

Temperature dependence of dielectric constant of crystals with fluorite structure

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Abstract. The experimental data on the temperature variation of dielectric constant of six crystals with fluorite structure are analysed using an approach proposed by Havinga and Bosman for ionic crystals. The temperature variation of dielectric constant is resolved in three components related to the thermal expansion, the pressure dependence of dielectric constant and the temperature variation of polarizability (the A , B , C terms). In the present work, the B term is calculated semiempirically, such that the analysis can be extended to crystals like EuF_2 for which high pressure dielectric constant data are not available. For the first time, such calculations have been made for EuF_2 and PbF_2 at elevated temperatures. The C term, which is related to the temperature variation of IR polarizability is seen to play a dominant role in determining the temperature variation of dielectric constant.

Keywords. Dielectric constant; fluorite-type crystals; strain derivative; polarizability.

1. Introduction

The temperature dependence of the dielectric constant of a number of cubic ionic crystals has been extensively studied (Bosman and Havinga 1963; Havinga and Bosman 1965; Samara 1968; Rao and Smakula 1971; Fontanella *et al* 1972). The temperature coefficient is either positive or negative in the low temperature range up to the vicinity of room temperature. It is positive for most of the crystals in the high temperature range due to various reasons like conduction, phase transition and other thermally-activated processes. Starting with the Clausius-Mossotti equation, Havinga (1960) showed that three effects contribute to the temperature dependence of the dielectric constant at low temperatures. The dielectric constant is given by,

$$\frac{\epsilon - 1}{\epsilon + 2} = (4/3)\pi\alpha \frac{1}{V}. \quad (1)$$

Here ϵ is the dielectric constant and α the polarizability of a small sphere of volume V . Differentiating, one gets,

$$\begin{aligned} \frac{1}{(\epsilon - 1)(\epsilon + 2)} (\partial\epsilon/\partial T)_p &= -\frac{1}{3V} (\partial V/\partial T)_p + \frac{V}{\alpha} (\partial\alpha/\partial V)_T \frac{1}{3V} (\partial V/\partial T)_p \\ &+ \frac{1}{3\alpha} (\partial\alpha/\partial T)_V. \end{aligned} \quad (2)$$

The three terms on the right side are denoted by A , B and C where

$$A = -\beta/3, \quad B = \frac{\beta V}{3\alpha} (\partial\alpha/\partial V)_T, \quad C = \frac{1}{3\alpha} (\partial\alpha/\partial T)_V,$$

and β is the thermal expansion coefficient. Differentiating (1) with respect to pressure, the following equation is obtained:

$$\frac{3}{(\varepsilon - 1)(\varepsilon + 2)} (\partial\varepsilon/\partial p)_T = K - K \frac{V}{\alpha} (\partial\alpha/\partial V)_T, \quad (3)$$

where K is the compressibility. $(A + B)$ is referred to as the total volume effect and C as the volume independent or pure temperature effect. Further it has been shown by Szigeti (1961) that the anharmonic contribution to dielectric constant is given by (Samara 1968, 1976)

$$\begin{aligned} G &= T(\varepsilon - 1)(\varepsilon + 2) \frac{1}{3\alpha} (\partial\alpha/\partial T)_V, \\ &= T(\varepsilon - 1)(\varepsilon + 2)C. \end{aligned} \quad (4)$$

From the knowledge of C values, the anharmonic contribution can be estimated. From (2) and (3) it can be seen that the evaluation of the terms A , B and C requires the measurements of dielectric constant, temperature and pressure dependence of dielectric constant and the data on thermal expansion and isothermal compressibility. Such evaluations have been carried out by Bosman and Havinga (1963) for a number of cubic ionic crystals, by Samara (1968) for thalious halides, alkaline earth fluorides and lead fluoride (Samara 1976) and by Young and Frederikse (1969) for cadmium fluoride. The quantities A and B are evaluated from experimental data and C is obtained as a difference between $(A + B + C)$ i.e. left side quantity in (2) and $A + B$.

Srinivasan and Narayanan (1982) have extended similar analysis to anisotropic crystal TiO_2 .

Havinga and Bosman (1965) have evaluated the B and C terms from a theoretical method based on a simple ionic model and obtained a reasonable agreement with the experimental values for the B term. For the C term, though exact agreement is not observed the magnitude is of the same order for the alkali halide crystals.

