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Electrical measurements on multiphased $(NaCl)_x(KCl)_{y-x}(KBr)_{1-y}$ single crystals

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ABSTRACT

Alkali halide mixed crystals were melt grown from NaCl, KCl and KBr starting materials. DC and AC electrical measurements were carried out on the resulting ternary compositions at temperatures ranging from 308 to 423 K. Activation energies and mean jump frequencies were also estimated. The present study indicates an increase of DC and AC electrical conductivities and dielectric constant with the increase of temperature. Also, it indicates a nonlinear variation of all the electrical parameters (both DC and AC) with the bulk composition, which is explained to be due to the enhanced diffusion of charge carriers along dislocations and grain boundaries.

1. Introduction

Alkali halides are useful for theoretical calculations of the energies for formation and migration of defects because of their electrostatic interactions. They are purely ionic conductors. Ionic conductivity studies provide valuable information on the state of point imperfections.

Ionic conductivity measurements as a function of temperature have been done by a number of researchers on pure alkali halide crystals and also on impurity (anionic as well as cationic)-added ones. Various defect parameters such as activation energy for migration, formation energy, etc. have been evaluated from these studies. Though an extensive amount of work has been done on pure and impurity-added alkali halide crystals, the work on mixed crystals of alkali halides is very limited [1–4].

The dielectric constant is one of the basic electrical properties of solids. The measurement of the dielectric constant and the dielectric loss factor as a function of frequency and temperature is of interest both from the theoretical point of view and from the applied aspects. Practically, the presence of a dielectric between the plates of a condenser enhances the capacitance. This effect makes materials with high dielectric constants useful in capacitor technology. There is limited work reported in the literature on the dielectric behaviour of alkali halide mixed (binary and ternary) crystals [2–5].

Mahadevan and co-workers [6] 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 the NaCl–KCl system may yield a new class of stable materials. The present work is a systematic addition to this previous study.

A research programme on the growth and characterization of $(NaCl)_x(KCl)_{y-x}(KBr)_{1-y}$ single crystals was planned and investigations were undertaken. Details regarding the growth of crystals, determination of density and refractive index along with estimation of bulk composition, indexing the X-ray powder diffraction data along with determining the lattice parameters, determination of thermal parameters like the mean Debye–Waller factor, the mean square amplitude of vibration, the Debye temperature and the Debye frequency from the X-ray powder diffraction data,

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determination of compressibility, mean sound velocity from the Debye temperature, etc. have been reported elsewhere [7].

The amount of substance in grams for preparing the required sample crystal of composition given by $(NaCl)_x(KCl)_{y-x}(KBr)_{1-y}$ may be obtained by using the following formula:

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

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

So, weight of NaCl to be taken $= P \times (x) \times$ mol.wt. of NaCl

weight of KCl to be taken $= P \times (y-x) \times$ mol.wt. of KCl

weight of KBr to be taken $= P \times (1-y) \times$ mol.wt. of KBr

It has been found that the density and refractive index values form a linear relationship with bulk composition for the binary mixed crystals [8]. Assuming that these values have linear relationships with composition for the ternary mixed crystals also, the following relations were considered [7]:

$$d = xd_1 + (y-x)d_2 + (1-y)d_3$$
$$n = xn_1 + (y-x)n_2 + (1-y)n_3$$

Here d, d_1, d_2 and d_3 represent the densities of mixed crystal, NaCl, KCl and KBr, respectively; n, n_1, n_2 and n_3 represent the refractive indices of mixed crystal, NaCl, KCl and KBr, respectively. Compositions of the grown mixed crystals were estimated by solving the above two equations for x and y values. The initial compositions taken for the crystallization and the final estimated bulk composition in the crystal for all the ternary mixed systems considered [7] are given in Table 1.

