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Crystalline ferroelectrics with glassy polarization behavior

Gerald Burns and F. H. Dacol
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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We report measurements of the optic index of refraction as a function of temperature, $n(T)$, in the crystalline ferroelectrics having the simple perovskite (ABO_3) structure. We show that these crystals possess a local, randomly oriented, nonreversible polarization below a temperature T_d several hundred degrees above the ferroelectric phase-transition temperature T_c. Using a simple model, we account for this behavior and understand quantitatively the values of T_d. This model, we believe, contains the basic physical understanding of ferroelectrics with a diffuse phase transition.

Ferroelectric materials have a transition temperature T_c below which the crystals show a reversible spontaneous polarization P_r. Materials with the simple perovskite (ABO_3) structure (e.g., $BaTiO_3$) transform at T_c from the high-temperature cubic structure to a structure with tetragonal or rhombohedral symmetry. We show that because of the built-in disorder, there is a much higher temperature T_d at which local dipoles condense out leading to a local, randomly oriented, polarization P_d. Furthermore, T_d can be quantitatively understood in terms of normal ferroelectric behavior.

Recently, there has been considerable interest in magnetic spin-glasses.[1] Actually, the analogous electric dipole glass was discussed a long time ago in terms of OH^- randomly oriented in alkali-halide crystals.[2] The crystalline ferroelectric analog was observed and discussed.[3] Random dipolar effects have also been reported[4(a)] in $KTaO_3$:Li and related systems, although this may be a standard ferroelectric material.[4(b)] Above T_c, in $BaTiO_3$ and related systems, effects attributed to thermal polarization fluctuations and the photoelastic constants, band edge, and index of refraction, were measured and discussed.[5] Randomly oriented elastic quadrupole behavior has been reported[6] in systems like $(KBr)_{1-x}(KCN)_x$. Also, a Jahn-Teller glass has been reported[7] in systems such as $(TmVO_4)_{1-x}(YVO_4)_x$, where the Tm^{3+} ion undergoes the Jahn-Teller distortion. The term glass refers to crystalline materials in which there is a randomness in a certain property (orientation of dipoles, quadrupoles, Jahn-Teller strains). For example, in a crystalline ferroelectric glass, one might expect to find randomly directed dipoles condensing out as the temperature is lowered. Then, at some lower temperature, there should be a standard ferroelectric phase transition (at T_c). Thus for crystalline ferroelectric glasses the long-range periodic crystal structure would be maintained; the randomness only refers to the positions of atoms within a few tenths of angstroms from their normal crystalline positions.

The type of crystalline ferroelectric material, which may show random behavior in some properties, is different from the type discussed by Lines[8] where the structure of the material itself is random (a structural glass or window glass with no long-range order). Structural glasses of this type have been studied, but it is not yet clear whether dipolar units condense.[9]

Recently, Courtens[10] has studied mixed crystals of $Rb_{1-x}(NH_4)_xH_2PO_4$, which have the KDP (potassium dihydrogen phosphate) structure. Ferroelectric and antiferroelectric behavior is observed for the end members $x=0$ and 1. For intermediate values of x, a glassy phase may occur.[10]

The materials studied here have the cubic perovskite (ABO_3) crystal structure. Measurements are made on ceramics (randomly oriented densely packed crystals) since large single crystals are very difficult to prepare. The materials are directly related to the ferroelectric system $Pb(Zr_yTi_{1-y})O_3$, which forms a complete solid solution for all y and is ferroelectric over most of the range.[11,12] In particular, we have studied materials where some Pb^{2+} is replaced with La^{3+}. Assuming that all of the La^{3+}, Pb^{2+}, and vacancies remain on the A site,[13] the chemical formula is $(Pb_{1-3x/2}La_x)(Zr_yTi_{1-y})O_3$. Thus the ions (and vacancies) are disordered on the A site, and we think that this disorder is fundamental in order to observe the effects discussed here. This material is usually referred to as PLZT (Refs. 14 and 15) and, for example, when $x=0.08$ (8 at. %) and $y=0.65$, it is called PLZT(8/65/35); the last two numbers refer to the ratio of the Zr to Ti. We have studied PLZT(x/65/35), where $x=7$, 8, 9, and 9.5 at. %; all of these crystalline materials have the cubic perovskite high-temperature phase and are rhombohedral below T_c. We have also studied PLZT(12/40/60), which is tetragonal below T_c.[14,15] Table I lists these materials and their values of T_c. With the addition of La, one can obtain ceramics with a density ~100% of the crystalline density, making