Jai Shanker and Sundaraj (1983) have analysed silver halides, thalious halides, alkaline earth fluorides and lead fluoride. In their approach, the volume derivative of dielectric constant which is contained in the B term is evaluated by using Born-Mayer theory of interatomic potential and the C contribution is obtained by adopting the model proposed by Havinga and Bosman (1965). As the authors themselves point out, the difficulty in their treatment is that in addition to the values of short range force constant and effective ionic charge, the higher order derivatives of the effective charge parameter are also required. While they find good agreement with the experimental values for volume derivatives, the calculated C terms differ.

Thus it is clear that the B contributions obtained either by Havinga and Bosman's treatment or by the method suggested by Jai Shanker and Sundaraj agree with the experimental results. For the C terms the values of Jai Shanker and Sundaraj differ both in magnitude and sign.

In the present work, the method proposed by Havinga and Bosman (1965) is extended to some crystals with fluorite structure. B values agree well with those obtained from experimental data on pressure dependence of dielectric constant in alkaline earth fluorides. In view of this agreement, the method is employed to estimate the B values for CdF_2 , PbF_2 and EuF_2 . $(A + B + C)$ is known from experimental data on $(\partial\varepsilon/\partial T)_p$. A , known from the data on thermal expansion and B obtained

semiempirically, the C term is evaluated from the difference between the $(A + B + C)$ and the $(A + B)$ terms. It has been shown that the C terms agree with the experimental values for all the crystals. For EuF_2 the experimental data for C is not available. The anharmonic contributions G have been evaluated from the C values. The results are compared with the earlier data.

2. Details of the method

The macroscopic polarizability α consists of two components, one the optical polarizability α_{op} due to the displacement of electrons and the other, infrared polarizability α_{ir} due to the displacement of ions. In terms of individual components, the temperature derivative of static dielectric constant is expressed as (Samara 1976)

$$\frac{1}{(\varepsilon - 1)(\varepsilon + 2)} (\partial\varepsilon/\partial T)_p = A + B + C = -\frac{\beta}{3} + \frac{\beta}{3} \left[\frac{\alpha_{\text{op}}}{\alpha} \left\{ \frac{V}{\alpha_{\text{op}}} (\partial\alpha_{\text{op}}/\partial V)_T \right\} + \frac{\alpha_{\text{ir}}}{\alpha} \left\{ \frac{V}{\alpha_{\text{ir}}} (\partial\alpha_{\text{ir}}/\partial V)_T \right\} \right] + (C_{\text{op}} + C_{\text{ir}}) \quad (5)$$

α_{op} is obtained from the data on refractive index n ($\varepsilon_{\text{op}} = n^2$). α is obtained from the experimental values of static dielectric constant ε . α_{ir} is the difference between α and α_{op} . The strain polarizability constant $(V/\alpha_{\text{op}})(\partial\alpha_{\text{op}}/\partial V)_T$ is evaluated using the following relation proposed by Jai Shanker *et al* (1979)

$$\frac{V}{\alpha_{\text{op}}} (\partial\alpha_{\text{op}}/\partial V)_T = \frac{1}{3\alpha} \left[\eta - \frac{2}{\eta - 2} \right] (2\alpha_{f-} - \alpha_{f+}) \left(1 - \frac{e^*}{e} \right). \quad (6)$$

Further, following Havinga and Bosman (1965), the strain derivative of IR polarizability is obtained from

$$\frac{V}{\alpha_{\text{ir}}} (\partial\alpha_{\text{ir}}/\partial V)_T = \frac{\eta^2 - 2\eta + 2}{3(\eta - 2)}. \quad (7)$$

In the above equations $e^*/e = q^*$ is the effective ionic charge and α_{f-} and α_{f+} are the free ion polarizabilities of cation and anion respectively. η is the stiffness constant occurring in the Born repulsion term in the potential function for the crystal.

Table 1. Input data for calculating the strain polarizability derivatives (polarizabilities are in units of \AA^3).

Crystal	η^a	n^b	α_{op}	α_{f+}	q^*
CaF_2	8.7	1.434	2.52	0.47	0.78 ^c
SrF_2	8.9	1.442	3.04	0.86	0.82 ^c
BaF_2	9.1	1.474	3.98	1.55	0.81 ^c
CdF_2	9.4	1.560	3.03	0.55	0.83 ^c
PbF_2	8.3	1.754 ^d	4.83	1.14	0.93 ^c
EuF_2	8.4	1.560 ^e	3.72	0.71	0.83 ^e

The α_{f-} value in all the cases is 1.04.

^a Rao (1977); ^b Hand book of chemistry and physics (1973);

^c Denham *et al* (1970); ^d Samara (1976); ^e Axe and Petit (1966).

