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Growth, characterization and high temperature XRD of $NaCl_xBr_{1-x}$ single crystals

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ABSTRACT

In this paper, $NaCl_xBr_{1-x}$ single crystals have been grown for x=0-1 by Czochralski method and its Characterization and High Temperature XRD have been studied. For all x, lattice parameter has been determined. We investigated the stability of grown crystal structure by high temperature x-ray diffraction patterns between 25-275°C. Micro-hardness experiments show, by increasing of NaBr, the hardness increased and will be maximum for $NaCl_{0.5}Br_{0.5}$ and then decreases.

KEYWORDS

Crystal growth;
Czochralski method;
Hardness;
Alkali-halid crystal;
High temperature x-ray.

INTRODUCTION

The Czochralski method, i.e. pulling a crystal from the melt, became the most important technology for the production of large semiconductor and optical crystals[1].

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[2-4].

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 mixed crystals of alkali halides are found to be harder than the end members and so they are more useful in these applications. physical property that limits the utility of alkali halides as device materials is their low hardness[2-4]. 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[4]. Ghadekar and other found there is a strigh relation between dislocation and etch-pit density in this cryetals.

In this paper we present the research results on the Physical, optical and thermal Properties $NaCl_xBr_{1-x}$ single crystals grown and microhardness in these crystals for all x measurs.

EXPERIMENTAL DETAILS

100 g of the substance, weighed according to the molecular ratio by weight, was thoroughly mixed and was taken in a silica crucible. The amount of substance in grams for preparing the required samples of composition given by $(NaCl)_x NaBr)_{1-x}$ may be obtained by using the formula

P[x × molecular weight of NaCl+(1-x)× molecular weight of NaBr]=100

$$P = \frac{100}{x \times \text{mol.wt.of}\ \ NaCl + (1-x) \times \text{mol.wt.of}\ NaBr}$$

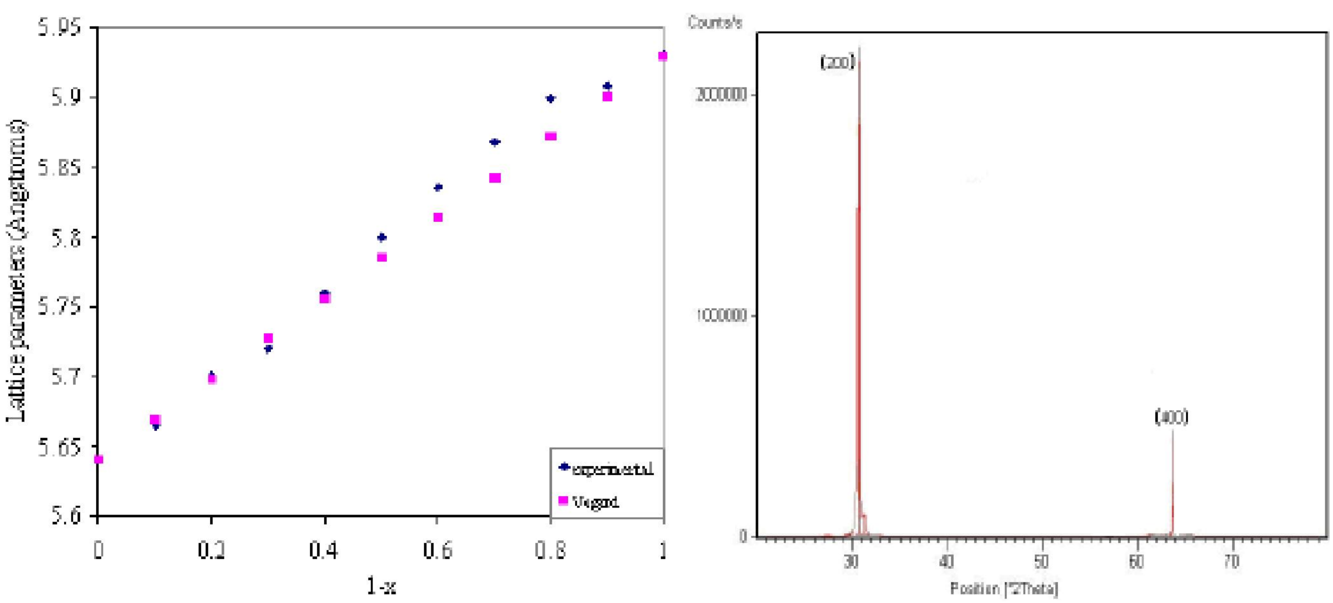
Weight of NaCl to be taken = P × x× mol. wt. of NaCl;
Weight of NaBr to be taken = P × x× mol. wt. of NaBr.

