

Microhardness studies in alkali halide mixed crystals

U V SUBBA RAO and V HARI BABU

Department of Physics, College of Science, Osmania University, Hyderabad 500 007

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Abstract. Microhardness measurements done in KCl, KBr and in different compositions of KCl-KBr mixed crystals show that it varies nonlinearly with composition. In order to investigate the nature of defects, several techniques such as etching, ionic conductivity and dielectric loss have been employed which showed that the mixed crystals of KCl-KBr are more defective, containing a high concentration of dislocations, low-angle grain boundaries and vacancies as compared to the end products KCl and KBr. These imperfections appear to be responsible for the nonlinear variation of microhardness in mixed crystals. The microhardness studies also revealed that the difference in size of the ions constituting the mixed system are responsible for the internal strains which in turn give rise to imperfections affecting the microhardness of mixed crystals.

Keywords. Mixed crystals; microhardness; etching; ionic conductivity; internal strains; imperfections.

1. Introduction

It is well known that single crystals of alkali halides are of considerable interest for use as infrared window materials (Sahagian and Pitha 1971). Since one of the main drawbacks of these halides is low mechanical strength, attempts have been made to improve their strength.

It has long been known that divalent cations are much more effective than monovalent ions in raising the strength of alkali halides (Edner 1932; Metag 1932; Shoenfeld 1932). Since then, detailed studies of mechanical properties have been made by Johnston (1962), Newey (1963), Dryden *et al* (1965), Newey *et al* (1966) and Suszynska (1971), to name a few. These studies have indicated that the defect structure of the crystals and the interaction of these defects with dislocations have a decisive role in hardening mechanism.

In recent years, some attempts have been made to improve the strength by precipitation hardening in NaCl-KCl system and solid solution hardening in KCl-KBr system (Armington *et al* 1973). However, the nature of defects and their role in hardening of mixed crystals is not clearly understood.

Our earlier work (Hari Babu *et al* 1975) on the density and distribution of dislocations in KCl-KBr mixed crystals as a function of composition both along and normal to the growth direction indicated a maximum dislocation density at the intermediate composition and a regular arrangement of low-angle grain boundaries in crystals cleaved along the growth direction. The formation of these boundaries is explained on the basis of Tiller's eutectic crystallization mechanism. The nonlinear

variation of ionic conductivity and activation energy with composition are described in terms of the diffusion of charge carriers along dislocations, whereas conductivity anisotropy is explained as due to the diffusion along the low-angle grain boundaries. In this paper, the results of a detailed study of microhardness and defects such as dislocations, vacancies and impurity-vacancy dipoles in KCl-KBr mixed crystals over the entire composition range and other systems such as KCl-KI and KCl-NaCl over a limited composition range are presented. A possible mechanism for hardening in these crystals is suggested.

2. Experimental

Single crystals of KCl, KBr and different compositions of KCl-KBr mixed crystals were grown in air in our laboratory by Kyropoulos technique. The starting materials used for the growth of these crystals being BDH analar grade salts. All these crystals were grown and annealed under identical conditions. These crystals were pulled at the rate of 1 cm per hour. After the growth, the crystals were brought to room temperature at the rate of 15°C per hour. The relative compositions of the end products in the mixed crystals were analysed chemically using potentiometric titration analysis. Single crystals of KCl-KI and KCl-NaCl systems were also grown in a similar way.

Etching technique has been employed to investigate the distribution of dislocations. An etchant consisting of doubly distilled methanol saturated with lead chloride was developed for this purpose.

Microhardness measurements have been performed by Vickers indentor, attached to Universal research microscope (Carl Zeiss, Jena). All the indentation measurements were done at room temperature and freshly cleaved samples of dimensions 5 mm × 5 mm × $\frac{1}{2}$ mm were used. The indentations were made at a load of 60 P and the time of indentation was kept at 10 sec. At least ten indentations were performed on each sample and a number of specimens were taken from each crystal. The final microhardness value is an average of all such measurements.

