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].

Acknowledgement

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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 BaF₂ 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

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

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, τ_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, $\tau_d^* = a/2$ and $\Delta G_v = \gamma^T/\tau_d^*$, we get

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

and

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

The rates of dissolution at dislocation emergence points, V_n, and at the perfect surface, V_d, are [1]:

$$V_n = a\nu \exp\left[-(\Delta G_n^* + \Delta H)/kT\right] \qquad (4)$$

$$V_d \approx \sigma x_d \nu \exp(-\Delta H/kT) \qquad (5)$$

where ν is the frequency factor, of the order of the Debye frequency, ΔH the free-energy change for a molecule going from the surface of the crystal into the solution, k the Boltzmann constant, T the absolute temperature, $\sigma = 1 - c/c_0$ the undersaturation, and x_d the displacement of an atom diffusing from a kink site to an absorbed position. Since [1]:

$$x_d = a \exp\left[(W_d - U_d)/2kT\right] \qquad (6)$$

where W_d is the free-energy change for a molecule going from an absorbed position into the solution and U_d is the energy barrier between equivalent positions on the surface, then

$$V_d = \sigma\nu a \exp\left(-\frac{\Delta H}{kT} + \frac{W_d - U_d}{2kT}\right). \qquad (7)$$

The values of dissolution activation energies at a dislocation, $E_n \simeq E_t$, and of the perfect surface, E_d, may be given as

$$E_n \simeq E_t = \Delta G_n^* + \Delta H \qquad (8)$$

$$E_d = \Delta H - \tfrac{1}{2}(W_d - U_d). \qquad (9)$$

It follows from Equations 8 and 9 that

$$\Delta G_n^* = E_t - E_d - \tfrac{1}{2}(W_d - U_d). \qquad (10)$$

Taking $U_d \approx 0$ [1], we get

$$E_{co} = \pi a \gamma' \tau_d^* - E_t + E_d + \tfrac{1}{2}W_d. \qquad (11)$$

For BaF$_2$ crystals we have $a = 6.2 \times 10^{-8}$ cm [2], $\gamma' = 2.17 \times 10^{-5}$ J cm^{-2} [3], $W_d = 3.2$ kcal mol^{-1} [4].

We have computed the value $E_d = 0.39$ eV for dissolution of BaF$_2$ crystals in HNO$_3$ and HCl (aqueous solutions) from the plot of the logarithm of the dissolution rates, V_d, versus $1/T$ [5]. We now compute $E_t = 0.68$ eV for dissolution on the {1 1 1} planes of BaF$_2$ crystals in HNO$_3$ and HCl form the plot log V_t versus $1/T$ (Fig. 1).

Substituting these values in Equation 11 we get $E_{co} = 0.62$ eV. We can estimate the value of the
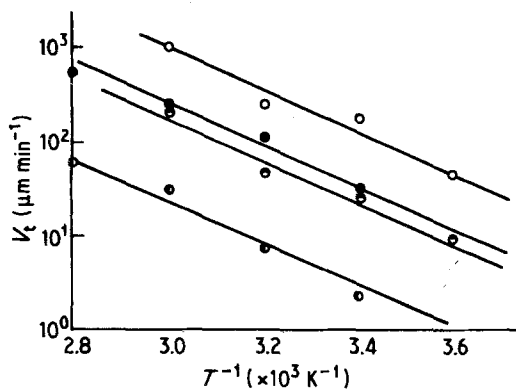

Figure 1 Log V_t versus $1/T$ for BaF$_2$ in aqueous solutions of HNO$_3$ and HCl for etching of the {111} planes. ○, 0.8 M HNO$_3$; ◐, 0.1 M HNO$_3$; ●, 1 M HCl; ◑, 0.1 M HCl.

core energy of dislocations without etching data [6] from

$$E_{co} = a\alpha Ab^2 \tau_d^* / \tau_0 \qquad (12)$$

where α is a constant, equal to 1.5 for screw dislocations and 1.8 to 2 for edge dislocations, $A = Gb^2/4\pi$ for screw and $Gb^2/4\pi(1 - \sigma)$ for edge dislocations, where σ is Poisson's ratio, b is the Burgers vector ($= a\sqrt{2}$), G is the shear modulus, and τ_0 the distance from the dislocation beyond which strain is negligible. Using $\tau_0 = 20Ab/G$ [1], we get

$$E_{co} = \frac{\alpha a^3 G\sqrt{2}}{40}. \qquad (13)$$

For BaF$_2$ crystals $G = 2.5 \times 10^{11}$ dyn cm^{-2} [2]. Then $E_{co} = 2$ eV for edge dislocations.

We compared our estimates of E_{co} for BaF$_2$ with E_{co} for MgO and NaCl (Table I). The computing of the value of the core energy of dislocations from etching data for MgO was accomplished in [7]. Other analytical estimations of $E_{co}^{11\dagger}$ and $E_{co}^{13\dagger}$ have been made by the authors of this letter. The results (Table I) show that the estimations of the dislocation core energy from etching data for MgO, BaF$_2$ and NaCl (E_{co}^{11}) agree with the theoretical estimates (E_{co}^{13}). The fact that $E_{co}^{11} < E_{co}^{13}$ means that the dislocation core energy determined on the basis of the elastic properties is not correct and one should take into account the surface properties. The decrease in the values

†According to Equations 11 and 13, respectively.

TABLE I Core energy of dislocations in some crystals (in electron volts)

Crystal	hkl	Etchant	E_t	E_d	E_{co}^{11}	Reference	E_{co}^{13}		E [9]
							Screw	Edge	
MgO	100	HNO$_3$	0.68	0.59	1.58	[7]	3.5	4.3	41
		HCl	0.68	0.55	1.52				
		CH$_3$COOH	0.81	0.66	1.55				
BaF$_2$	111	HNO$_3$	0.68	0.39	0.62	Authors's data	2.0	2.3	24
		HCl	0.68	0.39	0.62				
NaCl	100	CH$_3$COOH	0.67	0.37	0.37	Author's estimation according to [8]	0.56	0.75	8

of E_{co}^{11} and E_{co}^{13} in the series MgO, BaF$_2$, NaCl accords with the decrease in lattice energy of these crystals, E (Table I). Correlation of the values of E_{co}^{11} with E_{co}^{13} and E, and the independence of the dislocation core energy on etchant and solvent is evidence of the correct estimation of the dislocation core energy from dissolution and etching data.

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A. E. SMIRNOV
A. A. URUSOVSKAYA
Institute of Crystallography
USSR Academy of Sciences
Moscow
USSR

A mode of deformation in partially stabilized zirconia

This work describes the nature of deformation patterns associated with identations and scratches in partially stabilized zirconia. Surface deformation bands could be highlighted by chemical or ion-beam etching of the surface. The nature of the bands has been investigated using optical and transmission electron microscopy.

Partially stabilized zirconias have recently attracted considerable attention as a possible ceramic engineering material because of their exceptional mechanical properties [1–6]. In these materials a two- or three-phase microstructure exists which consists of a cubic stabilized matrix with monoclinic and/or tetragonal zirconia precipitates. It is the metastability of the tetragonal precipitates combined with the volumetric expansion and shear strains associated with their transformation to the monoclinic form that is responsible for the good mechanical properties of the material.

The materials used in this study are magnesia and calcia partially stabilized zirconia (Mg- and Ca-PSZ respectively). Previous studies of these materials have shown that the mechanical properties may be optimized by choosing suitable com-