Lattice Parameter, Density and Microhardness Studies on $Na_xk_{1-X}br$ Crystals Grown from Aqueous Solution

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Abstract: **- Mixed crystals of alkali halides find their applications in optical, opto electronics and electronic devices. Binary mixed crystals of NaBr and KBr were grown by the slow evaporation method. Densities and refractive indices of all the grown crystals were determined and also used for the estimation of the bulk composition in crystal lattice parameters and hardness values were determined by XRD and Vicker's micro hardness measurements respectively. The detailed results are reported in this paper.**

I. INTRODUCTION

A mixed crystal is obtained by crystallizing together two isomorphous crystals like NaBr and KBr with comparable lattice constants. For ionic crystals like alkali halides complete miscibility is possible only above a temperature TK given by $T = 4.5\ S^2$, S being the percentage difference in lattice constants [1]. Alkali halide mixed crystals are of the completely disordered substitutional type. Haribabu and Subbarao [2] have reviewed the aspects of the growth and characterization of alkali halide mixed crystals. Sirdesh Mukh and Srinivas [3] have reviewed the physical properties. More reports are available on binary mixed crystals of alkali halides.

A study of literature has shown that there are broad miscibility gaps in several binary systems of alkali halides. In the case of KBr_{1-x} crystals, Nair and Walker [4] observed that for the extreme concentration ranges $x < 0.3$ and $x > 0.7$ the system could be characterized by a single fcc lattice parameter, while in the intermediate region three fcc phases characterized by three lattice parameters. NaBr-KBr system is another example of not forming a continuous series of mixed crystals. The crystalline solutions in this system provide a useful model for comparison with more complex solutions such as those considered in the present study (NaBr-KBr). Thompson and Waldbaum [9] have analyzed the two phase region halite-sylvite in the system NaBr-KBr.

Alkali halide crystals are widely used as laser window materials, neuron monochromators, infra red prisms, infra red transmitters etc. But, the uses are limited by their mechanical properties and hence there exists the need to strengthen these. The mixed and impurity added (doped) crystals of alkali halides are found to be harder than the end members and so they are more useful in these applications. In addition, mixed alkali halides find their applications in optical, optoelectronic and electronic devices. In view of this, it becomes necessary and useful to prepare binary and ternary mixed crystals regardless of miscibility problems and characterize them by measuring their physical properties. Neelakanda Pillai and his co-workers [5-8] have grown binary crystals of alkali halides from the aqueous solutions. Growth of single crystals, density and refractive index measurements and determination of lattice parameters and Vicker's hardness values were under taken. Results are reported here in this paper.

II. EXPERIMENTAL DETAILS

2.1 Growth of Single crystals

$Na_xK_{1-x}Br$ single crystals were grown from the aqueous solutions by the slow evaporation method. Anal R grade samples of NaBr and KBr were used as the starting materials and doubly distilled water was used for the growth of the crystals.

Supersaturated solutions were prepared for various values of x ranging from 0.1 to 0.9 including two end member crystals in identical conditions. Crystals were harvested after three weeks.

2.2 Density measurements

Densities of all the grown crystals were determined by using the floatation method. Carbon tetra chloride of density 1.594 gm/cc and Bromoform of density 2.890 gm/cc were used as lower and higher density liquids respectively.

2.3 Refractive Index Measurement

Refractive index of an under saturated solution of the crystal in distilled water was measured using an Abbe's refractometer. Refractive index of the crystal was determined by using Gladstone's rule [9]

$$[(n-1)]P= [(n-1)/d_1]P_1 + [(n2-1)/d_2]P_2$$

Where n, n_1 and n_2 represents the refractive indices of the solution, solvent and solute respectively. d, d_2 and d_3 are the densities of the solution, solvent and solute respectively.

P, P_1 and P_2 are the percentage weights of the solution, solvent and solute respectively.

2.4 Estimation of bulk composition

It has been found that the density values form a linear relationship with composition for the binary mixed crystals[1] as $D = xd_1 + (1-x)d_2$
Here d_1 and d_2 represents the densities of NaBr and KBr

2.5 Lattice Parameter

X-ray Diffraction data were collected from powdered samples using an automated X-ray powder diffractometer with scintillation counter and monochromated CuKa (l = 1.5418 A^o) radiation. The reflections were indexed following the procedures of Lipson and Steeple [10]. Analysis of the X-ray diffraction peaks for the binary mixed systems considered in the present study by the available methods [11] shows that the mixed crystals can be indexed with single fcc lattices.