TABLE I. Values of T_c (Ref. 14) and T_d for the rhombohedral (Rh.) and tetragonal (Tet.) materials for PLZT($x/y/(1-y)$).

PLZT($x/y/(1-y)$)	T_c	T_d
	Rh. below T_c	
PLZT(7/65/35)	155 °C	347 °C
PLZT(8/65/35)	110 °C	350 °C
PLZT(9/65/35)	80 °C	366 °C
PLZT(9.5/65/35)	≈80 °C	354 °C
	Tet. below T_c	
PLZT(12/40/60)	130 °C	410 °C

them optically transparent,[14,15] and enabling measurements of the optic index of refraction $n(T)$ in the visible region of the spectrum. The measurements are made with the minimum deviation technique using prisms placed in an oven.[3,16] We again emphasize that the results pertain to *crystalline ferroelectric materials;* using the ceramic form allows us to obtain the materials.[17] Naturally, the ceramics angularly averages the crystalline properties as discussed below.

Figure 1(a) shows the index of refraction versus temperature $n(T)$ for PLZT(8/65/35) at four different wavelengths. Several things are clear. First, nothing happens at T_c (the arrow in the figure) contrary to what is expected in a normal ferroelectric.[16] Second, one can approximate, to a high degree of accuracy, the high-temperature $n(T)$ data with straight lines as indicated. Linear $n(T)$ is found for most ordinary materials. Third, for all the wavelenghts, the experimental points deviate from the straight lines at ~350 °C. This temperature, defined as T_d, is entered into Tables I for (8/65/35).

Figure 1(b) shows similar $n(T)$ results but for different La concentration, all measured at 6328 Å. Again, the high-temperature part can be approximated by a straight line. The values of T_d, which are about the same for all the compositions, are entered into Table I.

Figure 1(c) compares data at 6328 Å for the tetragonal PLZT(12/40/60) with that for (PLZT)8/65/35. Again, the high-temperature behavior can be approximated by a straight line as shown. However, $T_d \approx 410\,^\circ\text{C}$ for PLZT(12/40/60).

In Table I we see the following: (1) a range of ferroelectric T_c values, (2) values of T_d that are approximately independent of x for PLZT(x/65/35) but a different T_d for PLZT(12/40/60), and (3) behavior of $n(T)$ that is *qualitatively* different from what is expected in ferroelectrics in that the deviation from linear behavior is expected to occur at T_c, not 190–280 °C above T_c.

To understand these results, we investigate the changes in $n(T)$ due to the quadratic electro-optic effect. This effect occurs in all crystal classes and relates a change in the index of refraction to the square of a polarization P,

$$\Delta(n^{-2})_{mn} = \sum g_{mnop} P_o P_p \ ,$$

where g, a fourth-rank tensor, is the quadratic electo-optic coefficient, and the subscripts can have values 1, 2, and 3, signifying the a, b, and c direction, respectively. Using the standard contracted index notation,[18] and assuming that the polarization is along only a single axis, $\Delta(n^{-2})_i = \sum g_{ij} P_j^2$. Taking the polarization along only the 3 or c axis and expanding the left-hand side of this equation for small changes of the index, we obtain

$$\Delta n_i \equiv n_i^f - n_i^0 = -(n_i^0)^3 g_{i3} P_3^2/2 \ , \tag{1a}$$

$$\Delta n_3 = -(n_3^0)^3 g_{33} P_3^2/2, \quad \Delta n_1 = -(n_1^0)^3 g_{13} P_3^2/2 \ , \tag{1b}$$

where, as the polarization changes from zero to P_3, the index changes from n^0 to n^f. In Eqs. (1b) the change of indices along the polarization direction (n_3) and perpendicular to the polarization direction (n_1) are given.

