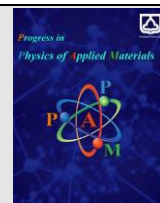




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Preparation and properties of polycrystalline aggregates of simple and hybrid alkali halides – An overview

C. K. Mahadevan*

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

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ABSTRACT

Alkali halides crystals occur in either NaCl structure or CsCl structure and the crystalline alkali halides are important both purely scientific and technological. The importance and applications in several optical, optoelectronic, and electronic devices led to the preparation and characterization of polycrystalline aggregates (with reduced crystallite sizes at or below micro level) of several pure and hybrid (mixed and/or doped) alkali halides in the recent decades. Polycrystalline aggregates of alkali halides can be cut into any shape and polished for their utility in device applications. There are several reports available in the past about two decades on the polycrystalline aggregates of simple and hybrid alkali halides. Presented herewith is an overview of various studies made on the preparation and properties of polycrystalline aggregates of simple and hybrid alkali halides (both single-phased and multi-phased) focusing the results reported by the present author and his co-workers. The reported results have indicated that the optical (particularly absorption and photoluminescence) and electrical (particularly dielectric) properties can be tuned significantly by reducing the crystallite sizes of the polycrystalline aggregates of alkali halides.

1. Introduction

The alkali (metal) atoms of the first group combine with the halogens of the seventh group to form the alkali halides or alkali metal halides; the significantly stable (simple) alkali halides considered are: LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, CsCl, CsBr, and CsI. The electronic configuration of the alkali metal atoms and the halogen atoms very much favor electron transfer and formation of ions. Alkali halides crystals occur in either NaCl structure or CsCl structure; the CsCl, CsBr and CsI crystallize in the CsCl structure and the others crystallize in the NaCl (halite) structure, under normal room temperature conditions. For the NaCl structure: the space group, coordination number, and number of molecules per unit cell are Fm3m, 6, and 4 respectively; and for the CsCl structure: the space group, coordination number, and number of molecules per unit cell are Pm3m, 8, and 1 respectively. Crystalline alkali halides are important both purely scientific and technological; and they have attracted the researchers for several decades and have always been at the center state of solid state materials

science. Development of lasers led to the development of polycrystalline alkali halides as materials for optical components; also, hybrid (mixed and/or doped) crystalline alkali halides find their applications in several optical, optoelectronic, and electronic devices [1,2]. If the end member alkali halide (simple compound) crystals are isomorphs with comparable lattice constants/volumes, it is expected to form a series of single-phased mixed crystals (proper solid solutions); otherwise, it is expected to form multi-phased mixed crystals (may be considered as improper solid solutions); and, in some cases (with alkaline earth halides), quasi mixed crystals are also possible. On forming a hybrid crystal, the added (impurity/guest or solute) ion goes to substitutional 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 [3]. There are several reports available (in the past about two decades) on the polycrystalline aggregates (with reduced crystallite sizes at or below micro level) of simple and hybrid alkali halides [2-15]. We consider here an overview of various studies made on the above

* Corresponding author.

E-mail address: mahadevan58@yahoo.co.in

polycrystalline materials focusing the results reported by the research group of the present author.

2. Preparation and Characterization

2.1. Preparation

It is generally understood that single crystals can be formed by slow cooling and amorphous materials can be formed by rapid cooling (quenching). Investigating systematically the melting and cooling processes is normally expected to provide the conditions required for the formation of polycrystalline aggregates (with crystallites of required sizes) of simple and hybrid alkali halides. Polycrystalline aggregates of alkali halides are normally 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. Highly transparent single crystals of alkali halides could be prepared by using the Czochralski pulling technique, with controlled slow cooling after pulling the crystal [16]. White coloration appears when the Czochralski pulled crystals are cooled naturally (without any control) [17,18]. When the melts are cooled naturally (without any control on cooling) polycrystalline aggregates (with white coloration) form [2,5,7-12,14]. Forming $\text{KCl}_{0.5}\text{Br}_{0.5}$ melt (at 800°C) and cooling it with different cooling times (nearly 0 to 14 h) lead to the gradual increase of crystal grain size (CGS) with the increase in cooling time [19]. Very recently, Raja and Mahadevan [15] have succeeded in preparing nanocrystalline solid slabs of undoped and CdS added KCl-KBr by using a melt quenching process.

