

Systematic hardness measurements on $\text{CsCl}_x\text{Br}_{(1-x)}$ and $\text{NH}_4\text{Cl}_x\text{Br}_{(1-x)}$ mixed crystals

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Abstract. Vickers hardness measurements have been made on polycrystalline blanks of $\text{CsCl}_x\text{Br}_{(1-x)}$ and single crystals of $\text{NH}_4\text{Cl}_x\text{Br}_{(1-x)}$. The composition dependence of hardness is highly nonlinear in both systems and follows an empirical model that includes a lattice contribution and a disorder contribution. The Gilman–Chin parameter (H/C_{44}) has been calculated and its significance discussed.

Keywords. Hardness; cesium halide mixed crystals; ammonium halide mixed crystals.

1. Introduction

The formation of mixed crystals with different proportions of two pure substances provides a means of having a new set of crystals with physical properties that are intermediate between those of the end-members. The physical properties of several mixed crystal systems were reviewed by Hari Babu and Subba Rao (1984) and Sirdeshmukh and Srinivas (1986).

The hardness is an important crystal property as it is a measure of the mechanical strength of a crystal. The reviews of physical properties of mixed crystals referred to above reveal two features. Firstly, the composition dependence of hardness is a highly nonlinear function of their composition. This behaviour becomes important in device materials; if the pure material has low mechanical strength, its strength can be increased by mixed crystal formation. Sirdeshmukh and Srinivas (1986) classified physical properties of mixed crystals on the basis of their composition dependence. According to this classification, if the composition dependence of a property is highly nonlinear, the property is affected by disorder caused by the difference in the sizes of the two mixing ions; hardness comes under this category. Secondly, while there is considerable work on the hardness of mixed crystals with NaCl structure, there is no work on the hardness of mixed crystals with CsCl structure.

The purpose of the present paper is to report the results of systematic hardness measurements on two mixed crystal systems with CsCl structure viz. $\text{CsCl}_x\text{Br}_{(1-x)}$ and $\text{NH}_4\text{Cl}_x\text{Br}_{(1-x)}$.

2. Experimental

2.1 Preparation of materials

Single crystal growth of cesium halides is difficult. Single crystals of pure cesium halides are commercially available, though they are very expensive. Cesium halide mixed crystals are not available commercially. Hence, small-sized polycrystalline blanks of the mixed crystals were prepared by melting mixtures of requisite quantities of CsCl and CsBr following the method described in a recent paper (Sirdeshmukh *et al* 2001). Ammonium halides cannot be grown by melting as they decompose, nor can they be grown from pure aqueous solution since they form dendrites. However, they can be grown as single crystals with a cubic morphology from aqueous solution to which urea is added (10% by weight).

2.2 X-ray characterization

The CsCl–CsBr mixed crystals were characterized by X-ray diffraction. Small portions of the blanks were crushed into fine powder. The powder diffractograms were recorded on a Jeol JDX-8P diffractometer fitted with a NaI(Tl) scintillation counter using filtered Cu radiation. The diffractograms revealed complete miscibility. As in the case of studies of pure cesium halides (Sirdeshmukh *et al* 2001), back-reflection X-ray photographs of the blanks obtained in the Laue geometry showed spotty powder lines superposed with a few intense spots indicating complete polycrystallinity and a slight degree of preferred orientation. Powder diffractograms of the NH_4Cl – NH_4Br mixed crystals showed single-phase patterns indicating complete miscibility.

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2.3 Composition determination

The composition determination of each sample was determined by potentiometric titration with an accuracy of 1%. In the $\text{CsCl}_x\text{Br}_{(1-x)}$ system, we could get mixed crystals covering the entire range of compositions. In the $\text{NH}_4\text{Cl}_x\text{Br}_{(1-x)}$ system, however, mixed crystals could be obtained in the ranges $x = 0-0.4$ and $0.7-1$. Several attempts were made to grow crystals in the intermediate range $x = 0.4-0.7$ by having growth solutions with these compositions. But the actual composition of the resulting crystals was outside this range.