Ionic conductivity measurements were carried out on KCl-KBr mixed crystals over the entire composition range and the experimental details were presented in Hari Babu *et al* (1975). The crystal holder used for dielectric loss measurements is similar to that used for ionic conductivity studies. Dielectric loss measurements were made at different temperatures in the frequency range 150 Hz to 15 kHz by using GR 1615-A capacitance bridge. A GR-1311 audio oscillator provided along the bridge is used as a signal generator. For obtaining a continuous variation of frequency a Philips oscillator of type PM-1500 is used in conjunction with the bridge.

3. Results

Microhardness measurements have been carried out on freshly cleaved samples of KCl, KBr and various compositions of KCl-KBr crystals in the grown state and also in the samples annealed at room temperature for about one year. Figure 1

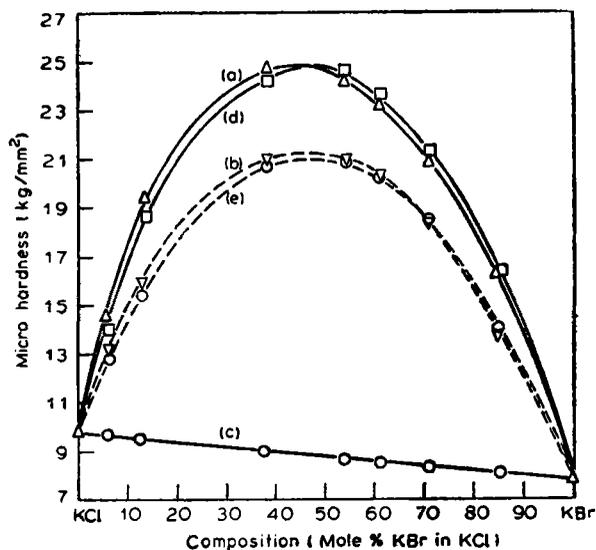


Figure 1. Variation of microhardness with composition (a) and (b) as grown and annealed KCl-KBr crystals; (c) obtained using equation (1); (d) and (e) obtained using equation (2) for the as grown and annealed samples.

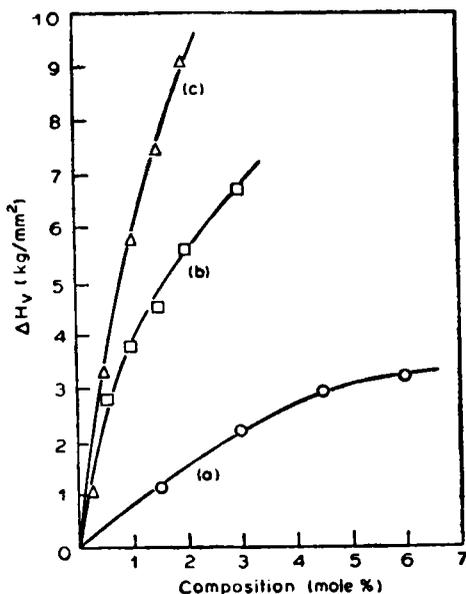


Figure 2. Change in microhardness ΔH_v against composition (a) KCl-KBr system; (b) KCl-KI system, (c) KCl-NaCl system.

shows the variation of microhardness against composition. From this figure, one can notice that the formation of a mixed crystal is accompanied by an increase in hardness and the microhardness attains a maximum value at an intermediate composition. Further, the hardness values in the crystals annealed at room temperature for one year were found to be less than the corresponding ones determined just immediately after growth. The hardness of the end crystals KCl and KBr, however, remain the same even after aging.

To study the effect of ionic size on microhardness in mixed crystals, microhardness measurements were carried out on various compositions of KCl-KBr, KCl-KI and KCl-NaCl mixed systems. Figure 2 shows the change in hardness ΔH_v drawn against composition in these mixed systems. From this figure it is clear that ΔH_v is found to increase with composition in all the three systems. Further, the change in hardness is found to be more in KCl-NaCl system and decreases as we move to KCl-KI and KCl-KBr systems.

Etching technique has been employed to study the density and distribution of dislocations present in these mixed crystals. For this an etchant consisting of distilled methanol saturated with lead chloride is developed. This etchant is capable of revealing dislocations in KCl, KBr and mixed crystals of KCl-KBr. It is observed that the density of dislocations is more in mixed crystals as compared to KCl and KBr. As composition of -KBr in KCl increases, the dislocation density increases and has a maximum value at an intermediate composition. Figure 3 shows the variation of dislocation density with composition.

