Low-temperature thermal properties of ferroelectrics

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Through measurements of the low-temperature thermal conductivity and specific heat, we show that two classes of ferroelectrics can be distinguished. One class exhibits behavior typical of crystalline solids and the other displays behavior identical to that seen in structural glasses. We correlate these observations with measurements of the dielectric constant and optic index of refraction in the vicinity of the ferroelectric transition at T_c. Near T_c, those ferroelectrics with crystal-like thermal properties at low temperature exhibit normal behavior (i.e., a sharp ferroelectric transition) while those with glasslike thermal properties display a diffuse phase transition and a glassy polarization phase. The similarity to the elastic dipole glass $(KBr)_{1-x}(KCN)_x$ is discussed.

In 1976 Lawless reported a $T^{3/2}$ dependence of the specific heat between 2 and ~ 5 K for the ferroelectrics $BaTiO_3$, $LiNbO_3$, triglycine sulfate (TGS), and KH_2PO_4 (KDP).[1] Thus attention was called to the fact that ferroelectrics have anomalous low-temperature thermal properties. Later, he added $NaNO_2$ to that list.[2] However, recent measurements by Grimm *et al.*[3] on $BaTiO_3$, $LiNbO_3$, TGS, and $NaNO_2$, which covered the extended temperature range 0.5—3 K, have shown that these ferroelectrics have no such anomalies. Instead, the magnitudes and temperature dependence of their specific heat agree with the Debye prediction. These authors suggested that the anomalies observed previously might have been caused by lattice defects, and were absent in their more perfect crystals. Following Lawless' early work,[1] Ackerman *et al.*,[4] Lawless *et al.*,[5] Lawless,[6] Henning *et al.*,[7,8] and Fischer *et al.*[9,10] reported a different kind of anomaly in several other ferroelectric materials. They observed behavior similar to that seen in structural glasses in both the thermal conductivity and specific heat for these solids.

In this paper, we will attempt to clarify this somewhat confusing situation. We will critically review the published results and add some of our own. We will see that there are in fact two kinds of ferroelectrics, those which display glasslike thermal properties and those which exhibit crystal-like thermal properties. Furthermore, we will show that from measurements of either the dielectric constant or the optic index of refraction at and above the ferroelectric phase transition it can be predicted to which class a ferroelectric belongs. Finally, we will discuss the origin of the glasslike behavior on the basis of breakdown of the translational symmetry occurring in these crystals.

Figure 1 shows the thermal conductivity of a variety of ferroelectrics: KH_2PO_4,[11] $LiNbO_3$ (this study), $Pb_5Ge_3O_{11}$ (this study), $BaTiO_3$,[12] and $Cd_2Nb_2O_7$.[5] None of these crystalline solids show the thermal conductivity characteristic for the amorphous state (see, for example, the dashed curve in Fig. 1, which is the thermal conductivity of amorphous silica, showing a T^2 dependence below ~ 1 K, and a plateau near 10 K, followed by a continued slow rise at higher temperatures[13]). With the exception of $Cd_2Nb_2O_7$ all samples were single crystals and have conductivities characteristic of somewhat imperfect single crystals [for comparison, see the curve for pure KBr (Ref. 14) in Fig. 1]. The sample of $Cd_2Nb_2O_7$ was a ceramic. Its thermal conductivity is characteristic of that of small-grain-size ceramics. For this sample, the data at lower temperatures ($T < 1$ K) approach a T^3 dependence with a magnitude approximately that expected on the basis of the grain size, i.e., 20 μm (Ref. 5). (Lawless *et al.*[5] had proposed that the thermal conductivity of the $Cd_2Nb_2O_7$ ceramic shown here indicated glasslike behavior; however, in view of the absence of a plateau, and because of the continued rapid increase up to 30 K, we believe that this interpretation must be rejected. Similarly, we argue that the thermal conductivity of polycrystalline antiferroelectric $PbZrO_3$ displays crystalline, and not glasslike behavior, as claimed by Lawless.[15])

The crystal-like thermal conductivity of the ferroelectrics shown in Fig. 1 differs greatly from that of certain other ferroelectrics. Figure 2 shows the thermal conductivity of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (this study), $(Sr_{0.61}Ba_{0.39})Nb_2O_6$,[10] $Pb(Mn_{0.5}Ta_{0.5})O_3$,[4,6] and $(Pb_{0.915}La_{0.085})(Zr_{0.65}Ti_{0.35})O_3$.[9] The first two were single crystals, the latter two almost 100% dense ceramics.[16] In all cases the similarity to glasses is striking, as shown by the comparison with silica.[17]

