Pure and hybrid Epsomite group crystals -An overview

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Abstract

The hydrogen bonded Epsomite group (Epsomite, $MgSO_4.7H_2O$; Morenosite, $NiSO_4.7H_2O$; and Goslarite, $ZnSO_4.7H_2O$) crystals, although they are considered to be old mineral crystals, have attracted the attention of researchers in the recent past about three decades. Several pure and hybrid (doped and mixed) crystals have been grown and characterized (structurally, optically, thermally, mechanically, electrically, etc.). They have been found to exhibit several interesting and stable physicochemical properties which are needed to realize a wide range of applications. In this article, we consider an overview of various studies made on the preparation and characterization of pure and hybrid Epsomite group crystals focusing the results reported by the research group of the present author.

Keywords: *Epsomite group crystals, Crystalline materials, Hybrid crystals, Crystal growth, Characterization, Physicochemical properties.*

1. Introduction

Crystal growth and characterization (an important area of materials science) has been a research field of immense interest, in the past, for many decades. Naturally occurring crystals have often been found to exhibit several imperfections in the arrangement of atoms, ions or molecules, *viz.* dislocation, twinning and other kinds of defects. But, the crystals for academic and industrial uses should be perfect and three–dimensional, which necessitates to grow artificially the required crystals in the laboratory rather than depending on the naturally occurring crystals. Development of new material crystals of enhanced performance is very much important to attain a significant progress in industries, science and technology. So, the researchers are now more concerned to discover new materials (pure and hybrid) for the purpose of academic and industrial uses.

It becomes important and highly desired to be able to control and alter the properties and functionalities of material crystals with greater flexibility and possibility. One useful approach, in this regard, is to prepare hybrid (doped and/or mixed) material crystals that have properties different from that of single component material crystals. Doping is a widely applied process in materials science, which involves incorporation of atoms/ions of appropriate elements (anionic/cationic substitution) into host lattices to yield hybrid materials. When the impurity ion behaves in the same way as the lattice ion making it possible to have a wide range of solubility, mixed crystals can be formed. Two or more elements/compounds are said to form a continuous solid solution (mixed crystal) if single lattice sizes/parameters can be assigned to the solid solutions at all compositions.

The minerals *Epsomite* ($MgSO_4.7H_2O$, magnesium sulfate heptahydrate), *Morenosite* ($NiSO_4.7H_2O$, nickel sulfate heptahydrate) and *Goslarite* ($ZnSO_4.7H_2O$, zinc sulfate heptahydrate) are hydrogen bonded crystals under the Epsomite group. They are isomorphous with each other and crystallize in the orthorhombic crystal system with a tetra-molecular unit cell having the space group $P2_12_12_1$ [1, 2]. The structures consist of octahedra formed by metal ions ($Mg^{2+}/Ni^{2+}/Zn^{2+}$) bonded to six water (H_2O) molecules and tetrahedra formed by S^{6+} ions bonded to four oxygen atoms (O^{2-}). One additional H_2O participates in linking these structural elements with a network of weak hydrogen bonds and this interstitial seventh H_2O is easily lost at near ambient temperatures to leave the material hexa-hydrated [1, 2].

The Epsomite group crystals are naturally occurring minerals and have been known to us from long back. However, single crystals (particularly pure and hybrid) of these have been grown artificially and characterized in the last about three

decades due to their importance. We consider here an overview of various studies made, in the past within three decades, on the preparation and characterization of pure and hybrid Epsomite group single crystals focusing the results reported by the research group of the present author.

2. Pure and Doped Epsomite Crystals

$MgSO_4.7H_2O$ is a widespread evaporate mineral and has played a number of roles of scientific interest over the last four centuries [1, 3, 4]. It has numerous medical and pharmaceutical applications, *for example*, in the treatment of cardiac arrhythmia, acute asthma, eclampsia and gallstones. It is used in agriculture (fertilizer), cotton and silk manufacturing, ore processing and as an additive in explosives. It is a raw material for manufacturing various chemicals containing magnesium and also has applications in the field of dosimetric measurements and luminescence studies [1, 3 - 5].

$MgSO_4.7H_2O$ crystal is colorless, transparent, with perfect cleavage in {010} and the unit cell parameters [1, 6, 7] are: a = 11.86, b = 11.99 and c = 6.858 Å. It is highly soluble in water and the solubility at room temperature (at 33 ^{o}C) is 115/100 ml of water [1]. The molecular weight, mean refractive index and density are 246.48, 1.485 and 1.68 g/cc respectively [8]. The pure *Epsomite* crystals have already been grown at low temperatures from aqueous solutions [1, 9 - 19].

