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Dislocation density and microhardness studies in KCl–KBr mixed crystals

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Crystals of KCl, KBr and different compositions of KCl–KBr mixed crystals are grown with a view to obtaining the maximum dislocation density. The density and distribution of dislocations in KCl–KBr mixed crystals have been studied as a function of composition employing the etch-pit technique. The results indicate a much greater dislocation density in the KCl and KBr crystals, compared with the mixed crystals. Microhardness measurements were carried out, using a Vicker indentation tester, for these crystals. The microhardness is found to vary non-linearly with compositio ı. These studies show that the microhardness variation with composition is independent of the variation of dislocation density with composition.

1. Introduction

The hardness of a crystal is generally defined as its resistance to structural breakdown under an applied stress. The general definition of indentation hardness, which relates to the various forms of indenter, is the ratio of the load applied to the surface area of the indentation.

Single crystals of alkali halides are of considerable interest for use as infrared window materials [1]. Since one of the main disadvantages of these crystals for use in this way is their low mechanical strength, attempts have been made to improve their strength by precipitation hardening in the NaCl–KCl system [2], solid solution hardening in the KCl–KBr system [2] and hardening involving dilute additions of di-valent cations [3].

It has been known since 1932 that di-valent ion additions are much more effective than the addition of mono-valent ions for raising the strength of alkali halides (see [4–6], Newey [8], Dryden *et al.* [9], Newey *et al.* [10] to name but a few). These studies have indicated that the defect structure of crystals and the interaction of these defects with dislocations play a decisive role in the hardening- mechanism. However, the nature of defects and their role in the hardening of mixed crystals is not clearly understood.

Smakula *et al.* [11], from their measurements of microhardness on KCl–KBr mixed crystals, have found that mixed crystals have higher hardness values than the pure components. It was found that the hardness reached a maximum value in the mixed crystals of composition 33 mol% KCl–67 mol% KBr. Bhima Sankaran [12], from his measurements of microhardness on NaCl–NaBr mixed crystals, has found that the hardness of mixed crystals shows a non-linear variation with composition. The maximum hardness appears to be present in the mixed crystal having equimolar composition, the maximum value being slightly more than two-times that of either of the components. He also pointed out that the hardness variation with composition is similar to the variation of dislocation density with composition. Similar observations were made by Subba Rao and Hari Babu, in the case of the KCl–KBr, KCl–KI and NaCl–KCl systems [13].

In this paper, the results of a detailed study of microhardness and defects such as dislocations in KCl–KBr mixed crystals over the entire composition range are presented. The purpose of the present work is to show that microhardness is independent of the dislocation density present in these crystals.

2. Experimental procedure

Single crystals of KCl, KBr and different compositions of KCl–KBr mixed crystals were grown from the melt in air using GR grade chemicals as starting materials. The main aim of this work was

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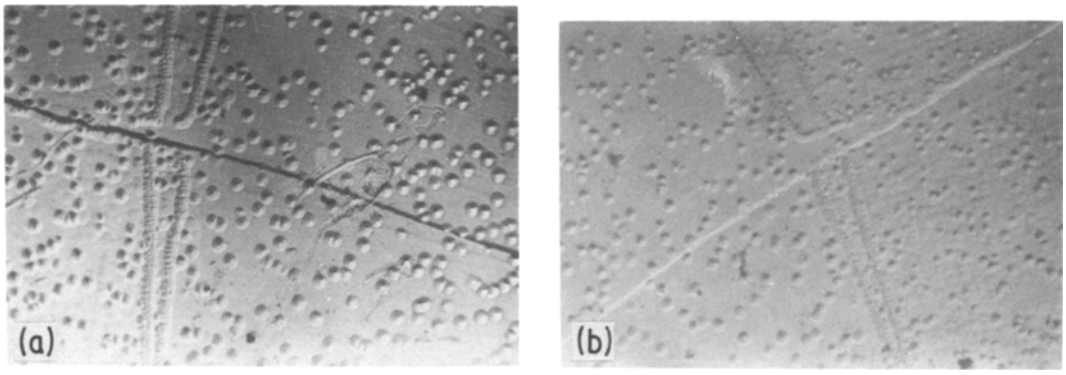


Figure 1 Matching faces of a KCl–KBr mixed crystal etched in a saturated solution of methanol and lead chloride (× 77).

