Madras Journal Series Pvt Ltd
Advanced Materials & Applications
Adv. Mater. App. 5 (2020) 31-45
ISSN: 2582-5070

Mixed crystals of alkali halides-An overview

C. K. Mahadevan

Department of Physics, Bharathidasan University, Tiruchirappalli-620024, Tamil Nadu, India.

Corresponding author: mahadevan58@yahoo.co.in

Received 23 June 2020, Received in final form 29 June 2020, Accepted 29 June 2020

Abstract

It becomes useful and necessary to prepare alkali halide mixed crystals (regardless of miscibility problem) and characterize them, as mixed crystals of alkali halides find their applications in several optical, optoelectronic and electronic devices. Moreover, development of lasers led to the development of alkali halide polycrystalline materials for use as optical components. Several reports are available, in the recent decades, on single phased and multiphased mixed crystals of alkali halides. This article contains an overview of various studies made in the preparation and characterization of single phased and multiphased mixed crystals (both single crystals and polycrystalline aggregates) of alkali halides focusing the results reported by the present author and his co-workers.

Keywords: *Alkali halide mixed crystals, Single crystal, Polycrystal, Crystal growth, Melt method, Solution method, Physical properties.*

1. Introduction

Alkali halide crystals have attracted the researchers for several decades and have always been at the center state of solid-state physics. A vast amount of information has been generated on all aspects of the alkali halides due to their dual importance-both purely scientific and technological. Also, the development of lasers revived the interest in alkali halides and led to the development of polycrystalline alkali halides as materials for optical components [1]. Moreover, as alloys are more useful than the pure simple metals in device fabrications, mixed alkali halides find their applications in several optical, opto-electronic and electronic devices [2].

If the end member crystals are isomorphous with comparable lattice constants/volumes, it is expected to form a series of single phased mixed crystals. Otherwise, it is expected to form multiphased mixed crystals. In some cases, quasi mixed crystals are also possible. While forming a mixed crystal (solid solution), the added (guest or solute) ion goes to substitutional position or interstitial position which can be understood by the ionic radius of the added ion and electronic configuration of the lattice (host or solvent) ion. There are three different possibilities, *viz.* substitutional, interstitial and defect solid solutions [3].

The mixed crystals of alkali halides are of the completely disordered substitutional type. In the recent decades, there are several reports available on binary, ternary and quaternary mixed (single/mono phased as well as multiphased) crystals (both single crystals and polycrystalline aggregates) of alkali halides [2, 4 - 58]. In this article (overview), we consider the studies made on single phased mixed crystals of alkali halides in general and multiphased mixed crystals of alkali halides in particular focusing the results reported by the research group of the present author.

2. Alkali Halide Crystals

The binary anhydrous compounds formed by the combination of alkali (metal) atoms of the first group and halogens of the seventh group are called alkali halides or alkali metal halides. There exist some alkali trihalides and pentahalides and some hydrated compounds, but, they are not considered under alkali halides. Moreover, compounds formed from Francium (alkali metal) and Astatine (halogen) which are rare or unstable, are also not considered. So, compounds considered under alkali halides are: LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, CsCl, CsBr and CsI. Electron transfer and formation of ions are very much favored by the electronic configuration of the alkali metal atoms and the halogen atoms. A comprehensive range of known physical properties of alkali halides have been brought in a single book by Sirdeshmukh *et al* [1] for the use of researchers in this millennium.

Crystals of alkali halides occur in either of the two structures, *viz.* the NaCl structure and the CsCl structure. At normal room temperature conditions,

the CsCl, CsBr and CsI crystallize in the CsCl structure and the others crystallize in the NaCl (*halite*) structure. For the NaCl structure: the point group, space group, coordination number, number of molecules per unit cell and the reciprocal lattice are m3m, Fm3m, 6, 4 and body centered cubic respectively; the atomic position coordinates are (0.0, 0.0, 0.0), (0.5, 0.5, 0.0), (0.5,0.0, 0.5), (0.0, 0.5, 0.5) for Na and (0.5, 0.5, 0.5), (0.0, 0.5, 0.0), (0.5, 0.0, 0.0), (0.0, 0.0, 0.5) for Cl. For the CsCl structure: the point group, space group, coordination number, number of molecules per unit cell and the reciprocal lattice are m3m, Pm3m, 8, 1 and simple cubic respectively; the atomic position coordinates are (0.0, 0.0, 0.0) for Cs and (0.5, 0.5, 0.5) for Cl.

Other than LiF and NaF, all the alkali halides are found to be soluble in water and, in principle, can be crystallized from their aqueous solutions. Moreover, as all the alkali halides have congruent melting points, their crystals can be grown from their melts. The alkali halides with NaCl structure cleave along the (100) plane whereas those with CsCl structure do not exhibit any cleavage. The CsCl transforms to NaCl structure at high temperatures and NaCl, K halides and Rb halides transform to CsCl structure at high pressures.

It has been found that while LiF, NaF and NaCl are useful in UV transmission KBr, KI, CsBr and CsI are useful in infrared transmission. Several alkali halides (pure and doped) have been employed in energy detection in X-ray, γ-ray and Cerenkov regions. LiF and NaCl have been employed as monochromators for X-rays whereas KCl-KBr mixed crystals have been found to be useful as neutron monochromators.

Some doped alkali halides are used as thermoluminescence dosimeter device materials: *for example*, Tl doped LiF is used in commercial dosimeters. CsI(Na), CsI(Tl), RbBr(Tl), etc are used as efficient X-ray imaging sensors. Doped alkali halides are used for (color-centre-based) information storage in visible and X-ray regions. Color-centre-based alkali halide lasers (tunable and have laser line of very narrow width when used in single wavelength mode) have been developed, some are commercially available.

NaCl is considered as a pressure marker and harmonic generation and superconductivity have also been observed in alkali halides. Results obtained in a recent study made by the present author along with his Chinese co-workers (Yongtao Li, Fanming Zeng and Jinghe Liu, School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China; *To be published*) indicate that the Ce^{3+} doped NaCl crystals grown in large size can be considered as promising materials for radiation dosimetry and scintillation applications due to their high hardness, low optical absorption, excellent photoluminescence and thermoluminescence performance and low fading advantages.

3. Mixed Crystals

Two or more elements/compounds form a continuous solid solution if a single set of lattice parameters (a, b, c, α, β and γ) can be assigned, at all compositions, to the solid solution. That is, if the guest ion behaves in the same way as the lattice (host) ion, a wide range of solubility may be possible. The term 'mixed crystal' is used to describe this effect. However, as the guest ions are all distributed at random throughout the lattice, it is more appropriate to use the term 'solid solution'.

The substitutional type solid solutions have some of the normal lattice sites in the solvent crystal (host) occupied by solute atoms (guest) leaving the structure of the solvent crystal unchanged. KCl and KBr, *for example*, form solid solutions (mixed crystals) of any composition between them. The interstitial type solid solutions arise when the solute atoms occupy the interstitial positions of the solvent crystal lattice. CaF_2-YF_3 is an example of this type. Defect type solid solutions are formed when some lattice sites of one of the mixing components remain vacant. Chemical compounds of transition elements, sulfides, selenides and some oxides are of this type.

Formation of single phased mixed crystal or solid solution, in general, requires that [59 - 61]: (a) The structures of the two (or more) crystals should be of similar type; (b) The bonds in the two (or more) crystals should be of similar type; (c) The radii of the substituent atoms should not differ by more than about 15 % from that of the smaller one; and (d) The difference between their lattice parameters should be less than 6 %.

For ionic crystals like alkali halides, Tobolsky's rule states that complete miscibility is possible only above a temperature T K given by $T = 4.5\ \delta^2$ where δ is the percentage difference in lattice constants [2, 56, 62]. For alkali halides at room temperature the δ takes a value of 6 %. This shows that, at room temperature, there are available broad miscibility gaps in several mixed systems of alkali halides. So, at near ambient temperatures, single phased mixed crystals are not possible to be prepared for these systems. Reports available on the growth of alkali halide mixed (single phased as well as multiphased) crystals (both single crystals and polycrystalline aggregates) have evidenced the Tobolsky's rule.

Mijangos *et al* [63] have found that the optical absorption F band allows to have a numerical criterion, based on the percentage respective of the F band energy, in order to predict possible solid solutions.