2.2. Characterization

The polycrystalline aggregates prepared and reported have predominantly been characterized by using the standard available techniques. They have been characterized structurally (by X-ray powder diffraction analysis), chemically (by X-ray powder diffraction analysis, atomic absorption spectral analysis, and energy dispersive X-ray absorption spectral analysis), optically (by optical absorption spectral analysis and photoluminescence spectral analysis), and electrically (by DC and AC electrical measurements at various temperatures). Composition dependence of the physical properties of alkali halide mixed crystals (single/poly) finds much importance when preparation and characterization of these mixed crystals are considered; this demands determining the composition in alkali halide mixed crystals, accurately. Law of composition dependence of lattice constants/volumes has been well established; and accurate determination of lattice parameters can be possible through X-ray diffraction analysis. Thus, for the estimation of composition in alkali halide mixed crystals (with anionic as well as cationic substitution), determination of lattice parameters through X-ray diffraction analysis can be considered as a simple and very reliable method [3]. The composition dependence of lattice constants (as alkali halides crystals

have cubic lattices) in an alkali halide mixed crystal series can be expressed, in general, as:

$$a^n = xa_1^n + (1-x)a_2^n \quad (1)$$

Here 'a₁' and 'a₂' are the lattice constants of the end member crystals and 'a' is the lattice constant of the mixed crystal. When lattice constants are assumed to be additive (n = 1), equation (1) becomes:

$$a = xa_1 + (1-x)a_2 \quad (2)$$

Showing a linear composition dependence (Vegard's law); and many alkali halide mixed crystal systems have well been represented by this law. When lattice volumes are assumed to be additive (n = 3), equation (1) becomes:

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

Showing an ideal mixed crystal (Retgers' rule); through theoretical investigations, it has been predicted that n = 3. When the difference between a₁ and a₂ is very small, then equation (3) is indistinguishable from equation (2). For all the seven crystal systems, equation (3) can also be expressed as:

$$V = xV_1 + (1-x)V_2 \quad (4)$$

Here 'V₁' and 'V₂' are the lattice volumes of the end member crystals and 'V' is the lattice volume of the mixed crystal.

Several relations were proposed, in a way similar to the above, to show the composition dependence of Debye temperatures of the mixed systems of alkali halides. The Kopp-Neumann relation has been found to be more significant, which can be expressed as [3]:

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

Here 'θ₁' and 'θ₂' are the Debye temperatures of the end member crystals and 'θ' is the Debye temperature of the mixed crystal. Values of density and refractive index were also found to form linear relationships with composition for the mixed crystals of alkali halides, which can be expressed as:

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

And

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

Here 'd', 'd₁', and 'd₂' represent the densities of mixed crystal, first component and second component respectively; 'n', 'n₁', and 'n₂' represent the refractive indices of mixed crystal, first component, and second component respectively. The above composition dependence of lattice constant (Retger's rule), Debye temperature (Kopp-Neumann relation), density (Eq. 6) and refractive index (Eq. 7) can be extended to ternary mixed crystals of alkali halides also as [3]:

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

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

$$d = xd_1 + (y-x)d_2 + (1-y)d_3 \quad (10)$$

$$n = xn_1 + (y-x)n_2 + (1-y)n_3 \quad (11)$$

Here 'a', 'a₁', 'a₂', and 'a₃' represent the lattice constants of mixed crystal, first component, second component, and third component respectively; 'θ', 'θ₁', 'θ₂' and 'θ₃' represent the Debye temperatures of mixed crystal, first component, second component and third component respectively; 'd', 'd₁', 'd₂' and 'd₃' represent the densities of mixed crystal, first component, second component and third component respectively; and 'n', 'n₁', 'n₂' and 'n₃' represent the refractive indices of mixed crystal, first component, second component and third component respectively.

