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TEM of the Relaxor Material $Pb(Sc_{0.5}Ta_{0.5})O_3$

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The transmission electron microscope (TEM) was used to directly observe ordered microdomains in $Pb(Sc_{0.5}Ta_{0.5})O_3$ (PST). The microstructure of both single crystal and polycrystalline PST was studied as a function of S, the degree of order (which was controlled by thermal treatment). The observed domain sizes were in good agreement with the results of prior X-ray studies. It was found that the domain coarsening kinetics are much slower for the single crystal than the polycrystalline material. Also evidence was obtained for the presence of short range order within PST.

§1. Introduction

Lead scandium tantalate $Pb(Sc_{0.5}Ta_{0.5})O_3$ is one of a number of ferroelectric compounds which exhibit so-called "relaxor behavior" i.e., these materials show a broad dielectric permittivity versus temperature peak, and dielectric dispersion at low frequencies. It has been postulated[1-3] that this type of behavior is due to the presence of microscopic regions within the material which are of slightly differing compositions (and hence Curie temperatures).

Setter and Cross investigated this model by studying the behavior of lead scandium tantalate (PST).[4,5] This material is particularly suited to this type of study because the degree of order of the B-site cations (Sc^{3+} and Ta^{5+}) can be controlled by thermal treatment. The structure of fully ordered PST is shown in Fig. 1; it can be seen that the Sc^{3+} and Ta^{5+} ions adopt a NaCl type structure on the B-site sublattice. Setter and Cross showed that in the disordered state, PST exhibited classic relaxor behavior. On ordering however, a pronounced sharpening of the permittivity versus temperature curves took place, thus supporting the model that the relaxor behavior is caused by chemical inhomogeneity on a nanoscopic scale.

Until very recently, evidence for the existence of ordered microdomains within PST has been indirect.[4] Harmer *et al.*[6] were the first workers to directly observe ordered microdomains in PST using the transmission electron microscope (TEM). The scale of the ordered structures was found to be of the order of 35-120 nm, which was in good agreement with the earlier X-ray results. A particularly interesting result from the study of Setter and Cross[5] was the difference in domain coarsening behavior exhibited by the single crystal and polycrystalline PST. On annealing the polycrystalline (ceramic) PST, the degree of order increased, and there was a corresponding increase in the size of the ordered domains (as determined by X-ray line broadening measurements). For the single crystal however, even for relatively high degrees of order (~80%), the domain size was determined to be <100 Å. The purpose of this study, therefore, was to use the TEM to directly examine the ordered domain configurations for both single crystal and ceramic PST, as a function of annealing conditions. In this way, it was hoped to gain a better understanding of the microstructure/property relationships in this system.

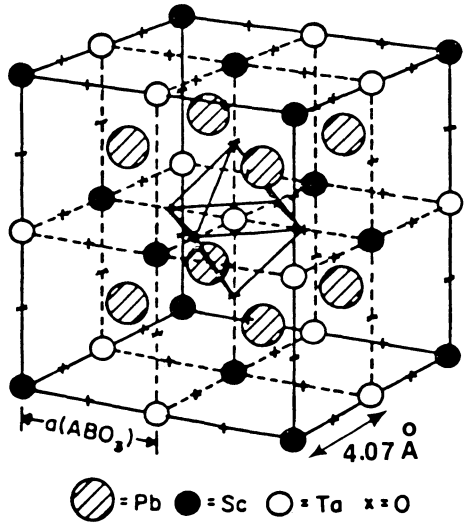

Fig. 1. Structure of ordered perovskite $Pb(Sc_{0.5}Ta_{0.5})O_3$ (after Galasso[11]).

Table I

PST		Heat Treatment	Degree of Order
Single Crystal	a)	As-grown	0.8
	b)	Annealed 24 hrs. 1000°C	0.8
	c)	1 hr. 1400°C air quenched	0.35
Polycrystal	a)	As sintered	0.37
	b)	2 hrs. 1000°C	0.86
	c)	30 hrs. 1000°C	0.86

§2. Experimental

The techniques used to prepare the PST single crystals[4] and polycrystalline sintered pellets[5] have been described in detail elsewhere. The samples studied, together with the corresponding heat-treatments are summarized in Table I. Lead loss during the annealing treatments was minimized by surrounding the specimens with a $PbZrO_3$-20 wt% PbO mixture. Thin foil TEM specimens were prepared by polishing down to ~30 μm, and argon-ion-beam thinning using 6 kV argon ions incident 15° to the foil plane. To prevent lead evaporation during ion-beam milling, a liquid-N_2 cooled cold stage was used.