A mixed crystal is found to have physical properties analogous to those of the pure (end member) crystals, but, with the composition dependence varying from system to system and property to property. Some of the physical properties change monotonically with composition, in several systems, in a linear or nearly linear manner. By establishing the trend in composition dependence, we will have a way to get a tailor-made crystal with a desired value for a given physical property. The composition dependence is highly nonlinear in a few properties and, in some systems, the magnitude of the given physical property for the mixed crystal even exceeds the values for the end member crystals. By this way, we can have a new crystal added in the family of crystals. This behavior, *for example*, is shown in the microhardness property of alkali halide mixed crystals. Moreover, some mixed crystals show exciting behavior such as the appearance of a first-order Raman spectrum in mixed crystals of alkali halides which is absent in the end member crystals.

4. Alkali Halide Mixed Crystals

Alkali halide mixed crystals have been found to be interesting and important as their end member crystals are. Several of these mixed crystals have found applications in information storage devices, as laser window materials and as neutron monochromators [59]. So, these alkali halide mixed crystals have created considerable interest and curiosity among a large number of investigators [64]. A treatise on mixed crystals by Kitaigorodsky [65], as it covers a wide range, has not considered in graet detail the alkali halide mixed crystals. It can be seen from the available literature that many investigations have been carried out and reported on alkali halide mixed crystal systems with the NaCl structure but not on systems with the CsCl structure.

Several researchers have reported the growth and characterization of binary mixed crystals (both single phased and multiphased) based on NaCl, NaBr, NaI, KCl, KBr, KI, RbCl, RbBr, *etc.* Harbabu and Subbarao [4] have reported a review on the growth aspects and characterization of binary alkali halide mixed crystals. Sirdeshmukh and Srinivas [5] have reported a review on the various physical properties of binary alkali halide mixed crystals. While Jayakumari [59] has provided some details on binary mixed crystals of sodium and potassium halides Priya [64] has provided some details on ternary and higher level alkali halide mixed crystals.

5. Binary Alkali Halide Mixed Crystals

Barrett and Wallace [66] have reported that a continuous series of single phased mixed crystals could not be formed with $Na_xK_{1-x}Cl$ system. Nair and Walker [67] have reported that multiphased (three f.c.c. phases characterized by three lattice constants) $KBr_{1-x}I_x$ crystals could be formed for the extreme concentration ranges $x < 0.3$ and $x > 0.7$. Padma and Mahadevan [36] could obtain multiphased mixed polycrystals of NaCl-KBr grown from miscible NaBr and KCl allowing it to be understood as Na^+ has more affinity towards Cl^- than Br^-.

Haribabu and Subbarao [4] have provided a survey of knowledge available by then about the nature of imperfections present and their role in understanding various properties associated with the alkali halide mixed crystals. They have attempted to distinguish different types of mixed crystals, the conditions for the formation of a mixed crystal, the local strains that arise in the lattice due to the difference in the size of the ions that constitute the mixed crystal. They have reviewed the results obtained from various studies such as ionic conductivity, dielectric loss, microhardness, radiation hardening, color centers, optical absorption, thermoluminescence, *etc.* on binary alkali halide mixed cryastals. Also, they have concluded that, as several authors reported very high defect concentrations in mixed crystals, the presence of higher concentrated defects have a decisive role on transport properties, microhardness, radiation hardening, *etc.* in mixed crystals.

Sirdeshmukh and Srinivas [5] have reviewed the physical properties of the binary alkali halide mixed crystals reported by then such as the experimentally determined quantities like the lattice constants, compressibility, elastic constants, thermal expansion, specific heats, Debye-Waller factors, dielectric constant, refractive index, infrared spectra and Raman spectra and also some calculated solid-state parameters like Debye temperatures and lattice energies. The composition dependence analysis made by them shows four types of alkali halide mixed crystals which are denoted as: Type A with properties varying linearly with composition, Type B with properties varying slightly nonlinearly with composition, Type C with properties depending highly nonlinearly on composition with the values for the mixed crystals exceeding the values for the end member crystals, and Type D with properties

which are peculiar to the mixed crystals and not exhibited by the end member crystals.

Anandakumari and Chandramani [26] have reported that they had grown, at room temperature from aqueous solutions, single phased $(KBr)_x(NaBr)_{1-x}$ single crystals. As per Tobolsky's rule, KBr and NaBr are miscible only at above 488 K. Later, Padma and Mahadevan [38] have reported that they had obtained multiphased $(KBr)_x(NaBr)_{1-x}$ polycrystals (polycrystalline aggregates) from melt. They inferred that the single crystals grown by Anandakumari and Chandramani ought to be multiphased. The earlier authors would have reported only the total average values of the lattice constants (obtained for two different f.c.c. phases).

A different approach was presented by Kikuchi [68] to evaluate the microcrystalline thermodynamic properties of solid solutions by combining the molecular dynamics (MD) method and a chemical thermodynamic approach. In alkali halide solid solutions (A,B)X, the coordination type of halide ions is classified into 7 types: X_n (n = 0 to 6) and that of cations into 13 types: A_n (n = 0 to 12) and B_n (n = 0 to 12) depending on the kind and coordination numbers of the nearest cation and entropy of mixing for a nonideal solid solution. The solvus curve of the NaCl-KCl mixed system exhibiting the asymmetric nature was well demonstrated. Also, the temperature of the apex of the solvus agreed well with the experimental data. The solvus curve of NaCl-KCl solid solution could also be estimated using the lattice constants of the end member crystals. Moreover, this approach can be applied to all kinds of solid solutions with different structure types.

Significant differences in composition have been found to occur in mixed crystals from region to region of a crystal. Nair and Walker [67] have observed local variations in composition up to 20 % in KCl-KBr crystals. This difference is found to be more in the case of solution grown crystals than in the case of melt grown crystals.

Composition dependence of the physical properties of mixed crystals is very important to be considered while carrying out the crystal growth and characterization studies on mixed crystals. This demands an accurate determination of the composition in a mixed crystal. For the composition determination the potentiometric titration method [69] can be used in the case of anionic substituted alkali halide mixed crystals. The atomic absorption spectroscopic (AAS) and X-ray fluorescence spectroscopic (XRFS) [67] techniques can be used for cationic substituted alkali halide mixed crystals. The law of composition dependence of lattice constants has been well established and X-ray diffraction techniques can very well be used to determine the lattice constants accurately. This affords a simple but reliable method for the estimation of composition in alkali halide mixed crystals with anionic as well as cationic substitution [70]. Assuming an additive rule, the measured macroscopic densities and refractive indices can also be used for the composition determination [2, 30, 31, 34, 67].

In general, the composition dependence of lattice constants in a mixed crystal series can be expressed as [59]:

$$a^n = \mathrm{x}a_1^{\mathrm{n}}+(1-\mathrm{x})a_2^{\mathrm{n}} \quad (1)$$

Here, a is the lattice constant of the mixed crystal and a_1 and a_2 are the lattice constants of the end member crystals. When n = 1 (lattice constants are assumed to be additive), equation (1) becomes:

$$a = \mathrm{x}a_1+(1-\mathrm{x})a_2 \quad (2)$$

predicting a linear composition dependence which is known as Vegard's law. The bulk of evidence indicates that the composition dependence of lattice constants in alkali halide mixed crystal systems can very well be represented by Vegard's law [59].

When n = 3 (lattice volumes are assumed to be additive), equation (1) becomes:

$$a^3 = \mathrm{x}a_1^3+(1-\mathrm{x})a_2^3 \quad (3)$$

predicting an ideal mixed crystal which is known as Retgers' rule. It has also been predicted, through theoretical investigations, that n = 3 [59]. If the difference between a_1 and a_2 is very small, then equation (3) is indistinguishable from equation (2). For all the crystal systems, equation (3) can also be expressed as [71, 72]:

$$\mathrm{V} = \mathrm{x}\mathrm{V}_1+(1-\mathrm{x})\mathrm{V}_2 \quad (4)$$

Here, V is the lattice volume of the mixed crystal and V_1 and V_2 are the lattice volumes of the end member crystals.

In a similar way, several relations have been proposed to describe the composition dependence of the Debye temperatures of the alkali halide mixed crystals. Among all, the Kopp-Neumann relation [73] is found to be more significant. This was obtained by assuming the additivity of specific heats and assuming the Debye T^3 expansion (the Debye theory expression for specific heat at low temperatures) and expressed as [71, 72]:

$$\theta^{-3} = x\theta_1^{-3}+(1-x)\theta_2^{-3} \quad (5)$$

Here, θ is the Debye temperature of the mixed crystal and θ_1 and θ_2 are the Debye temperatures of the end member crystals. All the seven alkali halide mixed crystals studied by Geetakrishna *et al* [16] have been found to satisfy the Kopp-Neumann relation.