2.4 Hardness measurements

Microhardness measurements were made with the help of a Leitz-Wetzlar Miniload Hardness Tester fitted with a diamond Vickers pyramidal indenter. The microhardness was calculated from the relation

$$H_V = 1854.4P/d^2, \quad (1)$$

where P is the load in g, d the length of the diagonal of the indentation impression in μm and H_V the Vickers hardness in kg/mm^2 . Measurements were made at several loads in the range 5–100 g. The hardness calculated from (1) showed a variation with load. A typical load vs hardness plot is shown in figure 1. The causes of the load dependence and the procedure for applying a correction have been discussed in detail in an earlier paper (Subhadra *et al* 2000). In the case of the polycrystalline blanks, measurements were repeated by changing the orientation of the sample surface with respect to the indenter to take care of the preferred orientation and the mean value was taken. The accuracy of the final corrected H_V value is about 10%.

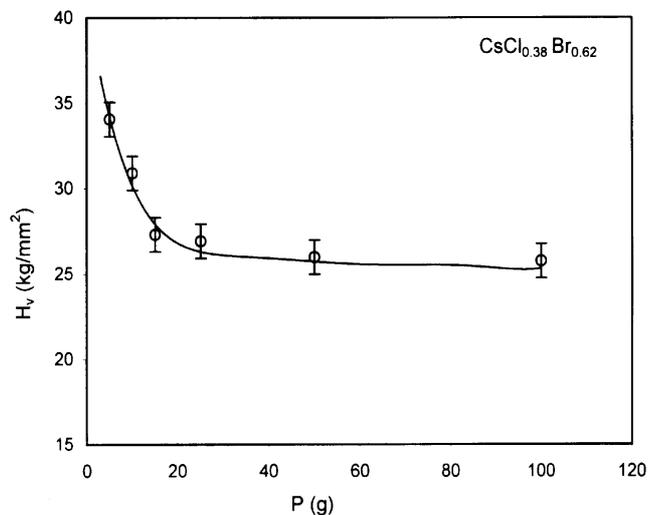


Figure 1. Typical plot of load vs hardness.

3. Results and discussion

3.1 Hardness of pure and mixed crystals

The values of the hardness of pure CsCl, CsBr and their mixed crystals and also of NH_4Cl , NH_4Br and their mixed crystals are given in table 1 along with values reported by earlier workers. It can be seen that the present values for the pure crystals are in fair agreement with values from other sources.

Mixed crystals invariably have higher hardness than the corresponding pure crystal. This behaviour is referred to as 'solid solution hardening' (Plendl 1971). We are not aware of a case where this trend is not followed.

The trends in composition dependence of hardness of mixed crystals studied in this work can be seen in figures 2 and 3. It is observed that the composition dependence is highly nonlinear with values for some of the intermediate compositions exceeding the values for the pure end members. This is similar to the composition dependence of hardness of several mixed crystals with the NaCl structure (Bhimasankaram 1974; Subba Rao and Hari Babu 1978; Thirmal Rao and Sirdeshmukh 1991). In the case of the $\text{CsCl}_x\text{Br}_{(1-x)}$ system, the hardness increases slowly with composition rising to a maximum value in the equimolar region which is about 20–30% of the value for the end members. On the other hand, in the $\text{NH}_4\text{Cl}_x\text{Br}_{(1-x)}$ system, the increase is very steep, the value for the equimolar composition being ten times the values of the pure crystals.

Sirdeshmukh and Srinivas (1986) classified the physical properties of mixed crystals on the basis of their composition dependence. According to them highly nonlinear composition dependence is exhibited in properties which are affected by the disorder caused by the

Table 1. Values of H_V (kg/mm^2) and ΔH_V (kg/mm^2) for $\text{CsCl}_x\text{Br}_{(1-x)}$ and $\text{NH}_4\text{Cl}_x\text{Br}_{(1-x)}$ mixed crystals.

