where $\eta = ck/\omega$. Suppose that the propagation is along the z axis and $\boldsymbol{\sigma}$ is of the form

$$\boldsymbol{\sigma} = \begin{vmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ \sigma_{y} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{vmatrix}. \qquad (A2)$$

Substitution of (A2) into (A1) leads to two homogeneous equations for the components E_x and E_y. The resulting secular equation has the solution

$$\eta^2 = \epsilon_0 - (2\pi i/\omega)\{\sigma_{xx} + \sigma_{yy} \pm [(\sigma_{xx} - \sigma_{yy})^2 + 4\sigma_{xy}\sigma_{yx}]^{\frac{1}{2}}\}. \qquad (A3)$$

The relations used in Sec. II are special cases of (A3) as they apply to bismuth.[13] In zero magnetic field, with $\mathbf{k} \| 3$,

$$\sigma_{xx} = \sigma_{yy} = \sigma_{22},$$

$$\sigma_{xy} = \sigma_{yx} = 0,$$

and

$$\eta_3{}^2 = \epsilon_0 - (4\pi i/\omega)\sigma_{22}. \qquad (A4)$$

Similarly, with the propagation along a binary axis $\sigma_{xy} = \sigma_{yx} = 0$ and

$$\eta_{12}{}^2 = \epsilon_0 - (4\pi i/\omega)\sigma_{22}, \qquad (A5)$$

$$\eta_{13}{}^2 = \epsilon_0 - (4\pi i/\omega)\sigma_{33}. \qquad (A6)$$

Equations (1a), (1b), and (2) are obtained from (A6), (A5), and (A4) by substituting the expressions for σ_{ii} given in reference 13. Equations (5) and (6) were obtained by expanding the radicand in (A3) treating σ_{xy} as small.

[13] B. Lax, K. J. Button, J. J. Zeiger, and L. M. Roth, Phys. Rev. **102**, 715 (1956).

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Ferroelectric Properties of $BaLi_{2x}Al_{2-2x}F_{4x}O_{4-4x}$

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Single crystals of $BaLi_{2x}Al_{2-2x}F_{4x}O_{4-4x}$, where $x = 0.15$ to 0.30, have been found to be ferroelectric with a Curie temperature in the range 127–153°C and a room-temperature spontaneous polarization along the hexagonal c axis of approximately 0.1 μcoul/cm^2. The structure of these mixed crystals is unrelated to that of any previously known ferroelectric, but appears to be very similar to that of $BaAl_2O_4$.

DURING an investigation of the chemical and dielectric properties of fluoride perovskites, a new type of room-temperature ferroelectric, $BaLi_{2x}Al_{2-2x}F_{4x}O_{4-4x}$, has been discovered. Crystals have been prepared in a composition range $x = 0.15$ to 0.30 and ferroelectric properties investigated.

The crystals were prepared from an equimolar mixture of LiF and BaF_2, where the BaF_2 was contaminated with 0.25 wt % Al. Crystals of $BaLi_{2x}Al_{2-2x}F_{4x}O_{4-4x}$ may also be prepared from an equimolar mixture of LiF and pure BaF_2 doped with about 0.11 wt % $AlF_3 \cdot H_2O$ with respect to BaF_2. All mixtures were heated at 1300°C in a Pt crucible and cooled at a rate of 40°C per hour to well below the reported 850°C melting point of $LiBaF_3$[1] before the furnace was shut off. The resulting product consists mainly of small cubes of $LiBaF_3$ interspersed with a much smaller amount of $BaLi_{2x}Al_{2-2x}F_{4x}O_{4-4x}$ in the form of hexagonal platelets 1 to 4 mm^2 in area and about 0.1 mm thick. They were collected and analyzed for fluoride and aluminum by standard techniques. In every case the value of x calculated from aluminum analysis agreed to within 10% with that calculated from fluoride analysis. x had a value of 0.30 when Al contaminated BaF_2 was used and $x = 0.20$ and 0.15 for crystals grown using pure BaF_2 doped with 0.113 wt % and 0.103 wt % Al, respectively.

The crystal structure of $BaLi_{2x}Al_{2-2x}F_{4x}O_{4-4x}$ is very similar to that found by powder pattern data for $BaAl_2O_4$.[2] The Weissenberg single-crystal data for the hexagonal unit cell of $BaLi_{0.6}Al_{1.4}F_{1.2}O_{2.8}$ gave $a = 10.44$ A and $c = 8.77$ A compared with $a = 5.209$ A and $c = 8.761$ A reported for $BaAl_2O_4$. We are attempting to grow crystals of $BaAl_2O_4$ in order to determine whether the a axis is also doubled in length in the pure compound as well as to investigate the dielectric properties.

Since the polar sixfold axis is perpendicular to the plane of the platelet, the dielectric properties of $BaLi_{2x}Al_{2-2x}F_{4x}O_{4-4x}$ were only investigated in this direction.

