

Systematic hardness measurements on mixed and doped crystals of rubidium halides

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Abstract. Efforts are made to improve the hardness of rubidium halide crystals by (i) solid solution hardening and (ii) impurity hardening. Systematic microhardness measurements have been made on rubidium halide mixed crystals (RbBr–RbI and KI–RbI) and rubidium halide crystals doped with Sr^{2+} ions. The composition dependence of the hardness of mixed crystals follows the law $\Delta H_V = K x (1-x)$, where ΔH_V is the enhancement in hardness, K a constant and x and $(1-x)$ the concentrations of the first and second component of the mixed crystals, respectively. The hardness of doped crystals increases with the concentration C of the dopant according to the law, $\Delta H_V = k C^m$, where k and m are constants. The relative efficacy of the two methods of hardening is discussed.

Keywords. Hardness; rubidium halide mixed crystals; doped rubidium halide crystals.

1. Introduction

Alkali halide crystals have several practical applications viz. as radiation detectors, as X-ray and neutron monochromators, as infrared optical components and also as laser host materials (Sirdeshmukh *et al* 2001a).

A physical property that limits the utility of alkali halides as device materials is their low hardness. Armington *et al* (1973) discussed two methods of improving the hardness of alkali halides: (i) solid solution hardening and (ii) impurity hardening. The hardness of several alkali halide mixed crystals is reviewed by Hari Babu and Subba Rao (1984). Chin *et al* (1973) studied the effect of divalent impurities (doping) on the hardness of sodium and potassium halides.

The rubidium halides have useful infrared transmission characteristics and have, recently, been found (Thomas *et al* 1994) to be efficient X-ray information storage sensors. Earlier studies from this laboratory (Thirnal Rao and Sirdeshmukh 1991) have shown that among the alkali halides with NaCl structure, for which hardness values are known, the rubidium halides have the lowest hardness. This paper reports results of hardness measurements aimed at improving the hardness of rubidium halide crystals both by solid solution hardening and impurity hardening. The mixed crystal systems chosen for this study are $\text{RbBr}_x\text{I}_{(1-x)}$ and $\text{K}_x\text{Rb}_{(1-x)}\text{I}$ and the impurity chosen for doping is Sr^{2+} .

2. Experimental

2.1 Crystal growth and characterization

Single crystals were grown by using a minifurnace described in detail elsewhere (Srinivas *et al* 1999). For the mixed crystals, the two components were taken in the required proportion. For growing Sr^{2+} doped crystals, different amounts of $\text{Sr}(\text{NO}_3)_2$ were added to the rubidium halides before melting.

The solidified ingot yielded single crystals with several mm linear dimensions. Their excellent cleavage itself was an evidence of single crystallinity. In addition, X-ray Laue photographs were obtained which showed spots with the expected distribution. X-ray powder diffractograms showed that the mixed crystals had a single phase.

Different techniques were employed to determine the compositions. The composition of the $\text{RbBr}_x\text{I}_{(1-x)}$ mixed crystals was determined by the method of potentiometric titration. In the case of the $\text{K}_x\text{Rb}_{(1-x)}\text{I}$ mixed crystals, the lattice constants were determined from the X-ray diffractograms and these were used to estimate the composition assuming Vegard's law (Bosch *et al* 1972). To determine the concentration of Sr^{2+} in the doped crystals, the technique of atomic absorption spectroscopy was used and a 902 GBC double beam atomic absorption spectrometer was employed.

2.2 Vickers microhardness measurement

Microhardness measurements were made with the help of a Leitz–Wetzlar Miniload Hardness Tester fitted with a

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Vickers diamond pyramidal indenter. The Vickers hardness (H_V) was calculated from the relation

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

where P is the applied load and d the length of the diagonal of the indentation mark. With P in g and d in μm , the units of H_V turned out to be kg/mm^2 . Indentations were carried out at different loads in the range 5–50 g. A load dependence of hardness was observed which was corrected by the procedure discussed by Sirdeshmukh et al (2000, 2001b). The method of error evaluation was given in a recent paper (Sirdeshmukh et al 2002).

3. Results and discussion

3.1 Hardness of mixed crystals

The Vickers microhardness values for the $\text{RbBr}_x\text{I}_{(1-x)}$ and $\text{KBr}_x\text{I}_{(1-x)}$ mixed crystals are given in table 1 for several compositions and are also shown in figure 1. In both cases the microhardness shows a nonlinear composition dependence with positive deviations from linearity. In the intermediate composition range, the hardness of mixed crystals is larger than the values of the end members.

