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The effects of isovalent and non-isovalent impurities on the ferroelectric phase transition in barium titanate

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Abstract. X-ray scattering experiments on lightly-doped powders of BaTiO₃ using the diffractometer on station 9.1 of the SRS at Daresbury have been extended to investigate transitions in materials doped with cations of lower valency than the ions they replace. These materials are insulators with a resistivity of about 10^{10} Ω cm at room temperature; the defect sites are therefore unscreened. Materials studied earlier had been doped with impurities of higher valency than the cations they replace: these are extrinsic n-type semiconductors with resistivity typically 10^2 Ω cm at room temperature, and so the impurities are screened. Surprisingly the behaviour of the two types is very similar: both types of impurity lower the transition temperature, even though they favour the formation of the low-temperature phase. The presence of small clusters of polarized material appears to inhibit the phonon softening, as first proposed by Halperin and Varma. We have also studied the phase transition in BaTiO₃-rich solid solutions; the critical behaviour in these materials is very different from that of the impure systems.

1. Introduction

Impurities can radically change the behaviour of a system undergoing a structural phase transition. Halperin and Varma [1] discussed how impurities change the static and dynamic response of a nominally pure crystal near a displacive phase transition. They focused on the symmetry and dynamics of the defect cell, and showed that a small concentration of such cells, in which the order parameter relaxes sufficiently slowly between different equivalent orientations, could account for the narrow central peak in the scattering, as well as the temperature dependence of the frequency of the soft mode (in SrTiO₃). The impurities were placed into one of two groups: A—those that occupy a site that breaks the symmetry of the high-temperature phase, and B—those that occupy a site that preserves the symmetry. Impurities of type A are likely to induce local, non-zero values of the order parameter above the transition temperature of the pure material, while those of type B are not expected to do so. However, as Halperin and Varma discuss in some detail, the situation is considerably more complicated than this simple division suggests. An A-type defect might hop between equivalent symmetry-breaking sites on a time scale short compared with the duration of the experiment, in which case it would appear to conserve the symmetry of the high-temperature phase. Also a symmetry-conserving impurity may alter the force constants in the cell to such an extent that the high-temperature phase becomes unstable, producing a spontaneous displacement of the atoms into one or other of the possible configurations of the low-temperature phase. These displacements could be static or dynamic and may or may not involve displacement of the impurity itself.

There are many examples of transitions in perovskites involving both A- and B-type impurities. Extensive studies of $(K_{1-x}Li_x)TaO_3$ (x typically 0.05) [2–4] have shown that the material belongs in category A. At elevated temperatures the lithium ion hops between equivalent symmetry-breaking sites, and as the temperature is lowered the hopping rate slows. Eventually a non-ferroelectric, dipolar glass forms. The tantalum-rich solid solution $K(Ta_{1-x}Nb_x)O_3$ falls into category B [5]. As the temperature is lowered, slowly relaxing polarized clusters begin to form around the niobium sites, yet the overall symmetry remains cubic. At low temperatures a transition to a rhombohedral ferroelectric phase occurs.

Here we describe some experiments performed on lightly-doped $BaTiO_3$. The pure material has a band gap of about 3 eV and resistivity of $10^{10} \Omega \text{ cm}$ at room temperature [6]. Doping with cations of higher valency than the replaced ion e.g. Ce^{3+} for Ba^{2+} or Ta^{5+} for Ti^{4+} , produces an *n*-type semiconductor. The reaction $Ti^{4+} + e^- \rightarrow Ti^{3+}$ occurs. The extra electron is not localized at room temperature, and, for concentrations around 0.3 mol.% of dopant, the resistivity is reduced to about $10^2 \Omega \text{ cm}$ [6]. Doping with a cation of lower valency than the ion it replaces e.g. Ga^{3+} for Ti^{4+} , does not produce a *p*-type semiconductor, since neither barium nor titanium can raise their valency from 2 to 3, or from 4 to 5 respectively. Charge neutrality is maintained through the introduction of oxygen vacancies [7].

