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Glassy polarization behavior in $K_2Sr_4(NbO_3)_{10}$-type ferroelectrics

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We extend our previous measurements of the temperature dependence of the optic indices of refraction, $n(T)$, of two crystals of the $K_2Sr_4(NbO_3)_{10}$ type with different amounts of disorder. These materials are axial ferroelectrics with the tetragonal tungsten-bronze crystal structure. As in other ferroelectrics where the translational symmetry is strongly broken, a glassy polarization P_d is observed far above the ferroelectric transition temperature T_c. However, in these noncubic materials, angular averaging of $n(T)$ need not be done, and so P_d is obtained rather directly. Below T_c it is in good agreement with the reversible, spontaneous polarization.

We extend earlier published measurements[1] of the temperature dependence of the index of refraction, $n(T)$, in two tetragonal ferroelectrics with the tungsten-bronze crystal structure. The ferroelectric system is $K_xSr_y(NbO_3)_{10}$. The results discussed here can be compared to two different systems[2,3] both of which have the rather simple cubic perovskite crystal structure, i.e., ABO_3 as in $BaTiO_3$ and $PbTiO_3$. All of these systems[1-3] are crystalline ferroelectrics but with built-in disorder. These materials have the usual ferroelectric transition temperature, T_c, below which there is an observable reversible spontaneous polarization P_r. However, at a much higher temperature, T_d, there is a randomly oriented local polarization, P_d, probably due to a freezing out of the local degrees of freedom leading to local dipole moments.

Two different crystals are studied. The more disordered material,[4] sample No. KSN92, has $x=0.74$ and $y=3.88$. The more ordered material,[4] sample No. KSN59, has $x=1.43$ and $y=3.76$. We report $n(T)$ measurements at two different wavelengths (6328 and 4416 Å). The reasons for extending our earlier 6328 Å measurements are several fold. First, dn/dT is larger at higher energies, i.e., nearer the band gap, which increases the accuracy of finding T_d. Thus, we have made measurements at 4416 Å, using a He-Cd laser. In addition we have taken more data points at 6328 Å which tends to increase the accuracy of the data. Second, by using two wavelengths we can use the known wavelength dependence of the quadratic electro-optic effect (discussed below) to check our interpretation of the data. Last, by extending the temperature range we can establish to greater certainty a high-temperature linear region for $n(T)$. We should also note that measurements on these tetragonal materials offer advantages over similar measurements in the cubic materials[2,3] because for tetragonal single crystals we need no angular average as is required for cubic crystals.

In Fig. 1(a) the temperature dependence of the index of refraction $n(T)$ for sample No. KSN92 is shown. The measurements are made at two wavelengths (using two different lasers) and, as indicated, a constant is subtracted from the data taken at 4416 Å so that both $n(T)$ results can be displayed on the same high-resolution plot. For most materials $n(T)$ has a weak linear temperature dependence[5] in a temperature range well above 0 K and well below the melting point. However, when a polarization develops there is a further contribution to $n(T)$ that depends on the square of the polarization. This term is described by the quadratic electro-optic effect, and for a polarization along the tetragonal axis (3 axis) the extra contribution to the index of refraction is

$$\Delta n_3 = -(n_3^0)^3 g_{33} P^2/2 \ , \tag{1}$$

where n_3^0 is the index of refraction if there were no polarization, Δn_3 is the difference between n_3^0, and the measured

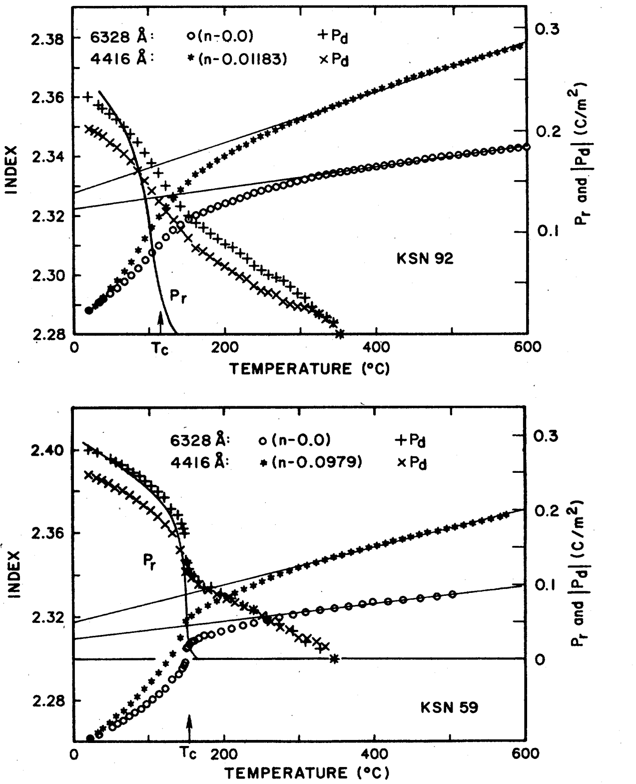

FIG. 1. (a) The indices of refraction at 6328 Å (o) and 4416 Å (*) for sample No. KSN92. Also shown are P_d values obtained from the $n(T)$ data at the two wavelengths (+ and ×, respectively). Last, the measured (Ref. 9) P_r results are sketched (the solid line). (b) The same results but for sample No. KSN59.

value g_{33} is the quadratic electro-optic coefficient, and P is the polarization along the tetragonal axis. In this expression, we assume that P is only along the tetragonal, ferroelectric axis, which for materials with this structure seems reasonable.[1] Note that the polarization that enters into Eq. (1) need not be P_r, spatially homogeneous or static. The long wavelength of the light will space and time average different regions in the crystal, and polarization that is up or down will contribute to Δn_3 with the same $\Delta n \propto P^2$.

