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Studies on $(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ solid solutions: 2. Electrical measurements

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Abstract Ternary solid solutions were melt grown from NaCl, KBr and KI starting materials. D.C. and A.C. electrical measurements were done on the resulting ternary compositions at temperatures ranging from 50 to 150 °C. Activation energies and mean jump frequencies were also estimated. The bulk composition has complicated influences on the electrical parameters.

Introduction

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

Ionic conduction occurs either through the migration of positive and negative ions in an external electric field (the ions originate either in the material in question or in interstice impurities) or through the motion of ions in vacancies, which reflects the migration of vacancies. If the sample is placed in a stationary electric field, the carriers may be considered to be contained in an enclosure bounded by the capacitor plates. As the carriers may not leave the enclosure, they accumulate in the regions close to the plates, which causes a concentration gradient to be formed and this gradient feeds a diffusion current. At equilibrium the diffusion current density equals that of the drift current. Charge accumulation is related to inhomogeneities of the material, the agglomeration of impurity ions by diffusion in the vicinity of electrodes or chemical changes in layers close to electrodes [1].

The Gibb's free energy of a crystal, at any particular temperature, is minimum when a certain fraction of ions leave the normal lattice. As the temperature rises, more and more defects are produced which, in turn, increases the conductivity. In the high temperature (intrinsic) region, the effect of impurity on electrical conduction will not change appreciably whereas in the low temperature (extrinsic) region, the presence of impurity in the crystal increases its conductivity. The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region. The presence of impurities and vacancies mainly determine this region. The energy needed to form the defect is much larger than the energy needed for its drift. The conductivity of the crystal in the higher temperature region is determined by the intrinsic defects caused by the thermal fluctuations in the crystals [2].

Processes like association, aggregation and precipitation, which become important at low temperatures and higher impurity levels, in general, reduce the 'free' point defects that are necessary for electrical conduction. Formation, migration and association of point defects are governed by characteristic activation energies. An artificial increase in the concentration of defects of one type affects the concentration of other

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defects both through the law of mass action and charge neutrality criterion. With the usual electric fields, the charge transported by electrons in ionic crystals is zero because of a large forbidden gap [3].

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 (solid solutions) of alkali halides is very limited. Electrical conductivity measurements have been carried out on some binary mixed crystals like KCl–KBr, KCl–RbCl, NaCl–NaBr, etc. [3]. However, there is no report of D.C. conductivity measurements available on ternary solid solutions of alkali halides.

The dielectric constant is one of the basic electrical properties of solids. The measurement of dielectric constant and loss as a function of frequency and temperature is of interest both from 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 crystals (solid solutions). Fertel and Perry [4] were the first to determine the static dielectric constant of the KCl–KBr system from Kramers–Kronig analysis of infrared reflectivity data. Their results of dielectric constant variation with composition were found to be haphazard. Kamiyoshi and Nigara [5] measured by the immersion method the dielectric constant of five mixed crystal systems, viz. KCl–KBr, NaCl–NaBr, RbCl–RbBr, KCl–RbCl and KI–RbI. They observed a nonlinear variation of dielectric constant with composition in all the cases. Large differences in the values of dielectric constant for the KCl–KBr system were observed when compared to the values obtained by Fertel and Perry. As a cross-check Premeela Devi [6] redetermined the dielectric constant of KCl–KBr mixed crystals for various compositions at room temperature. Her results favour the values obtained by Kamiyoshi and Nigara and differ considerably from those of Fertel and Perry. Later, Sathaiah [7] determined dielectric constant and loss at elevated temperatures up to about 400 °C as a function of frequency and also as a function of composition for KCl–KBr and RbCl–RbBr mixed crystals. Also, he has analysed the results empirically. However, there is no report of dielectric measurements available on ternary solid solutions of alkali halides.

A research programme on the growth and characterization of $(\mathrm{NaCl})_x(\mathrm{KBr})_{y-x}(\mathrm{KI})_{1-y}$ solid solutions 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 mean Debye–Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency from the X-ray powder diffraction data, etc. have been reported in the first part [8].