The lattice parameters determined for different compositions of NaCl-NaBr (miscible at room temperature) mixed system showed slight deviations from Vegard's law, the deviation being more in crystals with higher NaCl content and less in crystals with higher NaBr content [59]. Vesnin and Zakoryashin [74] determined the whole equilibrium decay curve of NaCl-KCl mixed system and showed that the rectilinear diameter rule and empirical rule of constancy of molar volumes sum at conjugate points on the decay curve. Jayakumari and Mahadevan [30] have found that, in the case of NaCl-KCl and NaCl-KBr binary mixed crystals, all the X-ray diffraction peaks could be indexed with two f.c.c. lattices (instead of one) showing the existence of two f.c.c. phases.

Shankar and Sharma [7] have calculated the electronic dielectric constant and fractional ionic character of the chemical bond for the mixed crystals (for the entire range of composition): NaCl-NaBr, KCl-KBr, KBr-KI and CsCl-CsBr (with common cations); CsCl-RbCl and CsCl-KCl (with common anions); *etc.* They have found that the calculated values depend sensitively on the composition of the mixed crystals. Sipani and Gupta [9] have analysed the thermal and elastic behavior of the mixed alkali halide systems, *viz.* NaBr-NaCl, KBr-KCl and KI-KBr by employing the Rydberg potential extending up to next nearest neighbors and including the van der Waals interactions.

Sirdeshmukh *et al.* [8] have measured the melting points of the mixed alkali halide systems, *viz.* KCl-KBr, RbCl-RbBr and KBr-RbBr and found that, in all the three mixed crystal systems, the melting points vary nonlinearly with composition (with negative deviations from linearity) and the maximum deviation being at about the equimolar concentration. The authors have explained this result qualitatively in terms of the enhanced concentration of point defects and dislocations in the mixed crystals considered.

KCl and KBr are miscible at normal room temperature and single crystals of KCl-KBr mixed system are expected to be grown. Haribabu and his co-workers [56, 75] have studied the density and distribution of dislocations in KCl-KBr mixed crystals. Their study indicates a maximum dislocation density in the intermediate composition range and a regular arrangement of low-angle grain boundaries consisting of edge dislocations in crystals cleaved along the growth direction. Mijangos *et al.* [14] have studied both experimentally and theoretically the Stokes shift in F-band of additively colored $KCl_{1-x}Br_x$ mixed crystals. They have obtained a maximum shift for the mixed crystal with x = 0.3 which indicates that a strong electron-phonon interaction takes place at this particular composition.

Samavat *et al.* [51] have grown the $KCl_{1-x}Br_x$ (x = 0.1, 0.3 0.5, 0.7 and 0.9) mixed crystals by the Czochralski method and characterized them (with γ-irradiated samples) by chemical etching, X-ray diffraction and optical absorption spectral analyses. The results obtained by them show that the configuration of defects in mixed crystals, in contrast with the end member crystals, is different. They observed a minimum F center intensity with $KCl_{0.5}Br_{0.5}$ crystal, in contrast with the other mixed crystals, which could be due to the lower pigmentation intensity (by the γ-ray source) for this mixed crystal.

Jayakumari and Mahadevan [30] have grown single phased $KCl_{0.5}Br_{0.5}$ crystal up to a size of 3.5 cm and characterized. Recently, Li Guo *et al.* [56] have grown large size (illustrated in Figure 1), high quality and single (mono) phased $KCl_{1-x}Br_x$ mixed crystals [with x = 0.0 (pure KCl), 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0 (pure KBr)] successfully and characterized. Results obtained by them indicate that mixing KCl with KBr leads to significant tuning of thermal, optical, mechanical and electrical properties without disturbing the crystal structure. Also, the dielectric constant is found to increase several times due to mixing and $KCl_{0.5}Br_{0.5}$ crystal has the maximum value.

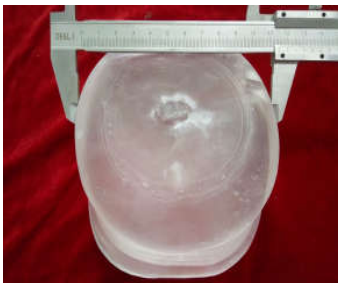

Fig. 1: *A photograph of the $KCl_{0.5}Br_{0.5}$ single crystal, $(KCl)_{0.484}(KBr)_{0.516}$ in crystal, grown by Li Guo et al. [56]*

The composition dependence of molar volume, bulk modulus and compressibility is found to be linear for NaCl-NaBr and KCl-KBr mixed systems and slightly deviating from linearity for the NaCl-KCl mixed system due to its poor stability [5].

Also, the microhardness measurements carried out on KCl-KBr, KCl-KI and KCl-NaCl mixed systems have indicated that the formation of a mixed crystal was accompanied by an increase in hardness and the microhardness attained a maximum at an intermediate composition [59].

The Debye-Waller factor (B) has been shown (theoretically) to be related to the mean square amplitude of vibration ($<u^2>$) and also the Debye temperature (θ_D) [76]. The B values of KCl_xBr_{1-x} and $NaCl_xBr_{1-x}$ crystals determined from X-ray diffraction measurements indicate that the B values of mixed crystals are found to vary nonlinearly with the composition deviating from linearity positively [16, 77]. In general, it is found that many properties vary nonlinearly with composition in these alkali halide mixed crystals.

Ketolainen *et al.* [13] observed light induced spectral shifts (F_{A1} band towards lower energy and F_{A2} band towards higher energy) in Li-doped KCl-KBr mixed crystals at liquid nitrogen temperature. They have attributed these shifts to the structural change when the electron-occupied vacancy finds a new location in relation to the neighbouring Cl^- and Br^- ions. Subrahmanyam *et al.* [17] obtained the lattice energies of NaCl-KCl, NaBr-KBr, KI-KBr and KCl-RbCl mixed crystals by making use of ultrasonic velocity data and Kudriavtsev's theory. They found a decrease of lattice energy with an increase in the concentration of the second component in these mixed systems. Subhadra *et al.* [23] have observed a highly nonlinear composition dependence of hardness in the case of polycrystalline blanks of $CsCl_xBr_{1-x}$ (prepared by melting and slow cooling) and explained as due to lattice and disorder contributions.

Padma and Mahadevan [38] formed (by the melt method) the polycrystalline aggregates of $(NaBr)_x(KBr)_{1-x}$ mixed (multiphased) crystals and characterized by density, refractive index, X-ray diffraction and electrical (DC and AC) measurements. The density and refractive index values obtained indicate linear dependence with bulk composition. The thermal parameters (B, $<u^2>$, θ_D and f_D) and electrical parameters (σ_{dc}, E_{dc}, ε_r, $\tan\delta$, σ_{ac} and E_{ac}) obtained are found to vary nonlinearly with bulk composition which has been attributed to the thermal defects formed in the crystals while cooling the crystal from the melting temperature to room temperature. Later, Katsika-Tsigourakou and Symeonidis [46] have found (for most of the compositions studied) the activation energy deduced from the temperature variation of their conductivity obeys a thermodynamical model that interrelates the defect Gibbs energy with the bulk elastic and expansivity data. Moreover, Katsika-Tsigourakou and Vassilikou-Dova [45] have quantitatively reproduced the larger temperature variation of dielectric constant observed for the $(NaCl)_{0.587}(KBr)_{0.413}$ crystal by means of a simple model which does not contain any adjustable parameter and solely makes use of the properties of the end members, *viz.* NaCl and KBr.

Mahadevan and his co-workers [40, 44, 78, 79], with an aim of discovering new materials, have prepared (from the melt) and characterized (by XRD, AAS and dielectric measurements) pure and II-VI compound (ZnO, CdO and ZnS) added simple (NaCl, KCl, NaBr, KBr and KI) and mixed (both mono and multiphased; NaCl-KCl and NaBr-KBr) polycrystalline aggregates of alkali halides. Their study indicates that the II-VI compound addition significantly changes the lattice and dielectric constants in both the simple and mixed alkali halide crystals prepared. Moreover, their study indicates that the multiphased mixed crystals (both pure and dopant added) prepared can be considered as of nanoparticle aggregation. Further, it is indicated that the II-VI compound addition creates different layers (with different physical properties) along the crystal with increase of dopant content from top to bottom.

