

Complete determination of electrostriction tensor components of KMnF_3 single crystals at room temperature

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Electrostriction is the basic electromechanical coupling effect in centric crystals, and is therefore of considerable fundamental interest. When it is remembered that the very widely used PbZrO_3 - PbTiO_3 poled ceramic piezoelectric transducers are in effect polarization biased electrostrictors, the phenomenon also becomes a very strong practical importance. Taking the first steps towards an atomistic understanding of the electrostriction effect, Achar *et al.* [1] in this laboratory, applied the shell model to the incipient ferroelectric and improper ferroelastic perovskite SrTiO_3 . For this crystal overall agreement with theory was not good, even though the trend of the temperature dependence is correct. Achar and Barsch [2]. A possible reason for the discrepancy was suggested to be in the large anisotropic polarizability of the oxygen ion. To test this hypothesis it is clearly desirable to move to a non-oxide perovskite and part of the reason for this study was to provide experimental data to test this hypothesis. The crystal chosen for study is potassium manganese fluoride KMnF_3 , one of the most widely studied of the halide perovskites. For this crystal the second and third order elastic constants have been measured as a function of temperature, Cao [3], necessary input data for the shell model calculation. A further advantage to choosing KMnF_3 is the possibility it affords to study the influence of the improper ferroelastic phase change upon the electrostriction behaviour. In many ways this study could be complementary to that of the perovskite oxides which encompass ferroelectric phase changes. The ultimate goal might be to combine soft electrical and mechanical modes in a single material so as to enhance the strain and reduce stress concentration for efficient electrically controlled high strain actuators.

In centric materials, odd rank tensors vanish according to Neumann's principle. Using the elastic Gibbs free energy function with stress (denoted as X), electric field (E), and temperature (T) as the independent variables, one can derive the following in heuristic notation

$$x = sX + MEE$$

$$D = \epsilon_0 KE + 2MEX = (\epsilon_0 K + 2MX)E$$

One can also use stress and polarization (P) as the independent variables and obtain

$$x = sX + QPP$$

For cubic symmetry, Q and M are related by

$$Q = M \frac{1}{[\epsilon_0(K-1)]^2}$$

M is mostly used by electrical engineers, which tells how much strain is developed under unit electric field. On the other hand, Q is used by physicists, which tells how much strain is developed by introducing polarization in the materials. As the electrostriction coefficient M appears in both equations for x and D , two methods for measuring the electrostriction coefficients are possible—the direct method and the converse method. The direct method is to measure the electrically induced strain. The widely used experimental techniques include the strain gauge method and the ultrasensitive dilatometer method which employs either a Michelson interferometer, Zhang *et al.* [4] or a capacitor dilatometer, Uchino and Cross [5]. The strain gauge method is not only sensitive to large strain but to minute strain. The dilatometer method is well suited for the oxide perovskite based materials which have large M coefficients. However, it becomes extremely difficult for low permittivity materials such as KMnF_3 with small M coefficients, because one has to avoid the mechanical resonance induced in the specimen holder and must perform measurements under very low electrical and mechanical noise environment. On the other hand, the converse method is to measure the minute changes in the dielectric permittivity in the materials induced by external mechanical stresses, where the difficulty is to make the precise measurements of dielectric permittivity. The General Radio 1621 precision capacitance measurement system does provide sufficient sensitivity and stability to handle this problem. Generally the converse method is easier and more stable than the direct method. For the direct method the equation is

$$2M_{ijk} = \left(\frac{\partial^2 x_{ij}}{\partial E_k \partial E_l} \right)_E$$

while for the converse method

$$2M_{ijk} = \left(\frac{\partial \epsilon_{kl}}{\partial X_{ij}} \right)_E$$

where ϵ_{ij} are the dielectric permittivity components. Since the measurable quantity is the capacitance

$$C = \frac{\epsilon_0 KA}{d}$$

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one obtains

$$\frac{\partial \ln C}{\partial X} = \frac{\partial \ln K}{\partial X} + \frac{\partial \ln (A/d)}{\partial X}$$

