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Hardness measurements on Pure and ZnS added $NaCl_x Br_{1-x}$ single crystals grown from aqueous solutions.

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ABSTRACT

Single crystals of pure and ZnS doped halides for different values of x were grown by slow evaporation technique. All the grown crystals were characterised by XRD patterns. The elemental analysis was made from the EDAX data. Microhardness measurements have been carried out using Zwick hardness tester fitted with a Vicker Diamond Pyramidal indenter. The results obtained are discussed.

Keywords: Alkali halides, Crystal Growth, Slow evaporation method, Microhardness, Stiffness Constant, Mixed crystals

INTRODUCTION

Alkali halide crystals are used as laser window materials, neutron monochromotors, infrared prisms, infrared transmitters and etc.[1]. But the uses are limited by need to strengthen them. The mixed and doped crystals of alkali halides are harder than the end members [2] and so they are more useful in these applications. In the present work, single crystals of binary mixed crystals of alkali halides $NaCl_xBr_{1-x}$ of different values of x were grown from aqueous solutions by slow evaporation technique and characterized by X-ray diffraction and the hardness of the grown crystals were measured using Vickers Method.

MATERIALS AND METHODS

Anala R grade NaCl and NaBr substances were taken. An aqueous solution of the salt with desired molecular constitutions was prepared at a supersaturated concentration and taken in a nucleation cell and kept in an undisturbed place. Seed crystals were used to grow the sample crystals. The temperature and volume were kept constant respectively at 32 ℃ and 25 ml for all the crystals. In the case of doped mixed crystals growth, 2.5ml of ZnS solution was added to each 25ml of aqueous mixed solution. In this present study, total of six mixed pure and 6 ZnS added mixed crystals from $NaCl_x Br_{1-x}$ solutions with x values 0.4,0.5,0.6,0.7,0.8, and 0.9 were grown in identical conditions.

The compositions of the mixed crystals were estimated from the EDAX Spectrum fig 02. X-ray diffraction data was collected from the powder sample of all the grown crystals (pure and ZnS doped) and the reflections were indexed following the procedure of H. Lipson and H. Steeple [3]. Micro hardness measurements were carried out using Zwick3212 hardness tester fitted with Vickers diamond pyramidal indenter.

The mixed crystals grown in the present study are found to be more hard, stable and transparent than the end member crystals. The photograph of the grown crystals is shown in fig .1.

