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Microhardness studies in mixed alum crystals

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The microhardness of mixed alum crystals of various compositions, $(NH_4)_{1-x}K_xAl(SO_4)_2$ $12H_2O$, has been determined. It is found that the microhardness varies non-linearly with composition, attaining its highest value for a crystal having nearly equimolar concentration. The observed behaviour is explained using the Kataoka and Yamada model.

1. Introduction

The hardness test has been used for a long time as a simple means of characterizing the mechanical behaviour of metals and minerals. Whenever hardness is of prime importance for a particular requirement, mixed crystals are used, because the microhardness of mixed crystals always exceeds the microhardness of the component single crystals. Smakula *et al.* [1], from their measurements of the microhardness of KCl–KBr mixed crystals, have found that mixed crystals show higher hardness values than the pure components. Similar results were observed by Subba Rao and Hari Babu [2] in KCl–KBr and KCl–KI, Bhimasankaram [3] in NaCl–NaBr, and Subramaniam and Bansigir [4] and Hopkins *et al.* [5] in KCl–KBr mixed crystals.

Ammonium alum, $NH_4 \cdot Al(SO_4)_2 \cdot 12H_2O$, and potassium alum, $K \cdot Al(SO_4)_2 \cdot 12H_2O$, form mixed crystals in all proportions. In this work, an attempt has been made to study the variation of microhardness of mixed alum crystals, $(NH_4)_{1-x}K_xAl(SO_4)_2 \cdot 12H_2O$, with composition and to see whether mixed crystals of these two alums show a similar behaviour as shown by mixed crystals of KCl–KBr, NaCl–NaBr and KCl–KI, in which the microhardness of mixed crystals having nearly equimolar composition is two or three times the microhardness of component single crystals. Microhardness of mixed alum crystals has been measured using the indentation technique. A theoretical analysis of the experimental results has also been included.

2. Experimental procedure

Mixed crystals of ammonium–potassium alums were grown from aqueous solution by an evaporation technique [6], at a constant temperature of 27° C, using GR grade chemicals as starting materials. All the crystals of varying compositions were grown simultaneously in the same environment so as to meet identical growth conditions. Transparent single crystals with (111) as-grown planes were thus obtained.

Microhardness measurements were performed at room temperature, by the indentation microhardness tester provided with the Universal Research Microscope NU2 (Carl Zeiss Jena) using loads of 20 g, on the as-grown (111) planes of the mixed alum crystals. Loads higher than 20 g produce cracks on the surface of the crystals. The time of indentation was maintained at 10 sec for each crystal. As many as five crystals were selected for each composition and at least ten indentations were made on each crystal. The diagonals of the indentation marks were measured with the help of a calibrated micrometer attached to the eye-piece of the microscope. The length of the diagonal was obtained by plotting a Maxwellian distribution. This value of the diagonal of indentation was used to calculate the microhardness, H_v (kg mm^{-2}), using the expression:

$$H_v = \frac{(1854.4)}{d^2} P, \qquad (1)$$

where P is the applied load in g and d is the length of the diagonal of indentation mark in μm.

3. Experimental results and discussion

The measured microhardness values of the mixed crystals of ammonium–potassium alum, $(NH_4)_{1-x}K_xAl(SO_4)_2 \cdot 12H_2O$ are shown in Fig.

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TABLE I Input data of the elastic constants and lattice constants of the NH_4–K alum system

Composition, x $(NH_4)_{1-x}K_xAl(SO_4)_2 \cdot 12H_2O$	C_{11} (10^{10} Nm^{-2}) (from [10])	C_{12} (10^{10} Nm^{-2}) (from [10])	C_{44} (10^{10} Nm^{-2}) (from [10])	b (10^{-8} cm) (from [11])
0.0	2.520*	1.09*	0.814*	12.214
0.1	2.515	1.084	0.819	12.206
0.2	2.509	1.077	0.825	12.197
0.3	2.504	1.070	0.830	12.190
0.4	2.498	1.064	0.836	12.181
0.5	2.493	1.057	0.841	12.173
0.6	2.487	1.051	0.847	12.165
0.7	2.482	1.045	0.852	12.157
0.8	2.476	1.038	0.858	12.149
0.9	2.470	1.032	0.863	12.140
1.0	2.465*	1.025*	0.868*	12.133

* S. Haussuhl and P. Preu, [9]

1. From Fig. 1 it is observed that the microhardness in NH_4–K alum mixed crystals shows a non-linear variation with composition. The mixed crystals show higher values of microhardness than the components. The maximum increase in the microhardness is obtained in crystals of nearly equimolar concentration (i.e. for x approximately 0.5) and the increase in the hardness is as high as 8 or 9 kg mm^{-2}, compared to the hardness of either of the single component crystals. The present study of the microhardness of the NH_4–K alum mixed crystals shows that the hardness is substantially increased when one component of NH_4–K alum system is added to the other.

If we compare our results with those of earlier workers [1–5], it is found that the variation of microhardness for mixed alums is similar to that observed in mixed alkali halides.

Alkali halides belong to a close-packed system and their slip system has been thoroughly studied, whereas alums are not as close packed as alkali halides. Apart from this, alums contain water molecules as well and their slip behaviour is also not well known. Since the variation of microhardness is similar to that of alkali halides, an attempt is being made to calculate the microhardness of these mixed crystals on similar lines, as has been done by Shrivastava [7] for mixed alkali halides.