In the second part of the programme, D.C. electrical conductivity (σ_{dc}) measurements along with determining the activation energy (E_{dc}) and mean jump frequency ($1/\tau$) and dielectric measurements along with determining the dielectric constant (ε_r), dielectric loss factor ($\tan\delta$), electrical conductivity (σ_{ac}) and activation energy (E_{ac}) have been made on all the 13 crystals grown [10 ternary solid solutions, viz. $(\mathrm{NaCl})_x(\mathrm{KBr})_{y-x}(\mathrm{KI})_{1-y}$ with x varying from 0.1 to 0.7 in steps of 0.2 and $y = 0.3$, 0.5, 0.7 and 0.9; three end member crystals, viz. NaCl, KBr and KI]. The results obtained in the present study are reported here.

Experimental

D.C. Measurements

The D.C. electrical conductivity measurements were carried out to an accuracy of ±2% for all the 13 grown crystals using the conventional two-probe technique at various temperatures ranging from 50 to 150 °C in a way similar to that followed by Freeda and Mahadevan [2]. The resistances of the crystals were measured using a million-megohmmeter. The observations were made while cooling the sample. Temperature was controlled to an accuracy of ±1 °C. The poly crystalline samples were cut into rectangular shaped to the desired thickness of 1–2 mm and polished. They were annealed for two hours at ~150 °C to remove moisture content if present. Opposite faces of the sample crystals were coated with good quality graphite to obtain a good ohmic contact with the electrodes. The samples were again annealed in the holder assembly at ~150 °C before making observations. The dimensions of the crystals were measured using a travelling microscope (L.C. = 0.001 cm). The D.C. electrical conductivity (σ_{dc}) of the crystal was calculated using the relation

$$\sigma_{\mathrm{dc}} = \frac{d}{RA},$$

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. The σ_{dc} values were fitted by the equation

$$\sigma_{\mathrm{dc}} = \sigma_{\mathrm{o}} \exp\left(\frac{-E_{\mathrm{dc}}}{kT}\right),$$

and the activation energy (E_{dc}) values were calculated. Here k is the Boltzmann's constant, T is the absolute temperature and σ_{o} is a constant depending on the material.

A.C. Measurements

The capacitance and dielectric loss factor measurements were carried out to an accuracy of ±1.5% using an LCR meter (Systronics mfs.) with a frequency of 1 kHz at various temperatures ranging from 50 to 150 °C in a way similar to that followed by Freeda and Mahadevan [9]. The observations were made while cooling the sample. Temperature was controlled to an accuracy of ±1 °C. The samples (rectangular crystals) were prepared and annealed in a way similar to that followed for the resistance measurement. Air capacitance was also measured. The dielectric constant of the crystal was calculated using the relation

$$\varepsilon_r = C_{\mathrm{c}}/C_{\mathrm{a}}$$

where C_{c} is the capacitance of the crystal and C_{a} is the capacitance of same dimension of air.

As the crystal area was smaller than the plate area of the cell, parallel capacitance of the portion of the cell not filled with the crystal was taken into account and, consequently, the above equation becomes

$$\varepsilon_r = \left[\frac{C_{\mathrm{crys}} - C_{\mathrm{air}}\left[1 - \frac{A_{\mathrm{crys}}}{A_{\mathrm{air}}}\right]}{C_{\mathrm{air}}}\right] \times \left[\frac{A_{\mathrm{air}}}{A_{\mathrm{crys}}}\right],$$

where C_{crys} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{crys} is the area of crystal touching the electrode and A_{air} is the area of electrode.

The A.C. electrical conductivity (σ_{ac}) was calculated using the relation,

$$\sigma_{\mathrm{ac}} = \varepsilon_{\mathrm{o}}\varepsilon_r\ \omega\tan\delta$$

where ε_{o} is the permittivity of free space (8.85×10^{-12} C^2 N^{-1} m^{-2}) and ω is the angular frequency ($\omega = 2\pi f$; $f = 1$ kHz in the present study). The σ_{ac} values were fitted by the equation

$$\sigma_{\mathrm{ac}} = \sigma_{\mathrm{o}} \exp\left[\frac{-E_{\mathrm{ac}}}{kT}\right],$$

and the activation energy values were calculated. Here k is the Boltzmann's constant, T is the absolute temperature and σ_{o} is a constant depending on the material.

Results and discussion

D.C. Electrical conductivity and mean jump frequency

The σ_{dc} values observed in the present study are provided in Table 1. They are found to increase with increase in temperature for all the 13 crystals measured.

