vogel-Fulcher equation[19-21]. It should be, however, stressed that though the difference in the ionic radii in PSN and PST is the same (0.09Å)[28] and the general dielectric behaviour is similar the temperature T^D of the dielectric anomaly of disordered PSN is higher than that of the ordered state T^O, whereas in PST the situation is opposite[6,9,19-21]. Moreover, the dielectric anomaly in PSN takes place at considerably higher temperature than that in PST.

Phase diagram of $Pb[Sc_{0.5}(Nb_{1-x}Ta_x)]O_3$ crystals was reported recently by Eremkin et al.[29]. Though it is evident that varying the crystallization conditions one can change the degree of order only isometric crystals of $x \leq 0.5$ were grown in the disordered state. One can expect, however, that for the mixed crystals of $x \sim 0.5$ the temperature of dielectric anomaly of the disordered phase should coincide with that of the ordered structure.

EXPERIMENTAL

PSN, PST and PSNT single crystals were prepared in two steps. Powdered materials were obtained by high temperature solid-state reaction in proper homogeneous mixture of consistent oxides of purity better than 0.995[29,30]. Single crystals were grown from a flux mixture of the weight ratio A/PbF_2-PbO-B_2O_3: 0.15/0.40-0.40-0.05 in a covered platinum crucible; A- denotes here PSN, PST and PSNT, respectively. The homogeneous mixture was heated to the temperature T_1 during 2 h and maintained at the temperature for 2 h. The crucible was then cooled to T_2 within the time t_2 and to room temperature during t_3 (Table 1).

Cube shaped crystals were extracted with hot dilute nitric acid and their chemical formula was verified by X-ray spectroscopy. The order

parameter s of the crystals was determined by X-ray using the method described earlier[7]. The s- value of as-grown PST crystals amounted to 0.82, s = 0.87 for PSNT, whereas s ~ 0.4 for PSN.

TABLE 1 Growth schedule of PSN, PST and PSNT single crystals

Crystals	T_1 (K)	T_2 (K)	t_2 (h)	T_3 (K)	t_3 (h)
PSN	1420	1070	55	273	20
PST	1470	1070	105	273	20
PSNT	1370	1020	45	273	10

Electron microscopy studies were carried out on as grown crystals at room temperature using Jeol 200 CX electron microscope.

RESULTS AND DISCUSSION

{111} superstructure reflections were observed in selected area diffraction patterns (<110>, <211>, and <123> zone axis) for all crystals studied. Figure 1 shows dark field micrographs obtained for as grown PSN, PST and PSNT crystals by setting the aperture around the F-type superlattice spot. The white regions are related to the domains of {111} ordering of the B-site cations.

The sizes of the ordered regions in as grown PSN are of 3-4 nm, whereas in PST crystals the {111} ordered regions are by one order of magnitude larger in agreement with those reported by Randall et al. for PST of similar order parameter[11]. The ordering in PSNT single crystals was higher and the sizes of the {111} ordered regions amounted to 60 - 100 nm.

To discuss the B-site cations ordering of the crystals in correlation with their dielectric behaviour we show in Figure 2 the temperatures of dielectric anomalies in disordered and ordered $Pb[Sc_{0.5}(Nb_{1-x}Ta_x)]O_3$ taken from literature and from our experiments. The temperatures T_f, obtained from the fit of temperature dependences of dielectric permittivity of disordered samples at various frequencies to Vogel-Fulcher equation, coincides with the phase transition temperatures from relaxor to ferroelectric state.