$\text{CsCl}_x\text{Br}_{(1-x)}$			$\text{NH}_4\text{Cl}_x\text{Br}_{(1-x)}$		
x	H_V	ΔH_V	x	H_V	ΔH_V
0	18.5	0	0	2.13	0
	18.47 ^a			2.4 ^b	
0.1	20.8	2.29	0.085	16.45	6.4
0.18	22.19	3.63	0.13	17.05	9.7
0.29	22.35	4.82	0.29	22.48	20.7
0.38	25.7	5.28	0.33	25.02	23.1
0.47	25.6	5.34	0.38	28.25	25.6
0.58	25.0	4.93	0.73	29.00	27.7
0.69	25.0	4.07	0.78	28.73	24.9
0.78	23.5	3.1	0.85	29.96	19.3
0.89	22.2	1.66	0.93	18.18	10.3
1.0	21.8	0	0.96	16.87	6.2
	21.84 ^a		1.0	3.31	0
				2.5 ^b	

^aSirdeshmukh *et al* (2001); ^bPratap and Hari Babu (1980).

difference in sizes of the mixing ions. Hardness belongs to this category. The co-existence of two ions of different sizes in a mixed crystal in place of a single ion in a pure crystal results in a disorder which causes an increase in dislocation density in the mixed crystals. The evidence of increased dislocation density in mixed crystals has

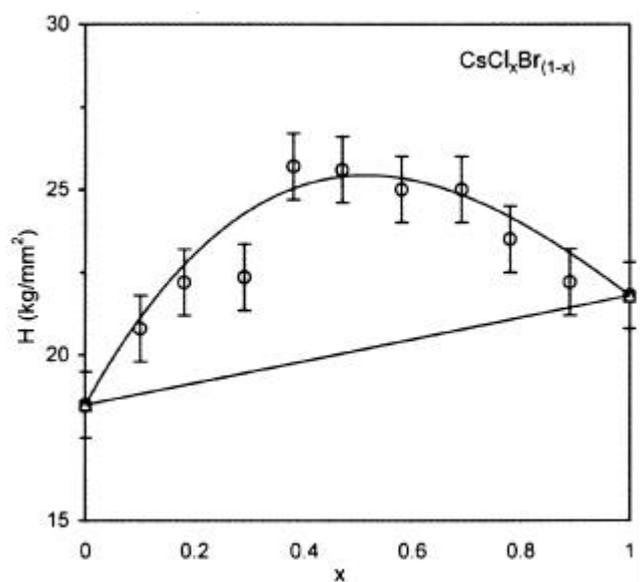


Figure 2. Plot of Vickers hardness (H_V) vs mole fraction, x , for the $\text{CsCl}_x\text{Br}_{(1-x)}$ system.

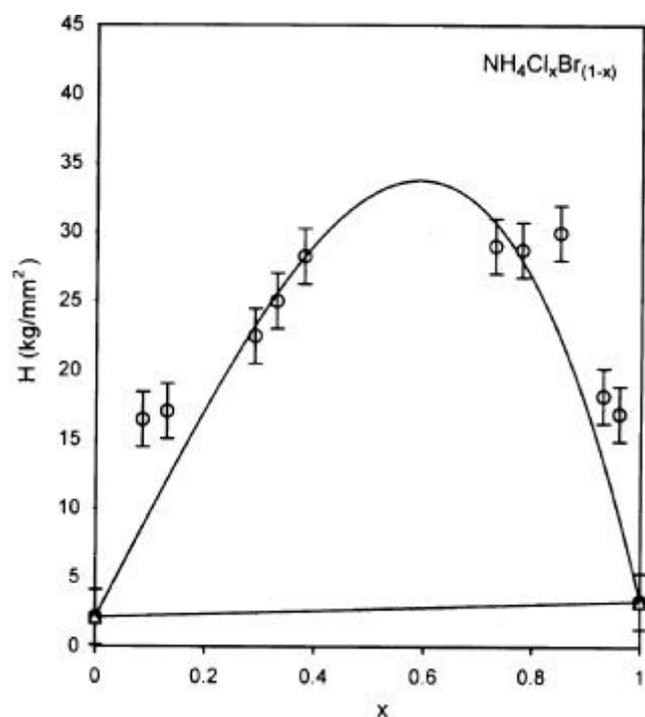


Figure 3. Plot of Vickers hardness (H_V) vs mole fraction, x , for the $\text{NH}_4\text{Cl}_x\text{Br}_{(1-x)}$ system.