2.6 Vicker's Microhardness Measurements

The hardness of a material is defined as [11] the resistance it offers to the motion of dislocations, deformation or damage under an applied stress.

Hardness testing provides useful information on the strength and deformation characteristics of materials [12]. It is correlated with other mechanical properties like elastic constant [13] and yield stress [14] Meyer [15] established a relationship between indentation hardness and plastic work hardening capacity of a material.

Vicker's microhardness measurement were done on all the 11 crystals grown using Zeitz Wetzler hardness test fitted with a diamond pyramidal indenter and attached with Leitz incident light microscope. Indentation test was done in air at room temperature. Different loads (25g,50g and 100g) were used for indentation. Diagonal length'd' of indented impression obtained for various loads were measured. The average value of the diagonal lengths of the indentation marks in each trial was calculated. Hardness of the crystal was calculated using the relation[6]

$$H_v = 1.8544\ (p/d^2)\ \text{kg/mm}^2$$

Where P is the applied load in kg and d, the average diagonal length. To know hardness of the material, a graph of log P versus log d is plotted. The slope of the best linear fit gives Mayer's work hardening co-efficient 'n'.

Table 1: Density, Refractive index and estimated compositions of all the grown crystals

System	Density	Refractive index	Estimated Composition
KBr	2.7254	1.554	
NaBr	3.1895	1.643	
$Na_{0.1}K_{0.9}Br$	2.7532	1.568	$Na_{0.132}K_{0.868}Br$
$Na_{0.2}K_{0.8}Br$	2.7703	1.578	$Na_{0.271}K_{0.729}Br$
$Na_{0.3}K_{0.7}Br$	2.7912	1.582	$Na_{0.321}K_{0.679}Br$
$Na_{0.4}K_{0.6}Br$	2.8356	1.591	$Na_{0.418}K_{0.582}Br$
$Na_{0.5}K_{0.5}Br$	2.8911	1.599	$Na_{0.509}K_{0.491}Br$
$Na_{0.6}K_{0.4}Br$	2.9198	1.607	$Na_{0.611}K_{0.389}Br$
$Na_{0.7}K_{0.3}Br$	2.9274	1.623	$Na_{0.793}K_{0.207}Br$
$Na_{0.8}K_{0.2}Br$	3.0123	1.631	$Na_{0.868}K_{0.132}Br$
$Na_{0.9}K_{0.1}Br$	3.1231	1.69	$Na_{0.923}K_{0.077}Br$

Table 2: Lattice parameter of all the grown crystals

System	Lattice Parameter		
	Experimental	Vegard's Law	Retger's Rule
KBr	6.5894		
NaBr	6.0995		
$Na_{0.1}K_{0.9}Br$	6.5339	6.5240	6.5280
$Na_{0.2}K_{0.8}Br$	6.4981	6.4566	6.4638
$Na_{0.3}K_{0.7}Br$	6.4538	6.4321	6.4401
$Na_{0.4}K_{0.6}Br$	6.3968	6.3846	6.3937
$Na_{0.5}K_{0.5}Br$	6.3302	6.3400	6.3494
$Na_{0.6}K_{0.4}Br$	6.2867	6.2374	6.2798
$Na_{0.7}K_{0.3}Br$	6.2440	6.2009	6.2073
$Na_{0.8}K_{0.2}Br$	6.1791	6.1641	6.1687
$Na_{0.9}K_{0.1}Br$	6.1319	6.1372	6.1401

Table -3: Hardness value and work hardening coefficient of all the grown crystals

System	Hardness value 25 g	50 g	100g	Work hardening Coefficient
KBr	48	70	74	0.339
NaBr	34	49	66	0.253
$Na_{0.1}K_{0.9}Br$	30	49	54	0.241
$Na_{0.2}K_{0.8}Br$	26	44	54	0.225
$Na_{0.3}K_{0.7}Br$	24	34	50	0.218
$Na_{0.4}K_{0.6}Br$	20	38	42	0.211
$Na_{0.5}K_{0.5}Br$	16	26	41	0.173
$Na_{0.6}K_{0.4}Br$	22	36	45	0.189
$Na_{0.7}K_{0.3}Br$	26	44	55	0.220
$Na_{0.8}K_{0.2}Br$	36	57	68	0.260
$Na_{0.9}K_{0.1}Br$	42	60	71	0.300