The important thing to realize about Eq. (1) is that the polarization enters as the square. We interpret the deviation of the index of refraction from the extrapolated high-temperature straight lines drawn in Fig. 1 as due to regions (probably of a size of the order of several unit cells) of local polarization. These regions are not uniform throughout the crystal, but the long wavelength of the light averages over a very large number of cells; whether the polarization is up or down, Δn is the same since it depends on P^2. T_d is far above T_c indicating that these regions of polarization are not reversible as in a normal ferroelectric crystal where one measures the reversible polarization P_r, typically by a Sawer-Tower circuit operating at

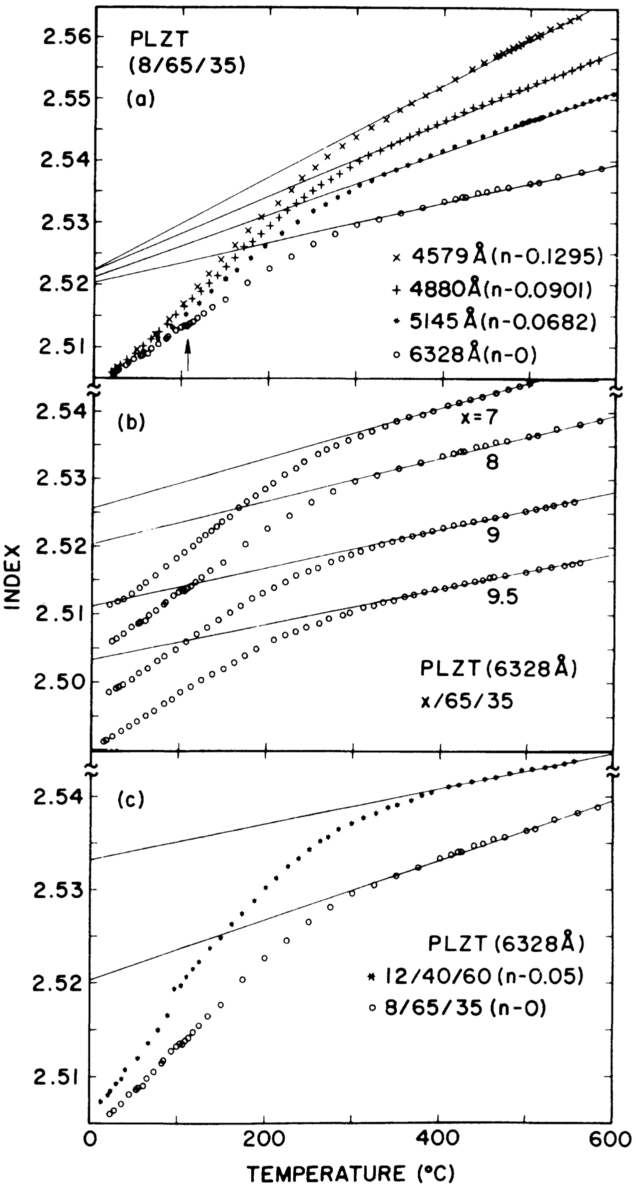

FIG. 1. Data points and the high-temperature extrapolations as discussed in the text. The arrow indicates T_c. (a) $n(T)$ measured at four different wavelengths with constants subtracted from three sets of data. (b) Similar to the above but all at 6328 Å and different values of La. (c) Different ratios of Zr to Ti (as well as La) measured at 6328 Å.

