

# Optical properties of ferroelectric $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ for $x=0$ and 0.02

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We report accurate measurements of the temperature dependence of the indices of refraction  $[n(T)]$  in ferroelectric single crystals of  $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$  for  $x=0$  and 0.02. Above the ferroelectric transition temperature  $T_c$ ,  $n(T)$  is linear with temperature. (It had been hoped that the  $x=0.02$  sample would show nonlinear results similar to those observed in  $\text{BaTiO}_3$ .) Analyzing  $n(T)$  below  $T_c$  in terms of the quadratic electro-optic effect,  $[\Delta(n^{-2})]_{ij} = \sum_{k,l} g_{ijkl} P_k P_l$ , reveals very large  $g$  values, 20–100 times larger than those observed in Pb perovskites.

## INTRODUCTION

In the ferroelectric  $\text{BaTiO}_3$  the temperature-dependent optic index of refraction measurements  $n(T)$  has revealed unexpected behavior<sup>1</sup> above the ferroelectric transition temperature  $T_c$ . In order to investigate this further, similar measurements of  $n(T)$  were made<sup>2</sup> in two other ferroelectrics,  $\text{PbTiO}_3$  and  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ . The former has the same simple perovskite structure as  $\text{BaTiO}_3$ , while the latter also is an axial ferroelectric but the structure is more complicated.<sup>3</sup>

In this paper we (1) extend the  $n(T)$  measurements, from 6328 to 4880 Å in  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ , (2) report results in  $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$  where  $x=0.02$ , measured to see if the

randomly located Ba ions would produce an effect similar to that observed in  $\text{BaTiO}_3$ , and (3) discuss the measurements below  $T_c$  for both  $x=0$  and 0.02.

## EXPERIMENT

The growth of  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  crystals has been described previously<sup>4</sup> and several studies of the ferroelectric properties have been published.<sup>5–7</sup> The ferroelectric properties of  $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$  for several values of  $x$  also have been published.<sup>8,9</sup> We have measured the indices of refraction by the minimum deviation method<sup>1,2</sup> which is capable of high accuracy. The indices with light polarized along the ferroelectric axis  $n_c$  and perpendicular to the ferroelectric axis  $n_a$  were separately measured.

## RESULTS ABOVE $T_c$

Figure 1 shows  $n(T)$  for  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  (i.e.,  $x=0$ ) emphasizing the values above  $T_c$  (the arrow in the figure). The index data are taken at two different wavelengths in the visible and  $n_c$  is displaced so that both  $n_c$  and  $n_a$  can be shown on the same high-resolution scale (0.001 or 0.002 between tic marks).

Figure 2 shows the same data but for  $x=0.02$  (i.e., 2 at. % Ba replacing the Pb). The  $x=0$  data generally are in agreement with published measurements using Na D light up to 300°C.<sup>5,6</sup>

For both  $x=0$  and 0.02, at 4880 Å,  $n_a$  above 350°C seems to deviate above the straight lines as can be seen. However, otherwise, in the high-temperature phase the indices depend linearly with temperature for several hundred degrees above  $T_c$ . We do not think that the deviation from linearity at high temperatures has anything to do with the specifics of the ferroelectric process near  $T_c$ . We feel this way because it is observed only along one axis, but more importantly, because it is observed only with the short-wavelength, higher-energy light. At this high energy one is close to the band gap in these materials so that a nonlinear temperature dependence of the bands would be emphasized.

