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Classical behavior of the index of refraction in two ferroelectrics in the high-temperature phase

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We report very accurate measurements of the optic index of refraction as a function of temperature $n(T)$ of two ferroelectric materials $PbTiO_3$ and $Pb_5Ge_3O_{11}$. In sharp contrast to results in $BaTiO_3$, $n(T)$ is linear in the high-temperature centrosymmetric phases. The implications are discussed.

We have recently published[1] very accurate measurements of the temperature dependence of the index of refraction $n(T)$ in the cubic phase of the ferroelectric material $BaTiO_3$. These results show[1] large polarizations above the paraelectric to ferroelectric phase transition temperature T_c extending up to $\approx T_c + 180\,°C$ and are contrary to what is expected from the soft-mode theory of structural phase transitions.[2] Similar disagreement with this theory in the ferroelectric tetragonal phase[3] has been explained by invoking linear coupling of the polarization with impurities or other local fluctuations.[4] In the cubic phase, due to symmetry, the impurity coupling model is less able to explain the disagreement. In a complementary experiment,[5] the infrared reflectivity of $BaTiO_3$ above T_c shows that the temperature dependence of the "soft mode" is inconsistent with the Curie-Weiss behavior of the low-frequency dielectric constant and deviations occur for temperatures extending to $\approx T_c + 120\,°C$. Infrared measurements in other perovskite ferroelectrics also show deviations from what is expected from the soft-mode picture.[6] Actually, much of the quantitative support for the soft-mode model of ferroelectrics comes from measurements of $SrTiO_3$ and $KTaO_3$, two perovskite crystals that are not ferroelectric.

It is therefore important to determine if any ferroelectric material actually shows behavior in agreement with the model. The first perovskite crystal that comes to mind is $PbTiO_3$. Unlike $BaTiO_3$, $PbTiO_3$ has underdamped soft modes in the ferroelectric and cubic phases as determined by Raman[7] and neutron[8] measurements. In this Communication we report measurements of the temperature dependence of the index of refraction in the cubic phase of $PbTiO_3$ and also of $Pb_5Ge_3G_{11}$. The growth of the $PbTiO_3$ and $Pb_5Ge_3O_{11}$ crystals has been described previously.[7,9,10]

Figure 1 shows the results for $PbTiO_3$ in the cubic phase.[11] As can be seen from the scale (0.001 between the tic marks) above T_c, $n(T)$ is highly linear with temperature. This is in sharp contrast to the results[1] in $BaTiO_3$ where at T_c we find (at 6328 Å) deviations of 0.0025 from the high-temperature linear behavior. If such deviations exist in $PbTiO_3$ they are at least 20 times smaller than in $BaTiO_3$.

Figure 2 shows similar results in the axial ferroelectric $Pb_5Ge_3O_{11}$, a material with a more complicated structure than the perovskites. As can be seen, below T_c ($\approx 180\,°C$) there is a strong deviation of $n(T)$ from the high-temperature linear behavior. These changes, due to the contribution to $n(T)$ from the spontaneous polarization via the electro-optic effect, will be discussed in the future. Here, we only emphasize $n(T)$ above T_c. Again, on the same scale as in Fig. 1 for $PbTiO_3$, $n(T)$ is linear with temperature for the indices both parallel (n_c) and perpendicular (n_a) to the ferroelectric axis. We find similar results for $n(T)$ at 5145 and 4880 Å.

The reasons for the deviations from the expected soft-mode behavior in $BaTiO_3$ are not clear. This effect has been discussed in terms of a crossover from

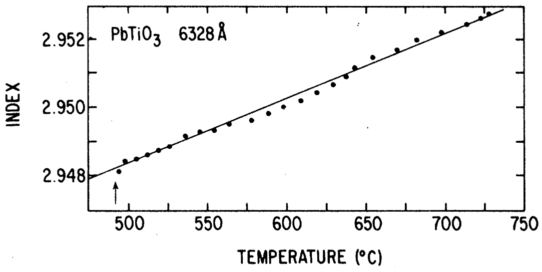

FIG. 1. Temperature dependence of the index of refraction in the cubic phase of $PbTiO_3$. The arrow indicates T_c.