Archana Gupta *et al.* [29] have investigated the ionic conductivities of mixed halide matrices $[(KCl)_{1-x}(NaCl)_x;\ 0\le x\le 0.4]$ and $[(BaCl_2)_{1-y}(KCl)_y;\ 0\le y\le 0.5]$ by using the impedance spectroscopic method. They found that the $(KCl)_{0.9}(NaCl)_{0.1}$ and $(BaCl_2)_{0.9}(KCl)_{0.1}$ crystals are highly conducting. The thermal characterization made by TG/DTA measurements indicate no evidence of new compound formation in these highly conducting crystals. They attributed, with the help of a simple model based on the wrong size substitution, the conductivity enhancement in the case of $(BaCl_2)_{0.9}(KCl)_{0.1}$ crystal to the net charge transfer across the interface of the biphasic mixture. However, they found that the wrong ionic size plays a significant role in the conductivity enhancement for the $(KCl)_{0.9}(NaCl)_{0.1}$ crystal.

Mahadevan and his co-workers [80-82] have attempted to prepare and characterize quazi mixed crystals based on an alkali halide (AH) and an alkaline earth halide (AEH) combined in the molecular ratio of AH:AEH as 3:1. They could grow, from aqueous solutions by the slow evaporation of solvent method, $K_{3.088}Ba_{0.912}Cl_{4.912}.1.369H_2O$ (KBC, from 3KCl + $BaCl_2.2H_2O$ solution), $K_{3.611}Ca_{0.389}Cl_{4.389}.1.177H_2O$ (KCC, from 3KCl + $CaCl_2.2H_2O$ solution) and $Na_{3.665}Ca_{0.335}Cl_{4.335}.0.153H_2O$ (NCC, from 3NaCl + $CaCl_2.2H_2O$ solution) single crystals. The results

obtained by them through temperature dependence of DC electrical conductivity measurement indicate that KBC is a dielectric material while the others (KCC and NCC) are ionic conductors. Less non-stoichiometry retains the dielectric nature (usual for ionic substances) and higher non-stoichiometry leads to ionic conduction (which could be due to the movement of loosely bound Cl^- ions) finding their utility in solid state batteries. All the three crystals grown by them belong to the triclinic crystal system with lattice parameters: a = 6.286, b = 6.294 and c = 6.309 Å, α = 90.04, β = 90.03 and γ = 90.30 °, V = 249.61 Å^3 for KBC; a = 6.267, b = 6.282 and c = 6.319 Å, α = 89.90, β = 90.73 and γ = 90.58 °, V = 248.71 Å^3 for KCC; and a = 5.633, b = 5.641 and c = 5.624 Å, α = 90.16, β = 89.93 and γ = 90.56 °, V = 178.71 Å^3 for NCC.

6. Ternary Alkali Halide Mixed Crystals

Mahadevan and his co-workers [10] have obtained larger and more stable $Na_xK_{1-x}Cl$ crystals from $(NaCl)_x(KCl)_{0.9-x}(KBr)_{0.1}$ solution than from $Na_xK_{1-x}Cl$ solutions. Their study, regardless of the miscibility problem, has made one to understand that a KBr addition to NaCl-KCl system may yield a new class of stable crystalline materials.

Mijangos and his co-workers [15, 28] have investigated the growth and optical properties of undoped (pure) and $EuCl_2$ (0.1%) doped $(KCl)_{0.50}(KBr)_{0.25}(RbCl)_{0.25}$ mixed crystals and found single phase behavior (f.c.c. type) in them. The results obtained by them show that the doped ternary mixed crystal, $(KCl)_{0.5}(KBr)_{0.25}(RbCl)_{0.25}$:0.1 % $EuCl_2$, is a promising material that could be interesting to future research related to luminescent and dosimetric processes [28].

Moroyoqui-Estrella *et al.* [50] have studied the anion composition dependence of the characteristic glow peak temperature of europium doped $(KCl)_{0.5}(KBr)_{0.25}(RbX)_{0.25}:Eu^{2+}$ (X = Cl, Br) mixed crystals. They have discussed, from the results obtained, a generalized rule to obtain the temperature from averaging the characteristic temperature as function of the composition.

Nagaveena *et al.* [57] have grown by the melt method and characterized lithium sulphate doped $(KCl)_{0.9-x}(KBr)_x(NaI)_{0.1}$ mixed crystals of different compositions. They have γ-irradiated using a ^{60}Co source and heated to at a uniform rate from room temperature to high temperature and recorded the thermoluminescence intensity-glow curves/peaks emitted by the sample crystal. The results obtained by them indicate appreciable shift in the peak position with composition change. Also, they have observed nonlinear variation of the trap depth.

Density and refractive index values have been found to form a linear relationship with composition for the binary mixed crystals of alkali halides [5]. Mahadevan and his co-workers [2, 30, 31, 34, 59, 64, 83, 84], assuming that the density and refractive index values have a linear relationship with the composition for the ternary mixed crystals also, have formed the following relations to determine the bulk composition of the ternary mixed crystals:

$$d = xd_1+(y-x)d_2+(1-y)d_3 \quad (6)$$

and

$$n = xn_1+(y-x)n_2+(1-y)n_3 \quad (7)$$

Here, d, d_1, d_2 and d_3 represent the densities of mixed crystal, first component, second component and third component respectively; n, n_1, n_2 and n_3 represent the refractive indices of mixed crystal, first component, second component and third component respectively. By solving the above two equations for x and y values, the bulk compositions of the grown ternary mixed crystals of alkali halides can be estimated.

In a similar way, Mahadevan and his co-workers [2, 30, 31, 34, 59, 64, 83, 84] have extended to ternary mixed crystals the Retger's rule and Kopp-Neumann relation as:

$$a^3 = xa_1^3+(y-x)a_2^3+(1-y)a_3^3 \quad (8)$$

and

$$\theta^{-3} = x\theta_1^{-3}+(y-x)\theta_2^{-3}+(1-y)\theta_3^{-3} \quad (9)$$

Here, a, a_1, a_2 and a_3 represent the lattice constants of mixed crystal, first component, second component and third component respectively; θ, θ_1, θ_2 and θ_3 represent the Debye temperatures of mixed crystal, first component, second component and third component respectively.

Jayakumari and Mahadevan [30, 43, 59] have reported the growth (by the Czochralski method) and characterization (by density, refractive index, X-ray diffraction and electrical (DC and AC) measurements) of ternary mixed (single) crystals: $(NaCl)_x(KCl)_{y-x}(KBr)_{1-y}$ with x varying from 0.1 to 0.7 in steps of 0.1 and y = 0.2, 0.4, 0.5, 0.6 and 0.8. The lattice parameters obtained by them show the existence of two phases (one nearly corresponds to the pure NaCl and the other corresponds to the mixed system, KCl-KBr) in crystals with NaCl content greater than 0.1 mole fraction. The thermal parameters (B, $\langle u^2 \rangle$, θ_D and f_D) along with compressibility and mean sound velocity obtained by them through X-ray diffraction measurements are found to vary nonlinearly with bulk composition. The values obtained for some mixed crystals even exceed those for the end member crystals which has

been attributed to the increase in vibrational entropy due to mixing. The electrical measurements made by them indicate that bulk composition has complicated influences on the electrical parameters (σ_{dc}, E_{dc}, ε_r, tanδ, σ_{ac} and E_{ac}) which has been attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries. Also, the ternary mixed crystals grown have been found to have large dielectric constants and are expected to be more useful than their end-member crystals. Moreover, the multiphased ternary mixed crystals grown have been found to be harder and less transparent than the other ones.

Katsika-Tsigourakou [47] has shown that these ternary mixed crystals, depending on their major constituent, are classified into three categories in each of which, the activation energy for the AC conductivity increases linearly with BΩ, where B is the isothermal bulk modulus and Ω is the mean volume per atom. The resulting three straight lines have been found to have the same slope.

Perumal and Mahadevan [31, 32, 84] have grown (by using the Czochralski method) and characterized (by carrying out density, refractive index, X-ray diffraction and electrical measurements) the multiphased ternary mixed (single) crystals of KCl, KBr and KI [$(KCl)_x(KBr)_{y-x}(KI)_{1-y}$ with x varying from 0.1 to 0.4 in steps of 0.1 and y = 0.2, 0.4, 0.6 and 0.8]. Figure 2 shows a photograph (as an illustration) of the $(KCl)_{0.1}(KBr)_{0.1}(KI)_{0.8}$ single crystal (multiphased) [the composition in crystal is $(KCl)_{0.155}(KBr)_{0.035}(KI)_{0.810}$]. Results obtained by them through X-ray diffraction measurements indicate the existence of two phases (one nearly corresponds to the pure KI and the other corresponds to the mixed system, KCl-KBr) in the ternary mixed crystals and the thermal parameters (B, $\langle u^2 \rangle$, θ_D and f_D) varying nonlinearly with bulk composition. Results obtained through electrical measurements indicate that the bulk composition has complicated influences on the electrical parameters (σ_{dc}, E_{dc}, ε_r, tanδ, σ_{ac} and E_{ac}) which has been attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries. The ternary mixed crystals grown have been found to have large dielectric constants and the multiphased crystals grown have been found to be harder than the other ones.