Sugaldino *et al.* [9] have reported the measurement of growth isotherms of the most important F forms ({110}, {010}, {111}, {100}, *etc.*) on *Epsomite* single crystals growing from pure aqueous solution at 30 and 40 °C. The presence of foreign particles in the growth medium has been found to change the growth habits of crystals [20, 21]. Jibbouri *et al.* [21] have found that the impurities ($KCl/K_2SO_4/NaCl/MgCl_2$) exert influence on the saturation and super-saturation limit. Mahadevan and Saravanan [22] have found that the critical nucleation parameters increase with the increase in concentration of impurity (KCl/KNO_3) in the $MgSO_4.7H_2O$ solution. Kasatkin [11] has studied (with the help of interferometric technique) the surface reaction controlled growth kinetics of $MgSO_4.7H_2O$ crystal in [110] direction at temperature, T = 15 – 32.5 ^{o}C. It has been found that, at lower supersaturations, the dislocation growth model fits with the experimental data. At higher supersaturations, the growth is accelerated due to poly-nuclear two-dimensional nucleation according to the 'Birth + spread' model.

Ruiz-Agudo *et al.* [4] have found that *Epsomite* nucleation is strongly inhibited in the presence of amino tri(methylenephosphonic acid), diethylenetriaminepentakis (methylphosphonic acid) and poly(acrylic acid) sodium salt. Moreover, these additives act as habit modifiers promoting the growth of acicular crystals elongated along the [001] direction. The hydrogen bonding available between the functional groups of additive molecules and water molecules in *Epsomite* {110} appears to be the principal mechanism of additive *Epsomite* interaction, as shown by FT-IR and molecular modeling.

Mahadevan [12] has observed larger DC electrical conductivity values for the impurity (KCl/KNO_3) added *Epsomite* single crystals. Urea/thiourea doped $MgSO_4.7H_2O$ single crystals were grown and characterized by X-ray diffraction (XRD) measurements [13]. The thermal parameters (Debye-Waller factor, mean-square amplitude of vibration, Debye temperature and Debye frequency) have been found to vary not in a particular order with respect to impurity concentration, which could be attributed to the random disturbance created by the impurity molecules in the hydrogen-bonding system of the $MgSO_4.7H_2O$ lattice. Ferdous and Podder [14] have found that KCl doping improves the optical quality of the *Epsomite* crystal. Their electrical measurements have shown that KCl doped *Epsomite* possesses low dielectric constant and low dielectric loss which could be suitable for electro-optic applications. Moreover, the dielectric constant is almost independent of the frequency up to 10^6 Hz but decreases with the increase in KCl concentration. The DC electrical conductivity has been found to increase in the temperature range 25 - 70 ^{o}C and also with the KCl concentration.

Kavitha and Mahadevan [16] have reported the growth and characterization of pure and glycine doped (with five concentrations) *Epsomite* single crystals. Analysis of X-ray powder diffraction (PXRD) data confirms the crystalline nature and indicates that glycine doping does not lead to significant distortion in the $MgSO_4.7H_2O$ crystal structure. The measured densities and lattice parameters indicate that the glycine molecules have entered into the crystal matrix. All the six grown crystals have been found to exhibit good optical transparency in the wavelength range 210 – 1100 nm, second harmonic generation (SHG) efficiency in the range 0.55 – 0.70 (in KDP unit), mechanical softness and normal dielectric behavior. The measured electrical conductivity (both DC and AC in the order of 10^{-6} - 10^{-7} mho/m) values can be understood as due to the proton transport within the framework of hydrogen bonds. Glycine doping (with some concentrations, 0.8 and 1.0 mole%) has

reduced the dielectric constant significantly (to < 4.0, from 7.403 for the pure to 2.359 at 35 °C) and consequently lead to low ε_r value dielectric material. This particular reported study has indicated that doping $MgSO_4.7H_2O$ with glycine leads to the discovery of promising NLO active and low ε_r value dielectric materials.

Sumithraj Premkumar *et al.* [17, 18] have reported the growth and characterization of pure and Cd/Hg/Histidine doped (with 0.005 M concentration) $MgSO_4.7H_2O$ single crystals. They have obtained by (adopting the simple slow evaporation of solvent method) good quality and transparent crystals in about 2-3 week time and observed an increase in thermal stability on doping with Cd and Hg but a decrease on doping with Histidine. The optical absorption (in the UV-visible range) spectral and electrical measurements (in the temperature range 30-100°C), they have made, indicate that the crystals they have studied possess a good transparency in the visible region (essential for photonic devices) and a normal dielectric behavior.