The input data for calculating the strain polarizability derivatives are given in table 1. The free ion polarizabilities for alkaline earth ions and F^- are those cited by Tessmann *et al* (1953). For Cd^{2+} , Pb^{2+} and Eu^{2+} the values are calculated from Ruffa's (1963) theory. Crystal polarizabilities are determined from the additivity rule taking the crystal polarizability of the F^- ion from Jai Shanker *et al* (1978). The $(V/\alpha)(\partial\alpha/\partial V)_T$ values thus calculated are given in table 2 along with those obtained by earlier workers from experimental data. Table 3 shows the input data for calculating A , B and C at room temperature for all the crystals.

3. Results and discussion

From table 2 it can be seen that the present values of $(V/\alpha)(\partial\alpha/\partial V)_T$ agree well with the values obtained by earlier workers. This agreement indicates the validity of the procedure based on the simple ionic model for evaluating the strain polarizability

Table 2. Calculated values of $\frac{V}{\alpha} \left(\frac{\partial\alpha}{\partial V} \right)_T$

Crystal	Experimental		Present work
	<i>a</i>	<i>b</i>	
CaF ₂	2.06	2.22	2.00
SrF ₂	2.03	—	1.90
BaF ₂	1.88	1.90	1.89
CdF ₂	—	—	1.80
PbF ₂	1.48	—	1.60
EuF ₂	—	—	1.66

a Samara (1976); *b* Jones (1967).

Table 3. Input data for calculating values of A , B and C (polarizabilities are in units of \AA^3).

	Crystal					
	CaF ₂	SrF ₂	BaF ₂	CdF ₂	PbF ₂	EuF ₂
$\beta \times 10^5 (\text{°K})^{-1}$	5.55 ^a	5.79	5.97	6.48	7.35	4.62
α	6.42	7.59	9.65	6.37	10.62	8.22
α_{op}	2.52	3.04	3.98	3.03	4.83	3.72
α_{ir}	3.88	4.48	5.66	3.47	5.80	4.50
$\frac{V}{\alpha_{\text{op}}} \left(\frac{\partial\alpha_{\text{op}}}{\partial V} \right)_T$	0.40	0.21	0.08	0.26	0.04	0.14
$\frac{V}{\alpha_{\text{ir}}} \left(\frac{\partial\alpha_{\text{ir}}}{\partial V} \right)_T$	3.00	3.07	3.14	3.23	2.88	2.90
ϵ	6.81 ^b	8.48 ^b	7.34 ^b	8.33 ^c	29.3 ^b	8.30 ^d
$(A + B + C) * \times 10^5 (\text{°K})^{-1}$	3.29 ^b	2.92 ^b	2.68 ^b	3.76 ^c	0.79 ^b	1.75 ^d

* $1/(\epsilon - 1)(\epsilon + 2)(\partial\epsilon/\partial T)_p$; ^a All values are from Rao (1980); ^b Samara (1976); ^c Young and Frederikse (1969); ^d Reddy and Sirdeshmukh (1984).

derivative for fluorite type crystals. The final values of A , B and C at room temperature are compared with the experimental values in table 4. They show reasonable agreement. For EuF_2 the B and C values have been estimated for the first time. The C values for the alkaline earth fluorides obtained in this work are of the same order as those for the alkali halides (Bosman and Havinga 1963). Further, the C values for CdF_2 and EuF_2 are of the same order as those for the alkaline earth fluorides. For PbF_2 , a negative value has been obtained for C at room temperature. This again is an agreement with the value obtained by Samara (1976) from experimental data.

In table 5 C values at room temperature obtained by different methods are compared. The experimental values of both Samara (1976) and that of Andeen *et al* (1972) agree very well. It may be mentioned that the values quoted by Jai Shanker and Sundaraj (1983) as from experimental data need to be multiplied by 10. Considerable difference is observed between the theoretical values of Jai Shanker and Sundaraj and the experimental values. On the other hand the values obtained by the semiempirical method in the present work show a good agreement with experimental values.

A comparison of anharmonic contributions $G/(\epsilon - \epsilon_{\text{op}})$ to dielectric constant, at room temperature is given in table 6. The present values agree well with those obtained using experimental data. The C contribution is negative for PbF_2 and positive for all the

Table 4. Calculated values of A , B and C .

Crystal	$A \times 10^5 (\text{°K})^{-1}$		$B \times 10^5 (\text{°K})^{-1}$		$C \times 10^5 (\text{°K})^{-1}$	
	Present work	Other work ^{a,b}	Present work	Other work ^{a,b}	Present work	Other work ^{a,b}
CaF_2	-1.85	-1.90	3.68	3.92	1.46	1.28
SrF_2	-1.93	-1.82	3.68	3.68	1.17	1.05
BaF_2	-1.98	-1.87	3.72	3.50	0.94	1.04
CdF_2	-2.16	-1.80	3.89	3.66	2.03	1.9
PbF_2	-2.45	-2.50	3.92	3.70	-2.26	-2.00
EuF_2	-1.54	—	2.56	—	0.73	—

^a Samara (1976) for all crystals except CdF_2 ; ^b Young and Frederikse (1969).