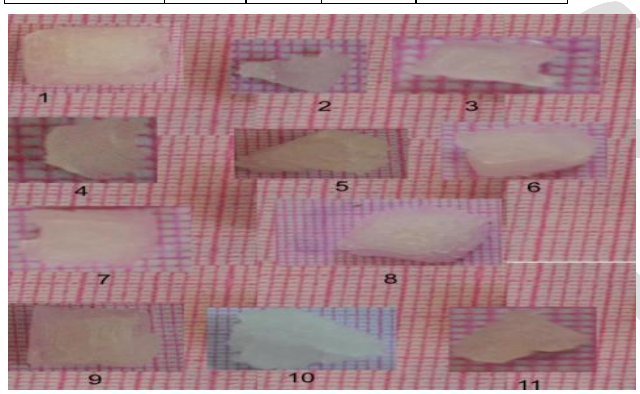

Figure 1: Photograph of pure and mixed $Na_xK_{(1-x)}Br$ single crystals (a) KBr (b) $Na_{0.1}K_{0.9}Br$ (c) $Na_{0.2}K_{0.8}Br$ (d) $Na_{0.3}K_{0.7}Br$ (e) $Na_{0.4}K_{0.6}Br$ (f) $Na_{0.5}K_{0.5}Br$ (g) $Na_{0.6}K_{0.4}Br$ (h) $Na_{0.7}K_{0.3}Br$ (i) $Na_{0.8}K_{0.2}Br$ (j) $Na_{0.9}K_{0.1}Br$ (k) NaBr

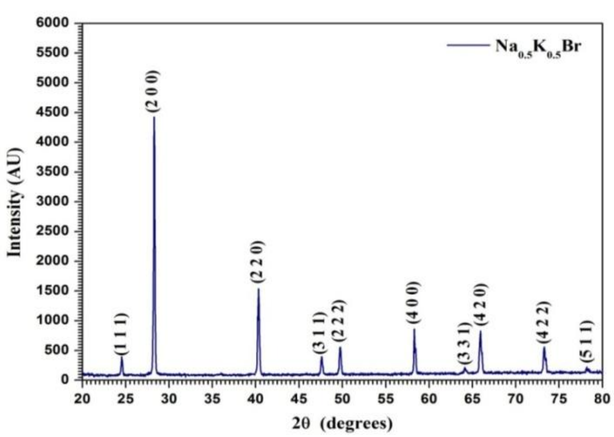

Figure 2: Indexed powder X-ray diffraction pattern for $Na_{0.5}K_{0.5}Br$ single crystal

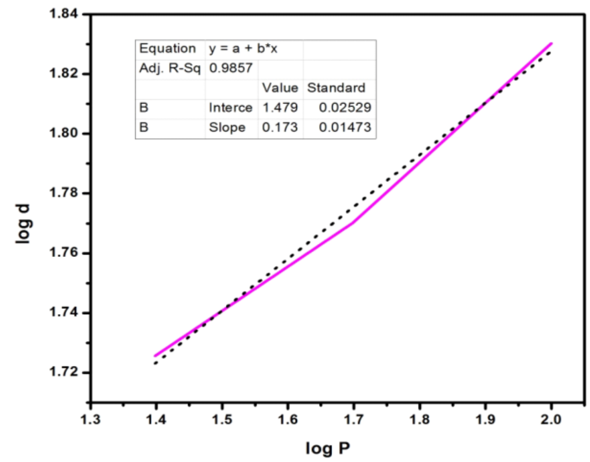

Figure 3 : Plot of log P *vs* log d for $Na_{0.5}$ $K_{0.5}Br$ crystal

III. RESULTS AND DISCUSSIONS

The binary mixed crystals are found to be transparent and harder than end member crystals. All the grown crystals exhibit cleavage properties which show that the grown crystals are single crystals. The maximum size of crystals grown is 10 mm x 10 mm x 5 mm. Photographs of all the grown crystals are shown in figure 1.

The density, refractive index and estimated composition of all the crystals are given in table 1. Observed density and refractive index of the end member compare well with those reported in the literature [1] (Reported values are given in brackets).