Vaitheeswari and Mahadevan [19] have grown $MgSO_4.7H_2O$ single crystals by the free evaporation of solvent method and investigated the effect of urea/thiourea (simple but interesting organic impurities) doping (dopant added in the solution used for the crystal growth with dopant concentration ranging from 0.2 – 1.0 mole%) on their structural, thermal, optical, mechanical and electrical (DC and AC) properties. Density and lattice volume variations observed indicate that the impurity molecules (urea/thiourea) have entered into the $MgSO_4.7H_2O$ (host) crystal matrix. They have found that all the eleven crystals they have grown are stable in the atmospheric air, non-hygroscopic, thermally stable up to about 70 °C, optically transparent in the wavelength range 210 – 1100 nm, mechanically soft and exhibit normal dielectric behavior (the electrical conduction explained as due to proton transport). Their study has indicated that urea/thiourea doping leads to tuning optical, mechanical and electrical properties and also leads to the discovery of new promising low ε_r value dielectric materials.

Microelectronics industry needs replacement of dielectric materials in multilevel interconnect structures with new low ε_r value dielectric materials, as an interlayer dielectric (ILD) which surrounds and insulates interconnect wiring. Lowering the values of the ILD decreases the RC delay, lowers power consumption, and reduces 'cross-talk' between nearby interconnects [23, 24]. Silica has ε_r ≈ 4.0, in part as a result of the Si-O bonds. Several innovative developments have been made for the development of new low ε_r value materials to replace silica. Reduction in ε_r value has taken place (with non-porous and porous thin films) but with several other problems. So, there is still a need for new low ε_r value dielectric materials [23, 24].

Goma *et al.* [24] have reported reduction in ε_r value in the case of potassium dihydrogen orthophosphate (KDP) single crystal added with 0.6 mole% urea. They observed, at 40 °C, ε_r = 2.86 along a-direction and 3.17 along c-direction. This illustrated that urea doping to KDP reduces the ε_r value. Meena and Mahadevan [25] have found that L-arginine addition makes it possible for the KDP and ADP (ammonium dihydrogen orthophosphate) crystals to become low ε_r value dielectric materials. Also, the study made by Meena and Mahadevan [26] has indicated that single crystals of L-arginine acetate (LAA) and L-arginine oxalate (LAO) are not only potential nonlinear optical (NLO) materials but also promising low ε_r value dielectric materials, expected to be useful in both the photonic and microelectronics industries. Moreover, material in the single crystal form would be very much interesting as thin wafers can be cut, polished and used. In addition, as the electronic circuits are in moisture-free (water proof) condition, these water soluble crystalline materials can very well be used. So, glycine/urea/thiourea doping leads *Epsomite* crystals to become potential materials useful in the microelectronics industry.

Gromnitskaya *et al.* [27] have reported the ultrasonic study of the elastic moduli of Epsomite in the temperature range 77 – 295 K at pressures up to 2.8 GPa along with the measurement of elastic properties at room temperature conditions (P = 0 – 2.8 GPa). They have identified the anomalies in dependences of elastic characteristics as phase transition points. Their results have shown that the elastic properties and the sequence of phase transitions for $MgSO_4.7H_2O$ and $MgSO_4.7D_2O$ are very similar at room temperature. But, the picture significantly changes below 285 K.

Salt hydrates exhibit water vapor sorption as one of the most promising means for compact, low-loss, and long-term storage of solar heat in the built environment. A theoretical study identified $MgSO_4.7H_2O$ as a very interesting salt hydrate for compact, seasonal, low-loss and long-term heat storage [1, 28]. The theoretical heat storage density of *Epsomite* is 2.8 GJ/m^3 which offers a more compact way of storing energy for the same volume in comparison to water (0.25 GJ/m^3 in the temperature range 25 – 85 °C) [1, 28, 29]. Moreover, *Epsomite* is cheap, non-toxic and non-corrosive and can be used under both ambient pressure and sub-

atmospheric pressure, thus being suitable for the application in open cycles or closed cycles [1, 30]. In addition, *Epsomite* salt can be efficiently regenerated at temperatures < 150 °C, compatible with the integration in low-grade heat recovery systems or solar systems in buildings [30, 31].

Epsomite was studied by van Essen and his co-workers [28] as a possible thermochemical material (TCM) for solar seasonal heat storage. Results of their study indicate that the application of *Epsomite* at atmospheric pressure is problematic for a heat storage system where heat is released above 40 °C using a water vapor pressure of 1.3 kPa. Also, if a heat storage system has to operate at atmospheric pressure, then the application of $MgSO_4.7H_2O$ for seasonal heat storage is possible for space heating operating at 25 °C and a water vapor pressure of 2.1 kPa. However, it can be expected that modification of the material as well as reducing the pressure may yield good results.

Ferchaud *et al.* [32] have studied the reversible water vapor sorption process of $MgSO_4.7H_2O$ under the conditions of seasonal solar heat storage. This study has shown that, under a water vapor pressure of 13 mbar, $MgSO_4.7H_2O$ dehydrates into an amorphous monohydrate phase when the system is heated until 150 °C and rehydrates after 100 h by recrystallizing the crystalline phase of $MgSO_4.6H_2O$. In effect, the material is able to take up 0.99 GJ/m³ of heat for a packed bed built with 50 % of porosity during the dehydration and released only 0.38 GJ/m³ of heat during the rehydration process. Their study has shown that $MgSO_4.7H_2O$ releases heat after a dehydration/hydration cycle with energy density of 0.38 GJ/m³. The heat release found for $MgSO_4.7H_2O$ is low and could be attributed mainly to the amorphization of the material during the dehydration performed at 13 mbar which reduces its sorption capacity during the rehydration. This low heat release could also be assigned to textural changes which influence the measurement conditions.