been established by Arends *et al* (1965), Hari Babu *et al* (1975) and Hussain *et al* (1988) by the etch-pit method. The increased dislocation–dislocation interaction results in enhanced hardness. Subba Rao and Hari Babu (1978) proposed that there are two contributing factors to the hardness of mixed crystals related to (i) the lattice and (ii) the disorder. The lattice contribution is additive (linear) in nature, whereas the contribution due to disorder is dependent on the product of the concentrations of the two mixing ions. Thus, they proposed that the hardness of a mixed crystal may be expressed as

$$H_{MC} = H_L + kx(1-x), \quad (2)$$

where H_{MC} is the hardness of the mixed crystal, H_L the value obtained from the additivity rule (from the linear plot between the values for the two end members), x and $(1-x)$ the concentrations of the two mixing ions and k a constant. Denoting the difference between the hardness of the mixed crystal (H_{MC}) and the value obtained by the additivity rule (H_L) for any composition by ΔH , (2) may be written as

$$\Delta H = H_{MC} - H_L = kx(1-x). \quad (3)$$

The plots of ΔH vs x for $\text{CsCl}_x\text{Br}_{(1-x)}$ and $\text{NH}_4\text{Cl}_x\text{Br}_{(1-x)}$ systems are shown in figure 4. The values of k can be obtained by substituting the experimental value of ΔH for a chosen concentration in (3). The values of k for the two systems are shown in table 2 along with values for a few systems with NaCl structure. While the present values are of the same order as those for the mixed crystals with NaCl structure, the value for the NH_4Cl – NH_4Br system is the largest. It may be mentioned that a rigorous derivation

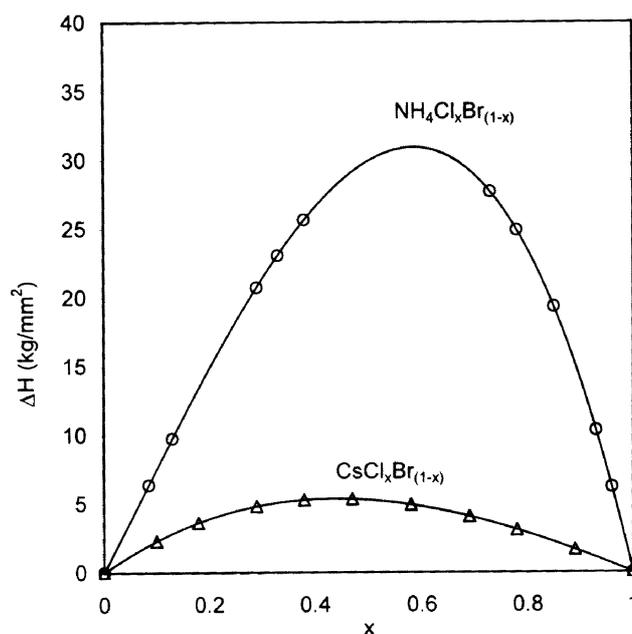


Figure 4. Plots of ΔH_V vs x for the $\text{CsCl}_x\text{Br}_{(1-x)}$ and $\text{NH}_4\text{Cl}_x\text{Br}_{(1-x)}$ systems.

Table 2. Values of constant k in (3).