Doping with an isovalent cation may produce a solid solution with random distribution of cations throughout the crystal e.g. Pb^{2+} or Sr^{2+} for Ba^{2+} . We use the term *solid solution* to describe materials which can be prepared over the whole compositional range, from one end member to the other, with relatively uniform composition throughout the crystal. They are clearly different from *impure systems*: one cannot consider one of the components of a solid solution as an impurity. Not all isovalent replacements produce solid solutions. $(K_{1-x}Li_x)NbO_3$ is not a solid solution in the sense used here since there is evidence that the lithium is not distributed at random [4]; there is a tendency for lithium-rich clusters to form, making the formula $[(1-x)KNbO_3 + xLiNbO_3]$ a better description when x is not very small. The structure of $LiNbO_3$, while in principal derivable from the perovskite structure by rotation of the octahedra through 30° about $[111]$ [8], is topologically different from the structure of $KNbO_3$.

Solid solutions can also be produced by the double substitution of non-isovalent cations on both A- and B-sites; e.g. $(Ba,K)(Ti,Nb)O_3$, $(Pb,K)(Ti,Nb)O_3$ and $(Pb,Bi)(Zr,Fe)O_3$ —see Landolt-Börnstein [9] for further examples.

The different types of system we will label as follows: H to describe an impure system with the impurity possessing a valency higher than the replaced cation; S, for solid solutions; and L, for systems with a dopant having a lower valency than the cation it replaces. Materials like $(K_{1-x}Li_x)NbO_3$ will be labelled as I. Clearly category S must be subdivided into two. Isovalent solid solutions, like $(Ba,Sr)TiO_3$, we will label SI, non-isovalent solutions, such as $(Ba,K)(Ti,Nb)O_3$, as SN.

The properties of solutions SI vary in a more or less linear fashion with composition. For example, changes in transition temperature to the cubic phase in $(Pb,Ca)TiO_3$, $(Pb,Sr)TiO_3$ and $(Pb,Ba)TiO_3$ decrease from the value for pure $PbTiO_3$ with increasing Ca, Sr and Ba content [10].

The same is not true for materials in category SN. $(Pb,K)(Ti,Nb)O_3$ shows a minimum in the cubic-tetragonal transition temperature at composition $(Pb_{0.2}K_{0.8})(Ti_{0.2}Nb_{0.8})O_3$ [11]; the transition temperature decreases linearly from 490°C for pure $PbTiO_3$ to its minimum of 180°C , then increases linearly to 440°C in pure $KNbO_3$. Bratton and Tien [12] investigated the system $(Ba,K)(Ti,Nb)O_3$ and found a tendency for alternate grains to be slightly rich in titanium and niobium. Linear changes in transition temperatures with composition occurred

near each end member, but 'complex' behaviour was reported for compositions between 40 mol.% to 80 mol.% KNbO₃. In this range, the transition temperature to the cubic phase is independent of composition.

Anomalously large distortions occur in some of the SN-type solid solutions. For example, the *c/a* ratio in tetragonal (Pb_{0.2}Bi_{0.8})(Ti_{0.2}Fe_{0.8})O₃ has a value approaching 1.2 [13]; *c/a* in BaTiO₃ at room temperature is about 1.01.

The resistivities of materials in categories S and L at room temperature are large, in the range 10⁸ to 10¹⁰ Ω cm [6]. As a result, the impurities in these groups are not screened by mobile charge carriers, while those in group H, with resistivities of 10² Ω cm or less, are screened.

We describe some recent x-ray scattering experiments performed on station 9.1 of the SRS at Daresbury on materials in class L, and compare their behaviour with those from categories H and SI, which have been reported before [14, 15]; the full list of materials studied by us is given in table 1.

Table 1. Experimental values for *T_t*, *T_s* and exponent *s*.

