important in limiting the low temperature strength achieved in hot-pressed material. Moreover, the anisotropy of grain shape and the crystallographic preferred orientation, which appear to be related phenomena, have been shown to introduce marked directionality of physical and mechanical properties in hot-pressings of Si_3N_4 [6]. Further microstructural investigation is required to establish clearly the quantity and distribution of the amorphous constituent.

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Electrochemical aspects of dielectric breakdown in alkali halides

In metal-insulator-metal sandwiches involving alkali halides, it is found that an application of a suitable voltage (i.e. field) across the sandwich gives rise to the decomposition of the insulator [1]. In an alkali halide MX, the reaction at the anode is

$$X^- + \text{Anode} \rightarrow \tfrac{1}{2}X_2 + e + \text{Anode} \qquad (1)$$

where X_2 is the molecular halogen gas. The corresponding cathodic reaction may thus be written as

$$e_{\text{cathode}} + \square_{\text{insulator}} \rightarrow \square^{-}_{\text{insulator}} \,. \qquad (2)$$

Greene *et al* [1] have noted that for the "forming" (ie. electrolysis) to occur, the forming voltage, V_F, must just exceed, ΔG, the free energy change involved in the overall electrolysis reaction, presumably because

$$\Delta G = -nFE_0 \qquad (3)$$

where E_0 is the electrode potential (i.e. reversible) of the electrolysis reaction to which ΔG refers; n is the number of charge carriers transferred in the overall reaction and F is the Faraday. For electrolysis to occur, V_f must exceed E_0 (and hence ΔG) because some overpotential must be developed before the electrolysis can occur.

This note attempts to correlate the V_f values of these alkali halides to their band gaps, E_g values. Also, the relation of these considerations to the experimental values of the dielectric breakdown field for several alkali halides [2] will also be examined.

Since for the solid-state electrolysis to commence, the (exothermic) free energy of formation of the insulator must be just exceeded by the formation voltage [1] it follows that

$$eV_f \simeq -\Delta G \qquad (4)$$

where V_f is the forming voltage of the insulator, e is the electronic charge and ΔG is its free energy of formation per mole. For the alkali halides, ΔG per *mole* is the same thing as ΔG_e, the free energy of formation per *equivalent* which may also be approximated as the heat of formation per equivalent, ΔH_e, so that*

$$V_f \simeq -\Delta G \simeq -\Delta G_e \simeq -\Delta H_e \,. \qquad (5)$$

Now, it may be noted that [3, 4]

$$E_g \simeq 2(-\Delta H_e) \qquad (6)$$

where E_g is the band gap of the compound, the

**Notes:* 1. Since alkali halide are uni-univalent, ΔG/mole = ΔG_e.
2. Since alkali halides are solids, entropy would be a rather negligible part of ΔG_e; for condensed phases in general, entropy considerations are relatively unimportant.

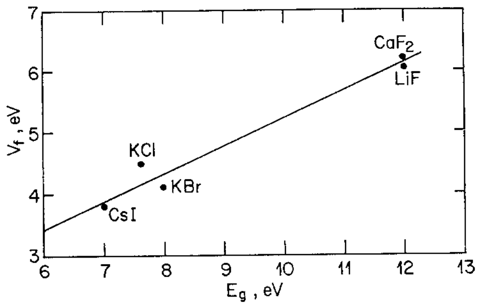

Figure 1 A correlation between the forming voltage, V_f, of the shown alkali halides (placed in a metal-insulator-metal sandwich configuration) versus their band gap, E_g values. See Table I for data and source references.

alkali halide in the present discussion. From Equations 5 and 6 one gets

$$V_f \simeq \tfrac{1}{2}E_g \qquad (7)$$

i.e. the forming voltage is half the band gap value. For the insulators where data on both V_f [1] and E_g [3, 4] exist, Equation 7 is roughly obeyed (Fig. 1); the data on V_f and E_g have also been given in Table I together with their source references.

TABLE I

Compound	V_f (eV)	E_g (eV)
CaF_2	6.2	12
LiF	6.1	12
KCl	4.5	7.6
KBr	4.1	8.0
CsI	3.8	7.0

Notes: 1. The V_f values are from [1] and the E_g values from [3, 4]. It is *not* indicated [1] that V_f values refer to single crystals.