The transparency of the single crystals grown (Czochralski pulled) by Mahadeven and his co-workers [30, 31, 59, 84] has been found to be reduced on cooling the crystals from high temperature (nearer to the freezing point) to the room temperature. They have explained that this could be due to the introduction of thermal defects while cooling the crystals (in about 12 h without a proper control, a sort of natural cooling only).

Fig. 2: *A photograph of the $(KCl)_{0.1}(KBr)_{0.1}(KI)_{0.8}$ single crystal (multiphased), $(KCl)_{0.155}(KBr)_{0.035}(KI)_{0.810}$ in crystal, grown by Perumal and Mahadevan [31]*

Selvarajan and Mahadevan [34, 35, 83] have melt grown the multiphased ternary solid solutions (polycrystalline aggregates) from NaCl, KBr and KI starting materials $[(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ 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]. Bulk compositions have been determined from the measured density and refractive index values. X-ray diffraction measurements carried out indicate the existence of three phases (each nearly corresponds to NaCl, KBr and KI) in the ternary solid solutions and the thermal parameters (B, $\langle u^2 \rangle$, θ_D and f_D) varying highly nonlinearly with bulk composition. The electrical (DC and AC) measurements carried out indicate that the bulk composition has complicated influences on the electrical parameters (σ_{dc}, E_{dc}, ε_r, tanδ, σ_{ac} and E_{ac}), attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries. The ternary solid solutions grown have been found to have large dielectric constants and are expected to be more useful than their end member crystals.

Neelakanda Pillai and Mahadevan [37, 42, 79] have grown (from the melt) single phased ternary mixed crystals (polycrystalline aggregates) from NaCl, NaBr and NaI starting materials: $(NaCl)_x(NaBr)_{y-x}(NaI)_{1-y}$ with x having the values of 0.1, 0.3, 0.5 and 0.7 and y having the values of 0.6 and 0.8. X-ray diffraction peaks observed could be indexed with only one f.c.c. phase indicating the single phased mixed crystalline nature and the estimated thermal parameters (B, $\langle u^2 \rangle$, θ_D and f_D) have been found to vary nonlinearly with bulk composition. The electrical (DC and AC) measurements carried out at various temperatures ranging from 40 to 150 ^oC indicate that bulk composition has complicated influences on the electrical parameters (σ_{dc}, E_{dc}, ε_r, tanδ, σ_{ac} and E_{ac}),

which has been attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries. They [44, 79] have also grown CdS doped $(NaCl)_x(NaBr)_{y-x}(NaI)_{1-y}$ crystals (polycrystalline aggregates) and found that CdS doping significantly changes the lattice and dielectric constants. The X-ray diffraction measurements carried out indicate that the CdS doped ternary mixed crystals grown can be considered as of nanoparticle aggregation. Further, their study has indicated that, in the case of $(NaCl)_x(NaBr)_{y-x}(NaI)_{1-y}$ crystals, the CdS doping creates different layers (with different physical properties) along the crystal with increase of dopant content from top to bottom.

Priya and Mahadevan [2, 64] have grown multiphased ternary mixed crystals (polycrystalline aggregates) of NaCl, KCl and KI [$(NaCl)_x(KCl)_{y-x}(KI)_{1-y}$ with x having the values of 0.1, 0.3, 0.5 and 0.7 and y having the values of 0.3, 0.5, 0.7 and 0.9] by the melt method (melt cooled) and characterized by density, refractive index, atomic absorption spectroscopic, X-ray diffraction and electrical (DC and AC) measurements. Their study has indicated that the ternary mixed crystals grown exhibit three f.c.c. phases (instead of a single f.c.c. phase) each nearly corresponds to NaCl, KCl and KI crystals. The thermal parameters (determined from the X-ray diffraction data), *viz.* B, $<u^2>$, θ_D and f_D have been found to vary nonlinearly with bulk composition. The electrical parameters (σ_{dc}, E_{dc}, ε_r, tanδ, σ_{ac} and E_{ac}) obtained have indicated that the bulk composition has complicated influences on them which has been attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries. Their study has indicated that the ternary mixed crystals grown are expected to be more useful than the end member crystals though their internal structures contain multiple phases.

Padma and Mahadevan [36, 41, 78] have prepared by the melt method (melt cooled), for the first time, multiphased mixed (binary and ternary) crystals of NaCl, NaBr, KCl, and KBr using the miscible NaBr and KCl as the starting materials. They have made density, refractive index and X-ray diffraction measurements and determeined the lattice constants and composition of the crystals prepared. They have determined the thermal parameters (B, $<u^2>$, θ_D and f_D) along with compressibility and mean sound velocity from the X-ray diffraction data. Also, they have made DC and AC electrical measurements at various temperatures ranging from 35 – 150 ^oC and determined the various electrical parameters (σ_{dc}, E_{dc}, ε_r, tanδ, σ_{ac} and E_{ac}).

The polycrystalline aggregates (melt cooled) prepared by Mahadevan and his co-workers [2, 34, 36 - 40, 64, 78, 79, 83] have been observed to be fairly transparent at temperatures nearer to the freezing point. When the crystals (frozen melt) were cooled from high temperature to the room temperature (without a proper control, a sort of natural cooling only) the transparency of the crystals have been found to be reduced and becoming white. They have explained this as due to the introduction of thermal defects during cooling and also the problem related to the degree of solubility of impurities introduced into the crystal. If the concentration of impurities (for a certain temperature T) is higher than allowable due to solubility limit, then the substance excess precipitates to form a new phase (the precipitate). When the precipitate tends to form on dislocations (may be observed by electron microscopy), the crystal becomes “milky” white [85]. If the crystal is doped with sufficient concentration, then the white color may change in accordance with the dopant used [44].

The DC and AC electrical measurents made on both single crystals (Czochralski pulled) and polycrystalline aggregates (melt cooled) at various temperatures (from room temperature to about 150 ^oC) by Mahadevan and his co-workers [2, 32, 35, 37, 38, 40, 41, 43, 44, 56, 59, 64, 78, 79, 83, 84] have indicated that the electrical parameters, *viz.* σ_{dc}, ε_r and σ_{ac} increase with increasing temperature. They have explained the results obtained in the following way [2].

Electrical conduction in simple or mixed alkali halide crystals (dielectrics) is mainly considered to be a defect controlled process, particularly in the low temperature region. In the high temperature region, it is determined by the intrinsic defects caused by the thermal fluctuations in the crystal. Formation, migration and association of point defects are governed by characteristic activation energies which, upon application of pressure, may increase or decrease [2, 64]. Also, through both the law of mass action and charge neutrality criteria, an artificial increase in the concentration of defects of one type affects the concentation of other defects. Moreover, the charge transported by electrons in ionic crystals (alkali halide crystals are considered to be ionic in nature), with the usual electric fields, is expected to be zero because of a large forbidden energy gap. Hence, the precipitating effect (discussed earlier) making the crystals to become “milky” white at lower temperature also influences the electrical conduction.

Temperature dependence of the dielectric constant (ε_r) is normally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects. For the alkali halide crystals, the major contributions to the dielectric constant are from electronic and ionic polarizations. It has been shown by Varatsos [2, 64] that the electronic polarizability practically remains constant. So, the increase in dielectric constant with increasing temperature is essentially due to the temperature dependence of ionic polarizability.

Maruthi and Chandramani [49] have grown (by the slow evaporation method) and characterized (by X-ray diffraction, EDAX, microhardness and dielectric measurements) well-defined and optically transparent single crystals of $(KCl)_x(KBr)_{0.9-x}(NaI)_{0.1}$ with x = 0.1, 0.4, 0.5 and 0.7. The results obtained by them indicate the formation of single phased ternary mixed crystals accompanied by an increase in hardness varying nonlinearly with composition. The dielectric measurements made by them indicate that the mixed crystals grown are more defective containing a high concentration of dislocations, low angle grain boundaries and vacancies when compared to the end member crystals.

Neelakanda Pillai and his co-workers [52, 53] have grown (from aqueous solutions) and characterized (by X-ray diffraction, EDAX, TG/DTA and microhardness measurements) single phased ternary mixed crystals (well-defined optically transparent single crystals) of $(NaCl)_x(NaBr)_{y-x}(KCl)_{1-y}$ with seven different compositions. The Debye temperatures determined by them from the measured melting points, Debye-Waller factors and microhardness values show nonlinear variation with composition, explained as due to the increase in vibrational entropy due to mixing.