The 1 kc/sec^{-1} dielectric constant, ϵ, and the 60-cps spontaneous polarization, P, were determined by standard techniques.[3,4]

The experimental error for ϵ is about 100% and the

[1] A. G. Bergman and J. I. Banascheck, Ann. secteur anal. physico-chim., Inst. chim. gén. (U.S.S.R.) **23**, 201 (1953).

[2] S. Wallmark and A. Westgren, Arkiv Kemi, Mineral. Geol. **12B**, 1 (1937).

[3] S. Triebwasser, Phys. Rev. **101**, 993 (1956).

[4] C. B. Sawyer and C. H. Tower, Phys. Rev. **35**, 269 (1930).

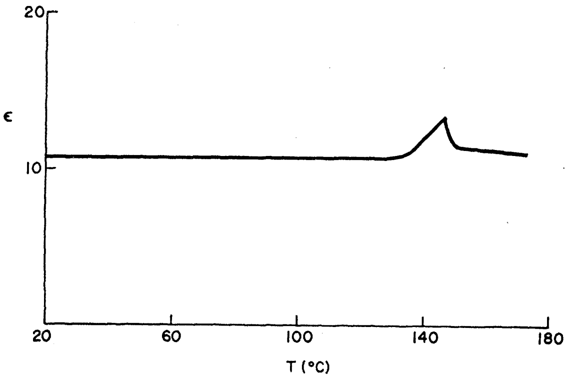

FIG. 1. Dielectric constant vs temperature for $BaLi_{0.6}Al_{1.4}F_{1.2}O_{2.8}$.

experimental error for P is about 30%. These large errors are largely caused by inaccuracies in thickness and area measurement for the small crystals obtained to date.

Representative data is shown in Table I. The dielectric constant data is reported as the ratio of the value of ϵ at the Curie temperature, T_c, to that at 25°C, because of the large experimental error for ϵ. ϵ has values of approximately 10 and 14 at 25°C and T_c, respectively. A plot of ϵ vs T is seen in Fig. 1. The value of P at 25°C is approximately 0.1 μcoul/cm^2. A typical plot of P and E_c, coercive field, vs temperature is seen in Fig. 2. Both these quantities as well as T_c which has an average value of 145°C are not significantly dependent on composition in the range investigated.

TABLE I. The ratio of the dielectric constant at the Curie temperature to that at 25°C, the Curie temperature, the 25°C spontaneous polarization and the 25°C coercive field for $BaLi_{2x}Al_{2-2x}F_{4x}O_{4-4x}$.

x	$\epsilon(T_c)/\epsilon_{25}$	T_c (°C)	P (μcoul/cm^2)	E_c (kv/cm)
0.30	1.27	148	0.15	7.5
0.30	1.34	153	0.11	5.1
0.20	1.51	127	0.12	4.7
0.20	1.52	134	0.08	13.7
0.15	1.68	140	0.14	20.1

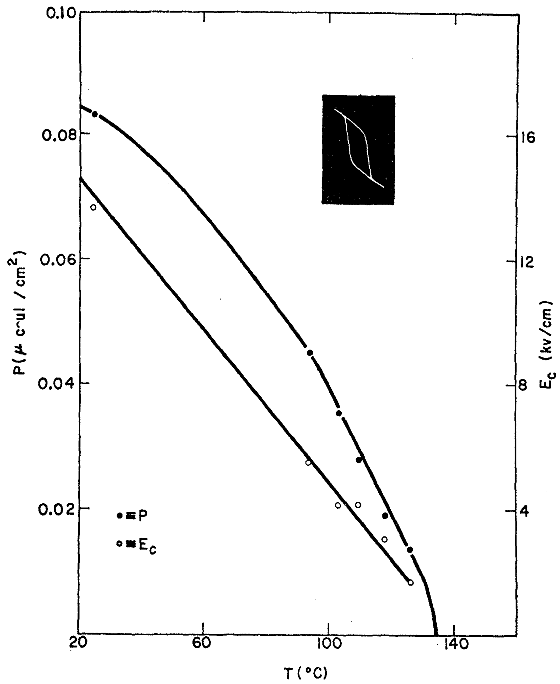

FIG. 2. Spontaneous polarization and coercive field vs temperature for $BaLi_{0.4}Al_{1.6}F_{0.8}O_{3.2}$ and a picture of a 25°C hysteresis loop.

In an investigation of the ferroelectric properties below room temperature, the coercive field was found to increase to the breakdown value at about −20°C and no further dielectric anomalies were found in the range from room temperature to −196°C.

A preliminary study of switching properties gives a switching time of under 5 μsec for 300-v pulses applied to a crystal of 0.1 mm thickness.

Work on systems similar to $BaLi_{2x}B_{2-2x}F_{4x}O_{4-4x}$ is now in progress.

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