Pressure dependence of the refractive index and dielectric constant in a fluoroperovskite, KMgF$_3$

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The hydrostatic-pressure dependence of the refractive index and the low-frequency dielectric constant of a perovskite-type single crystal, KMgF$_3$, have been determined at room temperature. The refractive index n for $\lambda = 589.3$ nm increases monotonously in proportion to pressure p with a slope of $\partial n / \partial p = 2.46 \times 10^{-4}$ kbar^{-1}. On the other hand, the dielectric constant at 10 kHz decreases with increasing pressure, from which the electric-displacement-related electrostrictive coefficient Q_h ($= Q_{11} + 2Q_{12}$) is calculated as 0.24 m^{4}C^{-2}. These data are compared with the $\partial n / \partial p$ values and the Q_h coefficients of various alkali fluorides and perovskite oxides.

I. INTRODUCTION

The electric-displacement-related electrostrictive coefficients of a cubic perovskite-type or a rocksalt-type crystal ($m\,3m$) are defined by

$$Q_{11} = \frac{1}{2} \frac{\partial^2 x_1}{\partial D_1^2} \tag{1}$$

and

$$Q_{12} = \frac{1}{2} \frac{\partial^2 x_2}{\partial D_1^2} , \tag{2}$$

where x_1 and x_2 are the longitudinal and transverse-induced strains, respectively. By using a Maxwell relation, Eqs. (1) and (2) are transformed as follows:

$$Q_{11} = -\frac{1}{2} \frac{\partial(1/\epsilon_0\epsilon_1)}{\partial X_1} \tag{3}$$

and

$$Q_{12} = -\frac{1}{2} \frac{\partial(1/\epsilon_0\epsilon_1)}{\partial X_2} . \tag{4}$$

These equations indicate that the electrostrictive coefficients can be obtained by measuring the stress X dependence of the reciprocal dielectric permittivity ($1/\epsilon$). When a hydrostatic pressure p ($= -X_1 = -X_2 = -X_3$) is applied to a paraelectric crystal, the pressure dependence of the dielectric constant is represented by

$$\frac{\partial(1/\epsilon_1)}{\partial p} = 2\epsilon_0 Q_h , \tag{5}$$

where $Q_h = Q_{11} + 2Q_{12}$ and ϵ_0 is the permittivity of free space.

Recent investigations of perovskite-type oxides have clarified the relationship between the electrostrictive effect and crystal structure.[1-4] The electrostrictive coefficient Q_h differs by an order of magnitude depending on the degree of order in the cation arrangement of complex perovskites. Because of these variations, it is interesting to examine perovskite-type halide crystals which are amenable to a rather simpler theoretical treatment than the oxides. This paper is concerned mainly with the electrostrictive properties of a perovskite-type fluoride, KMgF$_3$. If we assume that a certain ionic shift causes the same elastic strain in fluorides and oxides on the basis of an intuitive "ion-rattling" model,[5] then the electrostrictive Q coefficients in fluorides are expected to be larger than in oxides because the lower valences in fluorides result in smaller induced polarizations.

We have measured both the dielectric constant and the refractive index at room temperature as a function of hydrostatic pressure, so that the dielectric constant is separated experimentally into two parts, ϵ_{el} and ϵ_{ion}, which originate from the electronic polarizability and from the ionic shifts, respectively. It is also interesting to separate the contribution of the electronic polarizability to the electrostriction from that of the ionic polarizability, especially in simple low-permittivity dielectrics.

The fluoride used in this study, KMgF$_3$, was first synthesized by van Arkel[6] and has a simple cubic perovskite-type structure with a lattice constant of $a = 3.973$ Å at room temperature.[7] The elastic moduli have been measured precisely by the pulse superposition technique as a function of hydrostatic pressure and revealed no anomaly up to 2.5 kbars, showing only a gradual increase in stiffness.[8]