Electrical conductivity depends on thermal treatment of crystals, even in pure ones. Thus conductivity at low temperatures depends on the cooling speed from melting point to room temperature. Thus, for slow cooling the remaking of the lattice can occur by the migration of interstitials to vacancies, recombination of Schottky defects or migration of vacancies to the surface or to dislocation channels. On quenching or rapid cooling, a fraction of the vacancies freeze adding a pre-exponential term contribution [1].

Another problem relates to the degree of solubility of impurities introduced into the crystal. The concentration of impurities "dissolved" in the lattice increases as the temperature of the crystal increases. If for a certain temperature T the concentration of impurities is higher than allowable due to the solubility limit, then the excess material precipitates to form a new precipitate phase. This tends to nucleate on dislocations and may be revealed by electron microscopy; the crystal also becomes "milky". This effect also influences electrical conductivity [1].

In the case of $(\mathrm{NaCl})_x(\mathrm{KBr})_{y-x}(\mathrm{KI})_{1-y}$ crystals considered here, their transparency is reduced when the crystals are cooled from high temperature to room temperature. The observed lattice parameters indicated the existence of three phases in crystals; one phase each nearly corresponds to the end members, viz NaCl, KBr and KI [8].

The D.C. electrical conductivity is easily calculated [10] to be

$$\sigma_{\mathrm{dc}} = \mathrm{N}e^2a^2/(kT\tau),$$

Table 1 D.C. electrical conductivities (for NaCl, KBr, KI × 10^{-8} mho m^{-1}; for mixed crystals × 10^{-6} mho m^{-1})

System (with composition taken for crystallization)	σ_{dc} for temperatures (°C)										
	50	60	70	80	90	100	110	120	130	140	150
NaCl	0.46	0.55	0.58	0.67	0.82	1.00	1.14	1.39	1.68	2.13	2.46
KBr	0.24	0.25	0.27	0.29	0.30	0.36	0.42	0.52	0.69	0.95	1.20
KI	0.24	0.28	0.34	0.39	0.43	0.51	0.65	0.80	0.89	1.04	1.26
$(NaCl)_{0.1}(KBr)_{0.8}(KI)_{0.1}$	6.25	7.46	8.00	9.17	9.80	10.00	11.36	12.50	13.51	15.38	18.18
$(NaCl)_{0.3}(KBr)_{0.6}(KI)_{0.1}$	8.33	9.26	13.51	16.67	17.86	21.28	22.22	23.81	25.00	25.64	26.32
$(NaCl)_{0.5}(KBr)_{0.4}(KI)_{0.1}$	11.36	12.20	13.16	14.08	16.67	18.52	21.74	22.73	24.39	25.00	26.32
$(NaCl)_{0.7}(KBr)_{0.2}(KI)_{0.1}$	12.35	14.08	15.15	16.39	17.54	18.87	19.61	20.83	21.28	22.22	23.26
$(NaCl)_{0.1}(KBr)_{0.6}(KI)_{0.3}$	15.63	18.52	19.61	20.00	21.74	22.22	23.26	24.39	25.00	25.64	26.32
$(NaCl)_{0.3}(KBr)_{0.4}(KI)_{0.3}$	14.29	14.49	15.15	16.39	17.54	18.87	20.00	20.83	22.22	22.73	24.39
$(NaCl)_{0.5}(KBr)_{0.2}(KI)_{0.3}$	5.10	5.78	6.49	7.46	8.85	9.71	11.49	12.99	14.93	16.39	30.00
$(NaCl)_{0.1}(KBr)_{0.4}(KI)_{0.5}$	35.71	37.04	38.46	40.00	41.67	43.48	45.45	46.88	50.00	52.63	55.56
$(NaCl)_{0.3}(KBr)_{0.2}(KI)_{0.5}$	23.81	24.39	25.00	25.64	26.32	27.03	27.51	28.57	30.30	35.71	37.04
$(NaCl)_{0.1}(KBr)_{0.2}(KI)_{0.7}$	13.89	14.08	14.29	14.56	14.93	15.15	15.38	15.63	16.13	16.39	16.67

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

$$\frac{1}{\tau} = \frac{1}{\tau_o} \exp\left[\frac{-E}{kT}\right],$$

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 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}. Also $1/\tau \le 10^{11}$ s^{-1} and $1/\tau$ will be much smaller than this at temperatures well below the melting temperature.

