TABLE II

Compound	$\alpha_{\perp}(\times 10^6)$	$\alpha_{\parallel}(\times 10^6)$	$\beta(\times 10^6)$
Zircon [6]	3.47	4.36	10.79
$DyVO_4$ (Present study)	1.33	9.89	12.54

$$\alpha_{(30-604^\circ C)} = 4.30 \times 10^{-6} (^\circ C)^{-1}$$

$$\alpha_{(30-604^\circ C)} = 11.26 \times 10^{-6} (^\circ C)^{-1}.$$

The variation of the coefficient of thermal expansion with temperature is shown graphically in Fig. 2.

The lattice parameters ($a = 7.1483 \pm 0.0004$ Å, $c = 6.3075 \pm 0.0003$ Å) of $DyVO_4$ obtained by us at 30° C are in agreement with the parameters at 25° C ($a = 7.1434$ Å, $c = 6.3130$ Å) reported by Swanson and Tatge [5].

The coefficients of thermal expansion reported by Worlton *et al.* [6] in the case of zircon are given in Table II along with the present data. Although $\alpha_{\parallel} > \alpha_{\perp}$ in both cases, the anisotropy is more marked in the case of $DyVO_4$. From Table II, it is clear that the coefficient of volume expansion (β) is almost the same for both compounds.

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N. RAJASHEKHAR REDDY
K. SATYANARAYANA MURTHY
K. V. KRISHNA RAO
Department of Physics,
Osmania University
Hyderabad, 500 007 (AP),
India

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*Dipole ordering in dilute solutions of ferroelectrics in antiferroelectric materials**

Antiferroelectric materials such as $PbZrO_3$ and $NaNbO_3$ form solid solutions over the entire range of compositions with ferroelectrics such as $PbTiO_3$ and $KNbO_3$ that involve either cationic or anionic substitution. The solid solutions exhibit different kinds of dipole ordering depending on the composition. The antiferroelectric states of $PbZrO_3$, $NaNbO_3$ and such materials appear to be generally unstable with respect to such alteration in composition [1, 2]. Thus, for x greater than 0.10, $PbZr_{1-x}Ti_xO_3$ (PZT) is ferroelectric [3], a behaviour also shown by $Na_{1-x}K_xNbO_3$ (PSN) [4]. Compositions of PZT and $PbHf_{1-x}Ti_xO_3$ (PHT) close to $x = 0$, are antiferroelectric upto the paraelectric transition temperature [2, 5]; the nature of ordering in PSN around $x = 0.01$ is, however, not clear [4]. It has been considered interesting to investigate dilute solutions of ferroelectrics in antiferroelectric materials such as PHT, PZT and PSN with a view to understanding the nature of dipole ordering in the interface region between the antiferroelectric ($x \simeq 0$) and ferroelectric ($x \geqslant 0.1$) phases. This interface

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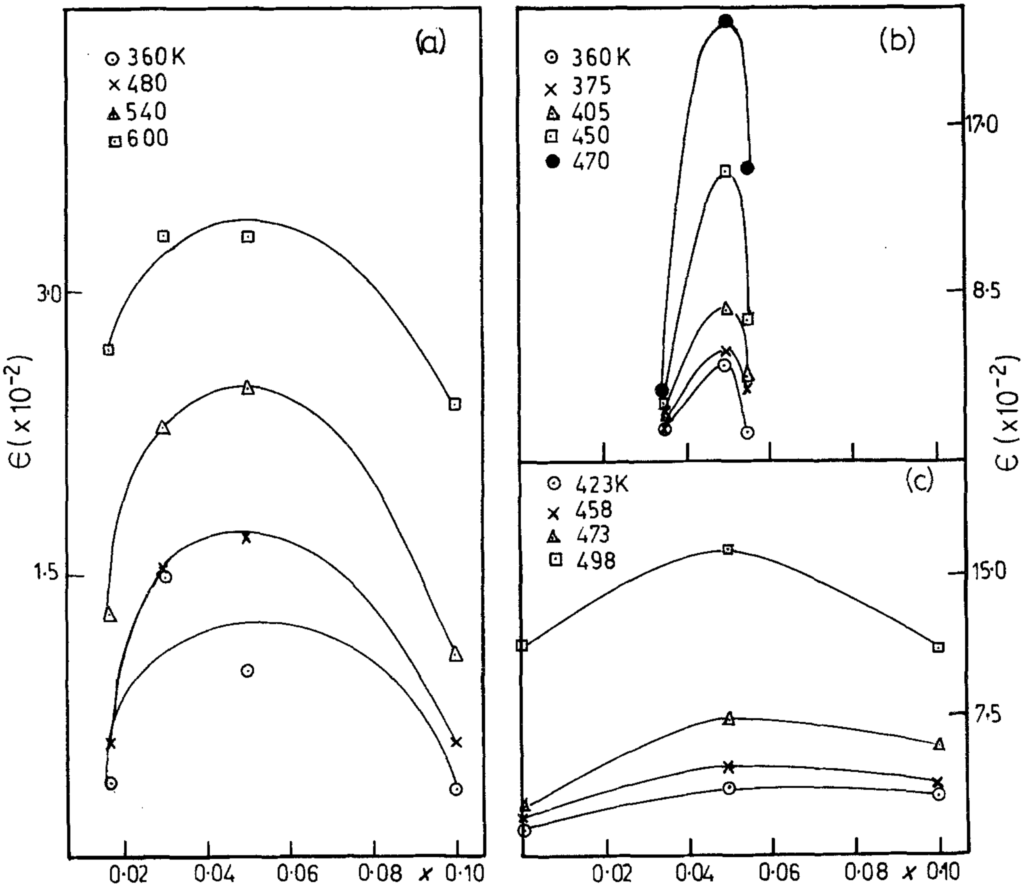