60 Hz. However, the quadratic electro-optic effect certainly does not demand that the polarization be reversible.

The next question is, if one has randomly oriented crystallites, what average index does one measure? There are several ways to take the averages.[19] We chose the simplest approach. Within any high-temperature cubic crystallite, we assume that the polarization lies along one of the six $\langle 001 \rangle$ directions, each having fourfold symmetry, as in the ferroelectric phase of PLZT(x/40/60), or the polarization is along one of the eight $\langle 111 \rangle$ directions, as in the ferroelectric phase of PLZT(x/65/35). In both cases, there is a unique index change parallel and perpendicular to the polarization given by $\Delta n_{\parallel}$ and $\Delta n_{\perp}$. For example, the results appropriate to PLZT(x/40/60) are given in Eqs. (1b). For a random orientation of crystallites, the observed change in index is

$$\Delta n = \frac{\Delta n_{\parallel} + 2\Delta n_{\perp}}{3} = -\frac{(n^0)^3}{2}\left[\frac{g_{33}+2g_{13}}{3}\right] P_d^2 , \qquad (2)$$

where the average random polarization is P_d. The second equality in Eq. (2) is appropriate for a polarization along either a $\langle 001 \rangle$ direction or a $\langle 111 \rangle$ direction. Since we measure $\Delta n, n^0$ and know the g's from other experiments, we can reverse the equations and determine $|P_d|$.

To use Eq. (2) we must know $(g_{33}+2g_{13})$ for the PLZT crystal. Thacher[20] measured $g_{33}-g_{13}=0.011$ m^4/C^2 at 6328 Å for these materials. This is reasonably close to the value of $+0.015$ m^4/C^2 found in the related[21] material Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$. In this latter material, by direct measurements using our prisms, we find[22] that $g_{33} \gg g_{13}$. Thus we use $g_{33}+2g_{13}=0.011$, 0.0126, 0.0132, and 0.0142 m^4/C^2, respectively, for the four wavelengths in Fig. 1(a); using the published wavelength dependence,[21] the largest g value corresponds to the highest energy light.

Figure 2 shows $|P_d|$ versus temperature for PLZT(8/65/35) and PLZT(12/40/60). Values of P_d for PLZT (8/65/35) obtained from the data taken at different wavelengths [Fig. 1(a)] are very similar and thus are not shown. The results for P_d obtained from the data for PLZT(x/65/35) [Fig. 1(b)] for the different values of x are very similar and thus are not shown. Also shown is the standard reversible polarization P_r. As discussed, P_d is observed several hundred degrees above T_c, yet at temperatures well below T_c, the two are similar in magnitude. Of the two polarizations, P_d is closer to the reversible spontaneous polarization found in[23,24] PBTiO$_3 \approx 0.57$ or 0.75 C/m^2.

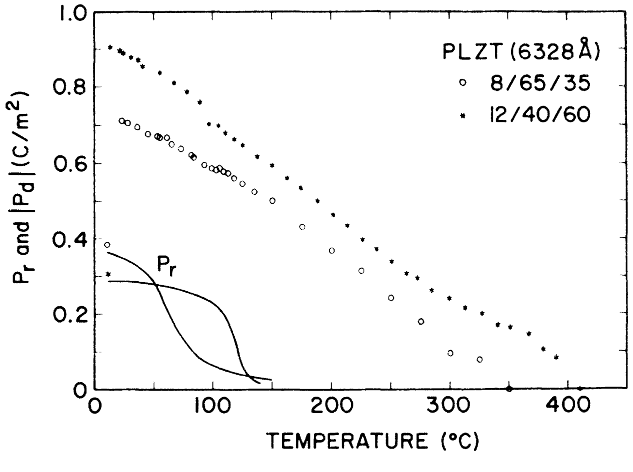

FIG. 2. P_d obtained from Eq. (2) and the reversible ferroelectric polarizations P_r [solid lines (Ref. 14)].

