Letters

A correlation between the magnitudes of dielectric breakdown fields in alkali halides and their lattice constants

Alkali halides represent a "simple" model class of dielectric materials on which one may conduct experimental and theoretical studies to determine the fundamental factors involved in the field-induced dielectric breakdown in solids. The experimental dielectric breakdown fields for several alkali halides have been assembled in an excellent review [1]. Also, the "forming" process observed in metal-alkali halide-metal sandwiches [2] have been shown [3, 4] to be nothing but cases of field-induced dielectric breakdown. A point of principal interest in the investigations of this subject is the delineation of factors that appear to be correlated with the magnitudes of the dielectric breakdown fields in these materials. In an electrochemical approach [4] to the problem, correlations between the dielectric breakdown fields and the free energies and heats of reactions (and thence the electrode potentials), and the band gaps of the alkali halides were successfully established.

The object of the present note is to show that a fundamental solid state parameter of alkali halides, namely, the lattice constant, appears to be correlated with the values of the dielectric breakdown fields for several alkali halides.

TABLE I

Compound	Lattice constant (Å)	F_{exp} (MV cm^{-1})
LiF	4.05	3.1
NaF	4.70	2.4
KF	5.30	1.9
NaCl	5.65	1.5
NaBr	5.9	0.81
KCl	6.25	1.0
RbCl	6.70	0.83
KBr	6.50	0.70
RbBr	6.70	0.63
KI	7.10	0.57
RbI	7.4	0.49

Notes: (1) The experimental dielectric breakdown values are from [1] and are *not* claimed to refer to single crystals.

(2) The values of lattice constants have been read from Fig. 26 of [5].

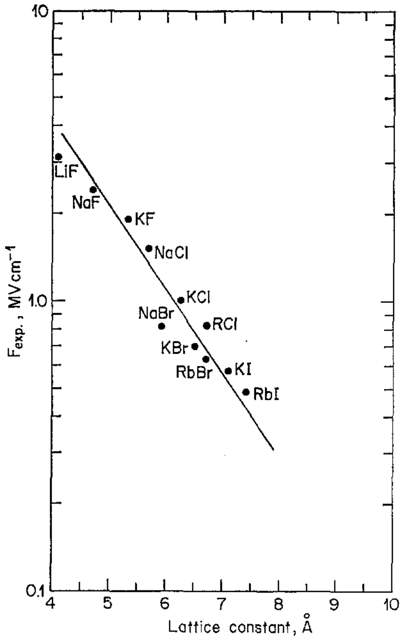

Figure 1 Experimental values of dielectric breakdown fields versus lattice constants for the alkali halides indicated. For details see Table I.

For the alkali halides for which the data are available, the values of the dielectric breakdown fields [1] and the lattice constant [5] are summarized in Table I. A plot of these data (Fig. 1) shows that a very good correlation is obtained between the two quantities. Increasing lattice constant heralds a decreasing value for the dielectric breakdown field for the series of alkali halides shown in Fig. 1.

Qualitatively, a higher lattice constant means high inter-nuclear distance between the atoms of an alkali halide, with the consequent poor solid state cohesion [6]. For a given value of the applied field, a lower solid state cohesion (or a higher lattice constant) would lead to an easier dielectric breakdown and hence a lower value of the dielectric breakdown field as is indeed observed (Table I, Fig. 1).

Quantitatively, the magnitude of the forces of solid state cohesion in ionic materials such as alkali halides is given by the lattice energy. This may be calculated via the Born equation [7]:

$$U = \frac{ANZ_1Z_2e^2}{R} - \frac{B}{R^m} \qquad (1)$$

in which U is the lattice energy (i.e. the magnitude of the solid state electrostatic cohesion in an alkali halide); A, B and m are constants; N is Avogadro's number; Z_1 and Z_2 are the charges ($Z_1 = Z_2 = 1$ for alkali halides) on the ions; e is the electrostatic charge and R is the internuclear distance. A higher lattice constant for an alkali halide implies a higher R and, correspondingly, a lower U value. The latter, of course, signifies weaker solid state cohesion and hence a relatively easier dielectric breakdown on application of a given field, as deduced above (Fig. 1). It should be added that the same conclusion would be reached even when U is calculated from other relationships such as the Born-Mayer equation, Kapustinski's equation or the Born-Haber cycle etc [7].

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Relationships for crystal structure transformations: MX, MX_2, MXO_3

The detailed crystallographic treatment of transformations of crystal structure depends upon the existence of a deformational relationship between the structures. This relationship implies that during the lattice deformation the displacements of atoms do not require any activated interchange of neighbours. The structures of many chemical compounds, however, contain so many atoms per unit cell that detailed examination of the displacements becomes necessary to decide whether particular structures are deformationally related ([1] and references therein). Most proposals for relationships and mechanisms for large changes of structure [2, 3] have concentrated on the sequence of displacements with little explicit attention to the lattice deformation and consequent misregistry and transformation twinning. The anion array has commonly been taken as the framework of the structure, or the relative arrangements of co-ordination polyhedra, usually octahedra, have been compared. This note points out some new deformational relationships referred either to a sub-cell which indicates the relationship or to a true cell from which the principal strains can be derived. Simple relationships between the well-known basic MX types are expected to be fundamental to the geometry for more complex stoichiometries.

In Fig. 1 either set of circles could represent anions, or the points of a sub-lattice. When small circles represent cations, Fig. 1 shows that the NiAs and CsCl structures are related by a pure strain, the site occupied by the central ion being displaced by the deformation. Quite similar geometry can be shown to relate the WC, MnP and NiAs structures.

When alternate pairs of cation sites are vacant, Fig. 1a represents rutile, TiO_2, regarded as having approximately hcp anions. The base of the prism corresponds to $(010)_r$. When the prism has been deformed to become two cubes the anion is at the centre of a tetrahedron, the anion array is simple cubic, and the result is the fluorite structure.

If the small black circles of Fig. 1 represent centres of triangular (CO_3^{2-}, NO_3^-) or flat pyramidal (BrO_3^-) anions then Fig. 1a represents the aragonite ($CaCO_3$) or KNO_3II structure (planes of anions parallel to the base of the prism) and Fig. 1b represents the cubic and distorted pseudo-cubic $CaNO_3$, $TlNO_3$ and low $RbNO_3$ structures which probably include that of KNO_3IV to which KNO_3II transforms under pressure. Except for aragonite it is convenient to