The linearity near  $T_c$  for all of the indices is observed in

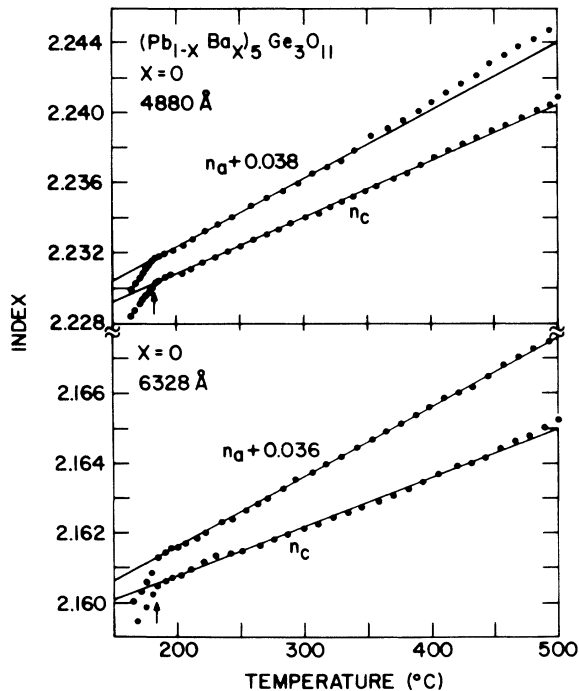


FIG. 1.  $n(T)$  for both indices of refraction in  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ , at two wavelengths, emphasizing the high-temperature nonferroelectric phase. The arrow indicates  $T_c$ .

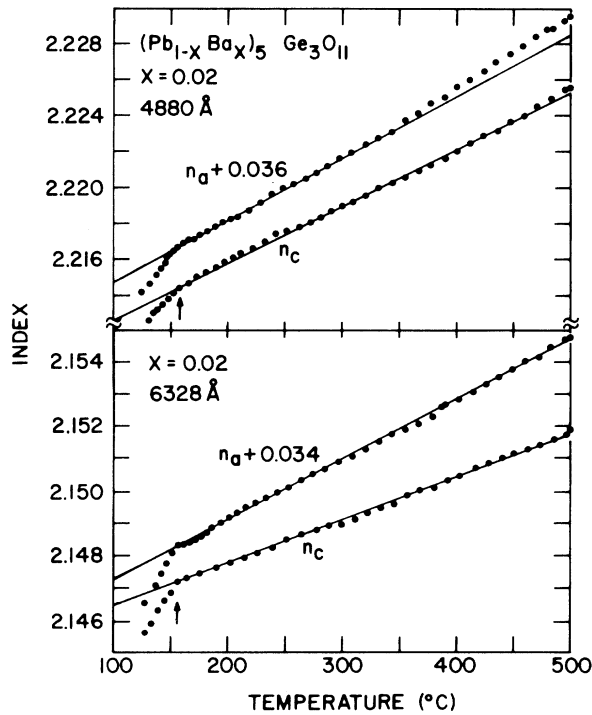


FIG. 2. Same as in Fig. 1 but for  $x=0.02$  in  $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$ .

$\text{BaTiO}_3$ .<sup>1,2</sup> Particularly surprising is that the linearity is observed for  $x=0.02$ . One might expect a local strain associated with each Ba ion which would result in the nonclassical  $n(T)$  observed in  $\text{BaTiO}_3$  above  $T_c$ . Clearly such is not the case. For the  $\text{BaTiO}_3$  samples used in Ref. 1 the impurities are in the parts per million range. Here if one takes the point of view that Ba ions are an "impurity," then a fraction  $\sim 0.004$  of the atoms in the crystal are impurities. Thus in the  $x=0.02$  sample there are greater than  $10^4$  more impurities than in the  $\text{BaTiO}_3$  samples. Yet the nonclassical behavior is not reproduced by the  $x=0.02$  samples. One might think that for crystals with larger  $x$  values the nonclassical effect could be observed but this seems unlikely since there are already greater than  $10^4$  more impurities present for  $x=0.02$  than for  $\text{BaTiO}_3$ . Apparently the nonclassical behavior in  $\text{BaTiO}_3$  is not due to local strain-type effects on the atom level.

Above  $T_c$  the straight lines, shown in Figs. 1 and 2, are

TABLE I. Values of  $A$  and  $B$  that describe  $n(T)$  ( $=AT+B$ ) above  $T_c$  at the two wavelengths, parallel ( $n_c$ ) and perpendicular ( $n_a$ ) to the ferroelectric direction.