A simple model is discussed here. Since the Pb and La ions are not ordered, one must have inhomogeneities over distances of the order of the average unit-cell size (≈ 4 Å). Consider a reference unit cell in which a Pb ion is on the A site (as opposed to a La ion). Consider a partiuclar grouping in which this reference unit cell is surrounded by nearest-neighbor cells (six nearest neighbors) each containing a Pb ion. This particular reference unit-cell grouping will have a tendency to have a local displacement and a local polarization at a higher temperature than a reference unit-cell grouping which contains a La ion. Furthermore, reference unit-cell groupings with more La ions will polarize at still lower temperatures. Thus a range of local polarization temperatures is expected; the direction of the local polarization being determined by a complex interplay of the positions of the ions (first, second, etc., neighbors) and the local strains due to these ions and the polarizations.

T_d is the highest temperature where we begin to observe a local polarization. What determines its value? Polarization occurs for a reference unit cell which has very few La ion neighbors. For PLZT(x/65/35) this corresponds approximately to the normal ferroelectric transition temperature for PLZT(0/65/35). From the phase diagram[12] or temperature-dependent dielectric constant measurements,[14] we find 352 and 366 °C, respectively, remarkably close to T_d measured for PLZT(x/65/35) (Table I). This explains why approximately the same T_d is found for all PLZT(x/65/35) materials (even though T_c varies with x). This also explains why T_d ($\approx$410 °C) for the PLZT(12/40/60) material has a different T_d from that found for PLZT(x/65/35). T_d for PLZT(12/40/60) is remarkably close to 416 °C found from the phase diagram[12] for PLZT(0/40/60) or the 414 °C obtained from birefringence data.[25] (Dielectric data are not available.[14])

The polarization measured for temperatures $T_c < T < T_d$ is not reversible, at least not in the standard ferroelectric sense. This undoubltedly is because the local P_d direction is determined by a fixed arrangement of atoms. It is not until T_c is approached and the cooperative coupling between different groupings of reference unit cells becomes important that an externally applied electric field can be used to reverse the local polarization.

Kirsch *et al.*[26] find that in order to understand their measurements of the lengths of PLZT versus temperature, our values of P_d (Fig. 2) must be used rather than P_r. This is strong supportive evidence for our interpretation of the $n(T)$ data. Besides observing these effects in PLZT as discussed here, we have also measured the same effects[22] in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, and the compound where Zn replaces Mg. These latter materials have been discussed in terms of ferroelectrics with a "diffuse phase transition"[27] and in terms of regions (with more than 10^4 cells) in which one should see standard ferroelectric soft-mode behavior.[27,28] The entire focus of these discussions[27,28] is concerned with the behavior at T_c (with some smearing). It is clear, however, from our discussion that the transition starts at T_d (several hundred degrees above T_c). One can always fit some of the behavior near T_c with Gaussian-broadened properties[27-29]; however, such a procedure does not display the fundamental physics of these materials.

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[1] There are many reviews of spin-glasses, two of which are K. Binder in *Ordering in Strongly Fluctuating Condensed Matter*, edited by T. Riste (Plenum, New York, 1980), p. 423; J. A. Mydosh, J. Magn. Magn. Mater. 7, 237 (1978).

[2] W. Kansig, H. R. Hart, and S. Roberts, Phys. Rev. Lett. 13, 543 (1964).

[3] G. Burns and B. A. Scott, Solid State Commun. 13, 423 (1973).

[4] (a) U. T. Höchli, H. E. Weibel, and L. A. Boatner, Phys. Rev. Lett. 41, 1410 (1978); J. J. van der Klink and D. Rytz, Phys. Rev. B 27, 4471 (1983); (b) L. L. Chase, E. Lee, R. L. Prater, and L. A. Boatner, Phys. Rev. B 26, 2759 (1982).