The two terms on the right side are denoted as

$$B_i = \frac{\partial \ln K}{\partial X}$$

$$S_i = \frac{\partial \ln (A/d)}{\partial X}$$

B_i and S_i are, respectively, linear combinations of the electrostriction coefficients and linear combinations of compliance tensor components. Both B_i and S_i depend on the crystal orientations, which are denoted by the subscript i . For convenience, the Voigt notation is used on the second order tensor. KMnF_3 has $m\bar{3}m$ symmetry. Therefore a second order tensor such as the electrostriction tensor M has the following form

$$M = \begin{bmatrix} M_{11} & M_{12} & M_{12} & 0 & 0 & 0 \\ M_{12} & M_{11} & M_{12} & 0 & 0 & 0 \\ M_{12} & M_{12} & M_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & M_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & M_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & M_{44} \end{bmatrix}$$

where M_{11} , M_{12} , and M_{44} are in matrix notation and are related to tensor notation by $M_{11} = M_{1111}$, $M_{12} = M_{1122}$, and $M_{44} = 4M_{1212}$. Samples in disk form were prepared with the major faces (100), (110), and (111). Uniaxial stress was applied perpendicular to the major faces of the disk. From Preu and Haussuhl [6], the effective electrostriction coefficients are

$$M'_{100} = M_{11} = \frac{\epsilon_0 K}{2} \left[\frac{1}{C} \left(\frac{\partial C}{\partial X} \right) + (s_{11}^T + 2s_{12}^T) \right],$$

$$M'_{110} = \frac{1}{2}M_{11} + \frac{1}{2}M_{12} + \frac{1}{2}M_{44}$$

$$= \frac{\epsilon_0 K}{2} \left[\left(\frac{1}{C} \frac{\partial C}{\partial X} \right)_{110} + \frac{1}{2}(s_{44}^T - 2s_{12}^T) \right],$$

$$M'_{111} = \frac{1}{3}M_{11} + \frac{2}{3}M_{12} + \frac{1}{3}M_{44}$$

$$= \frac{\epsilon_0 K}{2} \left[\left(\frac{1}{C} \frac{\partial C}{\partial X} \right)_{111} + \frac{1}{3}(2s_{44}^T - s_{11}^T - 2s_{12}^T) \right]$$

If the sample is under hydrostatic pressure, the appropriate coefficient is

$$M_h = M_{11} + 2M_{12}$$

$$= \frac{\epsilon_0 K}{2} \left[\left(-\frac{1}{C} \frac{\partial C}{\partial p} \right) - (s_{11}^T + 2s_{12}^T) \right]$$

The s_{ij}^T 's are isothermal elastic compliances, which are calculated from the adiabatic elastic constants measured by the ultrasonic pulse superposition technique, Cao [3].

There have been several uniaxial stress compressometers for the electrostriction measurements, Meng and Cross [7], Preu and Haussuhl [6]. Typically single

crystal disks having geometry of diameter/thickness being 23 mm/1.5 mm were prepared. Then gold sputtering or aluminium evaporation technique is used to make electrodes on the surfaces of samples. A guard ring electrode is used to prevent an apparent enhancement in the dielectric permittivity due to the fringe field. However, to be effective, the width of the guard should be at least twice as large as the thickness. For a 23 mm/1.5 mm geometry the guard should be 3.5 mm wide.

Unfortunately the KMnF_3 single crystal is very fragile. The crystal can easily crack in the process of cutting and polishing and also under stresses. To surmount this problem, smaller single crystals about 9 mm in diameter and 2.0 mm in thickness are used — not too thin to crack under mechanical stresses. However, this leaves little room for the guard ring; therefore one makes the electrode covering the whole surfaces. It will be shown in the discussion that such two terminal geometry is also adequate for converse electrostriction measurements on KMnF_3 .

The uniaxial compressometer built by Meng and Cross [7] was modified. A schematic drawing of the compressometer and associated equipment is shown in Fig. 1. For measurement of the capacitance, a General Radio 1621 capacitance measuring system was used. In the figure are shown the main parts of the sample holder and the system for stress application. The system is designed to keep the pressure