3. Results Obtained and Reported

3.1. Simple and binary mixed crystals

Multi-phased mixed poly-crystals (polycrystalline aggregates) of NaCl-KBr could be prepared by Padma and Mahadevan [7] from miscible (as per Tobolsky's rule [20]) NaBr and KCl by cooling naturally the NaBr-KCl melts, and characterized by X-ray diffraction measurement. This formation could be understood as Na⁺ has more affinity towards Cl than Br-. Padma and Mahadevan [9] could also prepare multi-phased (KBr)_x(NaBr)_{1-x} poly-crystals from KBr-NaBr melts (by natural cooling); the polycrystalline aggregates obtained were characterized by density, refractive index, X-ray diffraction and electrical (DC and AC) measurements. Density and refractive index values obtained indicate linear dependence with bulk composition; however, the thermal parameters (B, <u²>, θ_D and f_D) and electrical parameters (σ_{dc}, E_{dc}, ε_r, tanδ, σ_{ac} and E_{ac}) obtained indicate nonlinear variation with bulk composition, which could be attributed to the thermal defects formed in the crystals while cooling the melt to room temperature. B, <u²>, θ_D and f_D are respectively the Debye-Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency; σ_{dc}, E_{dc}, ε_r, tanδ, σ_{ac} and E_{ac} are respectively the DC electrical conductivity, DC activation energy, dielectric constant, dielectric loss factor, AC electrical conductivity and AC activation energy. For most of the compositions of (KBr)_x(NaBr)_{1-x} poly-crystals studied and reported by Padma and Mahadevan [9], Katsika-Tsigourakou and Symeonidis [21] have found that the activation energy estimated (from the temperature variation of conductivity) obeys a thermodynamical model (which interrelates the defect Gibbs energy with the bulk elastic and expansivity data). Moreover, Katsika-Tsigourakou and Vassilikou-Dova [22] have reproduced quantitatively the larger variation of dielectric constant with temperature observed for the (NaCl)_{0.587}(KBr)_{0.413} crystal by means of a simple model (which contains no adjustable parameter but solely uses the properties of the end members, viz. NaCl and KBr). With an aim of discovering new materials, Mahadevan and his co-workers [11, 14] have prepared (from the melt by cooling it

naturally) pure and II-VI compound (ZnO/CdO/ZnS) added simple (NaCl, KCl, NaBr, KBr and KI) and binary mixed (both mono and multi-phased (NaCl-KCl and NaBr-KBr) polycrystalline aggregates of alkali halides; they have characterized the prepared new materials by carrying out X-ray diffraction, atomic absorption spectroscopic and dielectric measurements. Their study has indicated that, in both the simple and binary mixed alkali halide crystals prepared, the II-VI compound addition significantly changes the lattice and dielectric constants; moreover, the study has indicated that the II-VI compound (with higher density) addition creates different layers (with different physical properties) with the increase of dopant content, from top to bottom along the crystal.