From Fig. 1 it can be seen that there is an effective

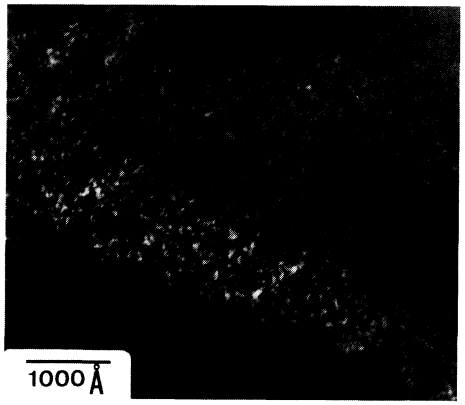

Fig. 2. Single crystal, as grown. Centered dark-field micrograph, bright regions are ordered microdomains.

Table II

Disordered			Ordered (NaCl structure)*			d-spacing (Å)
h	*k*	*l*		*h*	*k*	*l*	
—			F	1	0	0	8.14
—			F	1	1	0	5.76
—				1	1	1	4.70
1	0	0		2	0	0	4.07
1	1	0		2	2	0	2.88

F=forbidden reflection

doubling of the unit cell parameters when PST goes from the disordered to the ordered state. The effect of this on the observed reflections in the electron diffraction pattern is shown in Table II. The $(100)_s$ and $(110)_s$ super-lattice reflections are forbidden due to structure factor considerations, however the $(111)_s$ is allowed. It is this reflection therefore which can be used to image the ordered domains in dark field.

§3. Results

3.1 *Single Crystal*

i) As grown (S=0.8)

Figure 2 shows a centered dark-field micrograph of the as grown single crystal taken using the $(111)_s$ reflection. The bright regions are the ordered microdomains; the matrix (dark contrast) is disordered. The domain size was of the order 100–600Å. When this structure was annealed for 24 hrs. at 1000°C, no coarsening of the domains was observed, and the microstructure remained for the most part unchanged. This is in direct contrast to the behavior of the polycrystal which is discussed in a later section. Figure 2 is representative of the structure observed in the majority of the areas studied. In some isolated regions of the sample however, domains more resembling those reported by Harmer *et al.*[6] were observed. The reason for this variation in structure is unclear. It may be related to local variations in the degree of order occurring during the growth process.

ii) S=0.35

The degree of order of the as grown single crystal was relatively high. Disordering can be achieved however by annealing for 1 hr. at 1400°C, and air quenching. The resulting structure was very similar to that shown in Fig. 2. Despite the lower degree of order, ordered microdomains are still visible, the scale of the domains being similar to those of the "as grown" state.

3.2 *Polycrystal*

i) As sintered (S=0,34)

In the as sintered state, the degree of order is relatively low. Ordered microdomains ~200Å in diameter were observed, and the overall microstructure resembled that of the single crystal.

ii) Annealed at 1000°C (S=0.86)

After annealing for 30 hrs. at 1000°C, the structure underwent considerable coarsening as can be seen in Fig. 3. The wavy boundaries seen separating the domains are anti-phase domain boundaries (APB's). An APB is characterized by a disruption in the correct ordering sequence, and separates two fully ordered regions.[8] The observed domain size varied widely from ~200Å to over 4000Å. A similar structure was observed after annealing for only 2 hrs. at 1000°C, except in this case the maximum observed domain size was ~2000Å. This result confirms that coarsening of the domain structure occurs much more rapidly in the polycrystal than in the single crystal, and possible reasons for this will be discussed later.

3.3 *Anomalous* $(110)_s$ *Reflection*

As discussed previously, for the ordered NaCl structure, the $(110)_s$ superlattice reflection is forbidden due to structure factor considerations. Faint $(100)_s$ reflections were observed, however, for both single crystal and ceramic PST (Fig. 4). The possible origin of this anomalous $(110)_s$ reflection will be discussed more fully in the next section.

