JOURNAL OF MATERIALS SCIENCE 15 (1980) 2478–2482

The contribution of structural disorder to diffuse phase transitions in ferroelectrics

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Simple crystal-chemical arguments were used to suggest that in the ferroelectric perovskite lead–scanium–tantalate ($PbSc_{0.5}Ta_{0.5}O_3$) the B-site cations in this simple ABO_3 structure should be close to the boundary between order and disorder. Both polycrystal ceramic and single crystal materials of this composition have been grown. In this study X-ray powder diffraction is used to identify the strong superlattice reflections associated with the ordering of scandium and tantalum ions in the B-site, and to demonstrate quantitatively how the degree of ordering can be modified by suitable thermal treatment. Thermal changes associated with the ferroelectric Curie temperature have been measured by differential scanning calorimetry and show very clearly the manner in which the diffuse (broadened) transition in this crystal is sharpened by increase in the B-cation ordering.

1. Introduction

A number of ferroelectric compounds and solid solutions of complex composition in the perovskite and tungsten bronze families exhibit a characteristic low-frequency dielectric dispersion and several unusual associated dielectric, optical and thermal properties [1–3]. Materials with this characteristic "relaxor-type" behaviour and associated properties are often referred to as ferroelectrics with diffuse or broadened phase transitions [4]. One possible explanation for the "smearing" of the normally sharp ferroelectric phase change [4] is in the statistical composition fluctuations which must occur if crystallographically equivalent sites are occupied randomly by different cations. A statistical treatment based on a postulated Gaussian distribution of local Curie temperatures associated with composition fluctuations has been given by Rolov [5] and does provide reasonable agreement with experiment. Some experimental support suggesting a sharpening of the transition with increasing order in the cation arrangement can be found from data on several different solid-solutions [3], but a clear resolution of the problem is masked by the changing compositions used in these studies.

In the following, simple crystal chemical principles have been used to suggest a compound, lead–scandium–tantalate (PST) which should be on the boundary between the ordered and disordered B-site cation arrangements. Powders, ceramics and single crystals of PST have been grown. This paper describes the crystal-chemical arguments used in selecting PST, and the X-ray diffraction studies which establish that the degree of disorder in the B-site cation arrangement can be controlled by suitable thermal treatment. To demonstrate that ordering of the B-cations does effect the sharpness of the ferroelectric transitions at the Curie temperature, differential scanning calorimetry has been used to delineate the associated thermal changes in samples with identical composition but different degrees of ordering.

In subsequent papers the influence of the ordering upon the dielectric, ferroelectric and elastoelectric properperties of single crystals and ceramics will be discussed.

2. Crystal-chemical considerations

The simple crystal chemical arguments used to elaborate the structure and chemistry required may be briefly summarized as follows:

0022–2461/80/102478–05 $02.50/0

(1) Structure: In order to reduce the energy for ordering, a simple structure is preferred. There is some evidence in the literature [6] that the Curie temperature and the degree of ordering may be changed by annealing in some tungsten–bronze structure ferroelectrics. However, the perovskite of the form $A(B'B'')O_3$ is a considerably simpler form and is therefore preferred.

(2) Cation ratio: The same argument of simplicity to reduce ordering energy would suggest a cation ratio $B'/B'' = 1/1$ and thus eliminate the classical relaxors like $Pb(Mg_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$.

(3) Charge on B-site ions: Large differences in the valence between B' and B'', as in $PbMg_{0.5}W_{0.5}O_3$ result in a very strong tendency to order through electrostatic forces. In the case of identical charges the correlation energy is related to cation size [7]. Thus, an appropriate compromise might suggest an $A(B^{+3}_{0.5}B^{+5}_{0.5})O_3$ composition.

(4) B-site ion size: Materials with large size differences in the B-cations are driven strongly towards ordering by electric forces, whilst materials with near identical cation size, for example $Ba(Fe_{0.5}Nb_{0.5})O_3$, may stay disordered even after long annealing. Gallaso and Darby [8] suggest for $Ba(M_{0.5}Nb_{0.5})O_3$ structures that the critical differences in Ahrens radius for ordering must lie between 7 and 17%.

(5) A-site ion size: The role of the A-site ion in modulating the interaction may be seen by comparing the disordered $Pb(Zn_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$ and $Ba(Zn_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$ with the corresponding ordered $Sr(Zn_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$. As would be expected, reducing the size of A-site cation enhances the elastic drive towards ordering on the B-site.