3.2. Ternary mixed crystals

Polycrystalline aggregates of multi-phased ternary solid solutions (may be improper) [(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] have been prepared by Selvarajan and Mahadevan [5,6] (by cooling the melt naturally) from NaCl, KBr, and KI (the starting materials); from the measured density and refractive index values, the bulk compositions were determined. X-ray diffraction analysis has indicated the existence of three fcc phases (each nearly corresponds to NaCl, KBr, and KI), in the ternary solid solutions; and the thermal parameters (B, <u²>, θ_D, and f_D) have been found to vary highly nonlinearly with the bulk composition. DC and AC electrical measurements (at various temperatures) have indicated the complicated influences of the bulk composition on the electrical parameters (σ_{dc}, E_{dc}, ε_r, tanδ, σ_{ac}, and E_{ac}); and this has been attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries. The above prepared ternary solid solutions were found to have large dielectric constants, and are expected to be more useful than their end member crystals. Neelakanda Pillai and Mahadevan [8,13] have prepared polycrystalline aggregates (by cooling naturally the melt) of ternary mixed crystals [(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] from NaCl, NaBr, and NaI (the starting materials); X-ray diffraction analysis has indicated single phased mixed crystalline nature and the thermal parameters (B, <u²>, θ_D, and f_D) nonlinearly varying with the bulk composition. DC and AC electrical measurements (at various temperatures ranging from 40 to 150 °C) have indicated the complicated influences of the bulk composition on the electrical parameters (σ_{dc}, E_{dc}, ε_r, tanδ, σ_{ac}, and E_{ac}), which has been explained as due to the enhanced diffusion of charge carriers along dislocations and grain boundaries. They [14] have also prepared polycrystalline aggregates of CdS doped (NaCl)_x(NaBr)_{y-x}(NaI)_{1-y}, and found that CdS doping significantly changes the lattice and dielectric constants; further, the CdS doping has been found to create different layers (with different physical properties) with the increase in CdS content, from top to bottom along the crystal. Polycrystalline aggregates of (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) have been prepared (by cooling the melt naturally) and characterized by density, refractive index, atomic

absorption spectroscopic, X-ray diffraction, and electrical (DC and AC) measurements by Priya and Mahadevan [2]. Results obtained by them have indicated that the ternary mixed crystals prepared exhibit three fcc phases, each nearly corresponds to NaCl, KCl, and KI crystals; the thermal parameters obtained, viz. B , $\langle u^2 \rangle$, θ_D , and f_D vary nonlinearly with bulk composition. Electrical parameters obtained, viz. σ_{dc} , E_{dc} , ϵ_r , $\tan\delta$, σ_{ac} , and E_{ac} have shown complicated influences of the bulk composition on them; this could be attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries. Padma and Mahadevan [7,12] have prepared by the melt method (melt cooled naturally), for the first time, polycrystalline aggregates of multi-phased ternary mixed crystals of NaCl, NaBr, KCl, and KBr using the miscible (as per Tobolsky's rule [20]) NaBr and KCl as the starting materials. Compositions, lattice constants, and thermal parameters (B , $\langle u^2 \rangle$, θ_D , and f_D) along with values of compressibility and mean sound velocity have been determined through density, refractive index, and X-ray diffraction measurements. Also, they have determined the several electrical parameters (σ_{dc} , E_{dc} , ϵ_r , $\tan\delta$, σ_{ac} , and E_{ac}) through DC and AC electrical measurements at various temperatures ranging from 35 – 150 °C.

3.3. White coloration of crystals

Mahadevan and his co-workers [2, 5, 7-11] have observed the prepared polycrystalline aggregates to be fairly transparent at temperatures nearer to the freezing point. However, when the crystals (frozen melts) were cooled (by natural cooling, without any proper control) to the room temperature from the high temperature (the freezing point), the transparency of the crystals has reduced and the crystals have become white. This aspect was explained as due to the introduction of thermal defects during cooling, and also due to the problem related to the degree of solubility of impurities introduced into the crystal. When the impurity concentration (at a certain temperature T) is higher than allowable amount due to solubility limit, then the excess substance precipitates by forming a new phase (the precipitate); when this precipitate tends to form on dislocations, the crystal becomes "milky" white [23]. Moreover, if this crystal is doped with sufficient concentration, then the white color may change in accordance with the dopant used [14].

3.4. Electrical properties

The DC and AC electrical measurements made on the polycrystalline aggregates (prepared by cooling the melt naturally) at various temperatures (from room temperature to about 150 °C) by Mahadevan and his co-workers [2,6,8,9,11,12,14] have indicated that the electrical parameters, viz. σ_{dc} , ϵ_r , and σ_{ac} increase with the increase in temperature. The results obtained have been explained in the following way [2]. Electrical conduction in alkali halide crystals (dielectrics, including polycrystalline aggregates) is mainly considered to be a defect controlled process, particularly in the low temperature region; and in the high temperature region, it is determined by the