Mijangos *et al.* [54] have studied the thermoluminescence response of the ternary mixed crystal $(KCl)_{0.33}(KBr)_{0.33}(RbBr)_{0.33}:Eu^{2+}$ after γ-irradiation. They have found that the possibility of ternary mixed crystals in dosimetric application can be related to persistent traps nearer to dislocations as the mixed crystals have very good mechanical tensions and many dilocations.

Recently, Maruthi [58] has grown (by the slow evaporation method) and characterized (by EDAX and dielctric measrements) eight ternary mixed crystals, *viz.* $(KCl)_{0.2}(NaCl)_{0.1}(NaBr)_{0.7}$, $(KCl)_{0.2}(NaCl)_{0.2}(NaBr)_{0.6}$, $(KCl)_{0.2}(NaCl)_{0.5}(NaBr)_{0.3}$, $(KCl)_{0.2}(NaCl)_{0.6}(NaBr)_{0.2}$, $(KCl)_{0.1}(KBr)_{0.8}(NaI)_{0.1}$, $(KCl)_{0.4}(KBr)_{0.5}(NaI)_{0.1}$, $(KCl)_{0.5}(KBr)_{0.4}(NaI)_{0.1}$ and $(KCl)_{0.7}(KBr)_{0.2}(NaI)_{0.1}$, obtained significantly higher dielectric constants for some of these ternary mixed crystals.

7. Quaternary and Higher Alkali Halide Mixed Crystals

Mijangos *et al.* [20, 27] have grown and characterized (by refractive index, XRD, optical absorption and photoluminescence measurements) pure and 0.5 % Eu^{2+} doped $(KCl)_{0.25}(KBr)_{0.25}(RbCl)_{0.25}(RbBr)_{0.25}$ mixed crystals. From the results obtained, they have suggested that the symmetry of the Eu^{2+} site in the quaternary crystal is similar to a quenched sample of a single component crystal. Also, they have found that the Vegard's law extended to the quaternary crystal is in good agreement with the experimental results obtained.

Mohanlal and Pathinettam Padiyan [25] have grown by the melt method and characterized by XRD measurements three single crystals of the quaternary mixed system, $Rb_xK_{1-x}Br_yCl_{1-y}$ (with y = 0.25, 0.50 and 0.75 keeping x = 0.5). The resuls obtained by them indicate an enhancement of Debye-Waller factor B for the compositions y = 0.25 and 0.75, and for the intermediate composition y = 0.5, the factor B is close to the end member value.

Priya and Mahadevan [39] have prepared by the melt method, for the first time, multiphased mixed (ternary and quaternary) crystals of NaCl, NaBr, KCl, and KBr using the miscible alkali halides, *viz.* NaBr, KCl and KBr as the starting materials. XRD, density, refractive index and flame photometric measurements were made to determeine the lattice constants and composition of the crystals prepared. Figure 3 shows a photograph (as an illustration) of the polycrystal (multiphased) $[(NaCl)_{0.068}(NaBr)_{0.032}(KCl)_{0.570}(KBr)_{0.330}]$ prepared from $(NaBr)_{0.1}(KCl)_{0.6}(KBr)_{0.3}$ (starting material). This study has explored the possibility of preparing multiphased ternary and quaternary mixed crystals of NaCl, NaBr, KCl and KBr harder than the end member crystals using the miscible NaBr, KCl and KBr as the starting materials.

Fig. 3: *A photograph of the $(NaBr)_{0.1}(KCl)_{0.6}(KBr)_{0.3}$ polycrystal (multiphased), $(NaCl)_{0.068}(NaBr)_{0.032}(KCl)_{0.570}(KBr)_{0.330}$ in crystal, prepared by Priya and Mahadevan [39]*

Mijangos and his co-workers [33] have formed a crystalline nanocomposite from a melt of KBr, RbCl, RbBr, KI and RbI salts and characterized. They have found that this material consists of an aggregation of crystallites, ranging from 5 to 100 nm in size, of three different f.c.c. phases: one identified as single RbBr phase, another discussed to be the binary mixed KI(39 %):RbI(61 %) phase and the third discussed to be the ternary mixed KBr(47 %):RbCl(39 %):RbBr(14 %) phase.

8. Future Scope

Research work involving the preparation and characterization of new/modified solid state (particularly crystalline and nanostructured/low-dimensional) materials in order to explore potential applications is of paramount importance both academically and industrially.

It has been found that transparent single crystals could be formed by using the Czochralski technique with controlled slow cooling after pulling the crystal (illustrated in Figure 1) [56]. However, when the pulled crystals are cooled naturally (without any control on cooling) white coloration appears (illustrated in Figure 2) [30, 31]. Moreover, when the melts are cooled naturally (without any control on cooling) polycrystalline aggregates (with white coloration) form (illustrated in Figure 3) [2, 34, 36 - 40, 44]. In addition, the crystallite sizes determined for some polycrystalline aggregates (by using the Debye-Scherrer formula and X-ray diffraction data) indicate that these polycrystalline aggregates can be considered as of nanoparticle aggregation [44].

In principle, single crystals can be formed by slow cooling and amorphous materials can be formed by rapid cooling (quenching). A systematic investigation on this melting and cooling processes is expected to provide the required conditions for the formation of nanoparticle aggregation (aggregated nanocrystals) of simple and hybrid (mixed and/or doped) alkali (metal) halides which is expected to bring fruitful results. Also, further investigations into the growth of high quality and large size single crystals (both undoped and doped) and charcterization of mixed (both monophased and multiphased) and quazi mixed (with alkaline earth metal halides) alkali halide crystals are very much required particularly to explore the possible multifuctional materials for device applications. In addition, further studies are required to be carried out to understand the importance of polycrystalline aggregates (both undoped and doped) and characterization of simple, mixed (both monophased and multiphased) and quazi mixed (may be non-stoichiometrically with alkaline earth metal halides) alkali halide crystals as these are found to be hard materials and can be cut into any shape and polished for their utility in device applications. II-VI compounds, rare earths and transition metals can be considered as useful dopants in regard to industrial applications.

9. Conclusion

In effect, it is understood that the literature available in the past few decades carry a good amount of useful information on single crystals and polycrystalline aggregates of undoped and/or doped mixed (both monophased and multiphased) and quazi mixed alkali halide crystals. However, it is required to carry out a good number of further investigations on mixed and/or doped crystals of alkali halides in order to discover new materials for industrial applications, as discussed. This makes us to understand that the statement made by Seitz in 1946 [1, 36] on alkali halides remains relevant even now: In the field of solids, the properties of alkali halides have an enduring interest, since these crystals have continuously yielded to persistent investigation and have gradually provided us with a better and better understanding of the most interesting properties of all solids.

Acknowledgement

The support by the Council of Scientific and Industrial Research, New Delhi, India under the Emeritus Scientist Scheme (CSIR-ES Scheme No:21(1083)/19/EMR-II) is hereby gratefully acknowledged.

Funding

Preparation of this article received no specific grant from any funding agency.

Conflict of Interest

The author declares that this article was prepared in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References:

[1]. D. B. Sirdeshmukh, L. Sirdeshmukh, K. Subhadra (2001) “Alkali Halides-A Handbook of Physical Properties”, Springer Series in Materials Science-49, Springer, Berlin, Germany.

[2]. M. Priya, C. K. Mahadevan, “Studies on multiphased mixed crystals of NaCl, KCl and KI”, Cryst. Res. Technol. 44 (2009) 92.