The lattice parameters obtained in the present study are provided in table 2., along with estimated lattice parameters by Vegard's law and Retger's rule. Lattice parameter of the end member crystal compositions are well agreed with those reported in the literature [1](literature values are given in brackets). The lattice parameter of the mixed crystals is well agreed with those estimated from Vegard's law and Retger's rule.

According to Tobolsky [16] two alkali halide3s AC and BC will form continuous solid solutions A_xB_{1-x} C at 20^oC, provide the difference between their lattice parameters is less than 6%. Two compounds or elements are said to form a continuous solid solution if a single lattice parameter as measured by X-ray powder photographs can be assigned to the solid solution at all compositions. In the present work, from the Table-2, it is found that all the compositions are assigned single lattice parameter and it indicates that they form continuous solid solutions.

The micro hardness value and the work hardening coefficients of all the grown crystals are given in Table -3. The variation of log P vs log d for the crystal $Na_{0.5}$ $K_{0.5}Br$ is shown in figure 2 as an illustration. The hardness values for the mixed crystals are less than that of the end member crystals and it is high for $Na_{0.9}$ $K_{0.1}Br$ crystal and is low for $Na_{0.5}$ $K_{0.5}Br$ crystal. The work hardening coefficient shows that all the grown crystals are in the hard category materials. The 'n' values of all the samples are found to less than 1.6. According to Onitch [17] the 'n' values below 1.6 for hard materials and more than 1.6 for soft materials. The values obtained imply that the mixed crystals grown in the present study belong to hard category.

IV. CONCLUSION

Binary mixed crystals of NaBr and KBr were grown from the aqueous solution by slow evaporation method. Compositions of the grown crystals were determined using the measured density and refractive index values by assuming the additive rule, satisfying for them. Lattice parameters were estimated by the X-ray diffraction method and these values agreed with those estimated from Vigard's law and Ritger's rule. The lattice parameters show that the mixed crystals are single crystals. The work hardening coefficient values show all the crystals belong to hard category materials.

REFERENCES

[1] D. S. Sirdeshmukh, K. Srinivas, Physical Properties of mixed crystals of alkali halides, J. Mater. Sci 21(1986) 4117-4130

[2] V. Haribabu, V. Subbarao, Growth and characterization of alkali halide mixed crystals, Prog. Crystal Growth Charact. 8(1984) 189-260

[3] I.R. Nair, C.T. Walker, Raman scattering and X-ray scattering studies on $KBr_{1-x}I_x$, KCl_{1-x} and $K_{1-x}Rb_xCl$.

[4] J.B. Thompson Jr., D.R. Waldbaum, Analysis of the two-phase region halite-sylvite in the system NaCl-KCl. Geochim, Cosmochim, Acta 33 (1969) 671-690.

[5] Jayanthi T. S & N. Neelakanda Pillai. The Board of IJLTEMAScience Volume III(2014) P 28-29.

[6] S. Sivananthan and N. Neelakanda Pillai, Scholars Research Library Archives of Physics Research 2012, 3(3) : 239 -244

[7] C. V. Somasundari and Neelakanda Pillai IOSR Journal of Applied Physics (IOSR-JP) e – ISSN: 2278-4891. Volume 3, Issue 5(Mar-Apr 2013) PP01-07

[8] Lesly Fathima & N Neelakanda Pillai, Scholars Research Library Archives of Physics Research, 2012, 3(5):407-410

[9] A.E.H Tutton, Crystallography and Practical Crystal Measurement, Vol II, Today and Tomorrow's Book Agency, New Delhi, 1965. P 1014

[10] H. Lipson, H Steeple, Interpenetration of X-ray Powder Diffraction Patterns, Macmillan, New York 1970

[11] N.H. Ashby(1951), J. Nad. Engg. 6,33

[12] B.W. Mott (1956), Micro indentation Hardness Testing (Butterworth's, London)

[13] N.A. Wooster (1953), Ref. Progr. Phys. 16, 62

[14] J.H. Westbrook (1958), flow in rock salt structure (Report 58 RL 2003 of the G.E. Research Laboratory, USA)

[15] J.H. Westbrook and H Conard [Edn] 919730, The Science of Hardness testing and its Research Applications.

[16] A.V. Tobolsky, J.Chem. Phys. 10 (1942), 187.

[17] Onitch E.M [1947]Microscopic 2,131