System	k (kg/mm ²)	Reference
NaCl–NaBr	96	Bhimasankaram (1974)
KCl–KBr	53	Subba Rao and Hari Babu (1978)
KBr–KI	83	Subba Rao and Hari Babu (1980)
RbCl–RbBr	55	Thirnal Rao and Sirdeshmukh (1991)
RbBr–RbI	76	Kumaraswamy (1996)
KI–RbI	24	Geeta Krishna (1997)
CsCl–CsBr	22	Present work
NH ₄ Cl–NH ₄ Br	120	Present work

Table 3. Gilman–Chin parameter (H_V/C_{44}) for some pure cesium and ammonium halides and for NH₄Cl _{x} Br_(1- x) mixed crystals. Values in parenthesis are from Geeta Krishna (1997).

Cesium halides		NH ₄ Cl _{x} Br _(1-x)	
Crystal	H_V/C_{44}	x	H_V/C_{44}
CsCl	0.03 (0.03)	0	0.004 (0.003)
CsBr	0.02 (0.02)	0.2	0.025
		0.4	0.041
		0.6	0.045
		0.8	0.033
		1.0	0.003 (0.003)

for an equation similar to (2) for mixed crystals with NaCl structure has been given by Shrivastava (1980) based on the theory of dislocations. It is not possible to extend the derivation straightaway to mixed crystals with CsCl structure.

3.2 The Gilman–Chin parameter

Gilman (1973) showed that the ratio (H/C_{44}) is constant for the alkali halides with NaCl structure, C_{44} being the shear elastic constant. Chin (1975) evaluated this ratio for a large number of crystals and showed that the ratio takes definite values for crystal groups having different bond types. In particular, he showed that the value of this ratio is ~ 0.01 for ionic crystals and ~ 0.1 for covalent crystals. Sirdeshmukh *et al* (1995) extended these calculations to a large number of crystals with NaCl structure and showed that for ionic crystals this ratio has values in the range 0.01–0.03. Further, they termed this ratio the ‘Gilman–Chin parameter’.

Sirdeshmukh *et al* (1995) did not consider crystals with the CsCl structure. The Gilman–Chin parameter for some cesium halides and ammonium halides were evaluated by Geeta Krishna (1997) using the literature values of hardness and elastic constants. We have evaluated the values of the Gilman–Chin parameter for CsCl, CsBr,

NH₄Cl and NH₄Br using our values of H_V . Further, since the elastic constants for the NH₄Cl–NH₄Br mixed crystals are available (Garland *et al* 1979), we have also extended these calculations to the ammonium halide mixed crystals. For this purpose, the H_V and C_{44} values for chosen compositions were read off from smooth plots between these quantities and the composition. This could not be done for the cesium halide mixed crystals for lack of data on elastic constants. These results are given in table 3. The following features deserve to be noted. The Gilman–Chin parameter has values ~ 0.02 for the cesium halides; this is within the range of values given by Sirdeshmukh *et al* (1995) for ionic crystals. On the other hand, for the ammonium halides, the value of the parameter is ~ 0.004 . This value is too low and is, in fact, the lowest value to be reported for any crystal. The cause of this anomalously low value is not clear. The composition dependence of the Gilman–Chin parameter is highly nonlinear. The more interesting feature is that the values of the Gilman–Chin parameter for the mixed crystals are of the order of 0.04 which is close to the upper limit of the range of values given by Sirdeshmukh *et al* (1995) for ionic crystals.

4. Conclusions

Polycrystalline blanks of CsCl _{x} Br_(1- x) system were prepared by melting and slow cooling. Single crystals of NH₄Cl _{x} Br_(1- x) were prepared by slow evaporation of aqueous solutions to which urea was added. The mixed crystals were characterized by X-ray diffraction and their compositions were determined by potentiometric titration. Vickers hardness measurements were made. It is observed that the composition dependence is highly nonlinear with values of the intermediate compositions exceeding values of the pure crystals. The observed composition dependence is qualitatively explained in terms of a lattice contribution and a disorder contribution. The Gilman–Chin parameter (H/C_{44}) has been evaluated for the pure and mixed crystals and its significance discussed.

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