We have estimated the values of $1/\tau_o$ and $1/\tau$ using the f_D values estimated from X-ray diffraction intensity measurements on the systems considered in the present study [8]. The values of $1/\tau_o$ and $1/\tau$ are presented along with the E_{dc} values in Table 2. Since the present experimental temperature range is well below the melting temperatures (>650 °C), the values of $1/\tau_o$ and $1/\tau$ obtained in the present study compare well with those expected by the model.

Composition (bulk) dependence of σ_{dc} at 50 °C for $x = 0.1$ is shown (as an illustration) in Fig. 1. Composition (bulk) dependence of E_{dc} for $x = 0.1$ is shown (as an illustration) in Fig. 2. Results observed in the present study indicate that the composition has complicated influences on the values of σ_{dc}, E_{dc}, $1/\tau_o$ and $1/\tau$.

Haribabu and Subbarao have made conductivity measurements in the temperature range 100–450 °C in freshly cleaved (from single crystals) samples of KCl, KBr and various compositions of KCl–KBr mixed crystals [11, 12]. Their conductivity was found to increase gradually as the concentration of KBr increased. It attained a maximum value at an intermediate composition of 61.04 mole % of KBr in KCl. The results have been explained on the basis of a distortion model, where the observed nonlinear variation of ionic conductivity and activation energy occurs as due to the enhanced diffusion of charge carriers along the greater number of dislocations and grain boundaries found in their mixed crystals.

The nonlinear variation with composition observed here for the ternary (multiphased) solid solutions of NaCl–KBr–KI can be explained in a similar way and may be attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries which

Table 2 Values of E_{dc}, $1/\tau_o$ and $1/\tau$

System (with composition taken for crystallization)	E (eV)	$1/\tau_o$ ($\times 10^{13}$ s^{-1})	$1/\tau$ ($\times 10^{10}$ s^{-1})
NaCl	0.199	3.311	1.437
KBr	0.184	1.941	1.510
KI	0.194	1.527	0.805
$(NaCl)_{0.1}(KBr)_{0.8}(KI)_{0.1}$	0.112	0.865	11.080
$(NaCl)_{0.3}(KBr)_{0.6}(KI)_{0.1}$	0.138	1.297	6.042
$(NaCl)_{0.5}(KBr)_{0.4}(KI)_{0.1}$	0.109	1.407	20.255
$(NaCl)_{0.7}(KBr)_{0.2}(KI)_{0.1}$	0.085	2.053	75.187
$(NaCl)_{0.1}(KBr)_{0.6}(KI)_{0.3}$	0.111	1.363	18.152
$(NaCl)_{0.3}(KBr)_{0.4}(KI)_{0.3}$	0.066	1.362	104.466
$(NaCl)_{0.5}(KBr)_{0.2}(KI)_{0.3}$	0.158	1.366	2.922
$(NaCl)_{0.1}(KBr)_{0.4}(KI)_{0.5}$	0.051	1.038	142.709
$(NaCl)_{0.3}(KBr)_{0.2}(KI)_{0.5}$	0.047	1.140	183.125
$(NaCl)_{0.1}(KBr)_{0.2}(KI)_{0.7}$	0.055	1.523	179.212

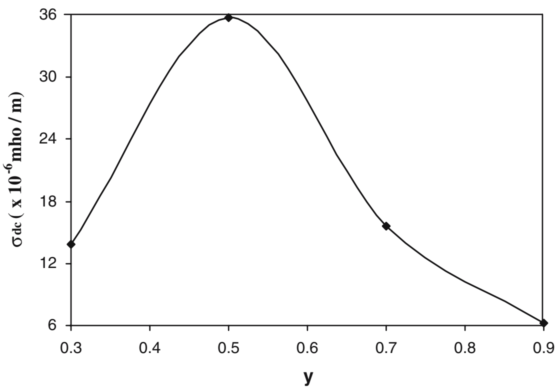

Fig. 1 Composition (taken for crystallization) dependence of σ_{dc} at 50 °C for $x = 0.1$