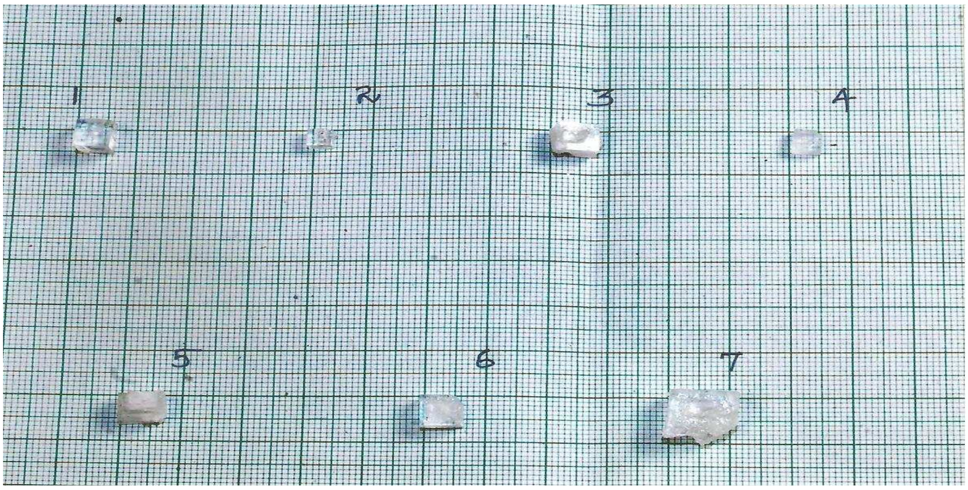

Fig 1 - Grown Crystals of $NaCl_x Br_{1-x}$

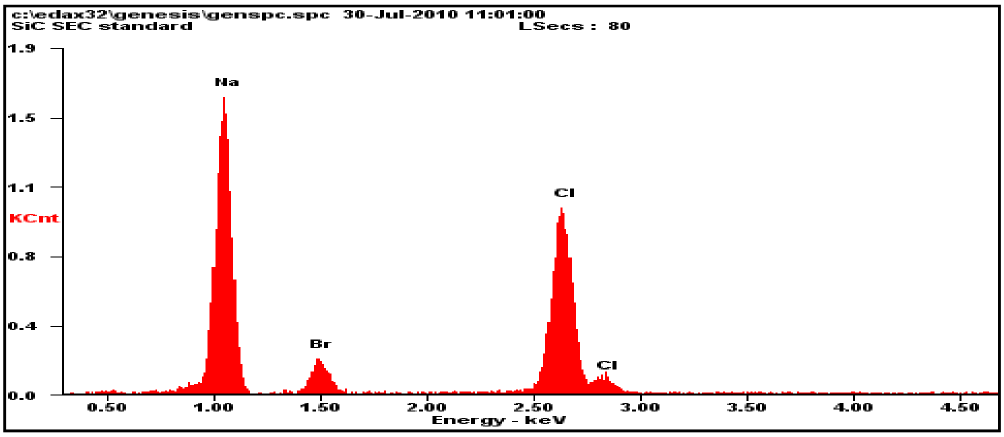

Fig 2 Edax Spectrum of the sample $NaCl_{0.5}Br_{0.5}$

The composition of the starting material and the estimated bulk composition of the sample crystals along with the lattice parameters are provided in the table 1.

Table 1 Actual compositions along with estimated composition and lattice parameters

Actual Composition		Estimated Composition		Lattice Parameter a			
				Pure Phase 1	Pure Phase 2	Doped Phase 1	Doped Phase 2
Nacl	NaBr	Nacl	NaBr	a	a	a	a
0.4	0.6	0.45	0.54	5.67	5.92	5.62	5.88
0.5	0.5	0.57	0.427	5.66	5.66	5.66	5.91
0.6	0.4	0.64	0.346	5.64	5.89	5.70	5.92
0.7	0.3	0.74	0.285	5.65	5.92	5.63	5.63
0.8	0.2	0.83	0.179	5.63	5.88	5.67	5.91
0.9	0.1	0.913	0.09	5.65	5.65	5.67	5.65

The micro hardness is calculated using the expression

$$H_v = 1.8544\ P/d^2\ Kgmm^{-2}$$

Where ‘P’ is the applied load in kg and ‘d’ is the average diagonal length of the Vicker’s impression in mm after unloading. The Meyers work hardening co-efficient ‘n’ can be determined by plotting log P vs log d ,the variation of log P vs log d for the sample $NaCl_{0.4}Br_{0.6}$ is fig 3 for illustration. The slope of the best linear fit graph gives ‘n’ value.

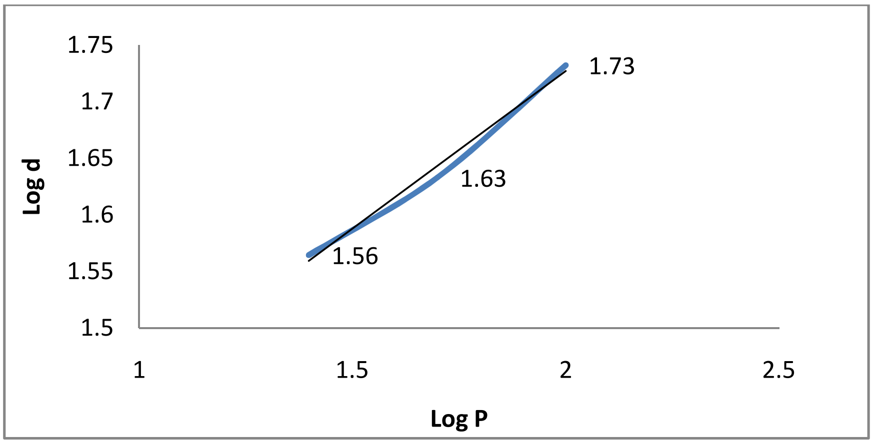

Fig 3 Variation of LogP with Logd for the mixed crystal $NaCl_{0.4}Br_{0.6}$

The elastic stiffness constant (C_{11}) for various compositions as well as different load have been estimated using Wooster's empirical formula.

$$C_{11} = Hv^{7/4}$$

RESULTS AND DISCUSSION

The calculated hardness value for all the grown crystals are provided in table 2. The variations of the hardness value with composition of NaCl in $NaCl_x\ Br_{1-x}$ are shown in fig4. It is found that the mixed crystals have more hardness.