In the second part of the programme, DC and AC (with a fixed frequency of 1 kHZ) electrical measurements were carried out at various temperatures ranging from 308 to 423 K for all the 26 crystals grown [20 ternary mixed crystals, viz. $(NaCl)_x(KCl)_{y-x}(KBr)_{1-y}$ with $x = 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 and $y = 0.8$, 0.6, 0.5, 0.4 and 0.2; three binary mixed crystals, viz. $(NaCl)_{0.5}(KCl)_{0.5}$, $(NaCl)_{0.5}(KBr)_{0.5}$ and $(KCl)_{0.5}(KBr)_{0.5}$; three end member crystals, viz. NaCl, KCl and KBr]. DC electrical conductivity (σ_{dc}), DC activation energy (E_{dc}) and mean jump frequency ($1/\tau$) were determined through the DC electrical measurements. Dielectric constant (ε_r), dielectric loss factor ($\tan\delta$), AC electrical conductivity (σ_{ac}) and AC activation energy (E_{ac}) were determined through the AC electrical measurements. The results obtained are reported here.

Table 1
The initial composition taken for crystallization and the final estimated bulk composition in the crystal

System (with composition taken for crystallization)	Estimated bulk composition in the crystal
$(NaCl)_{0.1}(KCl)_{0.7}(KBr)_{0.2}$	$(NaCl)_{0.078}(KCl)_{0.724}(KBr)_{0.198}$
$(NaCl)_{0.2}(KCl)_{0.6}(KBr)_{0.2}$	$(NaCl)_{0.159}(KCl)_{0.641}(KBr)_{0.200}$
$(NaCl)_{0.3}(KCl)_{0.5}(KBr)_{0.2}$	$(NaCl)_{0.282}(KCl)_{0.524}(KBr)_{0.194}$
$(NaCl)_{0.4}(KCl)_{0.4}(KBr)_{0.2}$	$(NaCl)_{0.389}(KCl)_{0.418}(KBr)_{0.193}$
$(NaCl)_{0.5}(KCl)_{0.3}(KBr)_{0.2}$	$(NaCl)_{0.479}(KCl)_{0.319}(KBr)_{0.202}$
$(NaCl)_{0.6}(KCl)_{0.2}(KBr)_{0.2}$	$(NaCl)_{0.595}(KCl)_{0.218}(KBr)_{0.187}$
$(NaCl)_{0.7}(KCl)_{0.1}(KBr)_{0.2}$	$(NaCl)_{0.704}(KCl)_{0.091}(KBr)_{0.205}$
$(NaCl)_{0.1}(KCl)_{0.5}(KBr)_{0.4}$	$(NaCl)_{0.063}(KCl)_{0.541}(KBr)_{0.396}$
$(NaCl)_{0.2}(KCl)_{0.4}(KBr)_{0.4}$	$(NaCl)_{0.159}(KCl)_{0.453}(KBr)_{0.388}$
$(NaCl)_{0.3}(KCl)_{0.3}(KBr)_{0.4}$	$(NaCl)_{0.292}(KCl)_{0.029}(KBr)_{0.419}$
$(NaCl)_{0.4}(KCl)_{0.2}(KBr)_{0.4}$	$(NaCl)_{0.361}(KCl)_{0.212}(KBr)_{0.427}$
$(NaCl)_{0.5}(KCl)_{0.1}(KBr)_{0.4}$	$(NaCl)_{0.505}(KCl)_{0.039}(KBr)_{0.457}$
$(NaCl)_{0.1}(KCl)_{0.4}(KBr)_{0.5}$	$(NaCl)_{0.133}(KCl)_{0.363}(KBr)_{0.504}$
$(NaCl)_{0.2}(KCl)_{0.3}(KBr)_{0.5}$	$(NaCl)_{0.230}(KCl)_{0.274}(KBr)_{0.493}$
$(NaCl)_{0.3}(KCl)_{0.2}(KBr)_{0.5}$	$(NaCl)_{0.261}(KCl)_{0.231}(KBr)_{0.508}$
$(NaCl)_{0.4}(KCl)_{0.1}(KBr)_{0.5}$	$(NaCl)_{0.389}(KCl)_{0.075}(KBr)_{0.536}$
$(NaCl)_{0.1}(KCl)_{0.3}(KBr)_{0.6}$	$(NaCl)_{0.110}(KCl)_{0.293}(KBr)_{0.597}$
$(NaCl)_{0.2}(KCl)_{0.2}(KBr)_{0.6}$	$(NaCl)_{0.240}(KCl)_{0.159}(KBr)_{0.602}$
$(NaCl)_{0.3}(KCl)_{0.1}(KBr)_{0.6}$	$(NaCl)_{0.272}(KCl)_{0.103}(KBr)_{0.625}$
$(NaCl)_{0.1}(KCl)_{0.1}(KBr)_{0.8}$	$(NaCl)_{0.104}(KCl)_{0.079}(KBr)_{0.817}$