To compare dislocation density in KCl-KBr, KCl-KI and KCl-NaCl mixed crystals, KCl containing 1.5 mole percent of KBr, KI and NaCl were etched in the methanol etchant, after all these three crystals were annealed at 500°C for 3 hr and cooled slowly to room temperature. From these studies we have observed that the dislocation density is more in KCl-NaCl crystal and is less in KCl-KI and KCl-KBr crystals.

Ionic conductivity measurements have been carried out on KCl, KBr and various compositions of KCl-KBr mixed crystals in the temperature range 100 to 450°C. Figure 4 shows the plots obtained for $\log \sigma T$ drawn against composition at different temperatures. From these curves, it is clear that at all temperatures, the conductivity is found to vary nonlinearly with composition and attains a maximum value at an intermediate composition.

Dielectric loss measurements have been made on mixed crystals to investigate the presence of impurity-vacancy dipoles (I-V dipoles). Figure 5 shows the plots of $\log \tan \delta$ against log frequency at different temperatures for 38.5 mole per cent KBr

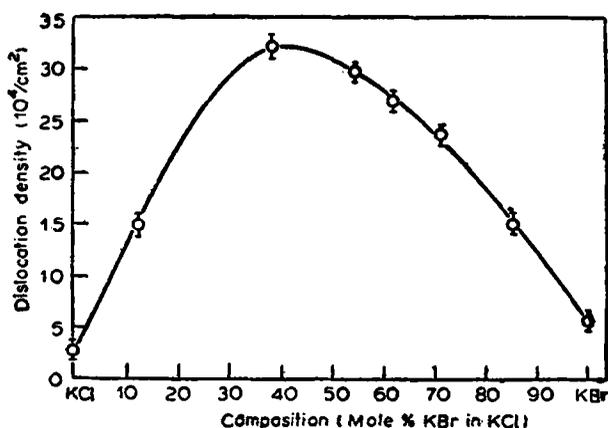


Figure 3. Variation of dislocation density with composition in KCl-KBr mixed crystals. The dislocation density is an average value of the density measured at different points on the specimen.

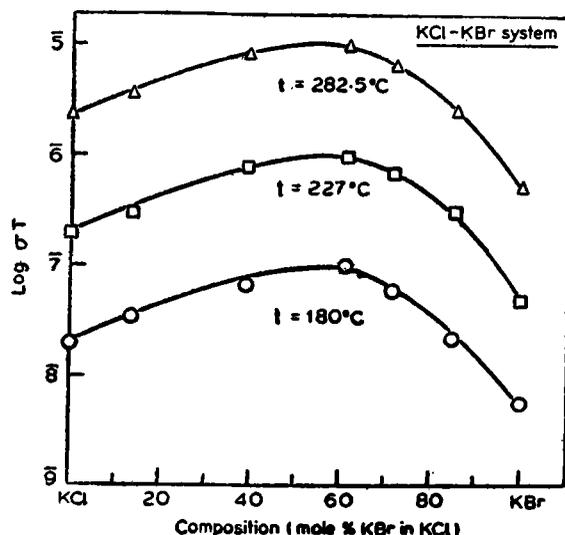


Figure 4. $\text{Log } \sigma T$ against composition at different temperatures in KCl-KBr mixed crystals.

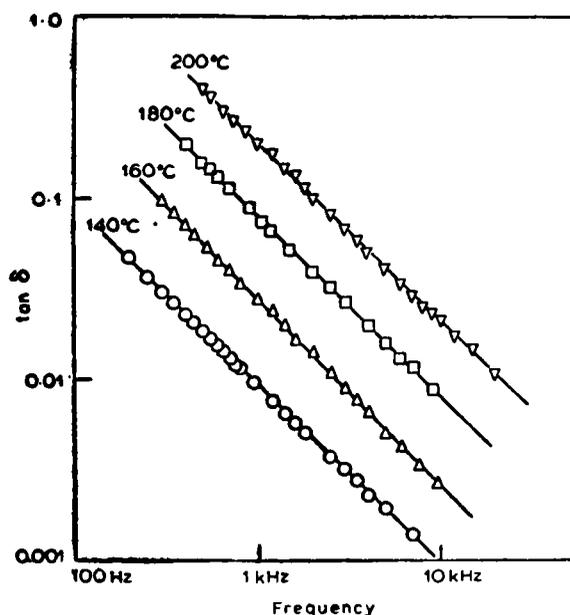


Figure 5. $\text{Tan } \delta$ vs frequency drawn on a logarithmic scale at different temperature in 38.5 mole percentage KBr in KCl.

in KCl mixed crystal. All the data points fall on a straight line at all temperatures and over the whole frequency range.