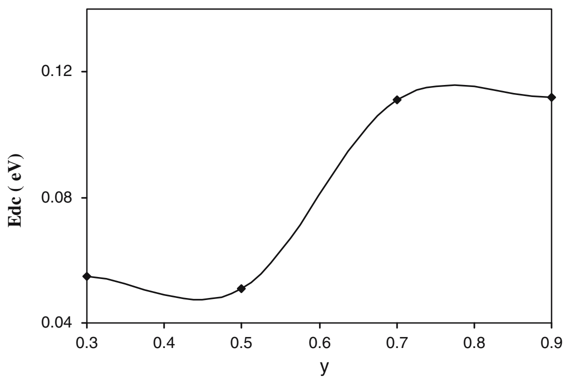

Fig. 2 Composition (taken for crystallization) dependence of E_{dc} for $x = 0.1$

are expected to be more in the multiphased solid solutions investigated here.

Dielectric parameters

The ε_r, tanδ and σ_{ac}values from the present study are provided in Tables 3, 4 and 5, respectively. The activation energies (E_{ac}), low frequency (static) dielectric permittivity, ε(o) and high frequency dielectric permittivity, ε_∞ are provided in Table 6. ε(o) in Table 6 is the ε_r value at 50 °C for 1 kHz frequency (assumed to be low) from Table 3. ε_∞ was evaluated from the refractive index in the optical range ($\varepsilon_\infty = n^2$) reported previously [8].

Dielectric constants determined for the end member crystals are nearly of the same order as those obtained by previous authors [13]. Small difference observed may be due to the difference in the method of preparation of crystals. Also, the samples prepared and used in the present study are polycrystalline. The ε_r values are found to increase with increase in temperature for the 13 crystals studied. This is similar to that observed for KCl–KBr and RbCl–RbBr mixed crystals [7]. The tanδ and σ_{ac} values are also found to increase with increase in temperature. The increase in dielectric constant with temperature observed in the present study is large when compared to that of earlier workers. This may be due to the difference in the method and conditions used for the growth of crystals and also to the thermal defects formed in the crystals while cooling them from the melting temperature to room temperature.

Composition (bulk) dependences of ε_r at 50 °C for $x = 0.1$ is shown (as an illustration) in Fig. 3. Composition (bulk) dependence of E_{ac} for $x = 0.1$ is shown (as an illustration) in Fig. 4. Results observed in the present study show that the composition has complicated influences on the dielectric constant, tanδ, σ_{ac} and E_{ac} values.

The dielectric constant of a material is generally composed of four types of contributions, viz. electronic, ionic, orientational and space charge polarizations. All of these may be active at low frequencies. The nature of variations of dielectric constant with frequency and temperature indicates the type of contributions that are present in them. The dipolar orientational effect can be seen in some materials at high frequencies and ionic and electronic polarizations below 10^3 Hz in others. The large value of ε_r at low frequency and at low temperature is due to the presence of space charge polarization, which depends on the purity and perfection of the sample. The orientational polarization does not exist for ionic crystals. The major contributions to dielectric constant for alkali halide crystals are from electronic and ionic polarizations.

Displacement of an ion from an equilibrium position is equivalent to the placing of a fictitious dipole at the state with the ion in equilibrium. Although positive and negative ions displace in opposite directions in an electric field, the induced moments all have the same sign. Since ionic (vibrational, displacement) polarization is related to the oscillations of ions, the proper frequencies are much lower than those of electrons due to large differences between masses [1].

The high frequency and low frequency permittivity values differ significantly for all the crystals. The ionic polarization is found to be very large in the case of almost all the ternary (multiphased) solid solutions when compared to that found for the three end member crystals. Moreover, the Debye frequencies (cut-off or limitation frequency of the vibration spectrum) obtained for these crystals [8] lie in the infrared range.