Table 2 Values of micro hardness for all the grown crystals

System	Microhardness (Hv)values for pure mixed crystals			Microhardness(Hv) values for doped mixed crystals		
	25 gm	50 gm	100 gm	25 gm	50 gm	100 gm
$NaCl_{0.4}NaBr_{0.6}$	**32.3**	52.65	63.5	18.75	21.95	32.05
$NaCl_{0.5}NaBr_{0.5}$	**48.5**	62.9	92.65	23.7	34.05	49.8
$NaCl_{0.6}NaBr_{0.4}$	**81.9**	93.2	106.5	29.65	44.15	63.95
$NaCl_{0.7}NaBr_{0.3}$	**74.5**	95.75	124	17.2	22.3	26.7
$NaCl_{0.8}NaBr_{0.2}$	**75.6**	98.2	128.5	11.45	17.1	23.2
$NaCl_{0.9}NaBr_{0.1}$	**87.1**	96.5	147	13.85	22	28.45

The measured micro hardness values for all the grown crystals are given in the table2. The variation of micro hardness with load is shown in the fig 4 and fig 5.

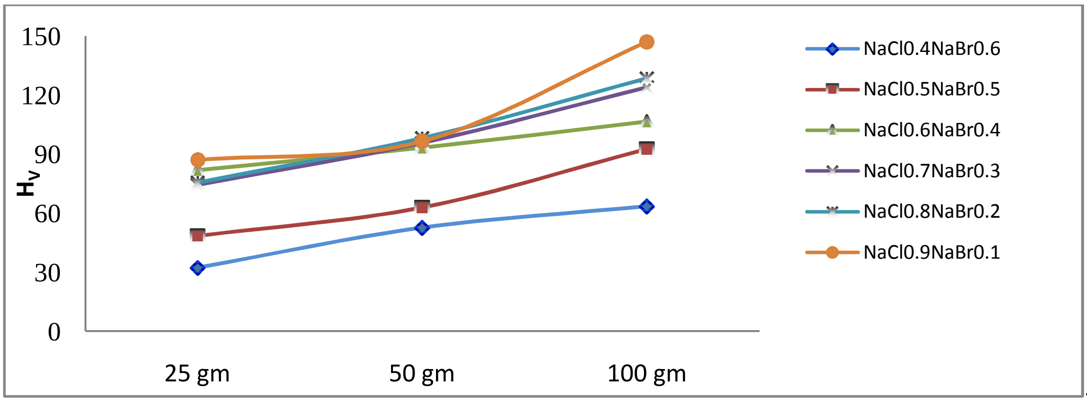

Fig 4 Variation of microhardness (Hv) with load for pure mixed crystals

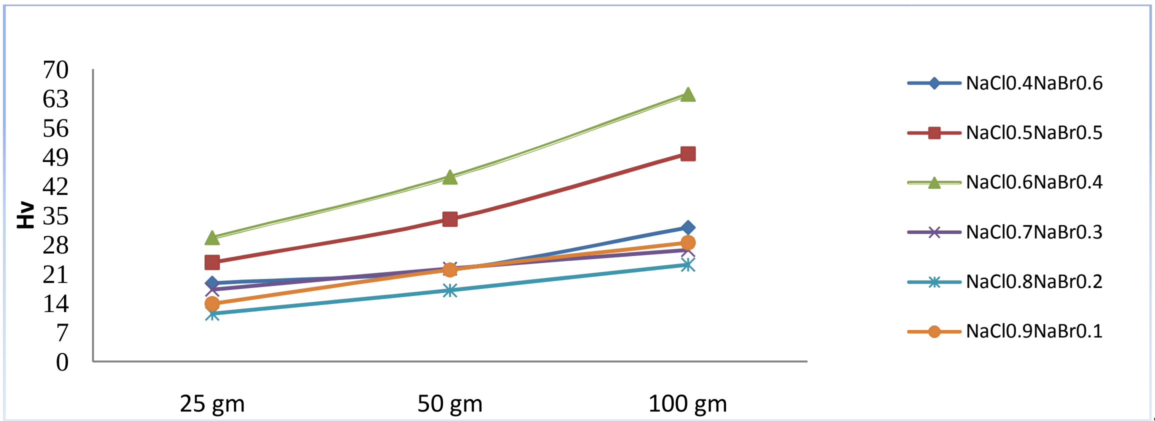

Fig 5 Variation of microhardness (Hv) with load for doped mixed crystals

The hardness value increases with the increase of load. The variation of micro hardness with composition of NaCl is shown in fig 6.