Donkers *et al.* [33] have studied the water transport in $MgSO_4.7H_2O$ during dehydration in view of thermal storage. Their thermogravimetric analysis (TGA) has indicated that the heating rate has a strong effect on the dehydration process. They have also shown, on the basis of a model, that pore water (an aqueous solution of $MgSO_4$ produced during dehydration) is produced as the vapor release is not sufficient at crossing a phase transition temperature.

In order to overcome the challenges presented by pure *Epsomite* in real application

during hydration/dehydration cycles, several matrices such as clay, pumice, zeolites and zeotypes, silica gel, activated carbon, and vermiculite have been proposed by several researchers in combination with *Epsomite* [34-38]. Results obtained by these researchers have demonstrated that, due to the increase in the thermal conductivity of the material, the use of composites allows for an increase of the thermal energy storage (TES) potentiality in terms of energy storage and dynamic performance. However, these matrices are rigid structures limiting the mechanical stability of the material over cycling, especially in view of the expansion/contraction of the grains of the salt (micro crystals) during hydration/dehydration. Also, the amount of salt that is possible to insert inside the structure is limited. Brancato *et al.* [39], in order to overcome such an issue, have employed a polymeric macro-porous foam to host $MgSO_4 \cdot 7H_2O$ salt.

Recently, Piperopoulos *et al.* [30] have investigated the composite foamed structure constituted by a porous silicone matrix filled with $MgSO_4 \cdot 7H_2O$ micro crystals by using a morphological and structural characterization protocol. Their study indicates that the dehydration process leads to a structural transition of the salt from a crystalline ($MgSO_4 \cdot 6H_2O$) to an amorphous state and, accordingly, the material dehydrates and hydrates suitably without cracks and damages. Also, they have observed a good adhesion to the silicone matrix support during the whole cycle. The results obtained by them indicate that their experimental protocol can be considered effective to better relate the composite microstructure to the hydration/dehydration processes. Moreover, their sorption enthalpy analysis confirmed the possibility to get TES energy densities up to 150 % higher than water under real operating conditions.

3. Pure and Doped Morenosite Crystals

$NiSO_4.7H_2O$ (*Morenosite*) is a chemical agent and is used for manufacturing of batteries, in fungicide mixtures, for production of catalysts, in food and oil industry, and in perfumery industry. $NiSO_4.7H_2O$ crystal is of emerald-green color, with perfect cleavage in {010} and its lattice parameters are [1, 2, 6, 7]: a = 11.86, b = 12.08 and c = 6.81 Å. *Morenosite* is soluble in water and the solubility at room temperature (at 30 °C) is 77.5 g/100ml of water [1]. Its molecular weight, mean refractive index and density have been reported as 280.88, 1.483 and 1.948 g/cc respectively [2, 8]. All forms of nickel sulfate (anhydrous or hydrated) are mildly toxic, carcinogenic and are paramagnetic.

Several researchers have already grown pure and doped *Morenosite* single crystals at low temperatures from aqueous solutions [1, 2, 13, 40 - 42]. Ptasiewiez-Bak *et al.* [43] have reported the determination of charge density distribution in pure $NiSO_4.7H_2O$ crystals at room temperature and 25 K. They have mentioned that all six water molecules around the nickel atom are crystallographically unique, which should provide a good internal comparison of the polarization according to coordination.

Mahadevan *et al.* [44] have measured the induction period (by the direct vision method) for various supersaturated aqueous solutions of $NiSO_4.7H_2O$ doped separately with $MgSO_4.7H_2O$ and $ZnSO_4.7H_2O$, and estimated the various critical nucleation parameters (based on the classical theory for homogeneous crystal nucleation). The results obtained by them indicate that the critical nucleation parameters decrease with the increase in concentration of $ZnSO_4.7H_2O$ doping but increase with the increase in concentration of $MgSO_4.7H_2O$ doping in the $NiSO_4.7H_2O$ solutions.

Mahadevan [13] has grown (by the free evaporation method) and characterized (by XRD measurement) urea/thiourea doped $NiSO_4.7H_2O$ single crystals. Results obtained by him indicate that the thermal parameters (Debye-Waller factor, mean-square amplitude of vibration, Debye temperature and Debye frequency) do not vary in a particular order with respect to impurity concentration, which he could attribute to the random disturbance created by urea/thiourea molecules in the hydrogen-bonding system of the $NiSO_4.7H_2O$ lattice.