Similar arguments could be advanced in consideration of $(A'A'')BO_3$ perovskites, but the smaller base of available experimental data would make system selection more difficult.

To facilitate the selection of a suitable boundary composition, at the edge of stability for ordering, structural data were collected from the literature for about 150 compounds with the $AB'_{0.5}B''_{0.5}O_3$ composition. A computer program tabulated the ionic radii R_A, R'_B, R''_B, and the information on ordering. A small section of the tabulated data is given in Table I.

Taking consideration also of the known ferroelectric properties, the tabulation clearly suggested $Pb(Sc_{0.5}Nb_{0.5})O_3$ as a suitable starting candidate. Since, however, it would be desirable to be able to use X-ray diffraction to detect B-site order, a composition with a larger difference in atomic number (scattering power) between B-site ions would be desirable. Since $Pb(Sc_{0.5}Ta_{0.5})O_3$ (PST) is also ferroelectric, with a convenient Curie range near room temperature and with very similar valence and size characteristics for its ions, this crystal was chosen for the initial study.

3. Experiment

3.1. Sample preparation

Powders of the PST composition were prepared from stoichiometric proportions of the constituent oxides, PbO, Sc_2O_3 and Ta_2O_5 using reagent or high purity grade chemicals. Following ball milling under alcohol for 20 hours, the milled powders were dried, then calcinated at 800° C for 2 hours. The calcinated powder was then reground, pressed into pellets and fired at 1300° C for 1 hour.

The degree of ordering in the Sc:Ta occupied B-sites was controlled by thermal annealing for different time periods at 1000° C. Disorder was induced by a short firing to between 1400 and 1560° C followed by rapid quenching. It may be noted, however, that the ease with which the state of ordering could be changed depended markedly upon the thermal prehistory of the sample. To avoid chemical differences between samples, weight loss throughout all thermal treatments was kept below 1 wt%.

3.2. Ordering studies

X-ray diffraction was used to establish quantitatively the degree of ordering in the scandium and tantalum. In the ordered form, scandium and tantalum ions alternate in adjacent B-sites, forming two interpenetrating sublattices and giving an effective doubling of the primitive *a*-spacing. Thus the X-ray diffraction pattern is characterized by the appearance of superlattice reflections corresponding to half-integer spacing of the disordered structure.

X-ray diffraction patterns, scanned at a rate of $0.2° \min^{-1}$, were taken using a General Electric diffractometer using CuKα radiation. Two superlattice reflections (1 1 1) and (3 1 1) were compared with adjacent normal lattice reflections (2 0 0) and (2 2 2) respectively (indices refer to the double-cell unit cell). The order parameter S for a particular sample was determined by comparing the ratio of the observed superlattice reflection to the base lattice reflection for that sample with the calculated ratio of intensities for perfect ordering.

TABLE I The relation between ordering and ionic size of A and B′ ions in A($B^{+3}_{0.5}$$Nb^{+5}_{0.5}$)$O_3$

A($B'_{0.5}Nb_{0.5}$)O_3	Ionic radii*			Order of phase	Reference
	A	B′	B″		
Ca(NbAl)O_3	1.49	0.78	0.67	ordered	[9]
Sr(NbAl)O_3	1.54	0.78	0.67	ordered	[10]
Ba(NbAl)O_3	1.74	0.78	0.67	ordered	[10]
Pb(NbNi)O_3	1.63	0.78	0.74	disordered	[11]
Ba(NbNi)O_3	1.74	0.78	0.74	disordered	[12]
Ca(NbCr)O_3	1.49	0.78	0.755	disordered	[9]
Sr(NbCr)O_3	1.54	0.78	0.755	ordered	[12]
Ca(NbFe)O_3	1.49	0.78	0.755	disordered	[9]
Sr(NbFe)O_3	1.53	0.78	0.755	disordered	[13]
Pb(NbFe)O_3	1.63	0.78	0.755	disordered	[14]
Ba(NbFe)O_3	1.74	0.78	0.755	disordered	[14]
Pb(NbMn)O_3	1.63	0.78	0.785	disordered	[15]
Ba(NbMn)O_3	1.74	0.78	0.785	disordered	[16]
Sr(NbSc)O_3	1.54	0.78	0.885	ordered	[10]
Pb(NbSc)O_3	1.63	0.78	0.885	partly ordered	[17]
				disordered	[14]
Ba(NbSc)O_3	1.74	0.78	0.885	disordered	[14]
				ordered	[10]
Ca(NbIn)O_3	1.49	0.78	0.94	ordered	[9]
Sr(NbIn)O_3	1.54	0.78	0.94	ordered	[9]
Pb(NbIn)O_3	1.63	0.78	0.94	disordered	[15]
Ba(NbIn)O_3	1.74	0.78	0.94	ordered	[18]
				partly ordered	
Ca(NbYb)O_3	1.49	0.78	1.008	ordered	[9]
Pb(NbYb)O_3	1.63	0.78	1.008	disordered	[14]
Ba(NbYb)O_3	1.74	0.78	1.008	partly ordered	[19]
				disordered	[14]
Ca(NbHo)O_3	1.49	0.78	1.041	ordered	[9]
Pb(NbHo)O_3	1.63	0.78	1.041	ordered?	[15]
Ba(NbHo)O_3	1.74	0.78	1.041	partly ordered	[19]