to have as many dislocations in these crystals as possible. Neither the pure or mixed crystals used in the present investigation were grown by the Kyropoulos technique or by the Bridgman method. The weighted salts were first ground separately to form a powder and then mixed, so that the two salts would amalgamate uniformly. The mixture was then furnace-melted in a silica crucible. In order to obtain a homogeneous solution the melt was held at a temperature of between 50 and 80° C above the melting-point temperature for a period of three to four hours. After the melt had attained a steady temperature, roughly 80° C above the melting-point, the temperature of the melt was allowed to decrease slightly so that solidifcation sets in on the surface of the melt and spreads all over the surface. The temperature of the melt is slowly decreased and brought to room temperature at the rate of $10^\circ\,C\,h^{-1}$. The temperature control is very critical and important in order that nucleation may be initiated. In this way, large, completely transparent crystals, without any cracks and free from strain were obtained. Neither immediately nor at some time after cooling did the mixed crystals show cracks as observed by Smakula *et al.* [11]. Mixed crystals of KCl–KBr have shown complete miscibility at room temperature. The crystals were stable and did not show any type of decomposition even after remaining for a prolonged time at room temperature. Care was taken to grow all the crystals in this way and it was possible to produce single crystals as large as 3 cm × 3 cm × 2 to 4 cm.

Single crystals, cleaved from the grown bulk sample, were used for the present investigation. Specimens for etching were cleaved from these single crystals of dimensions roughly 5 mm × 5 mm × 2 mm. Etching techniques have been employed to investigate the distribution of dislocations. An etchant consisting of freshly distilled methanol (spectroscopic grade) saturated with lead chloride was used for this purpose [14]. The etchant was truly selective with respect to dislocations in these crystals. This was confirmed by etching the matching faces of mixed KCl–KBr crystals. Fig. 1a and b shows photomicrographs of the matching faces after etching indicating a one-to-one correspondence. The above etchant gave octagonal etch pits with curved corners in KCl, KBr and all the mixed crystals. The etching time was adjusted carefully in all the samples. As the etching time was increased the size of the etch pit also increase and, with higher etching times the etch pits overlapped and for such cases it became difficult to count the individual pits. The etching time was therefore kept short to ensure good resolution of most of the dislocations. To obtain each value of etch pit density, counts were conducted on as many as twenty representative photomicrographs.

Microhardness measurements were performed using a Vickers indentor attached to Universal Research Microscope (Carl Zeiss, Jena). All the indentation measurements were made at room temperature using freshly cleaved samples of dimensions 5 mm × 5 mm × 3 mm. The indentations were made with a load of 40 g and the time of indentation was maintained at 10 sec. The diagonals of the indentation are measured with the aid of a calibrated micrometer attached to the eye-piece of the microscope. About twenty indentations were made on each sample and a number of samples were taken from each crystal. The final value of the diagonal was obtained by plotting a Maxwellian distribution. This value of the diagonal of indentation was used to calculate the hardness. Microhardness values of KCl, KBr and various

compositions of KCl–KBr mixed crystals were measured.

3. Results

Photomicrographs shown in Figs 2a to k illustrate the etched surfaces of KCl, KBr and various compositions of the KCl–KBr mixed system etched in methanol saturated with lead chloride [14]. It is observed that, as the concentration of KBr increases in KCl, the etching time also increases, indicating that surface dissolution becomes prominent and a number of layers have been removed from the crystal surface. When the solution near the crystal surface becomes saturated, etch-pit formation starts and thus the etching time increases.