Kavitha and Mahadevan [42] have grown *Morenosite* single crystals (by the free evaporation method) and investigated the effect of glycine (a simple and interesting amino acid) as an impurity (added in the $NiSO_4.7H_2O$ solution used for the growth of single crystals) with impurity concentration ranging from 0.2 – 1.0 mole% on the structural, mechanical, optical and electrical properties of *Morenosite*. The density and lattice volume variations observed by them indicate that the glycine molecules have entered into the $NiSO_4.7H_2O$ crystal matrix. Moreover, they have found that all the six grown crystals are transparent in the wavelength range of 210 – 1100 nm, NLO active, mechanically soft and exhibit normal dielectric behavior.

The SHG efficiency observed by Kavitha and Mahadevan [42] ranges from 0.93 (for the pure $NiSO_4.7H_2O$) to 1.35 (for the 1.0 mole% glycine added $NiSO_4.7H_2O$) (in KDP unit) which indicates that glycine addition leads to an increase in SHG efficiency. The electrical parameters (σ_{dc}, ε_r, $\tan\delta$ and σ_{ac}) have been found to increase with the increase in temperature (in the range 35 – 80 °C) but have nonlinear variation with the impurity concentration. Also, their study indicates that glycine addition (1.0 mole%) to $NiSO_4.7H_2O$ reduces the ε_r value from 11.391 to 3.745 in the temperature range of 35 - 60 °C leading to the discovery of promising NLO active and low ε_r value dielectric materials.

The SO_4 group in $MSO_4.7H_2O$ (M = Mg/Ni/Zn) may be considered similar to the PO_4 group (having tetrahedral geometry) in KDP [42]. Praveen and Mahadevan [45] have found that the electrical properties of tris(thiourea)zinc(II) sulfate (ZTS) have some similarities to those of KDP. The electrical conduction in $NiSO_4.7H_2O$ crystals could be understood (as in the case of $MgSO_4.7H_2O$ crystals [16, 19]) as due to proton transport within the framework of hydrogen bonds [42]. Two possible conductivity mechanisms (in combination) may be considered of which the first one is identical to that in ice (also containing hydrogen bonds). The second conductivity mechanism is associated with the incorporation of impurities into the crystal lattice and the formation of corresponding defects in ionic crystals.

Motion of protons accompanied by a D defect (excess of positive charge) may account for the proton conduction. Migration of these D defects may not change the charge at an electrode but modify the electric polarization [42, 46]. Enhancement of electrical conduction in $MSO_4.7H_2O$ (M = Mg/Ni/Zn) crystals due to increase in the crystal temperature is possible by the occurrence of weakening of the hydrogen bonding system due to rotation of the hydroxyl ions in water molecules. So, it has been understood that the proton transport depends on the generation of L-defects and, consequentially, the temperature dependence of the electrical conductivity can be understood as due to the temperature dependence of the proton transport [2, 16, 19, 42]. It is known that urea, thiourea and glycine are simple organic molecular substances and are expected to occupy mainly the interstitial positions in the host crystal lattice. To some extent, in addition to occupying the interstitial positions, these molecules are expected to replace the water molecules and ions ($Mg^{2+}/Ni^{2+}/Zn^{2+}$ and SO_4^{2-}) creating a disturbance in the hydrogen bonding system. This disturbance in the hydrogen bonding system is expected to cause the electrical parameters to vary nonlinearly with the impurity concentration.

The temperature dependence of the dielectric constant can generally be attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects [2, 16, 19, 42]. In the case of ionic crystals, as the electronic polarizability remains constant, the temperature dependence of dielectric constant is essentially due to the temperature variation of ionic polarizability [16, 19, 42]. Moreover, the electrical conductivity has been found to increase smoothly with the increase in temperature in the temperature range considered. No sharp increase in the electrical conductivity with the increase in temperature has been found that would be the characteristic of a super-protonic phase transition [42, 47].

4. Pure and Doped Goslarite Crystals

$ZnSO_4.7H_2O$ possesses a wide range of applications in the field of telecommunication, solar systems for solar energy storage, coagulation bath for rayon and optical information storage devices [1, 2]. It is also used as a direct emetic, antiseptic and disinfectant in the pharmaceutical industry [48]. $ZnSO_4.7H_2O$ crystal is colorless, strongly diamagnetic and optically transparent. The unit cell parameters [1, 2, 6, 7] are: a = 11.779, b = 12.050 and c = 6.822 Å. It is highly soluble in water, has an astringent taste and the solubility at room temperature (at 34 °C) is 184.8 g/100 ml of water [1]. The molecular weight, mean refractive index and density are 287.54, 1.474 and 1.957 g/cc respectively [2, 8]. The pure *Goslarite* crystals have already been grown at low temperatures from aqueous solutions [1, 2, 41, 49 - 55].