The crucible was kept inside a furnace (capable of heating up to 1250° C) having a temperature controller (accuracy is ±2°C) and heated till the whole substance was melted. The temperature was further increased to 800 °C and kept at this temperature for 15 min for homogeneous mixing to take place due to convection. Crystals were pulled from the melt by using a NaCl seed single crystal puller at the rate of 6 mm/h and rate of rotate is 15RPM. After growth crystal, the temperature slowly decries until 500°C, for 12 hours. In this temperature NaBr impurities بطور يكنواخت در…in all crystal and crystal is anneal whit rate of 0.6 ° C /min during 24 hours. The UV – V is spectral studies were carried out using Varian Cary 5E UV –V is spectrometer in the range190–900 nm.

RESULTS AND DISCUSSION

X-ray diffraction data were collected using an automated X-ray powder diffractometer with monochromated CuKα (λ=1.54Å) radiation. All of pattern diffraction are shown ther are two peaks (200) and (400) and (200)peak is longer then (400). Analysis of the X-ray diffraction peaks shows that, for the mixed Crystals whit increase NaBr, locations of all the X-ray diffraction peaks go to teta small. X-ray diffractograms for NaCl0.4Br0.6 crystal are shown in Figure 1 (a) as an illustration. The calculated lattice parameters are shown in Figure 1 (b.) whit increase in NaBr pecents lattice parameters is increase In this Figure result of experimental and theory of vegard is comparable.

In order to monitor the crystal structure of $NaCl_{0.9}Br_{0.1}$ material, high temperature x-ray diffraction measurements were carried out over the range 25–275°C with a sample on a Pt plate and 10^{-5} mbar vacuum during heated. The heating rate was 0.3°C min^{-1} and by 50°C steps. The sample cut from the as-grown crystal was crushed and finely ground into powder for the structure analysis. The accelerating voltage was 40 kV and the current was 30 mA. Figure 2 is shown X-ray diffraction spectra of $NaCl_{0.9}Br_{0.1}$ crystal at different temperature.



Figuer 1 : (a) X-ray diffractometer for $NaCl_{0.4}Br_{0.6}$ (b) Lattice parameters in Angstroms of NaClxBr1-x (for all x) in experimental and Law generalized of Vegard.