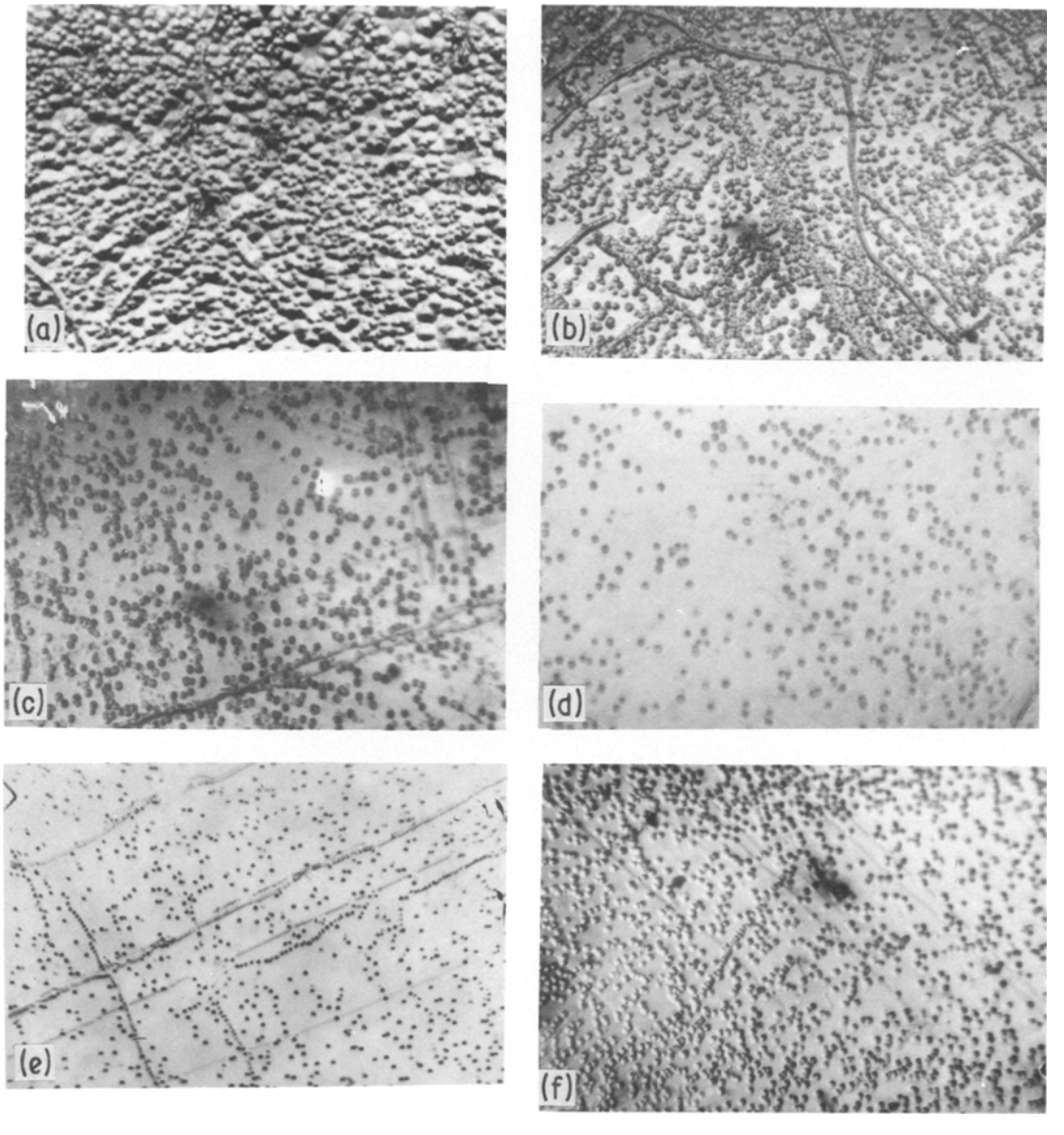
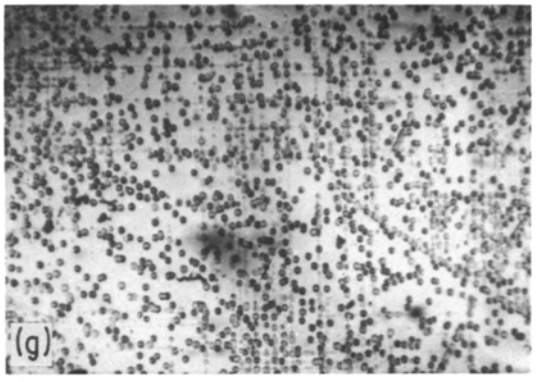
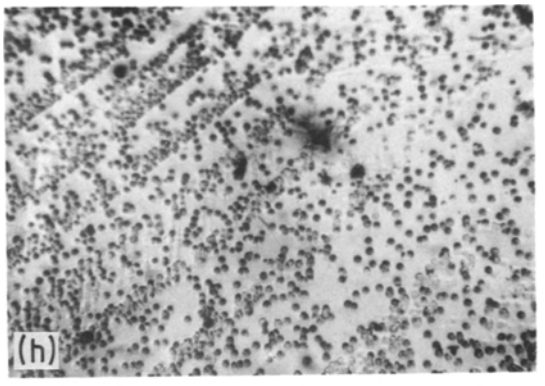
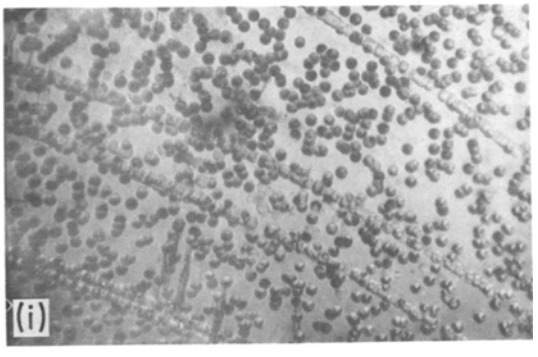
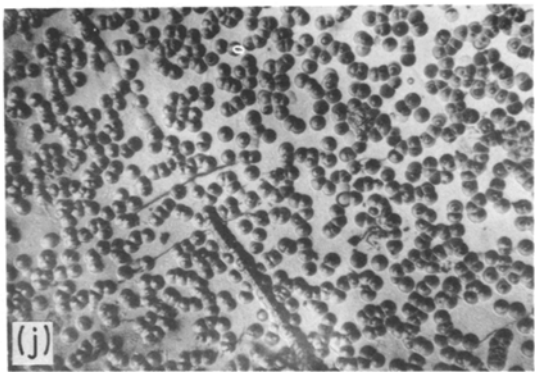