We define ΔH_V as the deviation of the measured hardness of a mixed crystal from the value expected from additive behaviour. These ΔH_V values are included in table 1 and are also shown in figure 2. The ΔH_V vs x curves are in the form of inverted parabolas. The two mixed crystal systems studied in this work and also the RbCl-RbBr system studied earlier (Thirnal Rao and Sirdeshmukh 1991) follow the equation

$$\Delta H_V = Kx(1-x), \quad (2)$$

where K is a constant. The values of K obtained by fitting the experimental data to (2) are given in table 2.

Table 1. Values of the Vickers hardness (H_V in kg/mm^2) and the deviation (ΔH_V in kg/mm^2) of the observed values from the additive values for the mixed crystals (error in H_V , 0.6 kg/mm^2).

$\text{RbBr}_x\text{I}_{1-x}$			$\text{K}_x\text{Rb}_{1-x}\text{I}$		
x	H_V	ΔH_V	x	H_V	ΔH_V
0	6.01	0	0	6.01	0
0.27	21.33	14.2	0.1	10.1	4.4
0.39	23.36	16.8	0.19	11.5	5.5
0.48	25.22	17.9	0.33	13.23	6.7
0.59	25.27	18	0.4	13.37	6.8
0.69	23.40	16.2	0.5	13.44	6.7
0.78	22.01	13	0.64	12.41	5.8
1	8.10	0	0.74	12.73	4.7
			0.87	10.30	2.9
			1	7.00	0

From (2), it can be seen that the maximum value of ΔH_V occurs at $x = 0.5$ and $(\Delta H_V)_{\text{max}} = 0.25 K$. Thus, K is a measure of the maximum hardening. In view of this significance of K , we may conclude from the K values given in table 2 that addition of RbI has a greater hardening

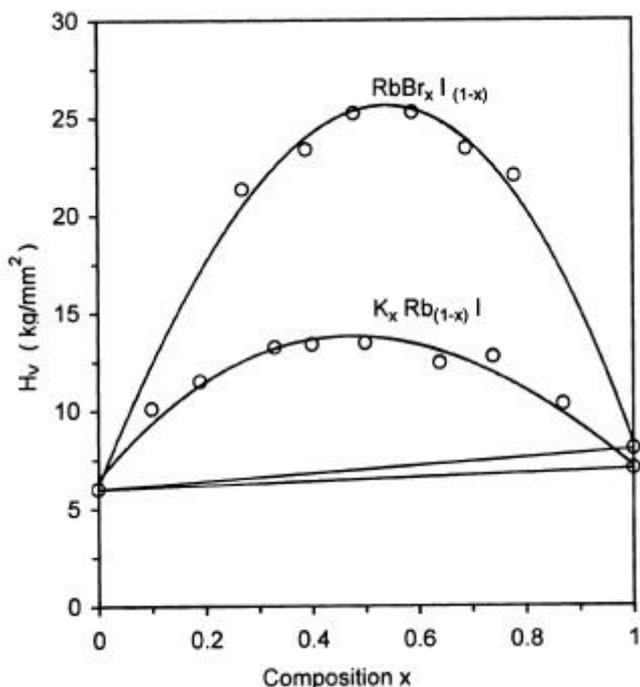


Figure 1. Plot of hardness, H_V , against the composition x for the mixed crystals.

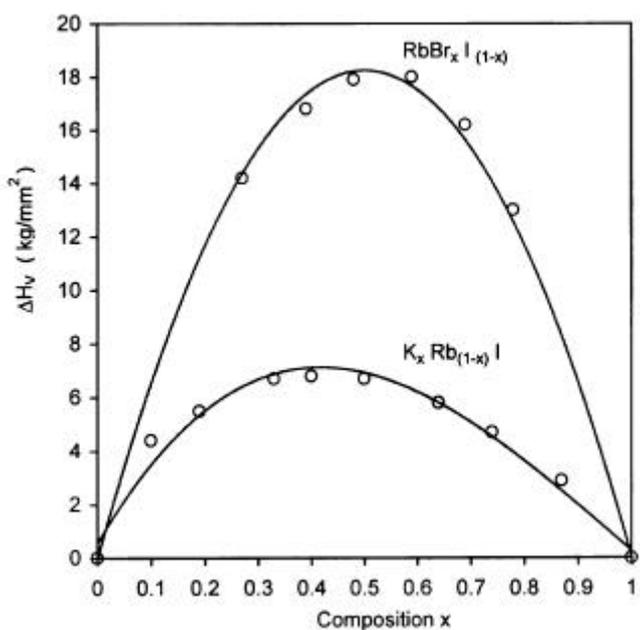


Figure 2. Plot of ΔH_V vs composition x for the mixed crystals.

effect on RbBr than the addition of RbCl. Similarly addition of RbBr has a far greater hardening effect on RbI than the addition of KI.