Unlike the cubic perovskites,[2,3] for the materials reported here the indices along the tetragonal axis and perpendicular to it can be measured separately. This enables us to proceed without the need for directional averaging.

We must know g_{33} to use Eq. (1) to obtain $|P_d|$ (the subscript implies a local randomly up or down dipole polarization). $g_{33}-g_{13}=0.10\ \mathrm{m}^4/\mathrm{C}^2$ has been measured[6] at 6328 Å, which is close to what is expected for these materials.[7,8] For this material, it has been estimated that $g_{33} >> g_{13}$ so we use $g_{33}=0.10\ \mathrm{m}^4/\mathrm{C}^2$ at 6328 Å and $0.135\ \mathrm{m}^4/\mathrm{C}^2$ at 4416 Å.[7]

Using these values of g_{33}, taking n_3^0 as indicated in Fig. 1(a) as the high temperature extrapolated $n(T)$, values for $|P_d|$ can be calculated. The results for the two wavelengths are shown in Fig. 1(a) as indicated ($T_d=352$ and 351 °C for the two wavelengths, respectively). Although g_{33} does not depend strongly on the wavelength, the agreement between P_d obtained from the two different measurements is indicative that our interpretation of the data in terms of the quadratic electro-optic effect is correct.

Figure 1(b) shows the same measurements and results for sample No. KSN59 which is closer to the ideal, ordered material. Again P_d obtained from the data at the two wavelengths is in good agreement as is $T_d(\approx 346\,^\circ\mathrm{C})$. Also, notice that T_d for both of these crystals is very close, much closer than their T_c values of ≈ 115 and 150 °C for sample No. KSN92 and sample No. KSN59, respectively, as indicated by the arrow in the figures.

Also shown in Figs. 1(a) and 1(b) is the reversible spontaneous polarization,[9] P_r, measured by the standard Sawer-Tower technique. As can be seen T_d is $\approx 200\,^\circ\mathrm{C}$ above either of the two T_c values. Also the values of P_d are large. This indicates, as previously discussed,[1-3,10] that above the ferroelectric transition temperature there are large regions which have nonreversible randomly oriented polarizations. In the more disordered material, sample No. KSN92, essentially nothing special is observed in $n(T)$ at T_c. However, in the more ordered material, Fig. 1(b), there is a sharp change in the index due directly to P_r. In normal ordered ferroelectric materials, Δn is only observed at T_c and below.[5] Note that at room temperature $P_d \approx P_r$. This agreement between the two results is indicative that the use of Eq. (1) is appropriate.

Unlike the Pb-based lanthanum-doped zirconate titanate (PLZT) results[2] where there is quantitative understanding, here it is less clear what determines T_d. From our simple model[2] one might guess that T_d is essentially the ferroelectric transition temperature for $x=2$ and $y=4$. However, from the model T_d should be the transition temperature for the arrangement of ions that locally have the highest transition temperature. Thus, it is satisfying to see approximately the same T_d for crystals with two different x values (with different T_c values).

We can now state the following conclusions. (1) As in the cubic perovskite ferroelectric crystals,[2,3] we can interpret the $n(T)$ data via the quadratic electro-optic effect. This leads to the findings that above the ferroelectric transition temperature a local nonreversible, randomly directed (up or down) polarization, P_d is determined, i.e., a glassy polarization. P_d is observed below a fairly distinct temperature T_d. (2) Since the crystals studied here have a unique tetragonal axis, the angular averaging of $n(T)$ in the cubic perovskites need not be used. This gives more certainty to the resultant P_d values. (3) Using the normal wavelength dependence measured[7] for g_{33}, the values obtained for P_d from $n(T)$ measured at the two wavelengths are in good agreement with each other. (4) Far below the ferroelectric phase transition $P_d \approx P_r$. In the $\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$ type of materials P_d is somewhat larger than the reversible spontaneous polarization,[3] while in PLZT materials P_d is two-times larger than P_r. In this latter system it is possible that the grain boundaries in the ceramics inhibit the reversibility of the polarization. The crystals, where the reversibility of the polarization should be inhibited the least, should be those studied here since P_r can only be in the $+c$ or $-c$ direction. Thus, it is possible that at low enough temperature most of the glassy polarization is reversible. This may be a property of all these systems.[4] The materials discussed here have a broadened, diffuse ferroelectric phase transition. We believe that the proposed model[2] for materials where the translational symmetry is strongly broken applies to these materials and may be applied to all ferroelectrics with a diffuse phase transition.

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