II. EXPERIMENTAL RESULTS

A. Pressure dependence of refractive index

Since the procedure for this measurement is the same as that described earlier,[9] only a brief outline is described here. In principle, Ramachandran's interferometric method[10] was adapted to an optical high-pressure cell. A schematic diagram of the experimental arrangement is shown in Fig. 1. A single-crystal plate of KMgF$_3$ with orientation $\langle 100 \rangle$ and dimensions of about $10 \times 10 \times 2$
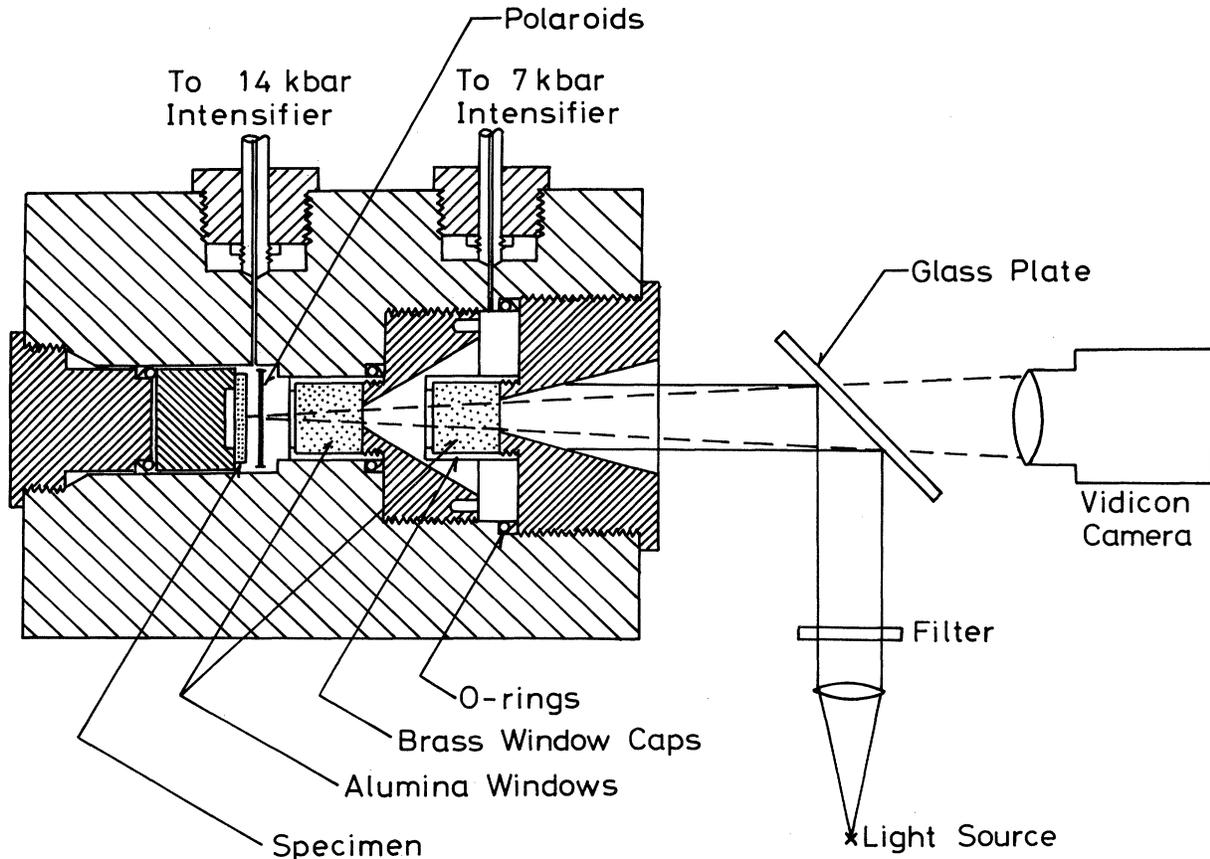
FIG. 1. Schematic drawing of the experimental arrangement for measuring the refractive-index change under high hydrostatic pressure.

mm^3 was cut, ground, and polished to be nearly optically parallel, so that localized Newtonian interference fringes could easily be observed across the major faces of the crystal. The major surfaces were then coated with a thin film of aluminum to increase the sharpness of the fringes. The two-stage optical pressure vessel was of conventional design, with two single-crystal alumina windows whose optically flat surfaces were kept pressed against matching optically flat faces of two steel plugs. The two windows are positioned in such a way that neither window experiences a pressure difference greater than 10 kbars at any time. Two Harwood intensifiers with conventional hand pumps served as the pressure generating system. Pressures up to 7 kbars could be read off directly with the help of a calibrated Heise gauge accurate to ± 7 bars. For higher pressures a manganin resistance gauge was employed in conjunction with a Carey-Foster bridge. Plexol 262 [di-(2-ethylhexyl) adipate] marketed by Rohm and Haas Co. was used as the fluid-pressure medium.