Sirdeshmukh and Srinivas (1986) pointed out in their review paper that the replacement of an ion by another ion of different size (the "size effect") in mixed crystals results in a highly non-linear composition variation in properties like the Debye–Waller factor, the dislocation density and hardness. Subba Rao and Hari Babu (1978) pointed out that in a mixed crystal, lattice interactions as well as the disorder due to size effect contribute to the hardness. On the other hand, Shrivastava (1980) considered the effect of the presence of substituted ions on the dislocation mobility and on the hardness. Both these approaches result in an equation exactly similar to (2) for the hardness of a mixed crystal in terms of its composition.

The experimental observations regarding the hardening of RbBr and RbI mixed crystals can be discussed qualitatively in terms of (2). The ionic radii of K^+ , Rb^+ , Cl^- , Br^- and I^- are 1.51, 1.65, 1.65, 1.80 and 2.01 (Å), respectively (Sirdeshmukh *et al* 2001a). In RbCl–RbBr mixed crystal the size difference is 0.15 Å whereas in RbBr–RbI, it is 0.21 Å. Since hardening is due to the size effect, it is more in the latter than in the former. Similarly, in RbI–KI the size difference is 0.14 Å whereas in RbI–RbBr it is 0.21 Å. Again, the hardening is larger in the latter.

3.2 Hardness of doped crystals

There are several earlier studies on the hardness of alkali halide crystals doped with divalent ions. Dryden *et al* (1965) measured the critical resolved shear stress (which is related to the hardness) of NaCl doped with Ca^{2+} and Mn^{2+} , KCl doped with Ca^{2+} and Ba^{2+} and LiF doped with Mg^{2+} . In all these cases they found an increase in hardness proportional to $C^{2/3}$, where C is the molar concentration of the impurity. Chin *et al* (1973) measured the microhardness of NaCl, NaBr, KCl and KBr doped with Ca^{2+} , Sr^{2+} and Ba^{2+} dopants. They observed that the increase in hardness (i) is proportional to $C^{1/2}$ and (ii) is independent of the host lattice. There is no reported study of the effect of doping on the hardness of the rubidium halides. In the present study the effect of addition of Sr^{2+}

ions on the hardness of rubidium halides is studied. The results are given in table 3 and are also shown in figure 3. It is seen that the hardness increases with increase in concentration C of the dopant. The results were fitted to the relation

$$\Delta H_V = k C^m, \quad (3)$$

where ΔH_V is the enhancement in hardness and k and m are constants; values of k and m are given in table 4. On comparing the present results with the results of Chin *et al* (1973) on the hardness of sodium and potassium halides, it is noted that the observed value of m (~ 0.6) is close to the value of 0.5 obtained by Chin *et al* (1973) and, theoretically, by Gilman (1974). On the other hand, the hardening is dependent on the host lattice increasing in the sequence RbI–RbBr–RbCl, unlike in the case of the sodium and potassium halides.

Fleischer (1962) developed a model to account for the hardening of alkali halides by divalent impurities. The divalent impurities are strongly attracted by positive ion vacancies resulting in large tetragonal distortions. A moving dislocation experiences a force due to the distortion. The resulting expression for the flow stress (which is a measure of the hardening) is proportional to $C^{1/2}$, where C is the concentration of the impurity. Considering the approximations in his model, Fleischer admit-

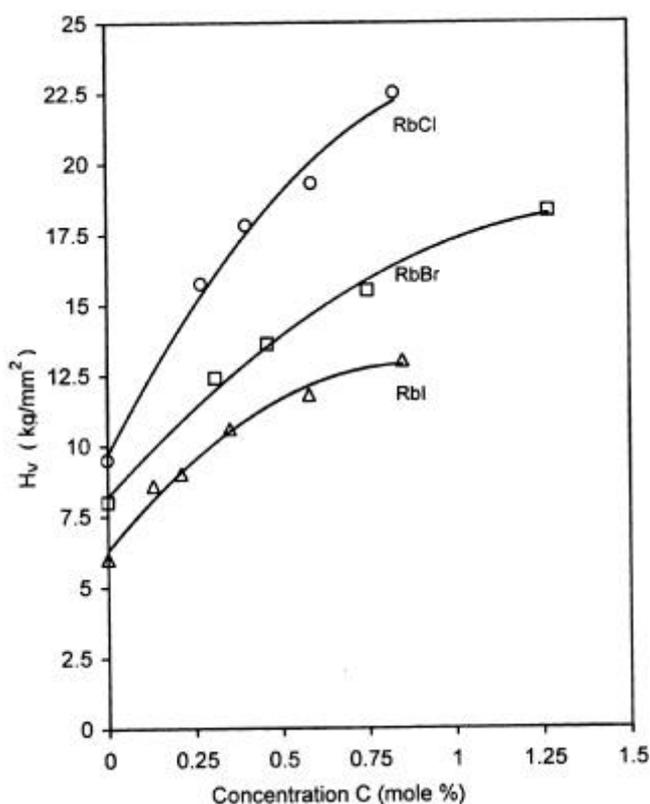


Figure 3. Plot of H_V as a function of concentration, C of Sr^{2+} ions in the doped crystals.