$x$	Index	$A$ ( $10^{-5} \text{ } ^\circ\text{C}^{-1}$ )	$B$
0	$n_c$ (4880 Å)	3.259 40	2.224 36
0	$n_c$ (6328 Å)	1.387 79	2.158 00
0	$n_a$ (4880 Å)	3.950 51	2.186 41
0	$n_a$ (6328 Å)	1.994 02	2.121 62
0.02	$n_c$ (4880 Å)	3.147 97	2.209 50
0.02	$n_c$ (6328 Å)	1.317 20	2.145 18
0.02	$n_a$ (4880 Å)	3.442 12	2.175 30
0.02	$n_a$ (6328 Å)	1.864 22	2.111 42

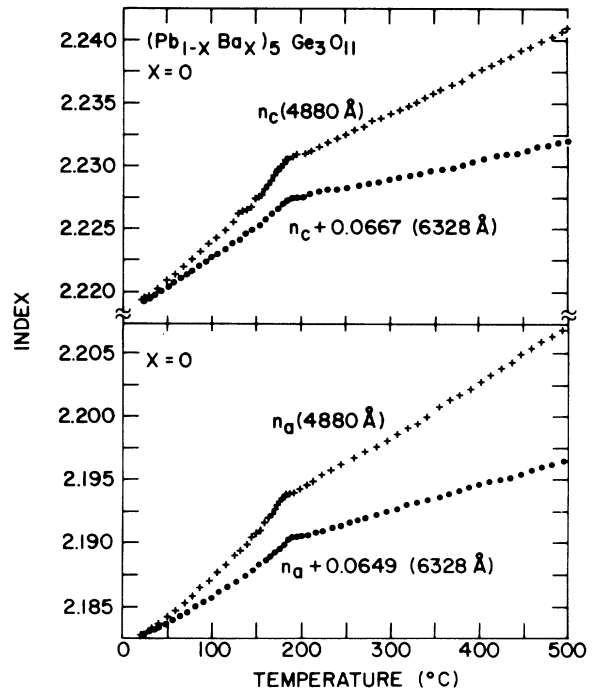


FIG. 3. Same as in Fig. 1 but the data in the ferroelectric phase are also shown.

of the form

$$n(T) = AT + B, \quad (1)$$

where  $T$  is the temperature in  $^\circ\text{C}$ ; values of  $A$  and  $B$  are listed in Table I.

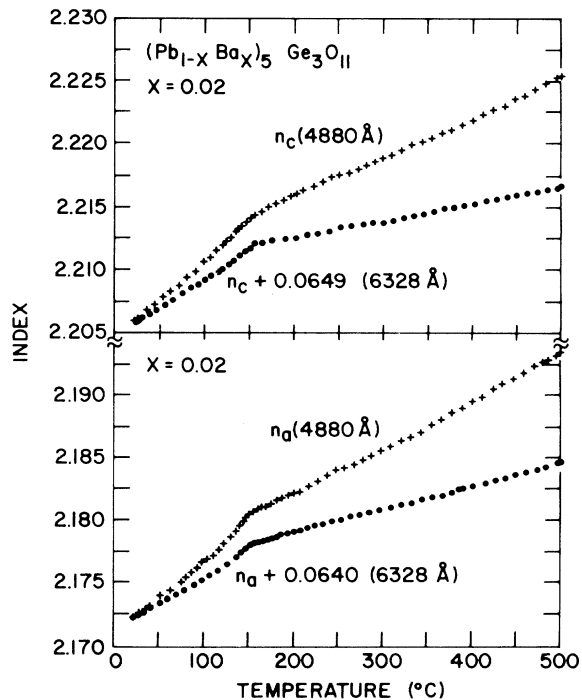


FIG. 4. Same as in Fig. 2 but also showing the data in the ferroelectric phase.