Figure 1 Compositional variation of isothermal dielectric constant of (a) PSN, (b) PHT, (c) PZT in the interface region.

region has not previously been explored adequately. It is not entirely unlikely that at some composition(s) in this region there would be some type of dipole ordering (giving rise to net polarization) distinct from either antiferroelectric or ferroelectric types of ordering. One possibility is the occurrence of orientationally frozen dipoles or dipole glasses [6, 7], somewhat analogous to spin-glasses.

Our observations on dilute solutions of ferroelectrics in antiferroelectric materials are as follows:

(i) Isothermal dielectric constants of PHT, PZT and PSN show maxima around $x = 0.05$ (Fig. 1).

(ii) A minimum in $\tan\delta$ is found at $x \simeq 0.05$ as shown for PSN (Fig. 2).

(iii) Dielectric hysteresis is not observed in the samples of composition $x \simeq 0.05$ even with high applied fields.

(iv) The solid solutions in the interface region show two phase transitions (as found by differential scanning calorimetry (DSC) and dielectric measurements), but the transitions are difficult to identify by DSC in the case of PHT. Ionic substitution affects transition temperatures, particularly of the low-temperature transition. We are unable to comment on the changes in dipole ordering accompanying these phase transitions in the composition range $0.01 \leqslant x \leqslant 0.06$.

The above observations can be understood if it is proposed that the dipolar arrangement in these solid solutions changes from antiferroelectric-type to ferroelectric-type at some concentration in the interface region through an intermediate phase. This intermediate phase does not appear to possess long-range ordering of dipoles; however, the uncompensated pairs of dipoles may form ferroelectric-type centres [8] in the phase. Increase in the concentration of such centres would make the phase unstable with respect to the ferroelectric

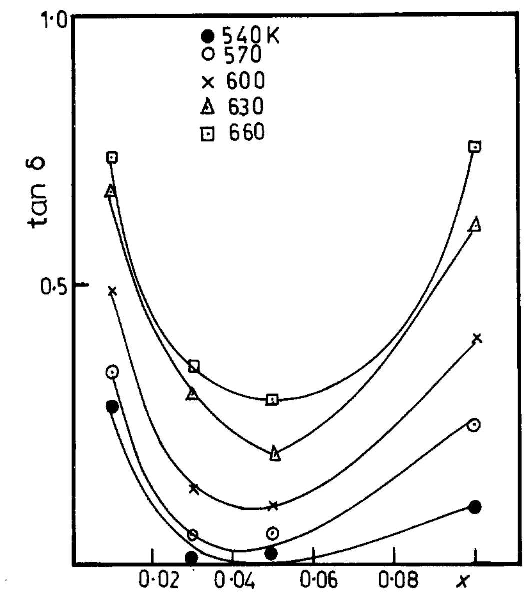

Figure 2 Compositional variation of isothermal tan δ of PSN in the interface region.

phase. The main feature of these systems is that concentration plays the role of temperature and the driving force for the transformation of the intermediate phase to the ordered ferroelectric phase is the chemical potential of the ordered dipoles. Relaxation times would be shorter in such an intermediate phase giving rise to a minimum in tan δ. The ferroelectric-type phase suggested here could, in principle, correspond to dipolar clusters or to a dipole glass, although the present observations may not strictly correspond to the kind of dipolar glass described recently by Kirkpatrick and Varma [6] or Höchli *et al.* [7].

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R. PARTHASARATHY
K. J. RAO
C. N. R. RAO
Solid State and Structural Chemistry Unit,
Indian Institute of Science,
Bangalore, 560 012,
India

Estimation of the dislocation core energy in BaF$_2$ crystals

Dissolution and etching data can be used to estimate the core energy of a dislocation [1]. In this letter the core energy of dislocations in BaF$_2$ crystals is estimated using the values of the activation energy of dissolution and formation of etch pits on the {1 1 1} planes. The method of estimation is described in the following.

The free-energy change for two-dimensional nucleation at a dislocation site during dissolution of a crystal has been given by Robinson [1] as

$$\Delta G_n^* = 2\pi a\gamma^T r_d^* - \pi a|\Delta G_v| r_d^{*2} - E_{co}(r_d^*) \quad (1)$$

where a is the height of a monomolecular ledge, γ^T the specific surface free energy of a molecule going from the solid to the solution, r_d^* the radius of the cavity of a unit pit, ΔG_v the Gibbs free energy per unit volume of the crystal, and E_{co} the dislocation of the energy core. Taking $\gamma^T = \gamma/2$, where γ is the surface free energy of the crystal in a vacuum, $r_d^* = a/2$ and $\Delta G_v = \gamma^T/r_d^*$, we get

$$\Delta G_n^* = \pi a\gamma^T r_d^* - E_{co} \quad (2)$$

and

$$E_{co} = \pi a\gamma' r_d^* - \Delta G_n^*. \quad (3)$$