Backiyam *et al.* [56] have measured the induction period (by the direct vision method) for various supersaturated aqueous solutions and estimated the various critical nucleation parameters [7] like interfacial tension of the solid relative to its solution, energy of formation of critical nucleus, the radius of the nucleus in equilibrium with its solution, *etc.* (based on the classical theory for homogeneous crystal nucleation) of $ZnSO_4.7H_2O$. Also, they have reported [49] the growth, dissolution and dielectric properties of $ZnSO_4.7H_2O$ along with that of $FeSO_4.7H_2O$ single crystals.

Anderson *et al.* [52] have determined and reported the structure of deuterated goslarite ($ZnSO_4·7D_2O$) crystal by a combined neutron powder diffraction and X-ray single-crystal data refinement technique. They have achieved the best overall agreement in the Rietveld refinement and reasonable geometry within structural units. The lattice parameters obtained by them are: a = 11.8176(6), b = 12.0755(7) and c = 6.8270(4) Å;

space group $P2_12_12_1$; Z = 4; *etc*. Their study has confirmed that the H-bonding scheme for the deuterated goslarite is the same as that of the other Epsomite group minerals. The observed small but significant variations of the Zn–O bond lengths could be attributed to details of the H bonds to the O atoms of the Zn octahedra.

Kanagadurai *et al.* [53] have made nucleation kinetics, growth and characterization studies on *Goslarite* crystal and found that (using the optimized growth parameters for growing bulk crystals) crystals up to a size of 70x11x4 mm³ could be grown over a growth period of 20 to 25 days by the temperature lowering method. They have observed that the optical absorption spectrum has no absorption band between 340 and 1100 nm and the UV cut off wavelength is 286 nm.

Saha and Podder [55] have obtained (from aqueous solutions by the isothermal evaporation method) pure $ZnSO_4.7H_2O$ single crystals up to a size of 25x15x8 mm³ within 30 days. They have confirmed the structure and material of the grown crystals by XRD and FT-IR spectral measurements. Their thermogravimetric (TG, DTA and DTG) analysis has shown the thermal stability up to 70 °C. Through optical transmission spectral analysis, they have found that the *Goslarite* crystal can be expected to be a useful material for optoelectronic applications in the visible and infrared region.

5. Mixed Crystals of Epsomite Group

Several reports are available on the formation of mixed crystals among Epsomite group minerals along with some other studies [1, 2, 40, 41, 50, 51, 54]. Mahadevan and his co-workers [57 – 59] have reported the results of their nucleation studies made on mixed crystals of $MgSO_4.7H_2O$, $NiSO_4.7H_2O$ and $ZnSO_4.7H_2O$. Jayakumari and Mahadevan [50] have reported the growth of $Mg_xZn_{1-x}SO_4.7H_2O$ (x value going from 0.0 to 1.0 in step of 0.2) single crystals from aqueous solutions by the slow evaporation method and measurement of their densities, refractive indices and refraction equivalents.

Single phased mixed crystals are the ones which can be assigned a single set of lattice parameters at all mixing compositions. The general conditions required for the formation of single phased mixed crystals are [60 – 63]: (a) The structures of the two mixing crystals should be of similar type (isomorphous crystals); (b) The bonding in the mixing crystals should be of similar type; (c) The difference in radii of the substituent atoms should be within 15 % with respect to the smaller one; (d) The difference in lattice volumes of the mixing crystals should be within 6 % with

respect to the smaller one. The Epsomite group crystals satisfy the above general conditions, and are expected to form single phased mixed (both binary and ternary) crystals at room temperature from aqueous solutions.

Mahadevan and his co-workers [40, 41, 51] have grown single crystals (by the slow evaporation method) and determined (through XRD analysis) the lattice variation and thermal parameters of $Ni_xMg_{1-x}SO_4.7H_2O$, $Ni_xZn_{1-x}SO_4.7H_2O$ and $Mg_xZn_{1-x}SO_4.7H_2O$ (x value going from 0.0 to 1.0 in step of 0.2) single crystals. In all these three mixed crystal systems, the lattice volumes obtained are found to be approximately additive obeying the relation,

$$V = xV_1 + (1-x)V_2$$

which is similar to Retger's rule [62, 63] applied to cubic system. Here, V, V_1 and V_2 are the lattice volumes of mixed crystal and first and second end members respectively.

No particular order with composition was observed in the case of thermal parameters, *viz.* Debye-Waller factor, mean-square amplitude of vibration, Debye temperature and Debye frequency. The values observed for some of the mixed crystals even exceed those for the end members. The Kopp-Neumann relation for the Debye temperature (obtained by assuming the additivity of specific heats and assuming the Debye T^3 expansion) [63, 64] is expressed as:

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

where θ, θ_1 and θ_2 are the Debye temperatures of mixed crystal and first and second end members respectively. This relation is valid for mixed crystals of cubic systems [63] and may not be for mixed crystals of orthorhombic systems. The orthorhombic mixed crystal systems we have considered here do not satisfy the above relation. Livingsta and Mahadevan [41] could attribute this nonlinearity in composition dependence of thermal parameters to the increase in vibrational entropy due to mixing. Moreover, they have explained that the vibrational entropy is less for cubic mixed crystal systems and more for orthorhombic (lower symmetry) systems due to the increase in anisotropy of the crystal system.