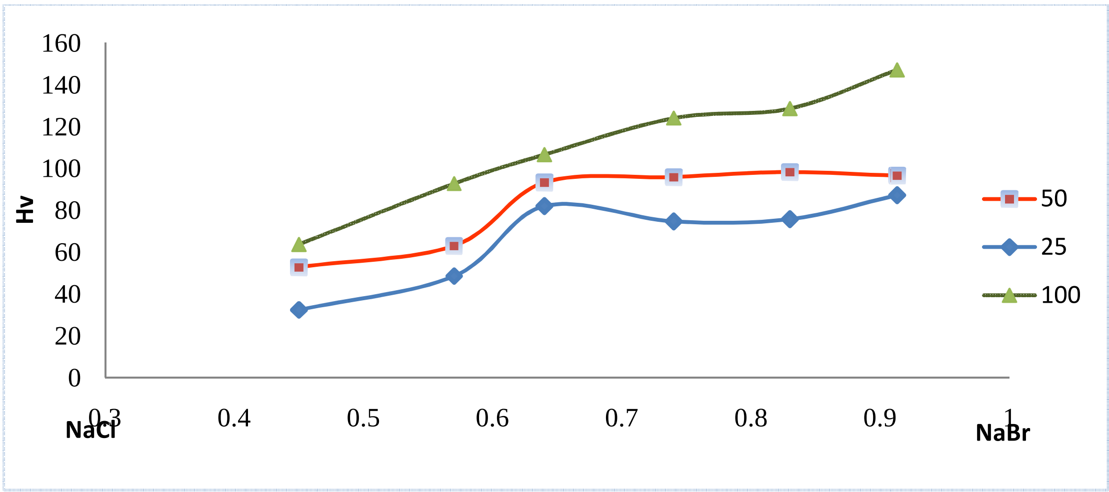

Fig 6 Variation of Hv values with composition for pure mixed crystals

It varies nonlinearly with composition. The non linear variation of micro hardness with composition is due the presence of imperfections. These imperfections can be vacancies, impurities, vacancy pairs, dislocations, low-angle grain boundaries etc. The studies made by so many authors [4] on conductivity measurement of binary and ternary mixed crystals shows that conductivity is high for mixed crystals compared to end crystals. Since Ionic crystals are solely due to the presence of charged vacancies, these results therefore indicate that mixed crystals contain excess of vacancies. The results on dislocation morphology [5] shows that the low-angle grain boundaries and dislocations are more in mixed crystals compared to end crystals. Also, Tillers Cutectice crystallization mechanism may responsible for the origin of low-angle grain boundaries in mixed crystals [6]. These imperfections may be responsible for the observed non linear variation of microhardness in mixed crystals.

In the case of ZnS added mixed crystals, the microhardness values decreases nonlinearly when compared with pure mixed crystals fig 7. This may also due to the increase in number of vacancies, dislocations, low angle grain boundaries and other defects [7] [8] when we doped.

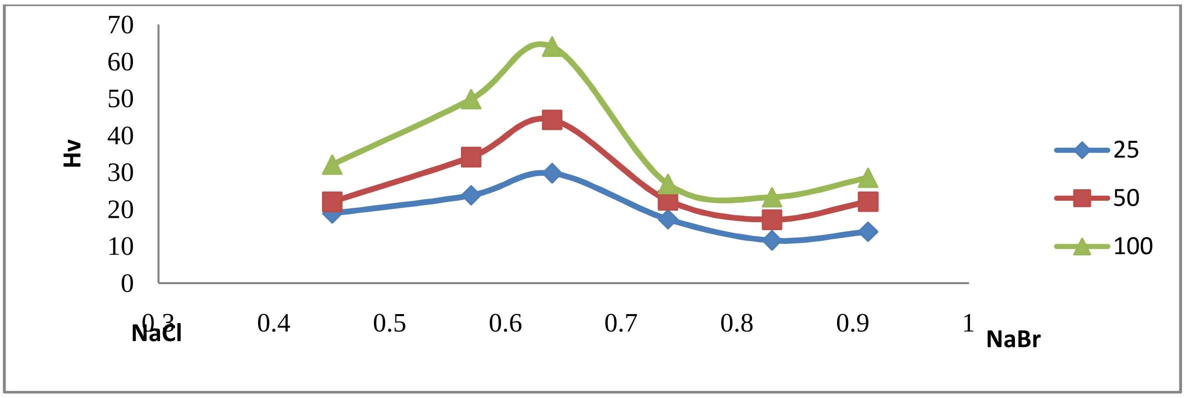

Fig 7 Variation of Hv values with composition for doped mixed crystals

Meyer's work hardening co-efficient "n" values for different composition are shown in table 3. According to Onitsh[9] and Hanneman[10] the 'n' value falls below 1.6 for hard materials and more than 1.6 for soft materials. The values obtained in the present study imply that grown crystals belong to hard materials category.