The same distinction can be made for the low-temperature specific heat: As mentioned above, Grimm *et al.*[3] had shown that the specific heats of $BaTiO_3$, $NaNO_2$, $LiNbO_3$, and TGS agree with the predictions of the Debye model. On the other hand, the specific heats C_v of $(Sr_{0.61}Ba_{0.39})Nb_2O_6$,[8] $Pb(Mg_{1/3}Nb_{2/3})O_3$,[4] and $(Pb_{0.9}La_{0.1})(Zr_{0.65}Ti_{0.35})O_3$ (Ref. 7) were reported to be glasslike, i.e., they had a linear anomaly of the order of $10T$ erg g^{-1}K^{-2}. For the sake of completeness, it should be pointed out that, when the specific heat of the latter crystals is plotted as C_v/T versus T^2 (Fig. 3), small devia-

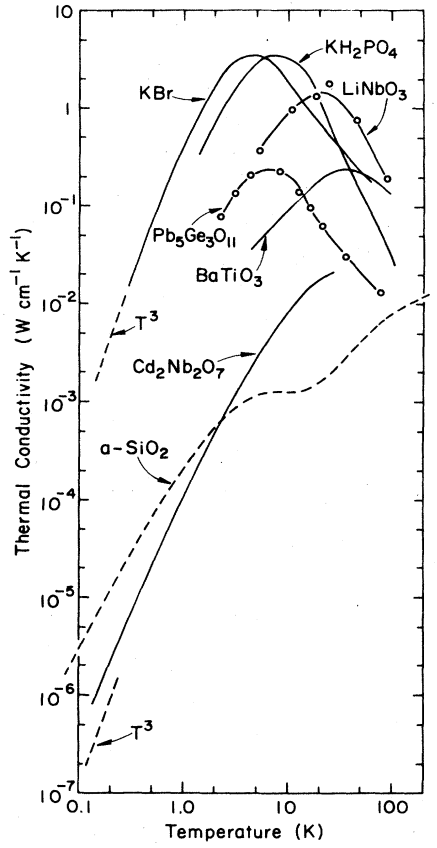

FIG. 1. Thermal conductivity of several ferroelectric single crystals (for references, see Table I). Single crystal KBr (Ref. 14) and amorphous SiO_2 (Ref. 17) for comparison. In the polycrystalline $Cd_2Nb_2O_7$, the thermal conductivity is determined largely by grain boundary scattering, the similarity to the thermal conductivity of Ge-Si ceramics is striking (see Kumar *et al.*, quoted in Ref. 16). Data points indicate results obtained in the present investigation.

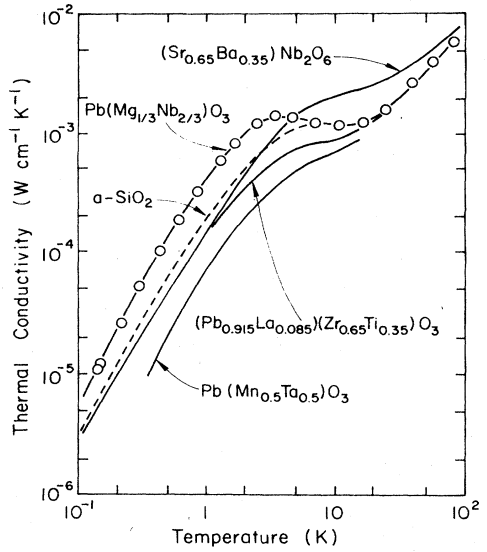

FIG. 2. Four ferroelectrics with glasslike thermal conductivity (for references see Table I). Single crystals, except for $Pb(Mn_{0.5}Ta_{0.5})O_3$ and $(Pb_{0.915}La_{0.085})(Zr_{0.65}Ti_{0.35})O_3$, which were polycrystalline. a-SiO_2 data, shown for comparison (Ref. 17), extend all the way to above 100 K, but merge with the $Pb(Mg_{1/3}Nb_{2/3})O_3$ data above 5 K. Similarly, the $(Pb_{0.915}La_{0.085})(Zr_{0.65}Ti_{0.35})O_3$ data (measured to 0.1 K) merge with those of $(Sr_{0.65}Ba_{0.35})Nb_2O_6$ below 1 K. Data points indicate results obtained in the present investigation.