* Ionic radii according to R. D. Shannon and C. T. Prewitt [20].

That is

$$S^2 = \left(\frac{I_{1\,1\,1}}{I_{2\,0\,0}}\right)_{\text{observed}} \Bigg/ \left(\frac{I_{1\,1\,1}}{I_{2\,0\,0}}\right)_{\text{calc.}\,S=1}$$

and

$$S^2 = \left(\frac{I_{3\,1\,1}}{I_{2\,2\,2}}\right)_{\text{observed}} \Bigg/ \left(\frac{I_{3\,1\,1}}{I_{2\,2\,2}}\right)_{\text{calc.}\,S=1}$$

Development of the (1 1 1) superlattice line on extended thermal annealing is clearly evident in the X-ray patterns shown in Fig. 1. The corresponding calculated order parameters are shown on each picture.

3.3. Ferroelectric transitions

In ferroelectric perovskites the transitions in the degree of ordering which occurs at the Curie point critical temperature, T_c is weakly a first order one: it is accompanied by a small latent heat and a peak in the specific heat. In the diffuse transition materials, since each microvolume transforms at a different temperature these heat changes are expected to be spread out, and the sharp peak reduced to a general rounded "hump". Thus, in samples where the degree of ordering can be controlled, it would be expected that the thermal change would sharpen and become larger with

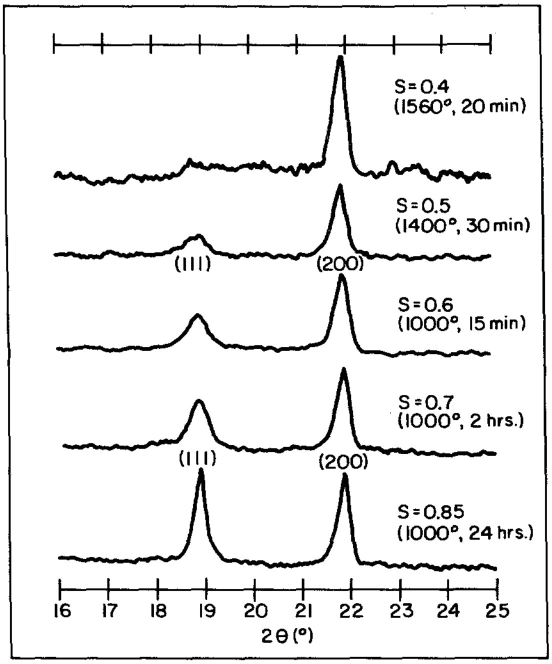

Figure 1 X-ray diffraction patterns of PST with varying degrees of ordering.

increasing order better defining the local composition.

Heat capacities for samples with differing degrees of ordering, established by the X-ray measurements described above, were measured for temperatures around the transition range (see Fig. 2) using a duPont 900 thermal analyser with a differential scanning calorimetric cell (DSC). The cell was first cooled by liquid nitrogen to a temperature of about -77° C and then heated at a rate of $12^\circ \mathrm{C\,min^{-1}}$ up to $+90^\circ$ C. The heat of transition for each sample was calculated by extrapolating a base line from the region outside the transition range, and determining the area between this extrapolated base and the measured thermal curve.