intrinsic defects caused by the thermal fluctuations in the crystal. The characteristic activation energies (which, upon application of pressure, may increase or decrease) govern the formation, migration, and association of point defects [2]; also, an artificial increase in the concentration of defects of one type affects the concentration of other defects (through both the law of mass action and charge neutrality criteria). Moreover, as the alkali halide crystals are considered to be ionic in nature, the charge transported by electrons in these crystals (with the usual electric fields) is expected to be zero due to the large forbidden energy gap. Hence, it can be understood that the precipitating effect making the polycrystalline aggregates to become "milky" white at lower temperature (discussed earlier) also influences the electrical conduction.

Dependence of dielectric constant with the temperature can normally be attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects. For the alkali halide crystals, electronic and ionic polarizations are the major contributors to the dielectric constant; moreover, the electronic polarizability practically remains constant. Hence, the increase in dielectric constant with increase in temperature can be essentially due to the temperature dependence of ionic polarizability.

3.5. Ternary and quaternary mixed crystals

Priya and Mahadevan [10] have prepared (by cooling naturally the melt), for the first time, multi-phased mixed (ternary and quaternary) crystals (polycrystalline aggregates) of NaCl, NaBr, KCl, and KBr using the miscible alkali halides (as per Tobolsky's rule [20]), viz. NaBr, KCl, and KBr as the starting materials. The lattice constants and compositions of the crystals prepared were determined through XRD, density, refractive index, and flame photometric measurements. Through this study they have explored the possibility of preparing multi-phased ternary and quaternary mixed crystals (in polycrystalline aggregated form) of NaCl, NaBr, KCl, and KBr harder than the end member crystals using the miscible NaBr, KCl, and KBr as the starting materials.

3.6. Crystalline nanocomposite

A crystalline nanocomposite has been prepared from the melt of KBr, RbCl, RbBr, KI, and RbI salts and characterized by Mijangos and his co-workers [4]. An aggregation of crystallites of three different fcc phases (ranging from 5 to 100 nm in size) has been understood to be formed: 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.

3.7. Nanocrystalline solid slabs

Very recently Raja and Mahadevan [15] have illustrated, for the first time, the possibility of preparing nanocrystalline solid slabs of pure and CdS added $\text{KCl}_{1-x}\text{Br}_x$ (with $x = 0.0, 0.25, 0.5, 0.75,$ and 1.0) with good quality, halite crystal structure, phase purity, reduced crystallite/grain size (average sizes are within 43 and 97 nm), and homogeneous morphology (with a cuboid shape) by using a melt quenching process. The surface ionization process has been found to be significant in the melt quenching process used in the synthesis. It has been understood that, for alkali halides like KCl and KBr, the optical band gap and photoluminescence emission can be significantly tuned not only by mixing and/or dopant addition, but also by decreasing the crystal grain size to nanoscale. It has been found that these melt quenched nanocrystalline solid slabs exhibit much higher dielectric constants than the bulk (single/poly) crystalline KCl-KBr (simple and hybrid) systems; this could be understood as due to their lower crystal grain/crystallite sizes. It is very interesting to note that, for example, the dielectric constant observed for the CdS added $\text{KCl}_{0.5}\text{Br}_{0.5}$ (with an applied field frequency of 1 kHz) increases from 2075 at 30 °C to 6188 at 190 °C.

4. Conclusion

It has been understood that the literature available in the past about two decades carry a good amount of useful information on polycrystalline aggregates of simple and hybrid (both monophased and multi-phased) alkali halides prepared (with the help of melting and cooling processes) and characterized (by using the available standard techniques). The recent achievement of preparing nanocrystalline solid slabs of pure and CdS added KCl-KBr with good quality, halite crystal structure, phase purity, reduced crystallite/grain size, and homogeneous morphology is found to be very interesting. However, in order to discover new materials for industrial applications, it is required to carry out a good number of further investigations on the polycrystalline aggregates (particularly with reduced crystallite sizes) of alkali halides (simple and hybrid).

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