4. Discussion

Although hardness has been defined earlier in several ways (Mott 1956), it is now generally accepted that it is the resistance offered to dislocation motion. There are several contributions to the resistance to the dislocation motion and they can be classified broadly into two types. (a) The intrinsic resistance and (b) the resistance

due to imperfections. The only intrinsic resistance to dislocation motion in an otherwise perfect crystal is the Peirels-Nabarro stress (Cottrell 1953) which is due to the periodic variation of strain energy as dislocation moves through the crystal. Most of the resistance to dislocation motion in many real crystals, however, seems to arise from imperfections that act as obstacles to dislocations. Hardness has been related to various physical parameters. Chin *et al* (1972, 1973) from their studies on alkali halides have established a correlation between hardness and yield strength of a crystal. Gilman (1973) derived an explicit expression for the indentation hardness number of pure alkali halides in terms of ionic bonding combined with the theory of plastic deformation. Plendl and Giellissie (1962) have studied many nonmetallic structures and related hardness to volumetric lattice energy. For intermetallic compounds, Wolff *et al* (1958) established a relation between hardness and interatomic distance and is given by

$$H = \text{const} \times r^{-m} \quad (1)$$

where H is the hardness number, r is the interatomic distance and m is a constant whose value is found to depend on the structure of the particular system under consideration. Hitherto the correlation of hardness with other physical parameters has been mostly confined to pure crystals. In order to correlate hardness of mixed crystals to one of the physical parameters, relation (1) is employed. The lattice parameters of KCl-KBr mixed crystals were determined by Debye-Scherrer x-ray powder technique and are shown in table 1. The calculated microhardness values are shown in curve (c) of figure 1. It shows that the hardness varies linearly with composition whereas experimentally determined values show a nonlinear variation. In order to account for this discrepancy, a disorder parameter KN_aN_b has been included in relation (1) so that

$$H = \text{const} \times r^{-m} + KN_aN_b \quad (2)$$

where K is the coefficient of hardening and N_a and N_b are the respective compositions of the two components in the mixed crystal. The values of K were found to be 65 kg/mm² and 49 kg/mm² for crystals immediately after the growth and aged after one year, respectively. Curves (d) and (e) of figure 1 show the hardness values calculated from relation (2). A comparison of curves (d) and (e) with curves (a) and (b) shows

Table 1. KCl-KBr system

Crystal	Lattice parameter Å	Interionic distance r Å
KBr	6.6038 ± 0.0004	3.3004
85 Mole% KBr	6.5623	3.2812
71.4 Mole% KBr	6.5064	3.2532
54.03 Mole% KBr	6.4594	3.2287
38.5 Mole% KBr	6.4096	3.2048
13.6 Mole% KBr	6.336	3.168
KCl	6.2941	3.147

that the agreement is good between the experimental values and those calculated from relation (2). These results, therefore, suggest that any expression for microhardness of a mixed crystal must have two terms, an intrinsic one which depends on some structure insensitive physical parameter of the crystal and a disorder parameter which depends on the concentration of imperfections. The nonlinear variation of microhardness with composition may then be due to the presence of imperfections. These imperfections can be vacancies, impurity-vacancy pairs, dislocations, low-angle grain boundaries, etc.

Our earlier studies (Hari Babu *et al* 1975) on ionic conductivity and the results presented in figure 4 all show that conductivity is high for intermediate compositions as compared to end crystals. Since ionic conductivity is solely due to the presence of charged vacancies, these results therefore indicate that mixed crystals contain excess of vacancies. Similarly the results on dislocation morphology published earlier (Hari Babu *et al* 1975) showed that the low-angle grain boundaries and dislocations are more in mixed crystals compared to pure end crystals. The authors have also suggested that Tiller's eutectic crystallization mechanism as responsible for the origin of low-angle grain boundaries in mixed crystals (Hari Babu *et al* 1975).