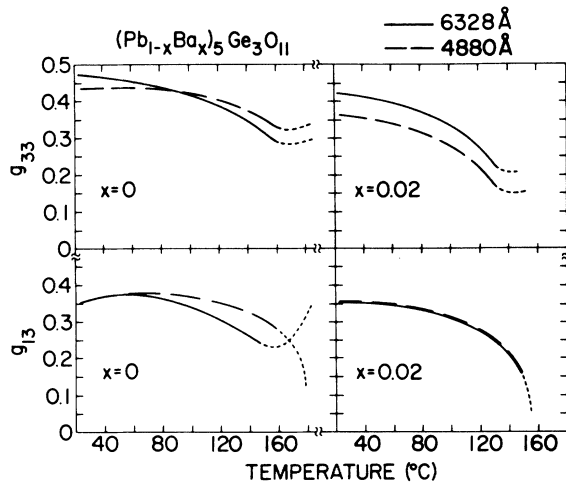


FIG. 5. Temperature dependence of the  $g$  values for  $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$  obtained from Eqs. (2).

### RESULTS BELOW $T_c$ —THE QUADRATIC ELECTRO-OPTIC EFFECT

Figure 3 shows the same measurements as in Fig. 1 but now  $n(T)$  is also shown in the ferroelectric region. The phase transition is second order<sup>5-7</sup> and the continuous nature of the transition can be seen. Figure 4 shows the same type of data for  $x=0.02$ . As can be seen (in Figs. 1-4) the phase transition shows up almost as clearly for  $x=0.02$  as for  $x=0$  in these homogeneous crystals; other than a shift in  $T_c$  to lower values for  $x=0.02$  there is little difference from the  $x=0$  materials.

To analyze the data below  $T_c$  we make an assumption often made for ferroelectrics: The index of refraction in the ferroelectric phase can be understood in terms of that in the high-temperature (centrosymmetric) phase but with a contribution from the reversible spontaneous polarization that comes about via the quadratic electro-optic effect.<sup>10,11</sup> For the materials discussed here, where the reversible spontaneous polarization  $P_r$  is along the  $c$  or three-axis, the change of the index of refraction due to this polarization is  $\Delta n_c$  (or  $\Delta n_a$  for the index perpendicular to the ferroelectric axis). Derived from the basic quadratic electro-optic effect,<sup>10,11</sup>  $[\Delta(n^{-2})]_{ij} = \sum_{k,l} g_{ijkl} P_k P_l$ , using the standard contracted index notation (Ref. 12) one easily obtains

$$\Delta n_c = -(n_c^0)^3 g_{33} P_r^2 / 2, \quad (2a)$$

$$\Delta n_a = -(n_a^0)^3 g_{13} P_r^2 / 3, \quad (2b)$$

where  $n_c^0$  (or  $n_a^0$ ) is the index of refraction given by Eq. (1), which is extrapolated from the high data and values can be found in Table I. The  $g$ 's are the quadratic electro-optic coefficients,  $P_r$  is the reversible spontaneous polarization,<sup>7</sup> and  $\Delta n_c$  (or  $\Delta n_a$ ) is the difference between the extrapolated  $n(T)$  and the experimental measurements.

Since we measure  $n_c$ ,  $\Delta n_c$ , and know<sup>7</sup>  $P_r$ , we can determine  $g_{33}$  from Eq. (2a). Similarly, we can determine  $g_{13}$  from Eq. (2b). Figure 5 shows the results for the two different  $g$ 's for  $x=0$  and 0.02 at two wavelengths. Before discussing these results it is worthwhile to investigate what is obtained from classical ferroelectrics. Thus we

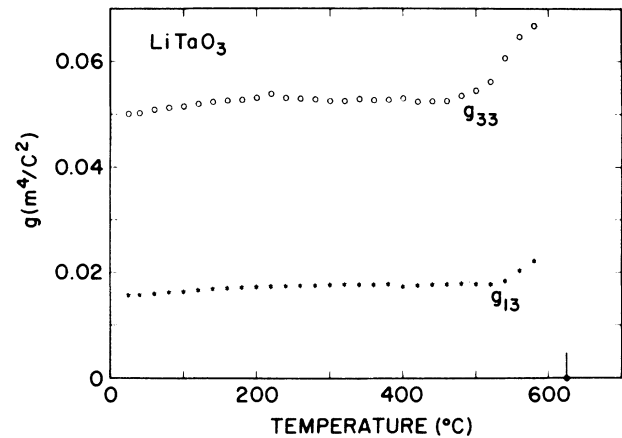


FIG. 6. Temperature dependence of the  $\text{LiTaO}_3$   $g$  values from Eqs. (2).

discuss two ferroelectric systems.