	<i>T_t</i> (°C)	<i>T_s</i> (°C)	<i>s</i>
Pure BaTiO ₃			
Annealed at 1200 °C	130	no fluctuations detectable	
As-purchased	130	112(fixed)	1.3(2)
Category H			
Ce(0.001) ^a	126	112(fixed)	2.7(3)
Ce(0.003) ^a	122	112(fixed)	2.8(2)
Sm(0.003) ^b	126		
Nb(0.003) ^a	120	112(fixed)	1.6(2)
Nb(0.003) ^b	122	112(fixed)	1.4(3)
Ta(0.003) ^b	122	112(fixed)	2.8(2)
Category SI			
Sr(0.003) ^b	123	55(80)	8(3)
Sr(0.010) ^b	110	50(80)	7(3)
Sr(0.100) ^b	100	20(40)	4(2)
Pb(0.010) ^b	134		
Category L			
Zn(0.003)	123	107(fixed)	2.8(3)
Zn(0.003)	122	107(fixed)	2.3(4)
Ga(0.003)	123	112(fixed)	2.7(3)

^a From [14].

^b From [15]; other entries this work.

As the transition temperature (*T_t*) is approached from above, anisotropic line broadening was observed as first described in [14] and [15]. We interpret this as evidence of small polarized clusters of the low-temperature phase existing above *T_t*. No line broadening was found in the pure sample that had been annealed at 1200 °C for 30 hours in air.

2. Experimental details

Samples with composition Ba(Ti_{0.997}Zn_{0.003})O_{2.994} and Ba(Ti_{0.997}Ga_{0.003})O_{2.997} were

prepared by the standard route described in [14] and [15]. The stated oxygen concentration has not been determined experimentally; the quoted formula is electrically neutral.

The diffractometer on station 9.1 was used in high-resolution mode, with a nearly constant resolution of 0.036 (FWHM $^{\circ}2\theta$) over the angular range studied [16]. The wavelength was 1.0 \AA . Temperature was controlled to an accuracy of better than 1°C using a Newtronic three-term controller. θ - 2θ scans through the reflections (110), (111), (200), (211) and (220) were recorded at a number of temperatures above and below the symmetry change. The steps were 0.006° in 2θ , and counts were accumulated for two seconds at each point.

3. Results

The effect of doping on the (200) reflection at room temperature is shown in figure 1; the peaks have been normalized to the same height. The scattering between the two resolved peaks in figure 1(a) is from material with spontaneous strain reduced from its maximum, most probable, value; we believe this material lies within 90° domain walls. Theory suggests that the magnitude of the strain varies in a tanh-like manner in passing through such a wall [17]. The profiles from the two doped samples are very similar to those obtained from all other doped samples. As strain couples electrostrictively to polarization, the doped samples possess a large spatial variation in the magnitude of the order parameter.