The specimen suitably supported in the pressure cell was illuminated with collimated light from a sodium lamp ($\lambda = 589.3$ nm) and the localized fringes on the specimen could be observed through a telemicroscope or a vidicon camera coupled to a TV monitor. When the specimen is subjected to hydrostatic pressure, both the thickness and the refractive index of the crystal change, with consequent shift of the fringes across a fiducial mark on the specimen. The change in the refractive index Δn is

calculated from the interference formula

$$\Delta n = (m\lambda - 2n\,\Delta t)/2t^0 , \qquad (6)$$

where m is the number of fringes shifted, t^0 is the initial thickness of the specimen, Δt is the change in thickness due to the compression, and λ is wavelength of the light. Elastic stiffnesses of $c_{11} = 138$ GPa and $c_{12} = 44$ GPa (Ref. 8) were used to evaluate Δt.

Figure 2 represents the variation of the refractive index n (the initial value $n^0 = 1.404$) of KMgF$_3$ at room temperature for hydrostatic pressures up to 14 kbars. The refractive index for $\lambda = 589.3$ nm increases linearly with a slope of 2.46×10^{-4} kbars^{-1} up to about 9 kbars, and thereafter a clear departure from linearity is observed. This could be interpreted as either (a) nonlinear piezo-optic behavior brought about by nonlinear elastic behavior at high pressures or (b) possible onset of a phase transition at 9 kbars causing a change in the slope $\Delta n / \Delta p$. Recent precision measurements by Jones[8] on the elastic constants of KMgF$_3$ and their variation with pressure up to 2.5 kbars indicate that KMgF$_3$ behaves quite normally like most other crystals, whose compressibility decreases with increasing pressure. On the other hand, all the crystalline materials studied thus far[9,11,12] exhibit either linear or sublinear $\Delta n / \Delta p$ relationships at high pressures, whereas KMgF$_3$ exhibits a superlinear $\Delta n / \Delta p$ relationship as shown in Fig. 2. Hence it is unlikely that this unusual
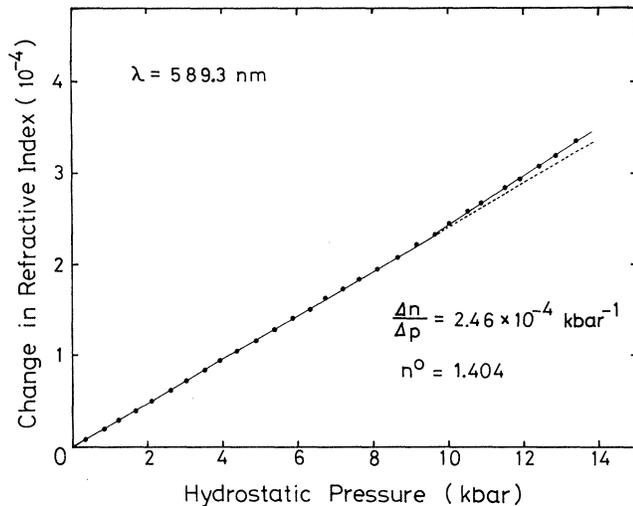
FIG. 2. Variation of the refractive index in $KMgF_3$ with hydrostatic pressure, measured with a sodium lamp ($\lambda = 589.3$ nm) at room temperature.

behavior is associated with the normal nonlinear piezo-optic behavior. At the same time it is felt that further optical, dielectric, and x-ray studies are necessary before we can definitely conclude that the unusual piezo-optic behavior above 9 kbars is due to a phase transition. Finally it may be mentioned that the pressure derivative of the refractive index $\partial n / \partial p$ is almost of the same magnitude as those of alkali fluorides such as LiF and NaF (see Table I).

B. Pressure dependence of dielectric constant

The effect of hydrostatic pressure on the dielectric constant has been investigated up to 1 kbar using a square

specimen $10 \times 10 \times 0.5$ mm^3 in dimensions with gold-sputtered electrodes. Capacitance was measured by a three-terminal method with an automatic capacitance bridge (Yokogawa-Hewlett-Packard, 4192A) over the frequency range 1 to 100 kHz. The stray capacitance of the high-pressure cell used (manufactured by Riken Seiki Co, Ltd.) is about 0.2 pF, much less than the sample capacitance of 10 pF. No significant dielectric dispersion was observed in the above frequency range. The initial dielectric constant ϵ^0 is 6.97 at 10 kHz, measured at $p = 1$ bar. The value of hydrostatic pressure generated by a conventional oil-pressure hand pump was monitored by a Riken gauge with an accuracy of ± 8 bars.