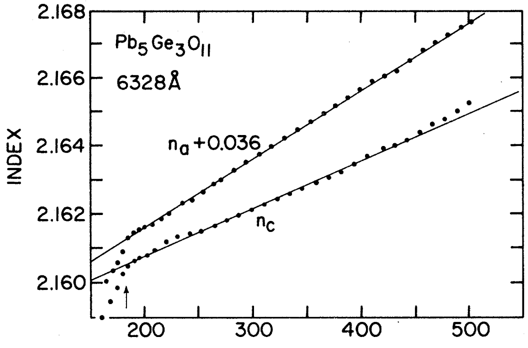

FIG. 2. $n(T)$ for both indices of refraction of $Pb_5Ge_3O_{11}$ emphasizing the high-temperture, nonferroelectric phase. The arrow indicates T_c.

displacive, at high temperatures, to order-disorder behavior within $T_c < T < \approx T_c + 150\,^{\circ}\mathrm{C}$.[12–14] So far there is no direct evidence to indicate that this is actually true. From renormalization-group theory it has been argued that in crystals with the perovskite structure ($BaTiO_3$, $PbTiO_3$, etc.) the crossover effect should be more pronounced than in $LiTaO_3$.[15] This comes about because the critical dimensionality of the former is larger than that of the latter.[15] Our results for $PbTiO_3$ (Fig. 1) argue against this proposal since we see classical behavior of $n(T)$ in $PbTiO_3$ but nonclassical results in $BaTiO_3$ (Ref. 1), and both have the same structure.

Another suggestion[16] is that the polarization fluctuations observed above T_c are related to random mean-square atomic displacements consistent with the high dielectric constant. Using the fluctuation dissipation theorem, the square of the polarization fluctuations δP^2 is related to the clamped dielectric constant ϵ,

$$\delta P^2 = kT\epsilon / V_c \ , \tag{1}$$

where V_c is a characteristic volume corresponding to the volume of the fluctuation.[16] If one assumes that V_c is not very temperature dependent, an assumption that might be supported by related x-ray results,[17] then $\delta P^2 \propto \epsilon = C/(T - T_0)$. Our polarization data above T_c in $BaTiO_3$ do not agree with this prediction. Further, although ϵ of $PbTiO_3$ has not been measured above T_c, a Curie-Weiss law is expected. Yet $n(T)$ in $PbTiO_3$ shows no indication of polarization fluctuations (Fig. 1).

The idea that the nonlinear behavior of $n(T)$ might be due to impurities (as is observed in most central peak experiments) is at odds with the fact that the same results are observed in $BaTiO_3$ grown in two entirely different ways.[1] In addition, the crystals of $PbTiO_3$ and $Pb_5Ge_3O_{11}$ probably have as many impurities as our $BaTiO_3$, yet no nonlinearities are observed in the former crystals.

Thus we have two materials $PbTiO_3$ and $Pb_5Ge_3O_{11}$ for which $n(T)$ is linear above T_c. In contrast, $BaTiO_3$ shows a nonlinearity in $n(T)$ (Ref. 1) and anomalous soft-mode behavior,[5] and two other perovskite ferroelectrics $KNbO_3$ and $NaNbO_3$ (Ref. 6) also show anomolous soft-mode behavior in the infrared measurements. There is one distinct difference between these two sets of materials. In the first set ($PbTiO_3$ and $Pb_5Ge_3O_{11}$) the soft mode is underdamped[7,8,18] while the soft mode is very overdamped for the latter three materials.[5,6] However, a comprehensive understanding of the effects discussed here cannot, as yet, be proposed. It would be interesting to measure the infrared spectrum in $PbTiO_3$ above T_c. From the results reported here, normal soft-mode behavior would be expected.

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