Sathaiah [7] has analysed the influence of lattice vibrational anharmonicity for KCl–KBr mixed crystals and found that the nonlinear variation with composition

Table 3 Dielectric constants

System (with composition taken for crystallization)	ε_r for temperatures (°C)										
	50	60	70	80	90	100	110	120	130	140	150
NaCl	5.78	6.49	7.87	9.58	10.64	11.01	13.07	15.10	16.20	17.80	18.00
KBr	4.93	5.26	5.59	6.26	6.93	7.59	8.60	9.93	11.26	12.93	14.26
KI	4.00	5.20	5.80	6.20	6.91	7.59	8.29	8.98	9.62	10.13	10.68
$(NaCl)_{0.1}(KBr)_{0.8}(KI)_{0.1}$	26.40	28.30	29.67	30.76	32.12	33.75	36.75	36.75	38.11	39.20	40.57
$(NaCl)_{0.3}(KBr)_{0.6}(KI)_{0.1}$	3.62	3.92	4.21	4.51	4.80	5.39	5.99	6.58	8.94	10.13	10.72
$(NaCl)_{0.5}(KBr)_{0.4}(KI)_{0.1}$	9.10	9.59	9.93	10.23	10.54	11.37	12.09	13.26	14.59	16.89	21.82
$(NaCl)_{0.7}(KBr)_{0.2}(KI)_{0.1}$	28.54	29.84	31.47	33.10	34.40	36.36	38.64	40.91	43.19	45.80	49.38
$(NaCl)_{0.1}(KBr)_{0.6}(KI)_{0.3}$	32.08	33.95	36.14	38.01	39.89	39.89	43.01	44.26	45.82	47.39	49.57
$(NaCl)_{0.3}(KBr)_{0.4}(KI)_{0.3}$	7.01	8.02	9.71	11.05	12.06	13.07	14.42	16.44	18.13	19.81	20.32
$(NaCl)_{0.5}(KBr)_{0.2}(KI)_{0.3}$	21.38	25.21	28.08	30.95	33.34	36.69	40.04	42.45	45.30	47.22	51.04
$(NaCl)_{0.1}(KBr)_{0.4}(KI)_{0.5}$	21.66	22.49	23.08	23.55	24.66	24.66	26.08	26.08	26.71	27.50	28.28
$(NaCl)_{0.3}(KBr)_{0.2}(KI)_{0.5}$	9.28	10.35	11.43	12.50	12.50	12.50	13.58	14.65	15.73	16.80	18.95
$(NaCl)_{0.1}(KBr)_{0.2}(KI)_{0.7}$	34.30	35.24	36.81	38.39	39.96	41.21	43.10	44.69	46.87	49.38	49.38

Table 4 Dielectric loss tangents

System (with composition taken for crystallization)	tan δ for temperatures (°C)										
	50	60	70	80	90	100	110	120	130	140	150
NaCl	4.32	5.75	6.37	7.45	9.10	9.89	10.31	10.75	11.21	12.05	13.33
KBr	2.69	3.09	3.82	4.51	4.88	5.41	5.87	6.21	6.67	7.40	7.93
KI	3.21	3.57	3.89	4.37	5.28	6.78	7.38	8.22	8.77	9.21	9.78
$(NaCl)_{0.1}(KBr)_{0.8}(KI)_{0.1}$	3.80	4.10	4.60	5.00	5.30	5.80	6.00	6.50	7.10	7.60	8.10
$(NaCl)_{0.3}(KBr)_{0.6}(KI)_{0.1}$	3.39	4.02	4.81	5.18	5.71	6.17	6.51	6.97	7.70	8.23	8.71
$(NaCl)_{0.5}(KBr)_{0.4}(KI)_{0.1}$	3.21	3.94	4.64	5.52	6.23	6.88	7.56	8.08	8.51	8.80	9.09
$(NaCl)_{0.7}(KBr)_{0.2}(KI)_{0.1}$	5.07	6.17	7.05	7.95	8.50	9.17	10.20	10.87	11.31	11.71	12.11
$(NaCl)_{0.1}(KBr)_{0.6}(KI)_{0.3}$	4.50	4.80	5.10	5.60	5.90	6.20	6.90	7.20	7.60	8.00	8.40
$(NaCl)_{0.3}(KBr)_{0.4}(KI)_{0.3}$	10.09	10.11	10.12	10.13	10.14	10.15	10.16	10.17	10.19	10.25	10.26
$(NaCl)_{0.5}(KBr)_{0.2}(KI)_{0.3}$	10.37	10.42	10.53	10.59	10.69	10.76	10.81	10.95	11.21	11.23	11.48
$(NaCl)_{0.1}(KBr)_{0.4}(KI)_{0.5}$	5.40	5.90	6.20	6.50	6.90	7.20	7.60	8.00	8.50	8.90	9.30
$(NaCl)_{0.3}(KBr)_{0.2}(KI)_{0.5}$	7.13	8.29	9.30	10.12	12.21	12.40	12.79	13.07	14.11	14.20	15.12
$(NaCl)_{0.1}(KBr)_{0.2}(KI)_{0.7}$	4.20	4.70	5.10	6.40	6.90	7.40	8.00	8.30	8.80	9.10	9.50