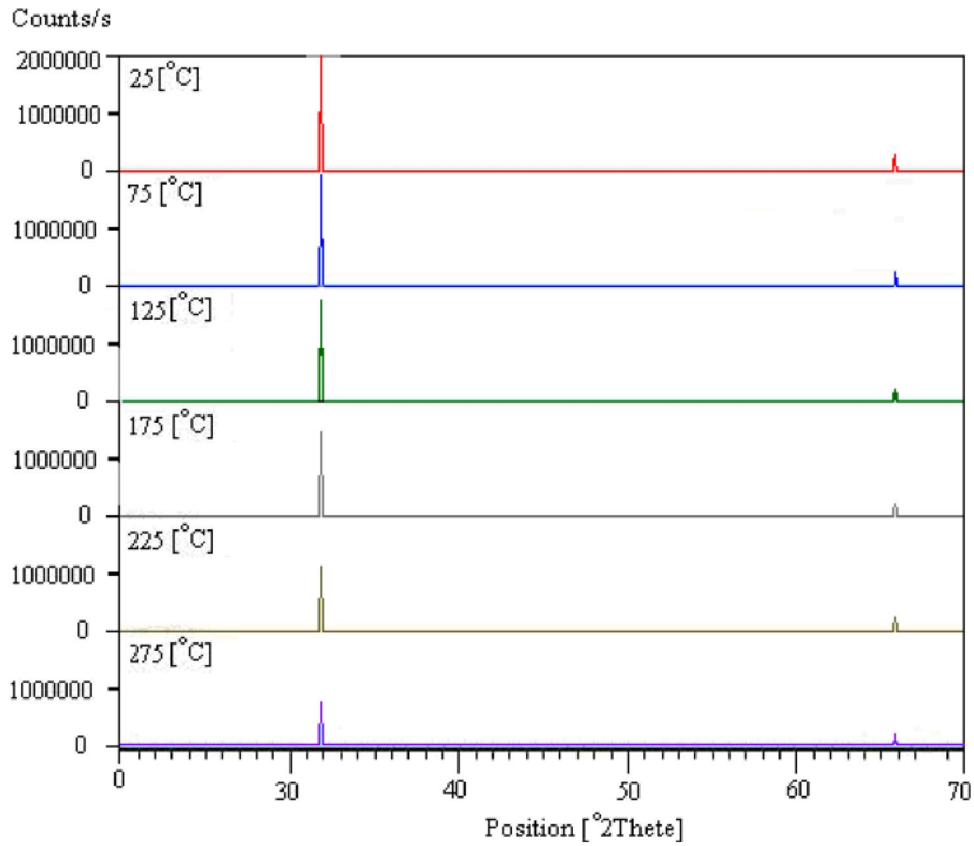


Figure 2 : X-ray diffraction spectra of $NaCl_{0.9}Br_{0.1}$ crystal at different temperature

The values of the linear thermal expansion coefficient (α_T) at any temperature can be obtained by the following equation[7]:

$$\alpha_T = \frac{\delta a}{\delta T} \times \frac{1}{a_{25}} \quad \textbf{(1)}$$

where δa is the variation of the lattice parameter corresponding to the change in temperature δT and a_{25} is the lattice parameter at 25°C, a_{25} = Å.

Linear thermal expansion coefficient versus temperature (°C) of $NaCl_{0.9}Br_{0.1}$ crystal is shown in Figure 3. The value of the average linear thermal expansion coefficient in the temperature range 25–275°C can be theoretically calculated from equation (2) to be 14.38×10^{-6} °C^{-1}. The volume coefficient of thermal expansion β = 3α is equal to 43.15×10^{-6} °C^{-1}.

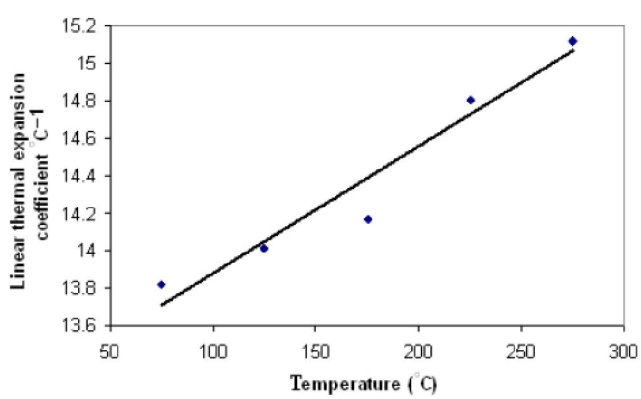


Figure 3 : Linear thermal expansion coefficient versus temperature (°C) of the $NaCl_{0.9}Br_{0.1}$ crystals.

The large thermal expansion coefficient suggests that in the process of the MIT crystal growth, a low cooling rate should be adopted. Otherwise, the ingots are likely to include large amounts of defects, such as microcracks, or crack into pieces due to thermal stress[7].

Microhardness measurements were made by Hardness Tester fitted with a Vickers diamond pyramidal indenter and whit ASTM Standard. Mixed crystals invariably have higher hardness than the corresponding pure crystal. 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 Denoting the difference between the hardness of the mixed crystal (H_{MC}) and the value obtained by the additive rule (H_L) for any composition by ΔH, (2) may be written as