Figure 2 (a) Distribution of dislocations in pure KCl (× 255), (b) distribution of dislocations in $KCl_{0.94}Br_{0.06}$ mixed crystal (× 102), (c) distribution of dislocations in $KCl_{0.86}Br_{0.14}$ mixed crystal (× 102), (d) distribution of dislocations in $KCl_{0.79}Br_{0.21}$ mixed crystal (× 102), (e) distribution of dislocations in $KCl_{0.71}Br_{0.29}$ mixed crystals (× 102), (f) etch pit pattern in $KCl_{0.61}Br_{0.39}$ mixed crystal (× 102), (g) etch pit pattern in $KCl_{0.52}Br_{0.48}$ mixed crystal (× 102), (h) distribution of dislocations in $KCl_{0.41}Br_{0.59}$ mixed crystal (× 102), (i) etch pit pattern in $KCl_{0.29}Br_{0.71}$ mixed crystal (× 102), (j) distribution of dislocations in $KCl_{0.15}Br_{0.85}$ mixed crystal (× 102) and (k) distribution of dislocations in pure KBr (× 255).









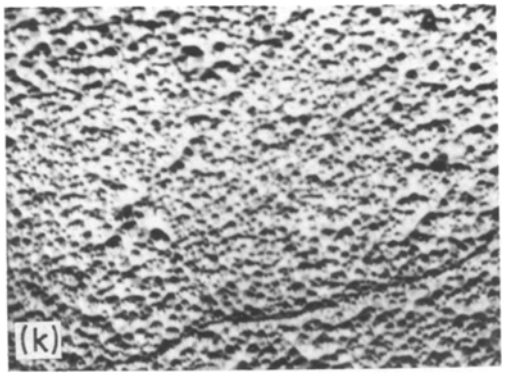


Figure 2 Continued.