Sumithraj Premkumar and Sahaya Shajan [54] have grown (by the slow evaporation method from aqueous solutions) mixed crystals based on $MgSO_4.7H_2O$ and $ZnSO_4.7H_2O$ up to a size of 50 x 15 x 10 mm³ and characterized by XRD, atomic absorption spectral (AAS) and thermogravimetric (TGA/DSC) analyses. They have found that the mixed crystals are thermally more stable than the end member crystals. Also, the crystals have been found to decompose in two thermal stages.

Kavitha and Mahadevan [2] have grown (by the free evaporation method at room temperature) and characterized (by density, XRD, AAS, FT-IR, UV-Vis spectral, SHG, micro hardness and electrical measurements) $Ni_xZn_{1-x}SO_4.7H_2O$ single crystals (with x having the values 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0). All the seven crystals grown by them are found to be stable in the normal atmospheric conditions and the green coloration reduces when the Zn content increases. The compositions (x values) of the mixed crystals obtained using the densities compare nearly with those obtained using the metal atom contents determined through AAS measurements. Also, it has been found that mixing does not lead to significant distortion in the host crystal structure and the observed FT-IR spectra have been found to be similar to that reported for Epsomite group crystals [4, 55, 65, 66].

The UV-Vis spectra observed for the $Ni_xZn_{1-x}SO_4.7H_2O$ crystals [2] are found to be similar and show wide transmission window with a small dip (except for x values of 0.2 and 0.4) at around 390 nm in the wavelength region from 210 – 1100 nm enabling these crystals to be potential candidates for optoelectronic applications. The observed cut-off wavelengths indicate that these crystals can be considered as promising NLO crystals [67]. The observed SHG efficiencies (in KDP unit) range from 0.55 – 1.63 with a maximum (1.63) for the mixed crystal with composition x = 0.5 and indicate that these crystals are NLO active. The micro hardness measurement indicates that these crystals are mechanically soft. The DC and AC electrical measurements indicate that these crystals exhibit normal dielectric behavior and mixing morenosite and goslarite with x = 0.2 and 0.5 leads to the discovery of promising low ε_r value dielectric materials.

6. Other Crystals Based on Epsomite Group

SHG from near-infrared (NIR) laser sources is an important technological problem that has attracted much attention and several new material crystals have been grown and characterized in the past about three decades. An ideal NLO material (to exhibit second order nonlinear effects) should crystallize in a non-centrosymmetric crystal class and should possess the characteristics like large nonlinear figure of merit for frequency conversion, high laser damage threshold, fast optical response time, wide transparency window, architectural flexibility for molecular design and morphology, ability to process into crystals, optical transparency, ease of fabrication, nontoxicity and growth environmental stability, higher mechanical strength

and thermal stability [68]. Epsomite group crystals have been found to be significantly NLO active. However, they have been found to be mechanically soft and thermally stable up to within 100 ^{o}C only. So, materials having better optical nonlinearity with chemical flexibility and mechanical properties have been required to be investigated. This has resulted in the preparation and characterization of semi-organic material crystals which are used as NLO devices in practice.

Zinc tris(thiourea) sulfate (ZTS) is such a semi-organic material crystal prepared from thiourea and $ZnSO_4.7H_2O$ and widely studied [68]. ZTS crystal is potentially useful for electro-optic applications and for the frequency doubling of NIR laser radiations [69]. It belongs to the orthorhombic crystal system with space group $Pca2_1$ and lattice parameters: a = 11.126, b = 7.773 and c = 15.491 Å [70]. The growth morphology of ZTS crystal has been studied by Verma $et\ al.$ [71]. Mahadevan and his co-workers [45, 68, 72 - 74] have grown and characterized pure and several doped (with both organic and inorganic impurities) ZTS crystals.

Ramachandran $et\ al.$ [75] have determined the electro-optic, piezo-electric and dielectric properties of ZTS crystal, and Desai and Gupte [76] have studied the variation of hardness with applied load, indentation time and temperature. Marcy $et\ al.$ [77] have found that ZTS is thermodynamically stable up to 200 ^{o}C and is nearly 1.2 times more NLO active than KDP. Venkataramanan $et\ al.$ [70] have determined the melting point of ZTS as 234 ^{o}C, and found that the high laser damage threshold and wide optical transparency observed for ZTS make it a better alternative for KDP crystals in frequency doubling and laser fusion experiments. Low temperature phase transitions in ZTS has been studied by Quassaid $et\ al.$ [78] using Raman scattering experiments. Vasantha $et\ al.$ [79] have made EPR and optical absorption studies on VO(II) doped ZTS crystals. Bhagavannarayana and his co-workers [80, 81] have investigated the effect of organic dopants on the crystalline perfection and some other properties of ZTS crystals.