2. The V_f values for MgF_2 and MnF_2 are available [1] but no E_g value could be found for them.

Forming destroys the insulator irreversibly and thus leads to dielectric breakdown; it is of interest, therefore, to compare the forming voltages [1] to, (F_{exp}), the experimental values of the dielectric breakdown fields [2] for the alkali halides for which the data are available (Fig. 2). Since log (F_{exp}) increases with increasing V_f (Fig. 2), increasing log (F_{exp}) should also be

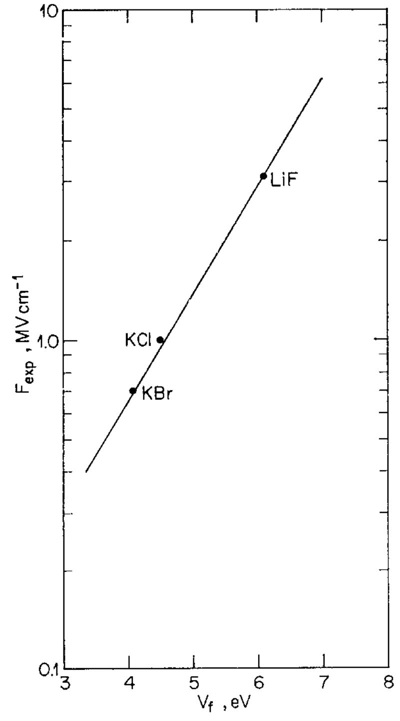

Figure 2 A plot of V_f against the experimental values of the dielectric breakdown field, F_{exp}, for the shown alkali halides. See Table II for data and source references.

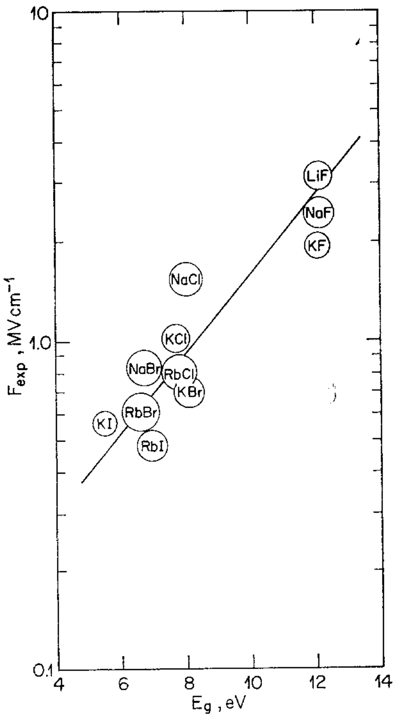

Figure 3 A plot of F_{exp} versus E_g values for the shown alkali halides. See Table II for the data and source references.

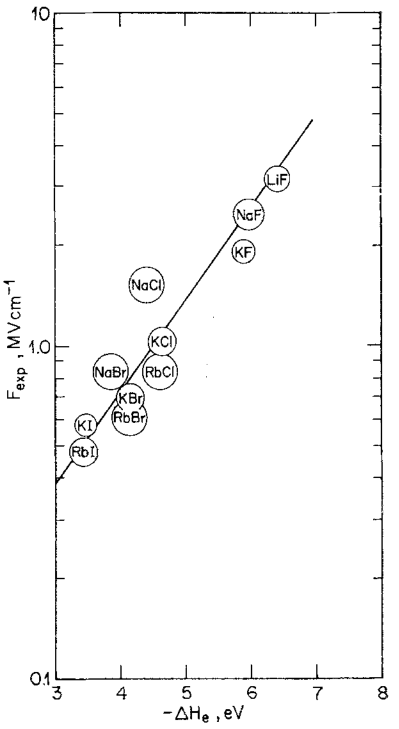

Figure 4 A plot of F_{exp} versus the heat of formation per equivalent (exothermic), $-\Delta H_e$, values for the shown alkali halides. See Table II for the data and source references.

TABLE II

Compound	F_{exp} (MV cm^{-1})	E_g (eV)	$-\Delta H_e$ (eV)
LiF	3.1	12.0	6.35
NaF	2.4	12.0	5.90
KF	1.9	12.0	5.84
NaCl	1.5	7.8	4.26
NaBr	0.81	6.5	3.73
KCl	1.0	7.6	4.51
RbCl	0.83	7.4	4.46
KBr	0.70	8.0	4.06
RbBr	0.63	6.4	4.04
KI	0.57	5.6	3.39
RbI	0.49	7.0	3.40

Notes: 1. The experimental dielectric breakdown values are from [2] and are *not* claimed to refer to single crystals.
2. The band gap, E_g, values are from [3, 4].
3. The (exothermic) heat of formation, $-\Delta H_e$, values are from [5].

associated with increasing E_g values. This is roughly verified on the basis of data in Table II, as plotted in Fig. 3. Equation 6 can also provide a means of relating F_{exp} of alkali halides to one of their fundamental thermodynamic parameters, namely, the $-\Delta H_e$ values. A good correlation is indeed obtained (Fig. 4) with log (F_{exp}) increasing with increasing ($-\Delta H_e$) values. The $-\Delta H_e$ data are listed in Table II and can be taken from any standard compilation, e.g. [5].

It should be stressed here that the line of reasoning developed here as well as the correlations depicted (Figs. 1 to 4) must be recognized as indicating rough correlative trends only and not as a formulation of a rigorous theoretical viewpoint. This is because the arguments presented are based on quasi-thermodynamic concepts derived from data on aqueous electrolytes and their application to solids may be somewhat debatable because in solids, the diffusion is slow, the activation energies involved are much greater and, several energy barriers of the same order of magnitude are usually encountered [6].

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