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Growth and characterization of multiphased mixed crystals of KCl, KBr and KI:1. Growth and X-ray diffraction studies

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Abstract

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 view of this, it becomes necessary and useful to prepare binary- and ternary-mixed crystals regardless of miscibility problem and characterize them by measuring their physical properties. In the present work, we have grown $(KCl)_x(KBr)_{y-x}(KI)_{1-y}$ crystals for various values of x and y by the melt method and physically characterized. Bulk composition of the crystals was measured using the measured density and refractive index values. X-ray diffraction analysis indicates the existence of two phases in the mixed crystals. Thermal parameters were determined using the X-ray powder diffraction intensity data.

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Keywords: Alkali halides; Mixed crystals; Crystal growth; X-ray diffraction; Density; Refractive index; Lattice variation; Thermal parameters

1. Introduction

The alkali halide crystals have always been at the center state of solid-state physics. They have been "model crystals" for testing many solid-state theories. In recent decades, they have also proved useful in several applications ranging from X-ray monochromators to tunable lasers.

The use of pure simple alkali halides is limited by the mechanical systems and hence there exist the need to strengthen them. The mixed- and impurity-added (doped) crystals of alkali halides are found to be harder than the end members and so they become more useful in these applications. Also, it is a known fact that alloys are more useful than the pure simple metals in device fabrications. In addition, mixed alkali halides find their applications

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in optical, opto-electronic and electronic devices. For these reasons, it becomes necessary and useful to prepare binary- and ternary-mixed crystals regardless of miscibility problem and characterize them by measuring their physical properties.

For ionic crystals like alkali halides complete miscibility is possible only above a temperature T (K) given by $T = 4.5S^2$, S being the percentage difference in lattice constants [1]. S takes a value of 8% for alkali halides at room temperature. There are broad miscibility gaps observed in several binary systems of alkali halides. NaCl–KCl [2] is an example. Barrett and Wallace [3] determined the lattice parameters of $Na_xK_{1-x}Cl$ crystals and found that this system does not form a continuous series of single-phased mixed crystals. Nair and Walker [4] observed that for the extreme concentration range $x<0.3$ and $x>0.7$ the $KBr_{1-x}I_x$ crystals could be characterized by a single FCC lattice parameter while in the intermediate region three FCC phases characterized by three lattice parameters.

Alkali halide mixed crystals are of the completely disordered substitutional type. Haribabu and Subbarao [5] have reviewed the aspects of the growth and characterization of alkali halide mixed crystals. Sirdeshmukh and Srinivas [6] have reviewed the physical properties. Several more reports are available on binary-mixed crystals of alkali halides [7–12]. Some reports are also available on ternary and quaternary mixed crystals of alkali halides [13–18].

Mahadevan and his co-workers [19] obtained larger and more stable crystals from $(NaCl)_x(KCl)_{0.9-x}(KBr)_{0.1}$ solutions than from $Na_xK_{1-x}Cl$ solutions. They grew the crystals from aqueous solutions only. Though the miscibility problem was there, their study has illustrated that a KBr addition to NaCl–KCl system may yield a new class of stable materials.

A research programme on the preparation and properties of multiphased ternary-mixed crystals of potassium and sodium halides was planned in this laboratory and a series of investigations were undertaken.

In the present investigation, studies on $(KCl)_x(KBr)_{y-x}(KI)_{1-y}$ mixed crystals have been considered: Preparation of mixed crystals, density and refractive index measurements and determination of lattice parameters and thermal parameters like Debye–Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency form the first part. DC and AC electrical measurements form the second part. Results of the first part are reported here in this paper.

2. Experimental

2.1. Crystal growth

$(KCl)_x(KBr)_{y-x}(KI)_{1-y}$ single crystals were grown from the melt, for the first time, by the Czochralski method. AnalaR grade samples of KCl, KBr and KI were used as the starting material for the growth of the crystals.

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 $(KCl)_x(KBr)_{y-x}(KI)_{1-y}$ may be obtained by using the formula

$$P[x \times \text{molecular weight of KCl} + (y-x) \times \text{molecular weight of KBr} + (1-y) \times \text{molecular weight of KI}] = 100$$

$$P = \frac{100}{x \times \text{mol.wt. of KCl} + (y-x) \times \text{mol. wt. of KBr} + (1-y) \times \text{mol. wt. of KI}}$$

$$\text{Weight of KCl to be taken} = \text{P} \times x \times \text{mol. wt. of KCl},$$

$$\text{Weight of KBr to be taken} = \text{P} \times (y-x) \times \text{mol. wt. of KBr},$$

$$\text{Weight of KI to be taken} = \text{P} \times (1-y) \times \text{mol. wt. of KI}.$$