Table 5. Comparison of values of $C \times 10^{-5} (\text{°K})^{-1}$.

Crystal	Experimental data Samara (1976)	Jai Shanker and Sundaraj (1983)		Present
		Experimental data*	Theoretical	
CaF_2	1.28	1.20	0.28	1.46
SrF_2	1.05	1.00	0.28	1.17
BaF_2	1.04	0.90	0.44	0.94
CdF_2	—	—	—	2.03
PbF_2	-2.0	-2.0	0.60	-2.26
EuF_2	—	—	—	0.73

* Andeen *et al* (1972).

Table 6. Comparison of values of $G/(\epsilon - \epsilon_{op})$.

Crystal	Experimental data Samara (1976)	Jai Shanker and Sundaraj (1983)		
		Experimental data*	Theoretical	Present
CaF ₂	0.040	0.04	0.009	0.046
SrF ₂	0.032	0.03	0.008	0.035
BaF ₂	0.036	0.04	0.015	0.033
CdF ₂	—	—	—	0.070
PbF ₂	-0.197	-0.20	0.060	-0.225
EuF ₂	—	—	—	0.028

* Andeen *et al* (1972).**Table 7.** A , B and C values at various temperatures.

Crystal	Temperature (°K)	$(A + B + C) \times 10^5$ (°K) ⁻¹	β values		
			$A \times 10^5$ (°K) ⁻¹	$B \times 10^5$ (°K) ⁻¹	$C \times 10^5$ (°K) ⁻¹
PbF ₂	180	-0.95	-2.41 ^a	3.86	-2.40
	295	-0.79	-2.45	3.92	-2.26
	395	5.30	-3.40	5.44	3.26
EuF ₂	295	1.75	-1.54	2.56	0.73
	395	5.43	-1.89	3.14	4.18

^a β values are from Rao (1980).

rest. Amongst the fluorite type crystals studied, the value is highest for CdF₂; the value for EuF₂ is comparable with those for alkaline earth fluorides.

To study the effect of temperature, the C contribution has been evaluated at temperatures up to $\approx 400^\circ\text{K}$ for EuF₂ and PbF₂. For this purpose the data on temperature variation of dielectric constant obtained by the present authors (Reddy 1980; Reddy and Sirdeshmukh 1984) are used. The results are given in table 7. For EuF₂, the temperature coefficient of dielectric constant is positive and the C value is also positive throughout the temperature range. However, in PbF₂, the temperature coefficient of dielectric constant is negative at low temperatures but becomes positive at elevated temperatures. Correspondingly, the parameter C also is negative at low temperatures and positive at elevated temperatures. It is to be noted that the A and B parameters are of the same sign in the entire suite of crystals and over the entire range of temperatures. Thus the contribution C plays a dominant role in determining the temperature variation of dielectric constant. It is to be noted that the C contribution reflects the anharmonic effects.

4. Summary and conclusions

The experimental data on temperature variation of dielectric constant of crystals with fluorite structure are analysed according to the method proposed earlier by Bosman

and Havinga (1963) for ionic crystals with NaCl and CsCl structures. Out of the three terms (A , B , C) which contribute to the temperature coefficient, the A term is obtained from thermal expansion and the B term is estimated semi-empirically from an ionic potential. From the difference between the experimental values of $A + B + C$ and $A + B$, the C term is obtained. Calculations of B and evaluation of C are made for six crystals with the fluorite structure *viz.* CaF_2 , SrF_2 , BaF_2 , CdF_2 , PbF_2 and EuF_2 . In the last two cases the calculations are made at different temperatures.

The semi-empirical method of calculations of strain derivative of polarizability yields values which agree with values from experimental data on pressure derivative of dielectric constant. Thus in crystals, like EuF_2 , for which high pressure data on dielectric constant are not available, one can confidently use the semi-empirical method.

The temperature coefficient of dielectric constant at room temperature is positive for all these crystals except PbF_2 . The C term is positive for all except PbF_2 . Further both the temperature coefficient of dielectric constant and C become positive at elevated temperatures. It is therefore concluded that the C contribution, which is related to the temperature variation of IR polarizability, plays a dominant role in determining the temperature variation of dielectric constant and anharmonic effects.

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