[3]. J. Haldik (1972) "Physics of Electrolytes", Academic Press, New York, USA.
[4]. V. Haribabu, V. Subbarao, "Growth and characterization of alkali halide mixed crystals", Prog. Crystal Growth Charact. 8 (1984) 189.
[5]. D. B. Sirdeshmukh, K. Srinivas, "Physical properties of mixed crystals of alkali halides", J. Mater. Sci. 21 (1986) 4117.
[6]. Y. C. Venudhar, L. Iyengar, K. V. Krishna Rao, "Thermal expansion and Debye temperatures of KCl-KBr mixed crystals by an X-ray method", J. Mater. Sci. 21 (1986) 110.
[7]. J. Shanker, S. C. Sharma, "Evaluation of electronic dielectric constant and fractional ionic character of mixed alkali halide crystals", Phys. Stat. Solidi (b) 136 (1986) 505.
[8]. D. B. Sirdeshmukh, K. G. Subhadra, K. A. Hassan, "Melting temperatures of some alkali halide mixed crystal systems", Pramana, 34 (1990) 235.
[9]. S. K. Sipani, V.P. Gupta, "The analysis of thermal and elastic behavior of mixed alkali halide systems using Rydberg potential", Indian J. Phys. 64A (1990) 454.
[10]. X. Sahaya Shajan, K. Sivaraman, C. Mahadevan, D. Chandrasekharam, "Lattice variation and stability of NaCl-KCl mixed crystals grown from aqueous solution", Cryst. Res. Technol. 27 (1992) K79.
[11]. G. S. Kumar, T. Bhimasankaram, G. Prasad, "Ionic conductivity of KBr-KI mixed crystals", Cryst. Res. Technol. 28 (1993)1001.
[12]. T. Kumaraswamy, K. G. Subhadra, D. B. Sirdeshmukh, "X-ray diffraction studies of RbBr-RbI mixed crystals", Pramana-J. Phys. 43 (1994) 33.
[13]. P. Ketolainen, P. Silfsten, P. Raerinne, "On light-induced spectral shifts of F_A bands in mixed alkali halide crystal", J. Phys.: Condens. Matter. 6 (1994) L517.
[14]. R. R. Mijangos, R. Perez-Salas, E. M. Sandoval, M. Barboza-Flores, "Stokes shift of the F center electronic transitions in mixed ionic crystals", Rad. Effects Def. Solids 138 (1996) 153.
[15]. R. R. Mijangos, A. Cordero-Borboa, E. Camarillo, H. Riveros, V. M. Castano, "A novel ternary alkali halide crystal", Phys. Lett. A 245 (1998) 123.
[16]. P. Geetakrishna, K. G. Subhadra, T. Kumaraswmy, D. B. Sirdeshmukh, "Debye-Waller factors and Debye temperatures of alkali halide mixed crystals", Pramana-J. Phys. 52 (1999) 503.
[17]. M. Subrahmanyam, E. Rajagopal, N. Manohara Murthy, "Lattice energy of mixed alkali halide crystals: Evaluation from sound velocity studies", Indian J. Pure Appl. Phys. 38 (2000) 495.
[18]. S. Hashimoto, M. Mori, N. Ichimura, H. Kondo, Y. Harada, "Composition dependence of the four A bands for thin-solid films of $KBr_{1-x}I_x:Tl^+$", Thin Solid Films 386 (2001) 14.
[19]. A. Jankowska-Frydel, B. Kuklinski, T. Nowosielski, M. Grinberg, "The influence of the heat treatment on luminescence and EPR spectra of mixed $Na_xK_{1-x}Cl$ single crystals", Radiat. Meas. 33 (2001) 773.
[20]. R. R. Mijangos, A. Cordero-Borboa, E. Alvarez, M. Cervantes, "Optical study in a novel quaternary ionic crystal doped with europium", Phys. Lett. A 282 (2001) 195.
[21]. Y. Kimura, Y. Saito, T. Nakada, C. Kaito, "Spontaneous mixing of binary alkali halide crystals by successive evaporation", Physica E 13 (2002) 11.
[22]. M. Kiguchi, K. Saiki, A. Koma, "Heteroepitaxial growth of alkali halide solid solution on GaAs(100)", J. Cryst. Growth 237-239 (2002) 244.
[23]. K. G. Subhadra, E. Balaiah, D. B. Sirdeshmukh, "Systematic hardness measurements on $CsCl_xBr_{1-x}$ and $NH_4Cl_xBr_{1-x}$ mixed crystals", Bull. Mater. Sci. 25 (2002) 31.
[24]. D. B. Sirdeshmukh, T. Kumaraswamy, P. Geetakrishna, K. G. Subhadra, "Systematic hardness measurements on mixed and doped crystals of rubidium halides", Bull. Mater. Sci. 26 (2003) 261.
[25]. S. K. Mohanlal, D. Pathinettam Padiyan, "X-ray studies on quaternary system $Rb_xK_{1-x}Br_yCl_{1-y}$", Cryst. Res. Technol. 38 (2003) 494.
[26]. R. Anandakumari, R. Chandramani, "Evaluation of lattice parameters and defect related studies

of $(KBr)_x(NaBr)_{1-x}$ mixed crystals grown from aqueous solutions", Indian J. Phys. 77A (2003) 219.

[27]. R. R. Mijangos, H. Riveros, E. Alvarez, M. Atondo, G. Vazquez-Polo, M. Gonzalez, "Defects in a novel ionic mixed crystallographic family", Rad. Effects Def. Solids 158 (2003) 513.

[28]. R. R. Mijangos, E. Alvarez, R. Perez Salas, C. Duarte, "Optical study of a novel dielectric ternary crystal doped with europium", Opt. Mater. 25 (2004) 279.

[29]. Archana Gupta, Anjan Sil, N. K. Verma, "Preparation and characterization of mixed halide systems as solid electrolyte base", Indian J. Eng. Mater. Sci. 11 (2004) 212.

[30]. K. Jayakumari, C. Mahadevan, "Growth and X-ray studies of $(NaCl)_x(KCl)_{y-x}(KBr)_{1-y}$ single crystals", J. Phys. Chem. Solids 66 (2005) 1705.

[31]. S. Perumal, C. K. Mahadevan, "Growth and characterization of multiphased mixed crystals of KCl, KBr and KI-Part 1: Growth and X-ray diffraction studies", Physica B: Phys. Cond. Matter. 369 (2005) 89.

[32]. S. Perumal, C. K. Mahadevan, "Growth and characterization of multiphased mixed crystals of KCl, KBr and KI-Part 2: Electrical measurements", Physica B: Phys. Cond. Matter, 367 (2005) 172.

[33]. A. E. Cordero-Barboa, R. R. Mijangos, P. S. Schabes-Retchkiman, "Structural characterization of a novel spatially coherent crystalline nanocomposite obtained from a melt of KBr, RbCl, RbBr, KI and RbI salts", J. Mater. Sci. 41 (2006) 7119.

[34]. G. Selvarajan, C. K. Mahadevan, "Studies on $(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ solid solutions: 1. Lattice and thermal parameters", J. Mater. Sci. 41 (2006) 8211.

[35]. G. Selvarajan, C. K. Mahadevan, "Studies on $(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ solid solutions: 2. Electrical measurements", J. Mater. Sci. 41 (2006) 8218.

[36]. C. M. Padma, C. K. Mahadevan, "On the preparation of multiphased mixed crystals from NaBr and KCl", Mater. Manuf. Processes 22 (2007) 362.

[37]. N. Neelakanda Pillai, C. K. Mahadevan, "Preparation and electrical properties of $(NaCl)_x(NaBr)_{y-x}(NaI)_{1-y}$ crystals", Mater. Manuf. Processes 22 (2007) 393.

[38]. C. M. Padma, C. K. Mahadevan, "Growth and characterization of multiphased mixed crystals of NaBr and KBr", Mater. Manuf. Processes 23 (2008) 144.

[39]. M. Priya, C. K. Mahadevan, "Formation of multiphased mixed crystals from miscible NaBr, KBr and KCl", Cryst. Res. Technol. 43 (2008) 1069.

[40]. M. Priya, C. K. Mahadevan, "Preparation and dielectric properties of oxide added NaCl-KCl polycrystals", Physica B: Phys. Cond. Matter. 403 (2008) 67.

[41]. C. M. Padma, C. K. Mahadevan, "Studies on mutiphased mixed crystals grown from NaBr and KCl", Physica B: Phys. Cond. Matter. 403 (2008) 1708.

[42]. N. Neelakanda Pillai, C. K. Mahadevan, "X-ray diffraction studies on $(NaCl)_x(NaBr)_{y-x}(NaI)_{1-y}$ crystals", Physica B: Phys. Cond. Matter 403 (2008) 2168.

[43]. C. K. Mahadevan, K. Jayakumari, "Electrical measurements on multiphased $(NaCl)_x(KCl)_{y-x}(KBr)_{1-y}$ single crystals", Physica B: Phys. Cond. Matter. 403 (2008) 3990.

[44]. C. K. Mahadevan, "Alkali halides and nanomaterials", NICE J. Emerging Technol. 3 (2008) 39.

[45]. V. Katsika-Tsigourakou, A. Vassilikou-Dova, "Estimating the temperature dependence of the dielectric constant of multiphased mixed crystals", J. Appl. Phy. 104 (2008) 026103.

[46]. V. Katsika-Tsigourakou, C. Symeonides, "Additional evidence for the interconnection of the conductivity activation energy with bulk properties in multiphased alkali halide mixed crystals", Physica B: Phys. Cond. Matter. 404 (2009) 1079.