Table 5 A.C. electrical conductivities ($\times 10^{-7}$ mho m^{-1})

System (with composition taken for crystallization)	σ_{ac} for temperatures (°C)										
	50	60	70	80	90	100	110	120	130	140	150
NaCl	13.88	20.74	27.86	39.67	53.81	60.52	74.89	90.22	100.93	119.21	133.35
KBr	7.37	9.04	14.98	15.70	18.81	22.83	28.07	34.29	41.76	53.21	62.88
KI	7.14	10.32	12.54	15.06	20.28	28.60	34.00	41.03	46.89	51.85	58.05
$(NaCl)_{0.1}(KBr)_{0.8}(KI)_{0.1}$	55.78	64.52	75.89	85.52	94.66	108.84	122.60	132.82	150.45	165.65	182.72
$(NaCl)_{0.3}(KBr)_{0.6}(KI)_{0.1}$	6.82	8.76	11.26	12.99	15.24	18.49	21.68	25.50	38.28	46.36	51.92
$(NaCl)_{0.5}(KBr)_{0.4}(KI)_{0.1}$	16.24	21.01	25.62	31.40	36.51	43.50	50.82	59.58	69.04	82.65	110.29
$(NaCl)_{0.7}(KBr)_{0.2}(KI)_{0.1}$	80.46	102.38	123.37	146.33	162.59	185.40	219.16	247.28	271.62	298.23	332.52
$(NaCl)_{0.1}(KBr)_{0.6}(KI)_{0.3}$	80.27	90.61	102.48	118.35	130.86	137.52	165.01	177.19	193.63	210.80	231.52
$(NaCl)_{0.3}(KBr)_{0.4}(KI)_{0.3}$	39.33	45.08	54.64	62.18	67.99	73.76	81.46	92.97	102.72	110.70	116.46
$(NaCl)_{0.5}(KBr)_{0.2}(KI)_{0.3}$	123.28	154.42	174.67	182.26	198.18	219.52	240.68	258.47	282.38	294.87	325.82
$(NaCl)_{0.1}(KBr)_{0.4}(KI)_{0.5}$	65.04	73.78	79.57	85.11	94.61	98.72	110.21	116.01	126.24	136.09	146.24
$(NaCl)_{0.3}(KBr)_{0.2}(KI)_{0.5}$	36.79	47.71	59.10	70.34	84.86	98.70	99.60	102.32	107.17	123.31	159.32
$(NaCl)_{0.1}(KBr)_{0.2}(KI)_{0.7}$	80.10	92.09	104.38	136.61	153.31	169.56	191.72	206.25	229.34	249.86	260.84

Table 6 Activation energies (eV), low and high frequency dielectric permittivities and ω_t/ω_l (=$[\varepsilon(o)/\varepsilon_\infty]^{1/2}$)

System (with composition taken for crystallization)	E_{ac}	$^a\varepsilon(o)$	$^a\varepsilon_\infty$	ω_t/ω_l
NaCl	0.261	5.78 (5.92)	2.409 (2.33)	1.549
KBr	0.244	4.93 (4.92)	2.458 (2.35)	1.416
KI	0.251	4.00 (5.11)	2.800 (2.64)	1.195
$(NaCl)_{0.1}(KBr)_{0.8}(KI)_{0.1}$	0.138	26.40	2.493	3.254
$(NaCl)_{0.3}(KBr)_{0.6}(KI)_{0.1}$	0.236	3.62	2.488	1.206
$(NaCl)_{0.5}(KBr)_{0.4}(KI)_{0.1}$	0.210	9.10	2.486	1.913
$(NaCl)_{0.7}(KBr)_{0.2}(KI)_{0.1}$	0.162	28.54	2.448	3.414
$(NaCl)_{0.1}(KBr)_{0.6}(KI)_{0.3}$	0.124	32.08	2.568	3.534
$(NaCl)_{0.3}(KBr)_{0.4}(KI)_{0.3}$	0.128	7.01	2.550	1.658
$(NaCl)_{0.5}(KBr)_{0.2}(KI)_{0.3}$	0.105	21.38	2.503	2.923
$(NaCl)_{0.1}(KBr)_{0.4}(KI)_{0.5}$	0.093	21.66	2.617	2.877
$(NaCl)_{0.3}(KBr)_{0.2}(KI)_{0.5}$	0.149	9.28	2.600	1.889
$(NaCl)_{0.1}(KBr)_{0.2}(KI)_{0.7}$	0.143	34.30	2.686	3.574