Figs 2a to k show the distribution of dislocations in KCl and KBr. All the other photomicrographs show the distribution in mixed crystals. The dislocation distribution studies are carried out on samples cleaved from different places of the crystal. From Figs 2a and k it is clear that the dislocation density in pure components, that is KCl and KBr, is much greater compared with the mixed system and is of the order of $10^6 cm^{-2}$. Figs 2b and c represent the etched surface of mixed crystals $KCl_{0.94}Br_{0.06}$ and $KCl_{0.86}Br_{0.14}$, respectively. They show a network of low-angle grain-boundaries distributed throughout the crystal surface and the density is much lower compared to the end products. The dislocation density is of the order of 46 to $48 \times 10^4 cm^{-2}$ in Fig. 2b and 19 to $21 \times 10^4 cm^{-2}$ in Fig. 2c. Figs 2d and e illustrate the dislocation morphology in mixed crystals $KCl_{0.79}Br_{0.21}$ and $KCl_{0.71}Br_{0.29}$, respectively. A regular array of pits is observed in these crystals. The etch-pit morphology can be seen to be identical in all the samples. The dislocation density is a minimum in the mixed crystal $KCl_{0.79}Br_{0.21}$ and is about 13 to $16 \times 10^4 cm^{-2}$. Figs 2f and g represent the etched surface of mixed crystals $KCl_{0.61}Br_{0.39}$ and $KCl_{0.52}Br_{0.48}$, respectively. The dislocation density here increases and is an average of between 35 and $37 \times 10^4 cm^2$. In these micrographs the network of sub-grain boundaries is not visible and the pits are distributed at random across the crystal surface. Figs 2h, i and j represent the dislocation morphology in the mixed crystals $KCl_{0.41}Br_{0.59}$, $KCl_{0.29}Br_{0.71}$ and $KCl_{0.15}Br_{0.85}$, respectively. Figs 2h, i and j show transverse cleavage bands as a result of fast cleaving. Fig. 3 shows the variation of dislocation density with composition.

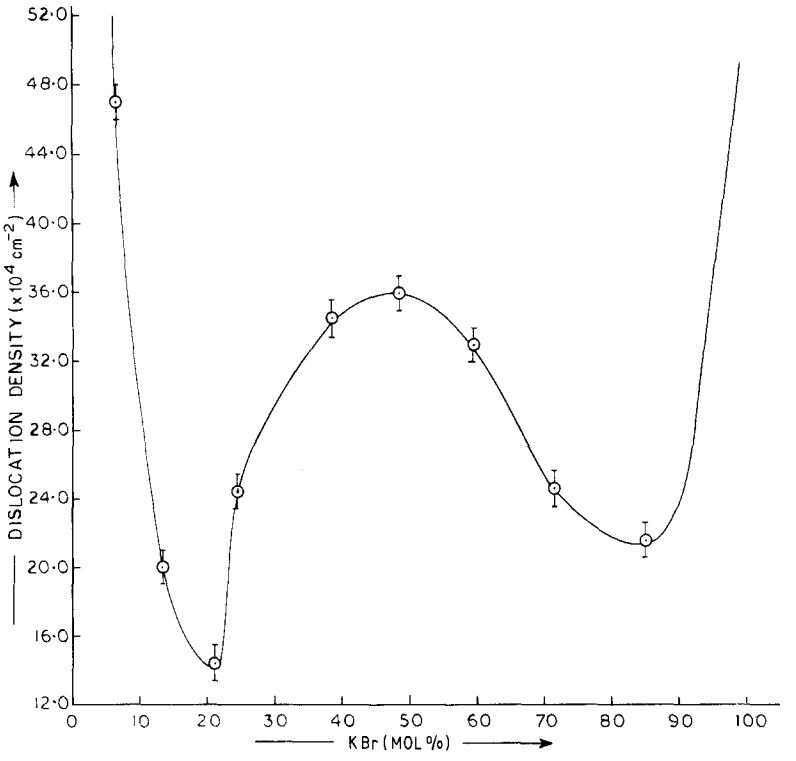


Figure 3 Variation of dislocation density with composition; x-axis represents the concentration of KBr in KCl (mol%); y-axis represents the number of dislocations cm^{-2}.

The Vickers indentation measurements have indicated that the microhardness in KCl–KBr mixed crystals shows a non-linear variation with composition. Mixed crystals show higher values of microhardness compared to the components, the maximum hardness being present in the equimolar composition. On either side of the equimolar composition, the microhardness values show a downward trend towards the two components. The variation of microhardness, H_v, with composition is shown in Fig. 4 which can be seen to be similar to the observations made by many workers [11–13].

4. Discussion

Several workers [11, 12, 14] have in the past observed the density of dislocations to be greater in the mixed crystals than in the end products. They have also observed that the dislocation density has a maximum value for the intermediate compositions and falls on either side towards the two components. The observations presented here for these crystals are entirely different (Fig. 3). The main difference lies in the growing technique. Our main aim was to have a high dislocation density in these crystals but that was obtained only in the pure components (the dislocation densities of KCl and KBr are of the order of $10^6\,cm^{-2}$). In the mixed crystals the dislocation density showed a small increase but was of the same order as that found in crystals grown by the Kyropoulos technique (typically between 10^4 and $10^5\,cm^{-2}$) although all the crystals are grown under identical conditions. A repetition of the process gave the same results. Thus it is concluded that KCl and KBr crystals with very large dislocation densities can be grown by this method but that the dislocation density of mixed crystals remains unaltered. A detailed study of this project is under consideration.