Table 2. Values of the constant, K (in kg/mm^2) in (2).

System	K
RbCl–RbBr*	55
RbBr–RbI	73
KI–RbI	27

*From Thirimal Rao and Sirdeshmukh (1991).

Table 3. Values of Vickers hardness (H_V) for the rubidium halides at different concentrations of C of the Sr^{2+} ions (error in H_V , 0.6 kg/mm²).

Crystal	C (mole%)	H_V (kg/mm ²)
RbCl	0	9.50
	0.27	15.75
	0.40	17.82
	0.59	19.30
	0.83	22.50
RbBr	0	8.10
	0.31	12.40
	0.46	13.61
	0.75	15.52
	1.27	18.30
RbI	0	6.01
	0.13	8.58
	0.21	9.00
	0.35	10.61
	0.58	11.81
	0.85	13.01

Table 4. Values of the constants, k (in kg/mm²) and m in (3).

Crystal	k	m
RbCl	14.36 ± 1.00	0.63 ± 0.05
RbBr	8.96 ± 1.00	0.60 ± 0.05
RbI	8.15 ± 1.00	0.62 ± 0.05

ted that the values of hardening predicted by his theory can be accurate “to within no better than a factor of two”.

Gilman (1974) criticized Fleischer’s model and proposed a theory in which hardening is associated with the change in electrostatic energy that occurs when a moving dislocation shears a divalent ion–cation vacancy complex. According to this model the hardening is proportional to $BC^{1/2}$ where the hardening coefficient, B , is given by

$$B = 4.7e^2(\epsilon a^4)^{-1}, \quad (4)$$

here e is the electron charge, ϵ the static dielectric constant and a the lattice constant of the host crystal. As Gilman’s immediate interest was in providing an explanation for the results of Chin *et al*, he adopted the unusual procedure of assuming average values for the static dielectric constant and the lattice constants of the four alkali halide crystals (NaCl, NaBr, KCl, KBr) and obtained an average value for B which was in fair agreement with the experimental value.

Chin *et al* have concluded that the impurity hardening observed by them in their study of sodium and potassium

halides is independent of the host crystal. However, a close look at their diagrams reveals that the data points for each crystal lie on different plots with slightly different slopes which means that the hardening is not altogether independent of the host lattice. Further, calculation of the term $(\epsilon a^4)^{-1}$ for the rubidium halides using individual values for ϵ and a (in Å) from literature (Sirdeshmukh *et al* 2001a) yields values 1.1, 0.96 and 0.73 (all in 10⁻⁴) for RbCl, RbBr and RbI, respectively indicating that the hardening expected from Gilman’s theory is host-dependent increasing in the sequence RbI–RbBr–RbCl. Our results are thus consistent with Gilman’s theory.

3.3 Comparative efficacy of the two methods of hardening

Armington *et al* (1973) pointed out that the optical absorption in the mixed crystals is not different from that in the pure crystals and, on the other hand, doping tends to form precipitates affecting the optical clarity. In the present study, although optical absorption was not measured, visual examination did not reveal any significant difference in the optical clarity of the mixed and doped crystals.

We have succeeded in improving the hardness of rubidium halides by 100–300% by the methods of solution hardening and impurity hardening. With regard to the relative efficacy of the two methods, the hardening is more pronounced in the doped crystals than in the mixed crystals. Thus, for instance, whereas a concentration of 0.1 mole% of Sr^{2+} increases the hardness of RbI by about 40%, the same amount of KI in RbI increases the hardness of RbI by only 10%.

4. Conclusions

Vickers hardness measurements have been made on $RbBr_xI_{(1-x)}$ and $KBr_xI_{(1-x)}$ mixed crystal systems. The composition dependence of hardness is nonlinear and the enhanced hardness, ΔH_V , follows the law: $\Delta H_V = Kx(1-x)$, where K is a constant. The hardness of RbBr is affected more by addition of RbI than the addition of RbCl while the hardness of RbI is affected more by the addition of RbBr than by the addition of KI. This is explained in terms of the relative sizes of the mixing ions. Hardness measurements on Sr^{2+} doped rubidium halides show that there is an enhancement of ΔH_V which follows the law, $\Delta H_V = kC^m$, where C is the concentration and k and m are constants. For a given concentration, the enhancement increases in the sequence RbI–RbBr–RbCl. This is shown to follow from Gilman’s theory of impurity hardening. It is found that impurity hardening is more effective than solid solution hardening.

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