tions from typical glassy behavior are seen for these samples. For a glass, a straight line is typical in this kind of a plot, perhaps with a slight downward trend at the lowest temperatures, indicating that the low-temperature anomaly varies slightly more rapidly than linearly with T [as an example, see the data for a-SiO_2 (Ref. 13) in Fig. 3]. The rise observed below $T \sim 1.5$ K in the ferroelectric crystals *above* the extrapolated straight lines is taken as evidence for additional (nonglasslike) excitations. It is known that impurities in very low concentrations can affect the specific heat not only of crystalline solids, but also of amorphous solids in the manner observed in these ferroelectric crystals.[17] In light of this problem, one may want to take the straight lines above $T \sim 1.5$ K in Fig. 3, which extrapolate to a positive value of C_v/T at $T=0$, as evidence for a linear, glasslike specific heat anomaly in these crystalline solids. However, these lines are observed clearly only in the limited temperature range 1.5 K $< T <$ 3 K, which is one in which phonon dispersion may influence the data in a way that a straight-line extrapolation towards $T=0$ is no longer permissible.[18] Thus evidence for glasslike excitations in these specific heat measurements must be viewed with some caution at this time. Better crystals are needed.

In measurements of the dielectric constant near the ferroelectric phase transition temperature T_c, it is also possible to distinguish between two types of ferroelectrics:[19,20] those which display a sharp peak indicative of a first- or second-order phase transition, and those which exhibit a

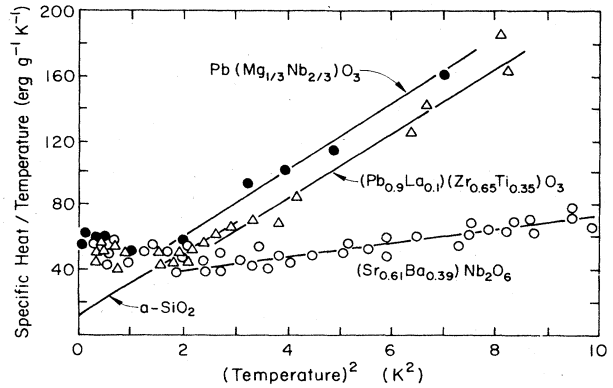

FIG. 3. Specific heat C_v of three ferroelectrics; the $(Sr_{0.61}Ba_{0.39})Nb_2O_6$ was single crystal, the others were polycrystalline. Plotted is C_v/T vs T^2 on linear scales. A linear specific heat anomaly, C_1T, would show up as a straight line intersecting the vertical axis at a finite value, as shown approximately for a-SiO_2 (Ref. 17). [Data on ferroelectric K_2SeO_4 single crystals do not extend to low enough temperatures ($T > 0.6$ K) to make a determination of a linear anomaly unambiguous; see I. Henning, E. Hegenbarth, and B. Brezina, Phys. Status Solidi A **78**, K167 (1983).]

broad peak. The members of this latter class are sometimes called ferroelectrics with a diffuse transition. Another distinction between these two kinds of ferroelectrics has been observed in measurements of the temperature dependence of the optic index of refraction, $n(T)$. Rather than observing an abrupt change in $n(T)$ at T_c, as occurs in normal ferroelectrics, Burns and Dacol[21–24] observed in ferroelectrics with a diffuse transition a gradual change in the slope of $n(T)$ beginning at a temperature T_d, which can be several hundreds of degrees above T_c.

The summary of the dielectric, optical, and thermal investigations of ferroelectrics, presented in Table I, shows a very remarkable correlation. All ferroelectrics can be grouped into two classes. (1) Ferroelectrics with diffuse transitions and a gradual change of slope of $n(T)$ have glasslike thermal properties. (2) Ferroelectrics with sharp transitions and an abrupt change of slope of $n(T)$ have crystal-like thermal properties.

In order to understand the glasslike behavior of the former class, we turn to the interpretation offered by Burns and Dacol for the origin of the gradual change in the slope of the index of refraction $n(T)$ observed in these ferroelectrics.[21–24] They explained the behavior in the temperature range $T_c < T < T_d$ by the presence of a ran-

TABLE I. Summary of the dielectric, optical, and thermal data on the glassy behavior of ferroelectrics. Entries without references are based on information obtained in this investigation. The second column indicates whether the crystalline ferroelectrics were single crystals (S) or polycrystalline ceramics (P).