[5] S. H. Wemple and M. DiDomenico, Phys. Rev. B 1, 193 (1970); M. G. Cohen, M. DiDomenico, and S. H. Wemple, *ibid.* 1, 4334 (1970); S. H. Wemple, *ibid.* 2, 2679 (1970).

[6] J. M. Rowe, J. J. Rush, D. G. Hinks, and S. Susman, Phys. Rev. Lett. 43, 1158 (1979); K. H. Michel and J. M. Rowe, Phys. B 22, 1417 (1980); A. Loidl, R. Feile, and K. Knorr, Z. Phys. B 42, 143 (1981).

[7] F. Mehran and K. W. H. Stevens, Phys. Rep. 85, 124 (1982); F. Mehran, K. W. Stevene, T. S. Plaskett, and W. J. Fitzpatrick, Phys. Rev. B 27, 548 (1983); see also references quoted in these papers.

[8] M. E. Lines, Phys. Rev. B 15, 388 (1977); 17, 1984 (1978).

[9] A. M. Glass, M. E. Lines, K. Nassau, and J. W. Shiever, Appl. Phys. Lett. 31, 249 (1977).

[10] E. Courtens, J. Phys. (Paris) Lett. 43, L199 (1982).

[11] E. Sawaguchi, J. Phys. Soc. Jpn. 8, 615 (1953).

[12] D. Berlincourt, IEEE Trans. Sonics Ultrason. SU-13, 116 (1966).

[13] K. H. Hardtl and D. Hennings, J. Am. Ceram. Soc. 55, 230 (1972).

[14] G. H. Haertling and C. E. Land, J. Am. Ceramic Soc. 54, 1 (1971); G. H. Haertling, *ibid.* 303 (1971).

[15] C. E. Land, P. D. Thacher, and G. H. Haertling, in *Applied Solid State Science*, edited by R. Wolfe (Academic, New York, 1974), Vol. 4, p. 138.

[16] G. Burns, Phys. Rev. B 13, 215 (1976); some work related to that reported here is in G. Burns and F. H. Dacol, Solid State Commun. 42, 9 (1982).

[17] Motorola Inc., 4800 Richfield Rd. NE, Albuquerque, NM 87113.

[18] G. Burns, *Introduction to Group Theory with Applications* (Academic, New York, 1977), p. 69.

[19] A. F. Devonshire, Philos. Mag. 42, 1065 (1951).

[20] P. D. Thacher, J. Appl. Phys. 41, 4790 (1970).

[21] W. A. Bonner, E. F. Dearborn, J. E. Geusic, H. M. Marcos, and L. G. Van Uitert, Appl. Phys. Lett. 10, 163 (1967).

[22] G. Burns and F. H. Dacol (unpublished). [The difference between T_c and T_d in $Pb(Mg_{1/3}Nb_{2/3})O_3$ is ~400 °C, which is indeed large.]

[23] J. P. Remeika and A. M. Glass, Mater. Res. Bull. 5, 37 (1970).

[24] V. G. Gavrilyachenko, V. G. Spinko, R. I. Martynenko, and E. G. Fesenko, Fiz. Tverd. Tela 12, 1531 (1970) [Sov. Phys.—Solid State 12, 1203 (1970)].

[25] S. Fushimi and T. Ikeda, J. Phys. Soc. Jpn. 20, 2007 (1965).

[26] B. Kirsch, J. Bamberg, and H. Schmitt (University des Saarlandes, Saarbrüken, Germany), private communication. I am indebted to them for discussing their work in progress with me.

[27] G. A. Smolensky, J. Phys. Soc. Jpn. Suppl. 28, 26 (1970); and some of the references quoted there; V. V. Kirillov and V. A. Isupov, Ferroelectrics 5, 3 (1973).

[28] K. Uchino, S. Nomura, L. E. Cross, and R. E. Newnham, Phase Transitions 2, 1 (1981); and some of the references quoted there.

[29] J. Kuwata, K. Uchino, and S. Nomura, Ferroelectrics 22, 863 (1979).