§4. Discussion

4.1 *Single Crystal*

For both the disordered (S=0.35) and ordered (S=0.8) single crystal, dark field imaging showed the structure to consist of ordered microdomains (200–600Å) within a disordered matrix. At first sight, the lack of dependence of the ordered domain size or density on the overall degree of order is difficult to understand. It should be remembered however that S (the degree of order) was estimated by ratioing the intensity of the $(111)_s$ X-ray reflection to that of the $(200)_s$. The value of

Fig. 3. Polycrystal, annealed 30 hrs. at 1000°C.

*Indexed using the ordered unit cell.

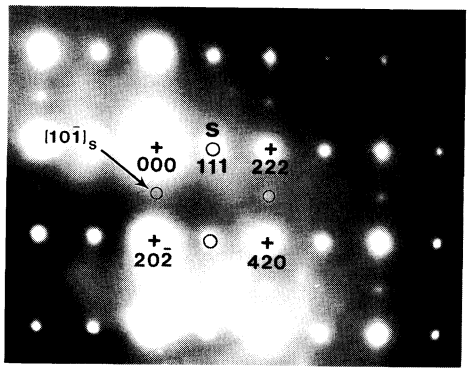

Fig. 4. [1$\bar{2}$1] diffraction pattern, note diffuse (110) reflections.

S obtained is thus an average for the whole specimen. The dark field imaging technique however only detects those volumes of material where the intensity of the $(111)_s$ is sufficient to produce an image in reasonable exposure times. Thus the X-ray and TEM techniques are measuring slightly different quantities, and in general one would expect the X-ray technique to give the higher value of S. Another factor which must be taken into consideration is the possibility of partial, short-range ordering (SRO). This is intermediate between disordered and fully ordered, and represents the stage where there is a marked preference for the B-site ions to have unlike neighbors, but the ordering extends over several unit cells only. This could account for the speckled contrast observed within the ordered domains.[9]

4.2 *Polycrystalline PST*

The ordered domain structure for the polycrystal (annealed 30 hrs. at 1000°C) is similar to that observed by Chang and Chen[10], however these workers did not state whether they were studying single or polycrystalline material, or the nature of the heat treatments carried out (if any). For the type of order occurring in PST, there is one unique type of APB whose anti-phase vector can be defined as 1/2 [001]. For this reason, no APB triple points can occur, and it is impossible to form a stable foam-like structure. Coarsening usually occurs readily for this type of APB configuration, and this was observed to be the case for the ceramic PST.

The reason for the lack of domain coarsening in the single crystal is not clear. One possibility is that it is related to differences in chemistry between the two samples, since the preparation techniques for the single crystal and polycrystal were completely distinct. If there is an excess of one of the B-site cations for example, this may have a stabilizing influence on a particular domain configuration.[12]

4.3 *Anomalous $(110)_s$ Reflection*

A series of experiments were carried out in order to determine the origin of the anomalous reflection $(110)_s$. The results were as follows:

a) It was determined that the $(110)_s$ reflection was not a thinning artefact, as the reflection was observed in thin specimens produced by crushing, as well as in ion-beam thinned samples.

b) It was shown to be unlikely that the $(110)_s$ reflection was the result of beam damage, because the d-spacing did not correspond to any reflections previously obtained from heavily damaged areas.

c) The $(110)_s$ reflection was determined not to originate from the APB's, since the reflection was observed even for selected area diffraction patterns taken from within a single domain.

Taking into account the above evidence, it is postulated that the observed $(110)_s$ reflections are the result of small regions within the crystal which have a type of order different from the NaCl structure. These regions could occur in either conventionally ordered or disordered regions of the crystal. Unfortunately this model is difficult to test because the diffuseness of these reflections made dark-field imaging of these regions impractical.

§5. Summary

Dark field imaging has been used to directly observe ordered microdomains in $Pb(Sc_{0.5}Ta_{0.5})O_3$. The size of the microdomains was in good agreement with the results of earlier X-ray determinations. The domain coarsening kinetics were much slower for the single crystal. Evidence has been obtained for the presence of short range order within PST. This study has focussed on the microstructural features of the ordered domains. These results will be presented more fully, together with the corresponding dielectric data, in a separate paper.

Acknowledgement

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