**BaTiO<sub>3</sub>.** By making  $n(T)$  measurements both above<sup>1</sup> and below<sup>13</sup>  $T_c$  in  $\text{BaTiO}_3$  and using the same analysis via Eq. (2a), we find that  $g_{33} = 0.115 \pm 0.008 \text{ m}^4/\text{C}^2$  between  $20^\circ\text{C}$  and  $T_c$ . Thus the value is independent of temperature over a  $100^\circ\text{C}$  range below  $T_c$ . Also one normally finds that the  $g$ 's become larger at shorter wavelength<sup>14</sup> (high energies) just as does the index of refraction; these dispersions are due to the strong valence- to conduction-band electronic resonances in the ultraviolet spectral region.

**LiTaO<sub>3</sub>.** This material has a second-order phase transition at  $T_c \approx 625^\circ\text{C}$ . By using the published  $P_r$  values<sup>15</sup> and published  $n(T)$  values<sup>16</sup> we have determined  $g_{33}$  and  $g_{13}$  via Eqs. (2). As can be seen in Fig. 6 the  $g$ 's are fairly independent of temperature except for  $\sim 100^\circ\text{C}$  below  $T_c$ . Although  $\Delta n$  is smallest in this temperature region, we suspect that this temperature variation is due largely to the  $P_r$  measurements.  $P_r(T)$  is steepest in this temperature region, and its measurement is inherently not very accurate. From the index data,<sup>16</sup> at room temperature we determine that the  $g$ 's have the following values (in  $\text{m}^4/\text{C}^2$ ) at the stated wavelengths:

$\lambda$	$g_{33}$	$g_{13}$
4680	0.050 05	0.015 70
4800	0.049 52	0.014 68
5090	0.048 27	0.013 05
6440	0.045 31	0.012 07

Now, via Fig. 5, let us observe how the  $g$ 's in  $(\text{Pb}_{1-x}\text{Ba}_x)_5\text{Ge}_3\text{O}_{11}$  behave. First, they are very large. Most ferroelectrics with the perovskite or related structures that do not contain Pb ions have  $g_{33}$ 's about<sup>10,11,14</sup>  $0.12 \text{ m}^4/\text{C}^2$ . However, the same perovskite materials with Pb ions replacing, e.g., the Ba ion in  $\text{BaTiO}_3$ , etc., have  $g_{33}$  values an order of magnitude smaller.<sup>17,18</sup> The reason for this has never been understood. Here we see  $g_{33}$  values in Pb-containing materials that are very large,  $\sim 0.4 \text{ m}^4/\text{C}^2$ . Second, the  $g$  values seem to have a temperature dependence. As can be seen they tend to decrease as  $T_c$  is ap-

proached from below. However, the measurements of  $\Delta n$  are not accurate enough near  $T_c$ , where  $\Delta n$  is small, to give reliable  $g$  values via Eqs. (2) and values of  $P_r$  are also not reliable enough to give accurate values of  $g$  via Eqs. (2). Thus the room-temperature  $g$  values are really an average value obtained via Eqs. (2). Third, the normal and expected tendency for the  $g$  values to increase at shorter wavelength is not observed here. (For example, see the above values for  $\text{LiTaO}_3$ .) Fourth,  $g_{13} \approx g_{33}$ , while for the perovskite materials<sup>11,14,17,18</sup>  $g_{13} \ll g_{33}$ .

A detailed microscopic understanding of these properties of the quadratic electro-optic coefficients in  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  undoubtedly requires a knowledge of the electronic energy bands of these materials<sup>11</sup> and how these bands shift with polarization. However, these results do show that salts with Pb ions can have some remarkable properties. These particular materials have quadratic electro-optic coefficients 20–100 times larger than those observed in Pb perovskites.

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