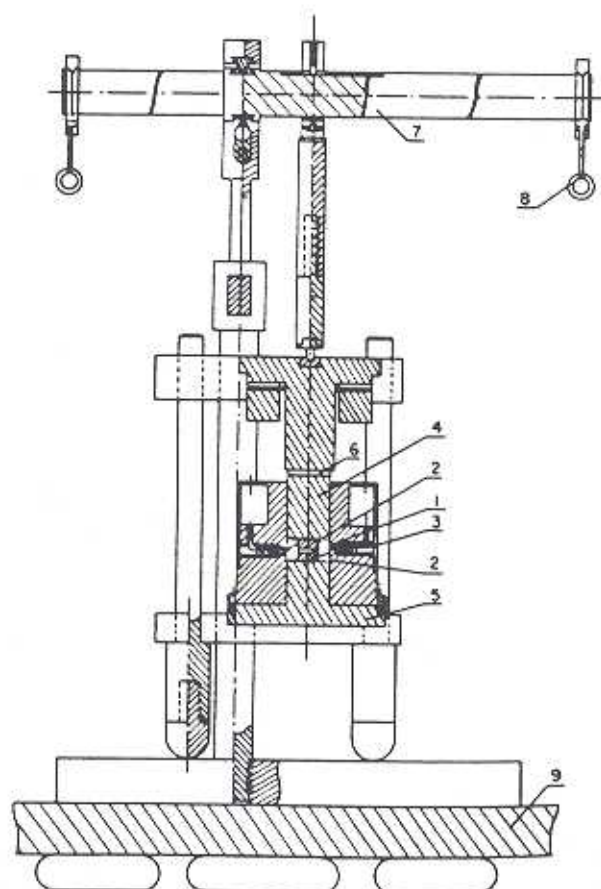


Figure 1 Schematic diagram of the dc compressometer. (1) Sample with electrodes, (2) stress transmitting ram extenders, (3) coaxial lead, (4) metal rod, (5) metal block (6) Teflon plate, (7) lever system, (8) dead weight, (9) vibration isolation table.

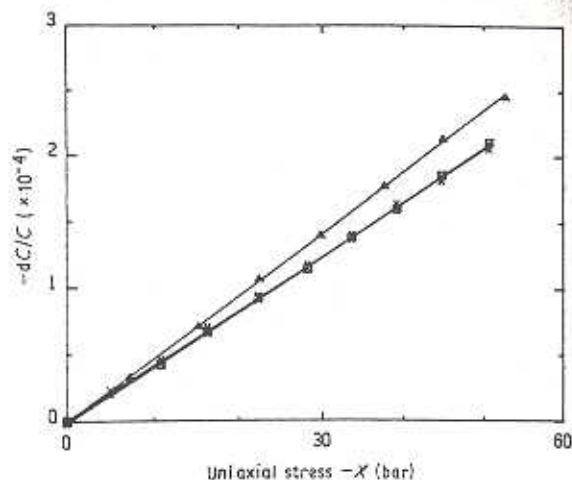
TABLE I Experimental results of KMnF_3 single crystals

	$1/C$ ($\partial C/\partial X$), (10^{-11} Pa^{-1})	S_i (10^{-11} Pa^{-1})	M_i ($10^{-21} \text{ M}^{-2} \text{ V}^2$)
(100)	4.708	-1.596	2.723
(110)	4.416	-2.118	2.712
(111)	4.087	-2.293	2.756

homogeneous and strictly uniaxial, the temperature stable for the period of measurement, and mechanical vibration isolated. The connections to the sample capacitance terminals are completely electrically shielded. The uniaxial stress is derived from a dead weight and is applied to the sample through a suitable lever arm. In the pressure cell, ram extenders are used, which are made of ordinary glass and cut strictly in the same diameter as the sample. A very thin mylar gasket is used between the bronze anvil and the ram surfaces to take up any surface roughness. Elaborate temperature control was found unnecessary for the system since the thermal capacity of the massive stressing jig was sufficient to smooth out any temperature fluctuations in the ambient in the already temperature controlled room.

The KMnF_3 single crystals were grown by a modified Bridgman method. The starting materials KHF_2 and MnF_2 in stoichiometric proportion were pre-heated at 350°C for 6 h. The diameter/thickness dimensions of the samples for (100), (110), and (111) orientations are, respectively, 9.13 mm/2.27 mm, 7.45 mm/1.64 mm, and 7.45 mm/1.45 mm. The results are shown in Fig. 2 and summarized in Table I. The electrostriction measurements were made under reasonable stress loadings well inside the elastic limit of KMnF_3 single crystals. The value $Q_h = 0.22 \text{ M}^4 \text{ C}^{-2}$ (having (X, D) as independent variables) is taken from Uchino *et al.* [8] so as to give a check on the present measurements. M_{11}, M_{12}, M_{34} are calculated by a least square fit, the fitting error is found to be less than 0.8%.