The dislocation density was very great in the end products. It decreased from KCl and became a minimum for the composition $KCl_{0.79}Br_{0.21}$. Increasing the KBr contents still further increased the dislocation density slowly to a maximum value for the intermediate compositions between 38 and 59 mol% KBr in KCl, but this is still quite low compared to the density of end products. The non-linear variation in the microhardness of these mixed crystals agrees with the results of earlier workers [11–13] as is evident from Fig. 4, although the variation of dislocation density with composition is contrary to the observations made earlier in [12, 14]. Although the dislocation density of KCl and KBr crystals is very great their microhardness values remain the same, i.e. 9.41 kg

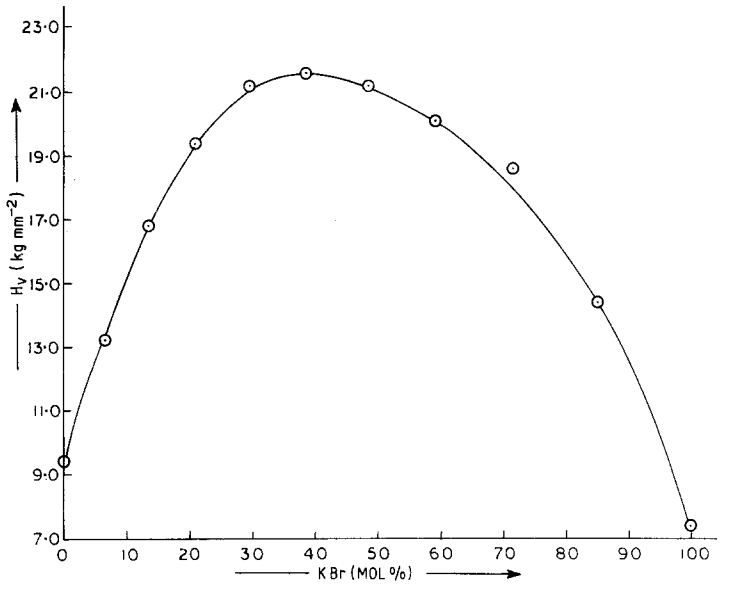


Figure 4 Variation of microhardness with composition; x-axis represents the concentration of KBr in KCl (mol%); y-axis represents microhardness values in kg mm^{-2}.

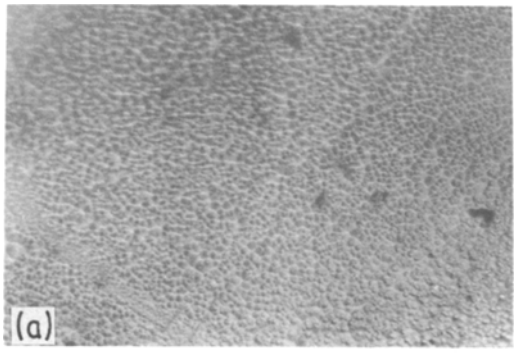
mm^{-2} and 7.43 kg mm^{-2}, respectively [13]. The mixed crystals having dislocation densities much lower than either the KCl or KBr crystals, have microhardness values that are much greater than those for the KCl and KBr crystals. The mixed crystal having composition $KCl_{0.61}Br_{0.39}$ has the maximum hardness value of 21.61 kg mm^{-2} which is slightly more than twice that of the hardness of KCl. This composition has a dislocation density of the order of 33 to 34 x 10^4 cm^{-2} which is much lower than the dislocation density of both KCl and KBr which have values of the order of 10^6 cm^{-2}. The hardness values and their corresponding dislocation densities for various crystal compositions are given in Table I. These observations reveal that microhardness values of mixed crystals are not dependent on the dislocation density. To establish this point, the hardness of crystals having different dislocation densities have been measured. Fig. 5a, b and c shows the distribution of dislocations in a pure KCl crystal. Anisotropic effects in the hardness measurements were taken into consideration. All the crystals were cleaved in the ⟨100⟩ direction. The crystal was aligned and indented in such a way that the pyramid impression had its sides along ⟨110⟩ direction. This is evident in Fig. 6 which shows an etched crystal of KCl with etch-pits orientated along the ⟨100⟩ direction illustrating the rosette pattern. From the figure it is clear that the sides of the impression are inclined at an angle of 45° to the sides of the etch-pits, that is in the ⟨110⟩ direction.