4. Theory

The microhardness of the mixed crystals of NH_4–K alum system may be calculated by the relationship given by Shrivastava [7] based on Kataoka–Yamada model [8]. The relationship is

$$H_v = \lambda_1 H_1 + \lambda_2 H_2 + A_H \frac{\mu^2}{\Gamma} \cdot \frac{\lambda_1 \lambda_2}{b^4}, \quad (2)$$

where λ_1 and λ_2 are the fractional molar concentrations, H_1 and H_2 are the microhardnesses of component single crystals, A_H is a constant for a given mixed system and b is the lattice constant. μ and Γ are defined as

$$\mu = \tfrac{1}{2}(C_{11} - C_{12}) \quad (3)$$

and

$$\Gamma = \tfrac{1}{2}(C_{11} + C_{12}) \times \left[\frac{C_{44}(C_{11} - C_{12})}{C_{11}(C_{11} + C_{12} + 2C_{44})}\right]^{1/2} \times b^2, \quad (4)$$

where C_{11}, C_{12} and C_{44} are elastic constants of the crystal.

5. Calculations and results

Calculation of microhardness of mixed crystals of the NH_4–K alum system has been performed using the input data of Table I. The elastic constants of the Cr–K alum mixed system have been

TABLE II Input data of microhardness of single crystal of pure potassium alum, ammonium alum and one composition of NH_4–K alum system, along with calculated value of A_H for the mixed alum system

Alum	H_v(Kg mm^{-2})	A_H (10^{-57} kg N^{-1} m^6)
$KAl(SO_4)_2 \cdot 12H_2O$	49.4	–
$NH_4Al(SO_4)_2 \cdot 12H_2O$	51.2	–
$(NH_4)_{0.5}K_{0.5}Al(SO_4)_2 \cdot 12H_2O$	58.9	11.75

experimentally determined by Bhagvantam [10]. From his observed values, it is found that elastic constant of this system varies almost linearly with composition. The same behaviour is also found in mixed alkali halides. In view of this behaviour, the elastic constants of mixed crystals of NH_4–K alum system have been computed by linear interpolation. Klug and Alexander [11] investigated this series of NH_4–K alum mixed crystals by means of X-ray diffraction to determine whether they were ideal from the standpoint of Vegard's law. From their results it is seen that the deviations from Vegard's additivity law are extremely small. The lattice constants of the present series of mixed crystals as reported by Klug and Alexander are believed to be accurate to $\pm 1.0 \times 10^{-4}$ nm and therefore used in the present work. The constant A_H for the system has been calculated using experimental values of microhardness of the mixed crystal (see Table II). The calculated values of the microhardness are presented in Table III. The variation of microhardness with composition is shown in Fig. 1, along with the experimental values. We find that the calculated results are in agreement with the experimentally observed results.

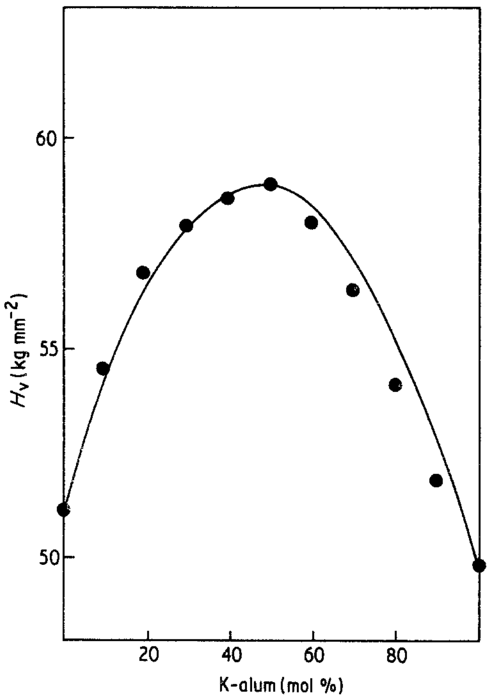

Figure 1 Microhardness of NH_4–K alum mixed crystals against concentration of K alum in mol %. • represent the experimental values and the solid line represents the theoretical calculation.

TABLE III Calculated values of microhardness of NH_4–K alum system

Composition, x $(NH_4)_{1-x}K_xAl(SO_4)_2 \cdot 12H_2O$	H_v(kg mm^{-2}) calculated from Equation 2
0.0	–
0.1	54.07
0.2	56.28
0.3	57.80
0.4	58.7
0.5	58.9
0.6	58.4
0.7	57.2
0.8	55.3
0.9	52.7
1.0	–

6. Summary and conclusion

Experimental study of the microhardness of $(NH_4)_{1-x}K_xAl(SO_4)_2 \cdot 12H_2O$ crystals shows that the hardness increases when one component of NH_4–K alum system is added to the other. Calculated values of microhardness are in good agreement with the observed ones.

It is observed that the increase in the microhardness at nearly equimolar composition is however not as high as in the KCl–KBr and NaCl–NaBr systems. This may be attributed to the small fractional change in volume, $\Delta V/V$, for the extreme components in the present system, compared to the other systems mentioned above. Fractional change in volume, $\Delta V/V$, in the case of alum mixed crystals is about 2 %, while in the case of NaCl–NaBr system it is 16 % and in KCl–KBr system it is 13 %.

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