[47]. V. Katsika-Tsigourakou, "Multiphased $(NaCl)_x(KCl)_{y-x}(KBr)_{1-y}$ single crystals: ac conductivity activation energy versus bulk properties", Physica B: Phys. Cond. Matter. 404 (2009) 3550.

[48]. P. Easwaran, A. Anbagi, S. Nagarajan, "Optical studies on KBr:Tl and KCl-Br:Tl mixed crystals", E-Journal of Chemistry 7(2) (2010) 425.

[49]. G. Maruthi, R. Chandramani, "Microhardness and dielectric studies of ternary mixed alkali halide crystals grown by aqueous solution method", Arch. Phys. Res. 2(2) (2011) 134.

[50]. G. Moroyoqui-Estrella, R. Perez-Salas, R. R. Mijangos, "A generalized rule of average for glow peak temperature of ternary alkali halide systems", Mexican Magazine of Physics. 57 (2011) 154.

[51]. F. Samavat, E. Haji-Ali, S. Shahmaleki, S. Solgi, "Growth of $KCl_{1-x}Br_x$ mixed crystals with different composition percent and study of KBr concentration effect on optical characteristics of mixed crystals", Adv. Mater. Phys. Chem. 2 (2012) 85.

[52]. T. S. Jayanthi, S. Radhika, N. Neelakanda Pillai, "Lattice parameters and Debye temperature of $NaCl_xNaBr_{y-x}KCl_{1-y}$ ternary mixed crystals", IOSR J. Appl. Phys. 5(3) (2013) 19.

[53]. T. S. Jayanthi, N. Neelakanda Pillai, "Bulk modulus and compressibility of $NaCl_xNaBr_{y-x}KCl_{1-y}$ ternary mixed crystals grown from aqueous solutions", International Journal of Latest Technology in Engineering, Management & Applied Science III(IX) (2014) 28.

[54]. R. R. Mijangos, R. Perez Salas, G. V. Polo, H. Riveros, P.G. Martinez, "Thermoluminescence response of a mixed ternary alkali halide crystals exposed to gamma rays", ISSSD, (2014) 717.

[55]. S. Kar, "Growth and characterisation of single crystals of alkali halides", Int. J. Sci. Res. 4(12) (2014) 34.

[56]. Li Guo, Weizhao Jin, Zekun Chen, Jinghe Liu, Priya Murugasen, Fanming Zeng, C. K. Mahadevan, "Large size crystal growth and structural, thermal, optical and electrical properties of $KCl_{1-x}Br_x$ mixed crystals", J. Cryst. Growth 480 (2017) 154.

[57]. V. M. Nagaveena, C. Ningappa, S. Prashantha, R. Ananda Kumari, "Thermoluminescence studies in ternary alkali halide mixed crystals $(KCl)_{0.9-x}(KBr)_x(NaI)_{0.1}$ doped with lithium sulphate", Mater. Today Proc. 4 (2017) 11260.

[58]. G. Maruthi, "Comparative study of dielectric properties of ternary alkali halide crystals", Int. J. ChemTech Res. 12(4) (2019) 24.

[59]. K. Jayakumari (2002) "Growth and characterization of $(NaCl)_x(KCl)_{y-x}(KI)_{1-y}$ single crystals", Ph.D. Thesis, Manonmaniam Sundaranar University, Tirunelveli, India.

[60]. I. S. Prameela Kumari, C. K. Mahadevan, Formation and characterization of mixed crystals based on bis(thiourea)cadmium chloride and bis(thiourea)cadmium iodide, Int. J. Eng. Res. Appl. 4(7:4) (2014) 125.

[61]. S. Benita Jeba Silvia, C. K. Mahadevan, T. Balu, A. Moses Ezhil Raj, S. Balakumar, S. G. Jebastin Andrews, "Urea doped crystals formed with potassium-sodium pentaborate ($K_{0.5}Na_{0.5}B5$)", Surf. Interfaces, 11 (2018) 14.

[62]. A.V. Tobolsky, "Solid solutions of the alkali halides", J. Chem. Phys. 10 (1942) 187.

[63]. R. R. Mijangos, G. V. Polo, J. J. Palafax, R. Perez Salas, "An optical criterion to obtain miscible mixed crystals in alkali halides", Rev. Mex. Fis (online), 54 (Suppl.2) (2008) 15.

[64]. M. Priya (2008) "Studies on some alkali halide mixed crystals", Ph.D. Thesis, Manonmaniam Sundaranar niversity, Tirunelveli, India.

[65]. A. I. Kitaigorodsky (1984) "Mixed Crystals", Springer-Verlag, Berlin, Germany.

[66]. W. T. Barrett, W. E. Wallace, "Studies of NaCl-KCl solid solutions.1. Heats of formation, lattice spacings, densities, Schotky defects and mutual solubilities", J. Am. Chem. Soc. 76 (1954) 366.

[67]. I. R. Nair, C. T. Walker, "Raman scattering and X-ray scattering studies on $KBr_{1-x}I_x$, $KCl_{1-x}I_x$ and $K_{1-x}Rb_xCl$", Phys. Rev., 37 (1973) 2740.

[68]. T. Kikuchi, "A new approach to the evaluation of thermodynamic properties of nonideal solid solutions by the molecular dynamics method: A mixing model of alkali halide solid solution", J. Solid State Chem. 153 (2000) 118.

[69]. U. V. Subbarao, V. Haribabu, "Microhardness studies in alkali halide mixed crystals", Pramana 11 (1978) 149.

[70]. K. Srinivas, D. B. Sirdeshmukh, "X-ray determination of mean Debye-Waller factors and Debye temperatures of the $K_xRb_{1-x}Br$ mixed crystal system", Pramana 25 (1985) 71.

[71]. M. Theivanayagom, C. Mahadevan, "Lattice variation and thermal parameters of $Ni_xMg_{1-x}SO_4.7H_2O$ single crystals", Bull. Mater. Sci. 24 (2001) 441.

[72]. A. Dahlia Queen Livingsta, C. Mahadevan, "Lattice and thermal parameters of $Ni_xZn_{1-x}SO_4.7H_2O$ crystals", Indian J. Phys. 76A (2002) 271.

[73]. R. A. Swalin (1962) "Thermodynamics of Solids", John Wiley, New York, USA.

[74]. Y. I. Vesnin, S. P. Zakoryashin, "About decay of solid solutions", Solid State Commun. 31 (1979) 635.

[75]. V. Haribabu, U.V. Subbarao, K. Venkata Ramiah, "Dislocations and ionic conductivity in KCl-KBr mixed crystals", Phys. Stat. Solidi 28 (1975) 269.

[76]. R. W. James (1967) The Optical Principles of the Diffraction of X-rays", G. Bell and Sons, London, UK.

[77]. S. K. Mohanlal, K. S. Chandrasekaran, C. Sanjeeviraja, "Bragg neutron diffraction studies on the crystalline solid solution KBr_xCl_{1-x}", J. Phys. C: Solid State Phys. 15 (1982) 4235.

[78]. C. M. Padma (2008) "Studies on some binary alkali halide solid solutions", Ph.D. Thesis, Manonmaniam Sundaranar University, Tirunelveli, India.

[79]. N. Neelakanda Pillai (2008) "Growth and characterization of ternary mixed crystals of NaCl, NaBr and NaI", Ph.D. Thesis, Manonmaniam Sundaranar University, Tirunelveli, India.

[80]. N. Manonmani, C. K. Mahadevan, V. Umayorubhagan, "Growth and studies of the new crystal formed with NaCl and $CaCl_2$", Mater. Manuf. Processes 22 (2007) 388.

[81]. N. Manonmani, C. K. Mahadevan, V. Umayorubhagan, "Growth and studies of two new potassium compound crystals", Mater. Manuf. Processes 23 (2008) 153.

[82]. N. Manonmani, R. Kesavamoorthy, C. K. Mahadevan, "Growth and vibrational spectroscopic studies of some incommensurate crystals", Physica B: Phys. Cond. Matter. 393 (2008) 228.

[83]. G. Selvarajan (2003) "Studies on $(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ solid solutions", Ph.D. Thesis, Manonmaniam Sundaranar University, Tirunelveli, India.

[84]. S. Perumal (2004) "Growth, structure and physical properties of the crystals grown from the starting compositions for x = 0.1 to 0.4 and y = 0.2 to 0.8 $(KCl)_xKBr)_{y-x}(KI)_{1-y}$", Ph.D. Thesis, Manonmaniam Sundaranar University, Tirunelveli, India.

[85]. I. Bunget and M. Popescu (1984) "Physics of Solid Dielectrics", Elsevier, New York, USA.