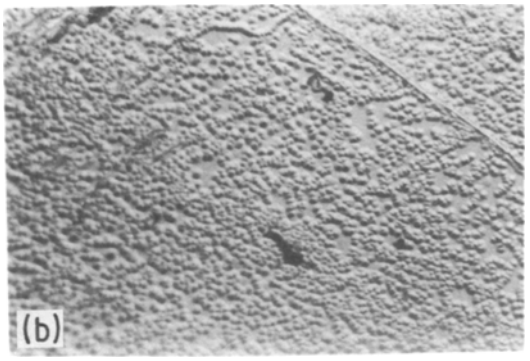
TABLE I Microhardness values and the corresponding dislocation density results

Hardness H_v (kg mm^{-2})	Dislocation density (× 10^4)	Composition
9.4	> 100	KCl
13.2	47	$KCl_{0.94}Br_{0.06}$
16.9	20	$KCl_{0.86}Br_{0.14}$
19.4	14.5	$KCl_{0.79}Br_{0.21}$
21.2	24.5	$KCl_{0.71}Br_{0.29}$
21.6	34.5	$KCl_{0.61}Br_{0.39}$
21.2	36	$KCl_{0.52}Br_{0.48}$
20.1	33	$KCl_{0.41}Br_{0.59}$
18.6	24.5	$KCl_{0.29}Br_{0.71}$
14.4	21.5	$KCl_{0.15}Br_{0.55}$
7.4	> 100	KBr

Hardness has been explained in terms of the resistance to the movement of dislocation during deformation. When an indentation is made, fresh dislocations move from the point of indentation [15]. These fresh dislocations created may have to move through a greater number of dislocations in mixed crystals since they have a greater dislocation density. These dislocations offer a resistance to the fresh dislocations due to interaction which causes an increase in the hardness. Using this model, earlier workers [12, 13] observed a correlation between dislocation density and microhardness in mixed crystals. However, according to our observations there appears to be no such correlation between dislocation density and microhardness.

The presence of two kinds of anions of different ionic radii in a KCl–KBr solid solution act as





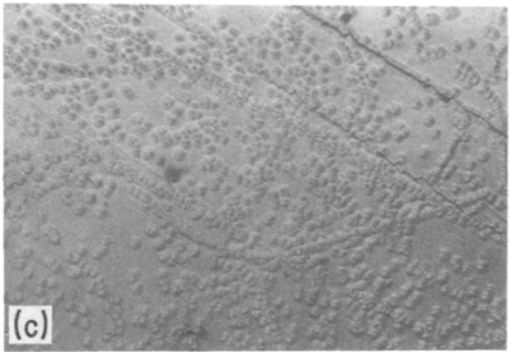


Figure 5 Variation in the dislocation density of a pure KCl crystal (× 190).

point sources of constriction and expansion and their random distribution produces a fluctuating stress field on the slip plane. An analytical model of the hardening mechanism was proposed by Kataoka and Yamada [16]. On the basis of the elastic interaction (size misfit) between an edge dislocation and solute atoms they have calculated the value of critical resolved shear stress. With the help of this model Shrivastava [17] has computed the extra hardness in mixed crystals from the amount of hinderance produced in the transport of ion-pairs in the fluctuating stress field due to the random distribution of anions of different sizes which behave like point source of expansion and constriction in the mixed crystal lattice. In the light of these models, the experimental observations reported here on the increased hardness of mixed crystals can very well be attributed to this size misfit in KCl–KBr solid solution rather than to the density of dislocations present in various compositions.

Figure 6 Etched surface of a pure KCl crystal with rosette (× 78).

5. Conclusions

The dislocation density and microhardness are measured for various compositions of KCl–KBr solid solutions.

(a) The variation of dislocation density with composition is found to be random and, for the pure components, the dislocation density is very high.

(b) The concentration dependence of microhardness is exhibited by a parabolic curve.

(c) Increased hardness of mixed crystals is attributed to the size misfit in KCl–KBr solid solutions rather than to the density of dislocations present in different compositions.

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