Figure 3 shows the relative permittivity change $\Delta\epsilon/\epsilon^0$ of $KMgF_3$ with pressure, measured at room temperature at 10 kHz. The experimental error results mainly from the readout precision of the capacitance bridge with four decimal digits. The capacitance change due to the dimensional change with compression was calculated by using the elastic moduli of Jones.[8] The dielectric permittivity decreases gradually with increasing hydrostatic pressure; this is quite similar to the behavior in alkali halides[13] and cubic perovskite-type oxides.[5] The electric-displacement-related electrostrictive coefficient Q_h is obtained from the pressure derivative of $\Delta\epsilon/\epsilon^0$ as $Q_h = 0.24$ m^{4}C^{-2}, by using Eq. (5).

It is well known that the low-frequency dielectric constant ϵ ($\epsilon^0 = 6.97$) can be separated into two parts, ϵ_{el} and ϵ_{ion}, which originate from the electronic and the ionic polarizabilities, respectively. The high-frequency dielectric constant ϵ_{el} can be estimated from the optical refractive index n as

$$\epsilon_{el} = n^2 \quad [\epsilon_{el}^0 = (1.404)^2] . \tag{7}$$

The pressure dependence of ϵ_{el} can, therefore, be derived from the experimental data in Sec. II A, and is inserted in

TABLE I. Refractive index n and its pressure derivative $\partial n / \partial p$, low-frequency dielectric constant ϵ, electrostrictive coefficient Q_h, and bulk modulus κ for several alkali fluorides, pervoskite-type oxides, and fluorides at room temperature.

Material	Refractive index n ($\lambda = 589.3$ nm)	$\dfrac{\partial n}{\partial p}$ (10^{-4} kbar^{-1})	Relative permittivity ϵ	Electrostrictive coefficient Q_h (m^{4}C^{-2})	Bulk modulus κ (GPa)
LiF	1.392	1.9[b]	9.06	0.32[e]	65[e]
NaF	1.328	2.17[b]	5.08	0.46[e]	46[e]
$KTaO_3$	2.252	-1.14[c]	173[d]	0.045[d,f]	230[f]
$SrTiO_3$	2.407	-0.85[c]	330	0.047[g]	175[g]
$KMnF_3$	1.450[a]		9.75	0.22[h]	65[i]
$KMgF_3$	1.404	2.46	6.97	0.24	75[j]

[a] $\lambda = 632.8$ nm.
[b] E. D. D. Schmidt, Ph.D. thesis, Solid State Science, Pennsylvania State University, 1972.
[c] J. L. Kirk, Ph.D. thesis, Solid State Science, Pennsylvania State University, 1972.
[d] At 450 K.
[e] Reference 13.
[f] Reference 14.
[g] Reference 15.
[h] K. Gesi (private communication) and Ref. 16.
[i] Reference 17.
[j] Reference 18.
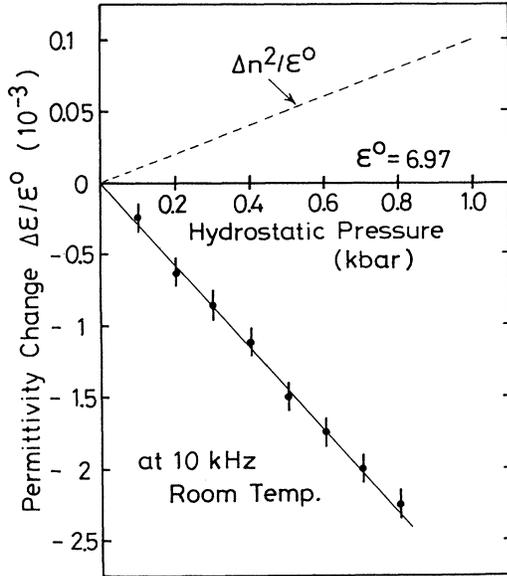
FIG. 3. Relative dielectric constant change $\Delta\epsilon/\epsilon^0$ in KMgF$_3$ with hydrostatic pressure, where ϵ^0 denotes the initial dielectric constant at $p=0$ kbar. The $\Delta n^2/\epsilon^0$ value which represents the dielectric constant $\Delta\epsilon_{el}/\epsilon^0$ originating from the electronic polarizability is also plotted with a dashed line.