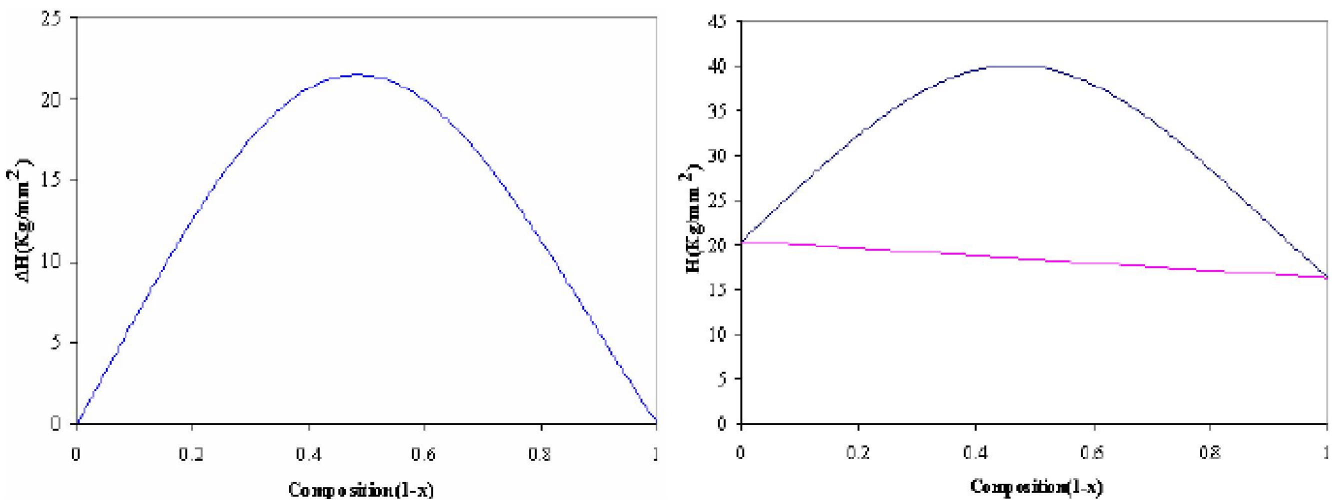


Figure 4 : (a) Plot of hardness, *H*, against the composition 1- *x* for the mixed crystals, (b) Plot of ?H vs composition 1- x for the mixed crystals.

$$\Delta H = H_{MC} - H_L = Kx(1-x) \quad (2)$$

where H_{MC} is the hardness of the mixed crystal, H_L the value obtained from the additive 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. The plots of systems are shown in Figure 4. The trends in composition dependence of hardness of mixed crystals studied in this work can be seen in Figures 4-a and 4-b. 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. In the case of the $NaCl_xBr_{1–x)}$ system, the hardness increases slowly with composition rising to a maximum value in the equimolar region which is about 50% of the value for the end members.

Figure 5 : NaCl0.5Br0.5 crystal Etched whit 400 magnification.

Dislocation structure in $NaCl_xBr_{1-x}$ grown from melt has been studied using the etch-pit method. Results is shown there is a straight relation between density of dislocations and hardness in this crystals. The average density of dislocations in crystals get les than 10^5 cm^{-2}. because measure density of dislocations for optical applications is les than 10^7 cm^{-2} then our crystals have good quality in optical applications.

Single crystals are mainly used in optical applications, the optical transmittance range and the transparency cutoff are important. The $NaCl_{0.9}Br_{0.1}$ has a good transmittance and the lower cut off wavelength is 200 nm (Figure 6). The large transmission in the entire visible region enables it to be a good candidate for optoel applications and low concentration of grown in defects[9].

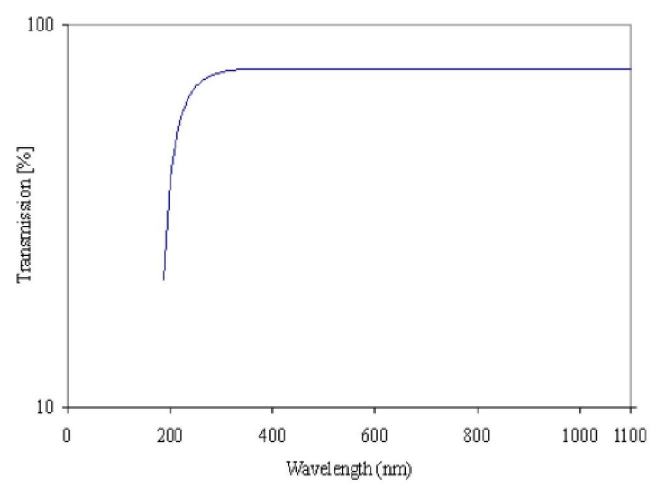


Figure 6 : Optical transmission spectrum half logarithmic of $NaCl_{0.9}Br_{0.1}$ crystal.

CONCLUSIONS

The good quality of transparent crystals of NaClx Br1-x was grown in different value of 'x' by Czochralski method and its Characterization and High Temperature XRD have been studied. For all x, lattice parameter has been determined. We investigated the stability of grown crystal structure by high temperature x-ray diffraction patterns between 25-275°C. Micro-hardness experiments show, by increasing of NaBr, the hardness increased and will be maximum for $NaCl_{0.5}Br_{0.5}$ and then decreases.

Results of dislocation show a straight relation between density of dislocations and hardness in this crystals. The average density of dislocations in crystals get les than 10^5 cm^{-2}. The hardness $NaCl_xBr_{1-x)}$ crystalincreases slowly with composition rising to a maximum value in the equimolar region which is about 50% of the value for the end members. The value of the average linear thermal expansion coefficient in the temperature range 25–275°C can be also theoretically calculated from equation (2) to be 14.38×10^{-6} °C^{-1}. The volume coefficient of thermal expansion $\beta = 3\alpha$ is equal to 43.15×10^{-6} °C^{-1}.

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