Chemical formula	Form	Specific heat	Thermal conductivity	Dielectric transition	Optic index of refraction
KH_2PO_4 (KDP)	S	a	cryst.[b]	sharp[c]	normal[c]
$BaTiO_3$	S	cryst.[d]	cryst.[e]	sharp[c]	normal[c]
$Pb_5Ge_3O_{11}$	S		cryst.	sharp[f]	normal[f]
$LiNbO_3$	S	cryst.[d]	cryst.	sharp[c]	normal[g]
TGS[h]	S	cryst.[d]		sharp[c]	normal[c]
$NaNO_2$	S	cryst.[d]		sharp[c]	normal[c]
$Pb(Zr_{0.65}Ti_{0.35})O_3$ (PZT 65/35)	P			sharp[c]	
$K(Ta_{1-x}Nb_x)O_3$ (KTN)	S		cryst.[i]	sharp[c]	normal[c]
$Cd_2Nb_2O_7$	P		polycryst.[j]	sharp[c]	
$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN)	S	glassy[k]	glassy[k,l]	diffuse[c]	glassy[n]
$(Sr_{0.61}Ba_{0.39})Nb_2O_6$ (SBN)	S	glassy[o]	glassy[p,q]	diffuse[c]	glassy[c]
$Pb(Mn_{0.5}Ta_{0.5})O_3$ (PMT)[r]	P		glassy[k,l]		
$(Pb_{1-3x/2}La_x)(Zr_{0.65}Ti_{0.35})O_3$[s]	P	glassy[t,u]	glassy[v,w]	diffuse[c]	glassy[x]

[a]Lawless' claim of a $T^{3/2}$ specific heat anomaly (Ref. 1) has not yet been disproved.
[b]Reference 11.
[c]Reference 20.
[d]Reference 3.
[e]Reference 12.
[f]Reference 24.
[g]This has not been measured at T_c or above, but below T_c, $n(T)$ shows the curvature typical of normal ferroelectrics.
[h]Triglycine sulfate.
[i]This is extremely sensitive to x; evidence for resonance scattering at $T \sim 10$ K even for $x = 0$. See B. Salce, A. M. de Goer, and L. A. Boatner, J. Phys. (Paris) Colloq. **42**, C6-424 (1981); W. N. Lawless, D. Rytz, and U. T. Höchli, Ferroelectrics **38**, 809 (1981). More recently the existence of a ferroelectric phase transition and the nature of that transition have been questioned. [See W. Kleemann, F. J. Schäfer, and D. Rytz, Phys. Rev. Lett. **54**, 2038 (1985), and references within.] Note that Salce *et al.* have reported evidence for a glasslike thermal conductivity in $KTaO_3$ doped with lithium, in which a glasslike orientational disorder of the Li^+ ions has been observed in dielectric measurements [U. T. Höchli, Phys. Rev. Lett. **48**, 1494 (1982)].
[j]Reference 5.
[k]Reference 4.
[l]Reference 6.
[m]Our own data, shown in Fig. 2, are close to those presented in Refs. 4 and 6.
[n]Reference 23.
[o]Reference 8.
[p]Reference 10.
[q]Another single crystal, with a Ba^+ concentration of 55% had a nearly identical conductivity.
[r]This is ferroelectric according to Lawless [Cryogenics **19**, 585 (1979)].
[s]This is abbreviated as PLZT $x/65/35$.
[t]Reference 7.
[u]Actual composition given as $(Pb_{0.9}La_{0.1})(Zr_{0.65}Ti_{0.35})O_3$.
[v]Reference 9.
[w]Actual composition given as $(Pb_{0.915}La_{0.085})(Zr_{0.65}Ti_{0.35})O_3$.
[x]Reference 22.