2. Experimental

The DC electrical conductivity measurements were carried out to an accuracy of $\pm 2\%$ for all the 26 crystals grown using the two-probe technique at various temperatures ranging from 308 to 423 K in a way similar to that followed by Mahadevan and co-workers [2–4]. The sample crystal was kept between two parallel plates (silver electrodes) to form a parallel plate capacitor. The resistances of the crystals were measured using a million megohm meter (AEC mfs; Model MOM 2). The observations were made while cooling the sample. The temperature was controlled to an accuracy of ± 1 K.

The samples (rectangular crystals) were cut parallel to the cleavage plane to the desired thickness of 1 and 2 mm using a sharp blade and polished using a soft emery paper. The samples were then etched with distilled water and dried to avoid the change taking place, if any, in the electrical properties of the surfaces of the crystals due to cutting and polishing. They were annealed for 2 h at ~423 K to remove moisture content if present. Opposite faces of the sample crystals were coated with good-quality graphite to obtain a good conductive surface layer. The samples were again annealed in the holder assembly at ~423 K before making observations. The dimensions of the crystals were measured using a travelling microscope (L.C. = 0.001 cm).

The DC electrical conductivity (σ_{dc}) of the crystal was calculated using the relation [2]

$$\sigma_{dc} = d/(RA)$$

where R is the measured resistance, d is the thickness of the sample and A is the area of the face in contact with the electrode.

Plots between $\ln(\sigma_{dc})$ and $1000/T$ were found to be very nearly linear (not shown here). So, the σ_{dc} values were fitted with the relation [2]

$$\sigma_{dc} = \sigma_o \exp[-E_{dc}/(kT)]$$

where E_{dc} is the DC activation energy, k is the Boltzmann constant, T is the absolute temperature and σ_o is a parameter depending on the material. E_{dc} values were estimated using the slopes of the above line plots ($E_{dc} = -(\text{slope})k \times 1000$).

The mean jump frequency ($1/\tau$) was estimated using the E_{dc} and Debye frequency (f_D) values (taken from Ref. [7]) in a way similar to that followed by Selvarajan and Mahadevan [3]. The DC electrical conductivity is easily calculated [9] to be

$$\sigma_{dc} = Ne^2a^2/(kT\tau)$$

where τ is a mean jump time, perhaps different from that for dipolar orientation but still given by an equation [9] like

$$\frac{1}{\tau} = \frac{1}{\tau_0}\exp\left(\frac{-E}{kT}\right)$$

where a is the distance of a jump. The factor $1/\tau_o = \omega_o$ (nearly equal to $2\pi f_D$ where f_D is the Debye frequency) is the ionic vibrational frequency around its equilibrium position and $\exp(-E/(kT))$ is the statistical Boltzmann factor. A jump is attempted with each vibration, but only a fraction succeeds, depending on the (activation) energy E_{dc} required in order to squeeze through the barrier to the neighbouring equilibrium position. N stands for the number of perfect bonds or the number of charges per unit volume. The frequency $1/\tau_o \approx 10^{13}\,s^{-1}$.