In alkali halides, there is a large increase in hardness due to the presence of divalent impurities (Edner 1932; Metag 1932; Shoenfeld 1932) and this increase has been attributed by Fleicher (1962) to the formation of impurity-vacancy dipoles which introduce tetragonal distortions in the lattice. Our dielectric loss results in figure 5 indicate that all data points fall on a straight line at all temperatures and over the entire frequency range. These results suggest that impurity-vacancy dipoles are not present in our mixed crystals. Thus vacancies, dislocations and grain boundaries appear to be the dominant imperfections in mixed crystals and these may be responsible for the observed nonlinear variation in microhardness in them.

Due to aging at room temperature for sufficiently long time, there is a decrease in hardness of mixed crystals compared to the corresponding ones immediately after the growth. The amount of change is maximum for middle compositions and this decreases on either sides. In KCl and KBr crystals, there is practically no change in hardness due to aging. Our studies also indicate that due to aging, there is no change either in dislocation density or low angle grain boundaries. The decrease in hardness may therefore be due to a decrease in the concentration of vacancies, which probably anneal out due to aging.

The change in hardness ΔH_v with composition is more in KCl-NaCl mixed system as compared to the other two systems KCl-KI and KCl-KBr. The dislocation density is also more in KCl-NaCl system as compared to the other two systems. It is

Table 2. Pauling ionic radii in Å

Ion	Ionic size Å	Percentage difference
Cl ⁻	1.81	Cl ⁻ to Br ⁻ = 8
Br ⁻	1.95	Br ⁻ to I ⁻ = 11
I ⁻	2.16	Cl ⁻ to I ⁻ = 19
K ⁺	1.33	K ⁺ to Na ⁺ = 26
Na ⁺	0.95	

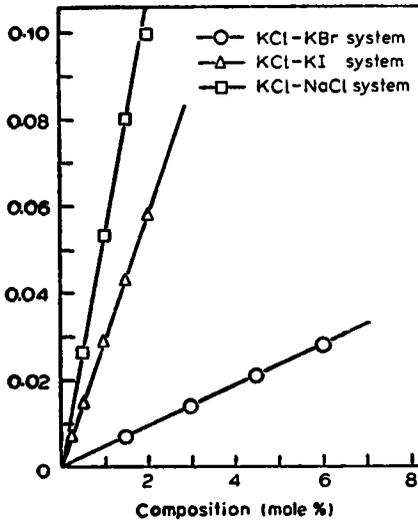


Figure 6. Variation of \bar{U}_{st}^2 against composition.

well known that lattice strains are developed in mixed crystals due to the difference in the size of the atoms or ions. The size of different ions and the percentage difference among them is shown in table 2 (Pauling 1927).

The amount of strain is determined by the magnitude of the mean square static displacement of the ions \bar{U}_{st}^2 from the equilibrium position. From the elastic model of a solid (Haldik 1972), we have

$$\bar{U}_{st}^2 = \gamma c (\Delta R)^2 \quad (3)$$

where γ is a numerical factor whose value is 7.8 for f.c.c. crystals, c is the composition and ΔR is the percentage difference in the ionic radii. Figure 6 shows the variation of static displacement calculated from (3) for KCl-KBr, KCl-KI and KCl-NaCl systems. A comparison of the curves in figures 2 and 6 shows a similar variation indicating a correlation between the static displacement and change in microhardness. Thus, as the difference in the size of the ions increases, the static displacement also increases resulting in large internal strains. The large change in microhardness with composition in KCl-NaCl system and also its high density of dislocations may be due to those large internal strains.

5. Concluding remarks

Internal strains arising out of the difference in ionic sizes may be responsible for the formation of dislocations, low-angle grain boundaries and other defects. These defects in turn appear to be responsible for hardening in mixed crystals. The results also suggest that microhardness in mixed crystals depends upon the difference in the size of the ions and not in the nature of the ions substituted.

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