[a] Values given in parentheses are taken from the literature (at 27 °C) [13]

of dielectric loss, A.C. electrical conductivity and A.C. activation energy could be attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries. The nonlinear variation with composition observed here for the ternary solid solutions can similarly be attributed to such anharmonicities.

It is seen that the nonlinear composition dependence reaches a maximum at intermediate compositions. Similar observations have been made by Sathaiah for KCl–KBr and RbCl–RbBr mixed crystals [7]. Sathaiah showed that the anharmonic contribution is enhanced for these intermediate compositions. In the present study, the nonlinear variation with bulk composition may possibly be explained as due to the influence of lattice vibrational anharmonicity.

The Lyddane–Sachs–Teller (LST) relation,

$$\frac{\omega_l^2}{\omega_t^2} = \frac{\varepsilon(o)}{\varepsilon_\infty},$$

establishes a direct link between the frequencies of the two oscillation modes and the ‘‘static’’ and ‘‘optical’’ values of the dielectric permittivities [1]. ω_l/ω_t (= $[\varepsilon(o)/\varepsilon_\infty]^{½}$) values were also calculated and provided in Table 6. The value obtained for KBr (1.416) compares well with that obtained by earlier workers (1.39 [1]).

In terms of utility, the multiphased ternary solid solutions with high dielectric constants are expected to be more useful than the end member crystals.

Conclusions

D.C. electrical conductivity measurements were carried out on multiphased $(NaCl)_x(KBr)_{y-x}(K(I))_{1-y}$ crystals. Activation energies and mean jump frequencies were determined. Capacitance and tanδ were measured, and ε_r, σ_{ac} and E_{ac} values were determined from the data obtained. The results indicate that composition has complicated influences on the σ_{dc}, E_{dc}, $1/\tau_o$, ε_r , tanδ, σ_{ac} and E_{ac} values. This has been attributed to enhanced diffusion of charge carriers along dislocations and grain boundaries. The multiphased ternary solid solutions are found to have large dielectric constants and are expected to be more useful than their end member crystals.

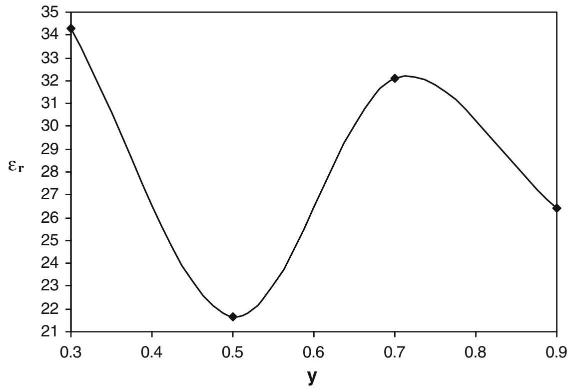

Fig. 3 Composition (taken for crystallization) dependence of ε_r at 50 °C for x = 0.1

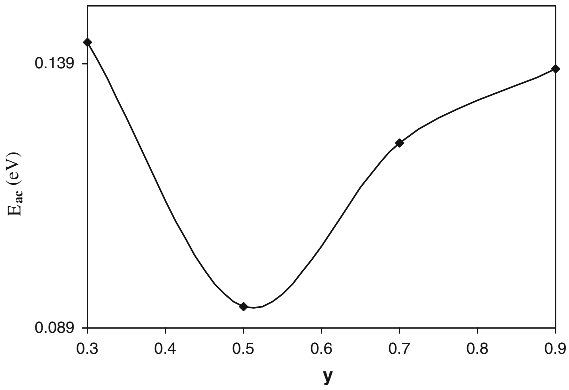

Fig. 4 Composition (taken for crystallization) dependence of E_{ac} for x = 0.1

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