It can be concluded from the following four arguments that the present sample geometry gives reliable results. First a linear dependence of $\Delta C/C$ on the stress X was obtained. Second, the capacitance was found to be decreasing with stress, which is opposite to the influence of the fringe field. The fringe field would rather increase the capacitance when a uniaxial stress is applied. Therefore the fringe field effect is at least not dominant. Third, the present data agree well (i.e., within 0.8%) with the Q_h value in the literature. Finally, the measurements on two (111) were made. One with three terminals and 23 mm/1.5 mm in

Figure 2 Uniaxial stress dependence of relative changes in the capacitance of KMnF_3 single crystals. (Δ) (100), (\square) (110), (\times) (111).

diameter/thickness geometry, and the other with two terminals and 7.44 mm/1.5 mm geometry. The results of these two measurements agree well with each other within 13%.

In Table II the electrostriction coefficients are summarized. As can be seen, and compared with data for other compounds, the electrostriction coefficients are very much structure dependent; those of the fluorites CaF_2 , BaF_2 , and SrF_2 are very much alike, and so are those of the perovskites. However, the magnitude of electrostriction coefficients Q_s depends upon the ionic charges. The larger the ionic charge, the smaller the magnitude of electrostriction coefficients Q —this is reasonable because if one assumes that a certain ionic shift causes the same elastic strain in fluorides and oxides on the basis of an intuitive "ion rattling" model, then the electrostriction Q coefficients in fluorides are expected to be larger because the lower valencies in fluorides result in smaller induced polarizations.

A number of neutron scattering, Gesi *et al.* [9] and ultrasonic experiments, Furukawa *et al.* [10] have been made around the improper ferroelastic phase transition at 186 K of KMnF_3 , which gives information on the dynamics of the soft mode involving the tilting of the MnF_6 -octahedra. It is interesting to measure the temperature dependence of the electrostriction coefficients in order to determine the influence of the ferroelastic phase transition on the electrostriction effect. This work is now under way.

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TABLE II Electrostriction coefficients of single crystals

	M_{11}	M_{12}	M_{34}	M_5	Q_{11}	Q_{12}	Q_{14}	Q_h
KMnF_3	2.72	-0.538	6.58	1.64	0.453	-0.0896	1.10	0.274*
BaTiO_3					0.11	-0.045		0.02†
CaF_2	-1.32	1.17	5.07	1.02	-0.508	-0.450	1.95	0.392
SrF_2	-1.16	1.09	5.38	1.02	-0.331	-0.311	1.53	0.291
BaF_2	-1.07	1.23	5.94	1.39	-0.340	-0.390	1.88	0.441

M coefficients are in unit of $10^{-21} \text{ M}^{-2} \text{ V}^2$ and Q in $\text{M}^4 \text{ C}^{-2}$.

*From Uchino *et al.* [11].

†From Uchino *et al.* [8].

‡From Meng *et al.* [12].

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References

1. B. N. N. ACHAR, G. R. BARSCH and L. E. CROSS, *Phys. Rev. B* **24** (1981) 1209.
2. B. N. N. ACHAR and G. R. BARSCH, to be published (1987).
3. W. W. CAO, PhD thesis, the Pennsylvania State University (1987).
4. Q. M. ZHANG and W. Y. PAN, *et al.* to be published (1987).
5. K. UCHINO and L. E. CROSS, *Ferroelectrics* **27** (1980) 35.
6. P. PREU and S. HAUSSUHL, *Solid State Comm.* **45** (7) (1983) 619.
7. Z. Y. MENG and L. E. CROSS, *J. Appl. Phys.*, **57** (2) (1985) 488.
8. K. UCHINO and L. E. CROSS, *et al. J. Appl. Phys.* **51** (2) (1980) 1142.
9. K. GESI, J. D. AXE and G. SHIRANE, *Phys. Rev. B* **5** (5) (1972) 1933.
10. M. FURUKAWA, *et al. J. Phys. Soc. Jpn* **29** (6) (1970) 1528.
11. K. UCHINO and L. E. CROSS, *et al. Phys. Rev. B* **29** (12) (1984) 6921.
12. Z. Y. MENG, Y. M. SUN and L. E. CROSS, *Mater. Lett.* **12** (6A & B) (1984) 544.

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