domly oriented array of polarizations (a glassy polarization phase) which occurs when there is a strong breakdown of the translational symmetry. This breakdown arises when ions with different valences are randomly distributed on a given type of site in the lattice. For example in $(Pb_{1-3x/2}La_x)(Zr_{0.65}Ti_{0.35})O_3$, Pb^{2+} ions and La^{3+} ions both randomly occupy the A sites in the ABO_3 perovskite crystal structure. Making the assumption that the effect is a result of local interactions, Burns and Dacol were able to predict T_d in the system $(Pb_{1-3x/2}La_x)(Zr_yTi_{1-y})O_3$. T_d should be approximately equal to T_c of the pure material, $Pb(Zr_yTi_{1-y})O_3$ (i.e., with $x=0$). Those very small regions with relatively little La^{3+} will tend to become polarized at T_c of $Pb(Zr_yTi_{1-y})O_3$, while those regions rich in La^{3+} will resist polarizing until lower temperatures. In the range of La^{3+} concentration $0.070 \leq x \leq 0.095$, for which the transition is diffuse, the experimental T_d does indeed coincide with T_c of the La^{3+}-free crystal $Pb(Zr_{0.65}Ti_{0.35})O_3$, for which a sharp transition has been seen in dielectric measurements. Unfortunately, since $Pb(Zr_{0.65}Ti_{0.35})O_3$ was available to us only as an opaque ceramic with 95% density and approximately 5-μm-grain size, there exist no measurements of the index of refraction and of the low-temperature thermal properties of this La^{3+}-free ferroelectric. However, based on the dielectric measurements, and the interpretation given above, we would expect it to be crystal-like.

Another interesting ferroelectric might be $(Sr_{1-x}Ba_x)Nb_2O_6$. This system exists as single crystals for $0.25 \leq x \leq 0.8$, and as x is decreased, the ferroelectric transition as seen in measurements of the dielectric constant and the optic index of refraction moves to lower temperature and changes from nearly sharp to diffuse (Ref. 20, Figs. 1261, 1265, and 1272). In addition the cusp seen in the specific heat at T_c also broadens as x is decreased (Ref. 20, Fig. 1269). However, samples spanning this wide a range in x and of a size sufficient for thermal conductivity measurements have not yet been located; in the single crystals measured by Fischer *et al.*,[10] x was 0.39 and 0.55; both had nearly identical, glasslike thermal conductivities.

Can such a glassy polarization phase lead to glasslike thermal properties? We will draw on an analogy with a crystal containing an elastic dipole glass, namely, $(KBr)_{1-x}(KCN)_x$.[25] This system forms cubic crystals in which CN^- ions are substituted randomly on bromine ion vacancies. In the concentration range $0.25 \leq x \leq 0.7$, these crystals display glasslike thermal properties at low temperatures.[26–28] For $x > 0.56$ this system undergoes a ferroelastic transition at a temperature T_c, which increases with increasing x. This transition can be observed through a peak in the specific heat at T_c which is sharp for $x = 1.0$ but broadens as x is decreased. This behavior is reminiscent of the behavior of the dielectric constant near T_c in $(Pb_{1-3x/2}La_x)(Zr_{0.65}Ti_{0.35})O_3$ as x increases from $x=0$ [and is also similar to what is seen in the specific heat of $(Sr_{1-x}Ba_x)NbO_3$ as x is decreased[20]]. Furthermore, inelastic neutron scattering measurements[29] in $KBr_{0.5}KCN_{0.5}$ have revealed the onset of freezing near T_c of pure KCN (168 K), which in analogy to the diffuse ferroelectrics we will call T_d. This is similar to what is seen in the optic index of refraction[22] of $(Pb_{1-3x/2}La_x)(Zr_{0.65}Ti_{0.35})O_3$ for $0.07 \leq x \leq 0.095$. It has been shown that the low-temperature glasslike excitations in $(KBr)_{1-x}(KCN)_x$ are due to the rotational tunneling of individual CN^- ions with low barriers against reorientation, while T_c and hence T_d are determined by those CN^- ions with large barriers.[28] The broad distribution of barriers is a result of the random grouping of the Br^- and CN^- ions.

On the basis of these similarities, we suggest that the ferroelectrics with diffuse transitions are the electrical analogues of the elastic dipole glass $(KBr)_{1-x}(KCN)_x$. In these ferroelectrics the random grouping and strong breakdown in translational symmetry result in a broad distribution of barriers against changes in the local polarization. As the temperature is lowered below T_d, local polarizations, and hence elastic distortions, begin to appear in those regions which have the greatest tendency to polarize. These polarizations are observed in optic index of refraction measurements below T_d. Changes between local polarizations with small energy differences result in the glasslike behavior seen in thermal conductivity and specific heat measurements below 1 K.

While the picture of local random polarizations leads readily to a broad distribution of tunneling states and hence a T^2 dependence in the thermal conductivity and a term in the specific heat proportional to T based on the so-called tunneling model developed for amorphous solids,[30] it remains to be demonstrated that it also leads to the proper magnitude of the density of tunneling states. Another fascinating question is whether this picture can in turn lead to an understanding of the physical nature of the tunneling states characteristic for structural glasses.

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