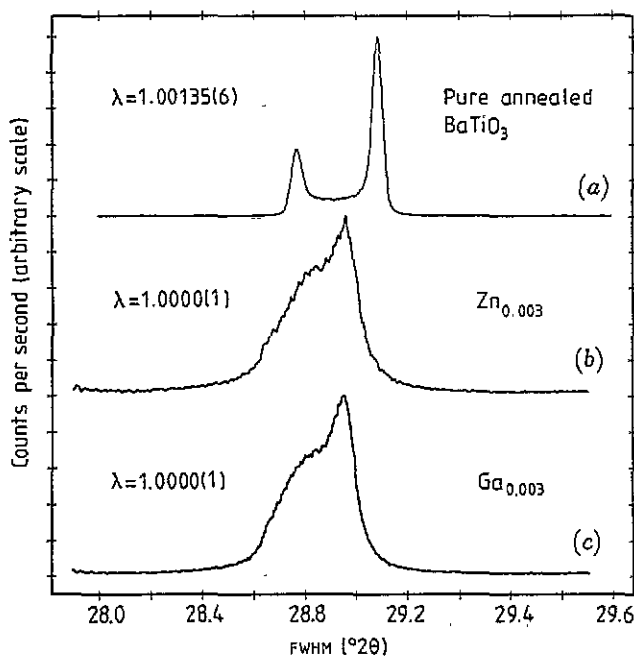


Figure 1. Profiles of the (200) reflection near room temperature from: (a) pure BaTiO_3 annealed at 1200°C for 30 hours; (b) $\text{Ba}(\text{Ti}_{0.997}\text{Zn}_{0.003})\text{O}_{2.994}$; (c) $\text{Ba}(\text{Ti}_{0.997}\text{Ga}_{0.003})\text{O}_{2.997}$. The peaks have been normalized to have the same peak heights.

4. Analysis

All profiles were fitted with pseudo-Voigt functions. The Lorentzian component was typically more than 70% for doped samples above their transition temperature, where the pure sample, annealed at 1200°C , gave linewidths equal to the resolution of the instrument and a Lorentzian component of about 25%.

The transition temperatures (T_t) were taken as the lowest temperatures at which line profiles were symmetric; that is, for temperatures above T_t the difference plot of observed profile minus calculated, symmetric profile was featureless. T_t is not well defined (± 2 K) and depends to some extent on the resolution of the instrument. Above T_t the average structure possesses cubic symmetry, while below, the overall symmetry is tetragonal, but the order parameter varies spatially.

A plot of FWHM versus temperature for the gallium-doped sample is shown in figure 2; these diverge as $T - T_t$ decreases. As described in [14] and [15] the critical broadening was fitted to the expression

$$\delta_c(2\theta) = W(T - T_s)^{-s} \quad (1)$$

where W , T_s and s are constants. The value of T_s was chosen to make the log-log plot of (1) linear. Values of T_t , T_s and s for the samples we have studied are given in table 1. T_s and s have been omitted for the samarium- and lead-doped samples, since there was evidence that the dopants were not evenly distributed throughout the sample [15].

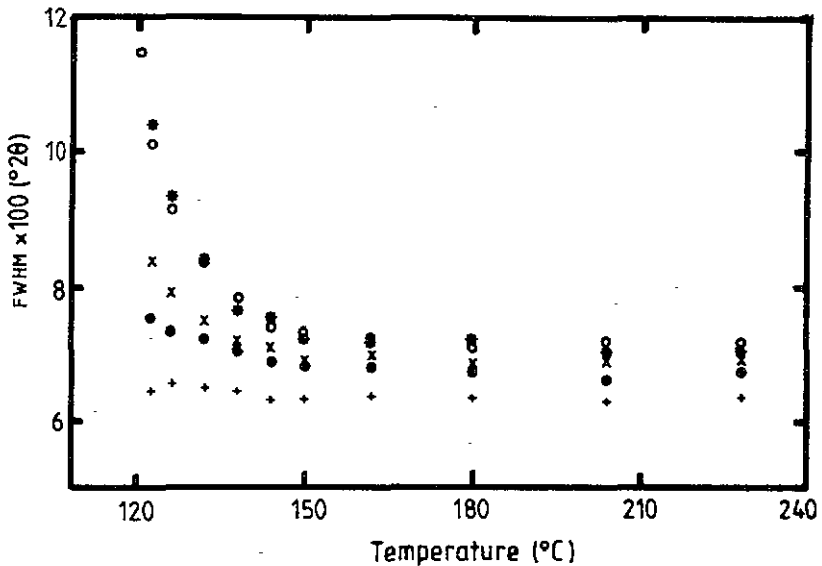


Figure 2. Temperature dependence of FWHM of several reflections from $Ba(Ti_{0.997}Ga_{0.003})O_{2.997}$ in the high-temperature phase (2θ is in degrees). Symbols denote: \circ (110); $+$ (111); \square (200); \times (211); $*$ (220).