4. Discussion

The X-ray diffraction measurements give clear evidence that $\mathrm{Pb(Sc_{0.5}Ta_{0.5})O_3}$, as expected from the crystal chemistry, is near to the boundary between order and disorder in the Sc : Ta arrangement, and that the degree of ordering can be controlled over quite a wide range by suitable thermal annealing. The simple thermal measurements give a clear indication that the degree of ordering does have a strong effect upon the ferroelectric Curie temperature with the Curie range narrowing markedly as a high degree of order is established.

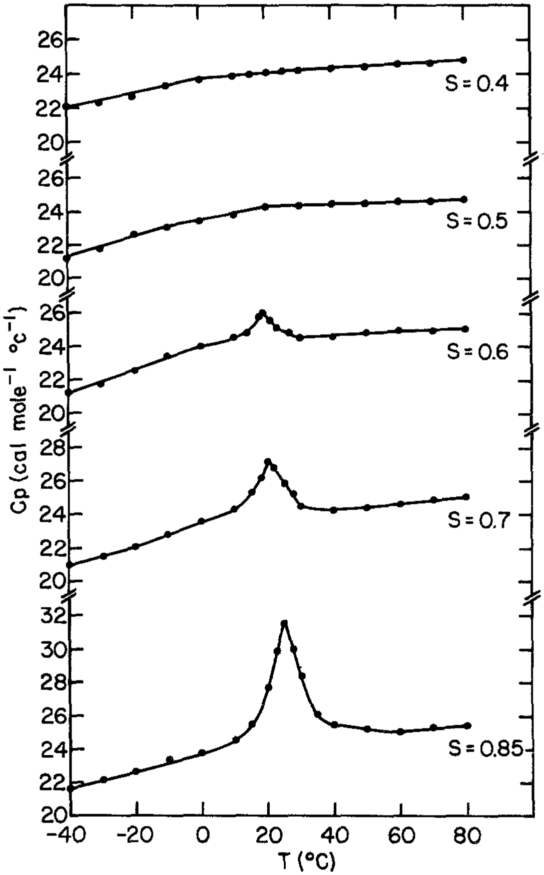

Figure 2 Variation of heat capacity of PST with degree of ordering.

Burggraaf and Stenger [20] correlate ΔS and $\Delta S/T_c$ at the Curie transition with the probability of occurrence of heterophase fluctuations. Large values of the ratio $\Delta S/T_c$ giving sharp transitions, and lower values leading to more diffuse behaviour. In Table II we have added our data for the differently ordered PST samples to the earlier compilation. It is interesting to note that the values fit in well, and link continuously the sharp transitions of $\mathrm{PbTiO_3}$ and $\mathrm{BaTiO_3}$, and those more diffuse transitions of the PLZTs.

The PST is apparently an excellent vehicle for study of the characteristics of ferroelectrics with diffuse phase transitions. In later papers we shall report dielectric, ferroelectric and elasto-electric measurements on both ceramic and single crystal specimens, and upon additional X-ray studies to determine the volume of the ordered regions and the manner in which this changes with increased ordering.

TABLE II Transition entropies and enthalpies of PST and other ferroelectrics

Compound	T_c (K)	ΔH (cal. mol $^{-1}$)	ΔS (cal. mol $^{-1}$K^{-1})	$\frac{\Delta S}{T_c} \times 10^3$ (cal. mol $^{-1}$K^{-2})	Type of transition	Reference
$PbTiO_3$	763	1150	1.51	1.98	sharp	[22]
$BaTiO_3$	393	47	0.12	0.30	sharp	[22]
PST ($S = 0.85$)	297	87	0.29	0.98	sharp	This work
PST ($S = 0.7$)	294	52	0.18	0.61	sharp	This work
PST ($S = 0.6$)	292	20	0.07	0.24	slightly diffused	This work
PST ($S = 0.5$)					diffused	This work
PST ($S = 0.4$)					strongly diffused	This work
PLZT 17/30/70	320	18	0.06	0.17	diffused	[21]
PLZT 11.1/55/45	325	11	0.03	0.10	strongly diffused	[21]

Acknowledgement

This work was carried out under contract No. N00014-78-C-0291 from the Office of Naval Research.

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Received 8 February and accepted 3 March 1980.