Fig. 3 as a dashed line. The subtraction $\Delta\epsilon/\epsilon^0 - \Delta n^2/\epsilon^0$ gives $\Delta\epsilon_{ion}/\epsilon^0$. Taking account of the initial dielectric constants $\epsilon_{ion}^0 = 5$ and $\epsilon_{el}^0 = 2$, it is very interesting that the pressure derivative $(\partial\epsilon_{ion}/\partial p)$ is about 30 times as large as the $(\partial\epsilon_{el}/\partial p)$ value with the opposite sign. This leads to the conclusion that ionic shifts are the principal contribution to electrostriction rather than electronic polarizability.

III. DISCUSSION

The refractive index n and its pressure derivative $\partial n/\partial p$, the low-frequency dielectric constant ϵ, the electrostrictive coefficient Q_h, and the bulk modulus κ of the fluoroperovskite crystal KMgF$_3$ at room temperature are summarized in Table I, and compared with corresponding data for several alkali fluorides (LiF, NaF), perovskite oxides (KTaO$_3$, SrTiO$_3$), and KMnF$_3$.

The refractive indices of perovskite-type fluorides are similar to those of alkali fluorides, and are much smaller than those of perovskite oxides. Very similar pressure derivatives are observed for the fluoroperovskites and alkali fluorides, in marked contrast to the negative $\partial n/\partial p$ values in oxide perovskites. In conclusion, the high-frequency dielectric constant ϵ_{el} originating from the electronic polarizability depends mainly on the anion species (fluorine or oxygen[11]) and is largely unaffected by the crystal structure (rocksalt or perovskite type).

On the other hand, the low-frequency dielectric con-

stant ϵ_{ion} is dependent on the crystal structure as well as the ionic species. It is concluded that the electrostrictive Q_h coefficient of fluoroperovskites lies near 0.23 m^{4}C^{-2}, intermediate between the Q_h values of alkali fluorides and perovskite oxides. In other words, it appears that the electrostrictive coefficient in fluorides is larger than in oxides, and that the Q_h value in perovskites is smaller than in rocksalt compounds. It is important to mention here that the bulk modulus κ in fluoroperovskites also lies between those in alkali fluorides and in perovskite oxides. This interrelation between the electrostrictive coefficients Q_h and the elastic moduli κ of fluorides and oxides can be understood on the basis of the discussion presented in our previous paper.[19]

Consider a rigid ion model of the rocksalt structure with $+q$ and $-q$ ion species as the simplest case, for which the ion-pair potential energy is represented by the following anharmonic function:

$$\Delta U = U(r) - U(r_0) = f(r-r_0)^2 - g(r-r_0)^3 , \qquad (8)$$

where r is a distance between a cation and the neighboring anion, and r_0 denotes the equilibrium position. Using a Boltzmann distribution, the averaged induced strain $\langle x_1 \rangle$ under an applied electric field E_1 is calculated to be

$$\langle x_1 \rangle = (3gq^2/4f^3r_0)E_1^2 . \qquad (9)$$

Taking account of the polarization P_1 per unit volume of the form

$$P_1 = (q^2/4fr_0^3)E_1 , \qquad (10)$$

the electrostrictive coefficient Q_{11} is given by

$$Q_{11} = 12gr_0^5/fq^2 . \qquad (11)$$

Note here that the hydrostatic Q_h is related to the Q_{11} coefficient through the Poisson ratio σ:

$$Q_h = (1-2\sigma)Q_{11} . \qquad (12)$$

If we assume that f, g, and r_0 are of the same order of magnitude for the same crystal structure, the Q_h value will be nearly inversely proportional to the square of the valence q. Since the ratio of the valence of fluorides to that of oxides is about $\frac{1}{2}$, the electrostrictive coefficient of fluorides should be about four times larger than that of oxides. This rough estimation is comparable with the averaged ratio 0.23/0.046 obtained experimentally for the fluoride and oxide perovskites (see Table I). In a similar manner a relation between the elastic modulus κ and the Q_h value,

$$\kappa \propto Q_h^{-1} , \qquad (13)$$

can be obtained.

Detailed calculations taking into account the crystal-structure difference and the electronic polarizability (e.g., a shell model), will be required for further quantitative discussions.

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