5. Discussion

For impure samples—those in categories H and L— T_s is about 18 °C below the transition temperature of the pure, annealed sample; a better fit for the zinc-doped sample was obtained with T_s a little less than this, which may be because the sample is oxygen deficient. T_s in the fully oxygenated samples is independent of dopant, so it seems reasonable to propose that its magnitude is determined by the host material—pure barium titanate. The fluctuation–dissipation theorem connects the dielectric susceptibility, χ_T , with fluctuations in polarization, P , caused by temperature to give

$$k_B T \chi_T = V_c ((P^2) - \langle P \rangle^2)$$

where V_c is the volume within which the polarization is correlated and k_B is the Boltzmann constant. There is evidence that the magnitude of V_c does not diverge at T_t [18], so the increase in χ_T is caused by polarization fluctuations alone. The reciprocal susceptibility extrapolates to zero at a temperature T_0 , which is about 15 °C less than T_t of the pure material— T_0 is therefore approximately the same as T_s —so it is tempting to identify T_s with T_0 [14]. With $T_t > T_s$, the transition is discontinuous. The discontinuity is unobservable because of fluctuations in the magnitude of the order parameter.

The correlation length of the order parameter, r_c , diverges as the transition temperature is approached, with $r_c \sim |T - T_0|^{-\nu}$. For a point-like defect one would expect s to equal 4ν , for a linear defect 3ν , and for a planar defect 2ν . Values of ν for various theoretical models are listed in table 3 in [15]. Doped BaTiO₃ is three dimensional and the order parameter has three components; all relevant models with these parameters have $\nu \simeq 0.7$. Materials in categories H and L, apart from the niobium-doped sample, give values of s close to 4ν , and therefore can be described as host (pure barium titanate) and point-like defect—as expected. *The barium-rich solid solutions in category SI clearly do not behave in this way. T_s depends on composition as does the magnitude of exponent s . Even in very barium-rich solutions, strontium does not behave as an impurity; the host material is not pure barium titanate. The values obtained for T_s and exponent s are not well-defined because $(T_t - T_s)$ is large.*

The value of s for pure barium titanate annealed at 1000 °C (the ‘as-purchased’ material), suggests the presence of planar defects. The line profiles, even at room temperature, were symmetric and very broad [14], indicating that the most probable value of the order parameter at room temperature is zero with large variance. We believe that this is because the density of 90° domain walls is high, and these are planar—see, for example, [10]. Why the niobium-doped sample gives a different value for exponent s than other materials in category H is not understood.

The magnitudes of the parameters describing the critical broadening in groups H and L are very similar, which suggests that screening of the charge carriers has little effect on the transition process. This is surprising since one would expect the electron–ion correlations to modify the Coulombic ion–ion correlations and thereby reduce T_t [19]. The experimental values for T_t in these categories are about the same.

In all the impure samples we have studied, the transition temperature is less than the transition temperature of the pure material. This is surprising too, since the impurities favour formation of the low-temperature phase.

Halperin and Varma [1] argue—within the framework of the soft-mode theory of displacive phase transitions—that the presence of small clusters of the low-temperature phase would inhibit phonon softening, and hence inhibit the growth in correlation length of the order parameter which, in turn, would depress the transition temperature.

For many years the notion that there is a component of order-disorder behaviour in the dynamics of a displacive transition (in ideal systems) has been discussed in the literature [20]. As T_t is approached from above, quasi-local ordering occurs i.e. clusters of the low-temperature phase form. This view is entirely consistent with the conventional view that displacive transitions are driven by phonon softening, since the softening leads to an increase in correlation length and hence coherent motion of atoms.

An extreme view [21] is that at elevated temperatures the titanium atoms are displaced along all eight $\langle 111 \rangle$ directions, and become partially ordered in the tetragonal phase with displacements along $[111]$, $[\bar{1}11]$, $[1\bar{1}1]$ and $[\bar{1}\bar{1}1]$ only. However, as T_t is approached the soft mode becomes overdamped [22] making the distinction between the two models—of a slowly relaxing, displaced titanium, and the soft mode picture—blurred. The terms ‘displacive’ and ‘order-disorder’ describe only limiting behaviour.