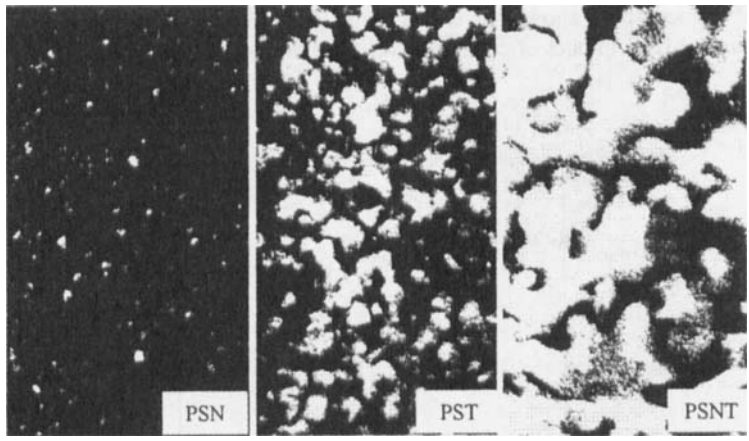

FIGURE 1 Dark field electron micrographs obtained for as grown PSN, PST and PSNT single crystals. White regions are related to {111} B-site ion ordered domains

As it could be expected, the difference in the temperature of dielectric anomaly of ordered and disordered PSNT is rather small in comparison with those of PSN and PST. Also the sizes of {111} ordered domains are the greatest in PSNT crystals.

Recently published refinement of the crystal structure from high resolution neutron time-of-flight powder diffraction data show that large displacement parameters are associated with both lead and oxygen ions in the paraelectric phase of PST[36]. It was interpreted that the ions are locally displaced from their equilibrium sites but without long range coherence in the orientation of the displacements. Calculation yield 0.18 Å displacements of the oxygen ions in the direction perpendicular to the Sc-O-Ta bond and isotropic 0.21 Å displacements of the lead ions at 400 K.

The results confirm the model of mixed ferroglass phase with a coexistence of long and short range order in the 1:1 type relaxors [24,37-39]. Randomly oriented oxygen and lead ion displacements are, besides the substitutional disorder and vacancies, the sources of the random field in PST (and PSN) crystals. Calculations of the distribution function

of random field show that the random field determines the order parameter (the number of coherently oriented dipoles)[37].

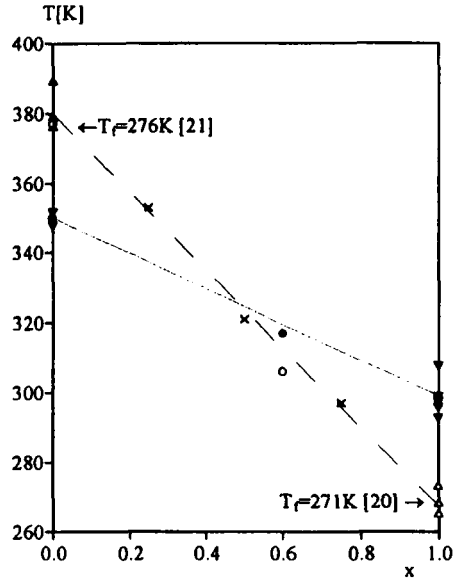

FIGURE 2 Temperatures of dielectric anomalies of disordered (open symbols) and ordered (solid symbols) $Pb[Sc_{0.5}(Nb_{1-x}Ta_x)]O_3$; open and solid triangles - from [7, 9, 11, 20, 21, 31-34], crosses – from [35], open and solid circles – our crystals

The phase diagram of a disordered system is determined by the ratio of the mean field E_0 to its dispersion ΔE[37]. When $E_0 \gg \Delta E$ ferroelectric order appears, whereas for $E_0 \ll \Delta E$ short range order, characteristic of dipolar glass state is observed. The situation $E_0 \approx \Delta E$ leads to a mixed ferroglass phase, where only a part of dielectric dipoles is coherently ordered. It was shown that a nonlinear contribution of random field sources to the random field distribution function f(E) allows both nonlinear and spatial correlation effects[38,39]. Taking into account that the coefficient of nonlinearity is larger for Nb-O octahedra than that of Ta-O (the Ta-O bonds are more covalent[26,27]) one can expect stronger

nonlinear contribution of the random field in PSN. This can explain the fact that the dielectric anomaly in PSN appears at higher temperatures than that in PST. It has been shown, moreover, that at a certain concentration of random field sources, the temperature of dielectric anomaly of disordered state could be higher than that of the system with long-range order (Figs. 2 and 3 in Ref. [38]) and we believe that this is the case of PSN.

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