Table 3 Work hardening co-efficient for the grown crystals

Composition	n	Composition	n
$NaCl_{0.4}NaBr_{0.6}$	0.28	**$NaCl_{0.4}NaBr_{0.6}ZnS_{0.1}$**	0.31
$NaCl_{0.5}NaBr_{0.5}$	0.24	**$NaCl_{0.5}NaBr_{0.5}ZnS_{0.1}$**	0.23
$NaCl_{0.6}NaBr_{0.4}$	0.31	**$NaCl_{0.6}NaBr_{0.4}ZnS_{0.1}$**	0.21
$NaCl_{0.7}NaBr_{0.3}$	0.41	**$NaCl_{0.7}NaBr_{0.3}ZnS_{0.1}$**	0.34
$NaCl_{0.8}NaBr_{0.2}$	0.35	**$NaCl_{0.8}NaBr_{0.2}ZnS_{0.1}$**	0.22
$NaCl_{0.9}NaBr_{0.1}$	0.39	**$NaCl_{0.9}NaBr_{0.1}ZnS_{0.1}$**	0.24

The elastic stiffness constant C_{11} for various compositions as well as for different loads are shown in table 4.

Table 4 Elastic Stiffness Constant for various compositions pure and doped mixed crystals

System	C_{11}- Pure $NaCl_x$ Br_{1-x} Crystals GPA			C_{11}- Samples doped with ZnS GPA		
	25 gm	50 gm	100 gm	25 gm	50 gm	100 gm
$NaCl_{0.4}NaBr_{0.6}$	437.6	1029.1	1428.4	168.9	222.6	431.7
$NaCl_{0.5}NaBr_{0.5}$	889.7	1404.9	2766.8	254.6	480.0	933.6
$NaCl_{0.6}NaBr_{0.4}$	2229.7	2795.6	3530.7	376.7	756.2	1446.2
$NaCl_{0.7}NaBr_{0.3}$	1889.2	2930.8	4607.7	145.3	228.8	313.6
$NaCl_{0.8}NaBr_{0.2}$	1938.3	3063.3	4904.3	71.3	143.8	245.2
$NaCl_{0.9}NaBr_{0.1}$	2483.3	2971.1	6205.9	99.4	223.5	350.5

The values give the idea about the tightness of the bonding between neighbouring atoms [11]. It is found that, the stiffness value increases with increase in NaCl content. In case of doped mixed crystals the stiffness constant of all the samples are found to decrease considerably when compared to pure mixed crystals. This may be due to the creation of vacancies by the addition of impurity.

CONCLUSION

The good quality of transparent crystals of **$NaCl_x$ Br_{1-x}** was grown in different value of 'x' by slow evaporation from aqueous solution. The compositions were estimated from Edax. Micro hardness value have varied non linear with composition. The hardness value decrease when impurities added to the mixed crystals, this may be due creation of vacancies and other defects. The 'n' values reveal that all the grown crystals belong to hard category. The stiffness constant value indicate that the bonding neighbouring atoms increases with increased NaCl constant and also indicate that for doped mixed crystals , the bonding is very low.

REFERENCES

[1] D.B. Sirdeshmukh, L. Sirdeshmukh ,K.g, Subhdra – *Alkali halides – A Handbook of Physical properties Springer series in Materials science Vol.49, Springer , Berhim ,* **2001**
[2] N.Neelakanda Pillai, C.K. Mahadevan – *Physica B 403 (***2008***) 2146 – 2172*
[3] H. Lipson, H. Steeple, Interpretation of X-ray powder diffraction pattern, *Maxmillan, Newyork , 1970.*
[4] V. Har Babu, U.V. Suba Rao and K. Venkata Ramaiah, *Phys. Stat. Sol(a), 28 (***1975***) 269.*

[5] U.V. SubaRao and V. Har Babu, *Pramana, 2 (***1978***) 149.*
[6] U.V. Suba Rao, *Indian.J. Phys., 54A (***1980***) 147.*
[7] C.W.A. Newly, *Trans. Br. Ceram, Soc, 62 (***1963***) 739*.
[8] K. Kamiyoshi and Y. Nigara, *Physc. Stat. Soil.(a), 6 (***1971***) 223.*
[9] E.M.Onitsch, *Mikroscopia 2(**19i47**)131*
[10] M.Hanneman, *Metall, Manch 23(***1941***)135*
[11] G.Ananth Babu, P.Ramaswamy, *Mater. Chem. Phys.113(***2009***)727-733*
[12] Tanmoy Roy Choudhury, Amitabha Basu *Journal of Ovonic Research vol.4. No.2 (***2008***) 35-42*