At high temperatures the line broadening is nearly isotropic, so the impurities conserve the symmetry of the high-temperature phase; the systems fall into category B. Following the description given by Bruce and Cowley [20], the impurities are symmetry conserving but soft; the transition in the neighbourhood of an impurity occurs at T_t which is greater than T_t of the pure material by about 40 °C.

The ground state of the low-temperature phases is ferroelectric [6], like the solid solution $K(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$, but unlike $(\text{K}_{1-x}\text{Li}_x)\text{NbO}_3$ which forms a dipolar glass.

For solid solutions of type SI, rich in barium and titanium, the ferroelectric transition temperature is either raised or lowered depending on the transition temperature of the other end member. The addition of PbTiO_3 , in which the transition occurs at 490 °C, raises the transition temperature, but it is lowered in $(\text{Ba,Sr})\text{TiO}_3$; pure SrTiO_3 is not ferroelectric at any temperature. In similar fashion, the addition of KNbO_3 to KTaO_3 produces ferroelectric behaviour; pure KTaO_3 is cubic at all temperatures [5]. This is one further difference between solid solutions of type SI and impure systems.

References

- [1] Halperin B I and Varma C M 1976 *Phys. Rev. B* **14** 4030
- [2] Doussineau P, Frenois C, Levelut A, Ziolkiewicz S and Höchli U T 1991 *J. Phys.: Condens. Matter* **3** 8369
- [3] Höchli U T, Hessinger J and Knorr K 1991 *J. Phys.: Condens. Matter* **3** 8377
- [4] Christen H-M, Höchli U T, Chatelain A and Ziolkiewicz 1991 *J. Phys.: Condens. Matter* **3** 8387
- [5] Fontana M D, Bouziane E and Kugel G E 1990 *J. Phys.: Condens. Matter* **2** 8681
- [6] Saburi O 1959 *J. Phys. Soc. Japan* **14** 1159
- [7] Heywang W 1971 *J. Mater. Sci.* **3** 1214
- [8] Megaw Helen D 1973 *Crystal Structures: A Working Approach* (Philadelphia, PA: Saunders)
- [9] Mitsui T 1982 *Ferroelectrics and Related Substances: Volume 16a: Oxides; Landolt-Börnstein; New Series* (Berlin: Springer)
- [10] Jona F and Shirane G 1962 *Ferroelectric Crystals* (Oxford: Pergamon)
- [11] Tien T Y, Subbarao E C and Hirzo J 1962 *J. Am. Ceram. Soc.* **45** 572
- [12] Bratton R J and Tien T Y 1967 *J. Am. Ceram. Soc.* **50** 90
- [13] Smith R T, Achenbach G D, Gerson R and James W J 1968 *J. Appl. Phys.* **39** 70
- [14] Darlington C N W and Cernik R J 1991 *J. Phys.: Condens. Matter* **3** 4555
- [15] Darlington C N W and Cernik R J 1992 *J. Phys.: Condens. Matter* **4** 4387
- [16] Langford J I, Cernik R J and Louer D 1990 *J. Appl. Crystallogr.* **24** 913
- [17] Salje E K H 1990 *Phase Transitions in Ferroelastic and Co-elastic Crystals* (Cambridge: Cambridge University Press)
- [18] Wemple S H 1970 *Phys. Rev. B* **2** 2679
- [19] Lines M E and Glass A M 1977 *Principles and Applications of Ferroelectrics and Related Materials* (Oxford: Clarendon)

- [20] Bruce A D and Cowley R A 1981 *Structural Phase Transitions* (London: Taylor and Francis)
- [21] Comès R, Lambert M and Guinier A 1968 *Solid State Commun.* 6 715
- [22] Harada J, Axe J D and Shirane G 1971 *Phys. Rev. B* 4 155