Praveen and Mahadevan [45] have grown ZTS crystals by the free evaporation method from aqueous solutions and carried out electrical measurements (both DC and AC) along all the three (a-, b- and c-) directions at various temperatures ranging from 40 – 150 ^{o}C by the conventional parallel plate capacitor method. They have explained the conduction mechanism in ZTS crystal as due to the proton movement (as explained in the case of KDP and Epsomite group crystals) and also due to

rotation of the sulfate ions (as explained in the case of tartrate crystals by Torres $et\ al.$ [82]).

Praveen $et\ al.$ [68] have grown (from aqueous solutions) and characterized (by XRD, FT-IR spectral and multi-crystal XRD measurements) pure and impurity (urea/Mg^{2+}/Ni^{2+}) added ZTS single crystals. The results obtained by them indicate that the impurity added crystals are basically ZTS but incorporated with a small amount of impurity molecules in the crystal matrix. They have found that urea/Ni^{2+} added ZTS single crystals have good crystalline perfection when compared to the Mg^{2+} added ZTS single crystal.

Krishnan $et\ al.$ [72] have investigated the effect of KI as an impurity on the structural, optical, thermal and electrical properties of ZTS single crystal. They have found that the KI addition leads to change in ZTS crystal morphology, no distortion in crystal structure, small increase in thermal stability, no significant change in SHG efficiency and increase in electrical parameters (σ_{dc}, ε_r, $\tan\delta$ and σ_{ac}). Praveen $et\ al.$ [73] have studied the effect of urea as an impurity on the dielectric properties of ZTS single crystal. They have observed no systematic variation in the dielectric parameters (ε_r, $\tan\delta$ and σ_{ac}) with impurity addition and direction (a-, b- and c-) which could be explained by considering the complex situation created by the urea impurity in the dielectric phenomenon of ZTS crystal. Rajasekar $et\ al.$ [74] have investigated the effect of transition metal (Ni^{2+}) doping on the optical, thermal and dielectric properties of ZTS single crystal. They have found that the doping results in an increase in the surface roughness, defects and SHG efficiency.

Very recently, Durgababu $et\ al.$ [83] have investigated the effect of 2,4-dinitrophenol (DNP) dye on ZTS bulk single crystals (grown from aqueous solutions by the slow evaporation method) with regard to their structural, mechanical, thermal, electrical and optical properties for NLO device applications. They have found that the doping leads to enhancement of the SHG efficiency and optical range of photoluminescence (PL) in ZTS crystals.

Pasupathy and Philominathan [84] have grown from aqueous solutions and characterized structurally, thermally, optically and mechanically tris(thiourea)magnesium sulphate (MTS) crystals and found that this crystal belongs to the monoclinic crystal system with lattice parameters: a = 7.67, b = 5.48 and c = 8.56 Å; β = 131.1 ^{o}.

Mahadevan and his co-workers [85, 86] have grown (by the free evaporation of solvent method) mixed crystals of ZTS and MTS [$(ZTS)_x(MTS)_{1-x}$ with x = 0.0 – 1.0 in step of 0.1] by using the molecular isomorphism (cationic substitution) even though the

end members are non-isomorphous [62], and characterized by XRD, density, FT-IR spectral, AAS, thermogravimetric, micro hardness, optical absorption spectral, SHG efficiency and electrical measurements. They have found that, except MTS crystal (belonging to monoclinic crystal system), all the other ten crystals belong to the orthorhombic crystal system. All the eleven crystals they have grown have been found to have good transmission in the UV-visible region, considerable SHG efficiency, density in the range of 1.921 – 2.090 g/cc, considerable mechanical and thermal stabilities and normal dielectric behavior. The electrical parameters (σ_{dc}, ε_r, $\tan\delta$, σ_{ac}, E_{dc} and E_{ac}) have been found to vary nonlinearly with composition (x value). Their study indicates that ZTS-MTS crystals are going to play a vital role in the field of optoelectronics and laser technology.

7. Conclusion and Future Scope

It has been understood that the pure and hybrid Epsomite group (*Epsomite*, *Morenosite* and *Goslarite*) crystals and their extensions like ZTS (pure and doped), MTS and ZTS-MTS mixed crystals have been studied widely by several researchers in the past about three decades. Also, it has been understood that these crystalline materials are expected to find potential applications in solar energy (thermal) storage, photonic, optoelectronic, microelectronic, magnetic, etc. devices. However, lot more studies have to be carried out to understand the full potential of these crystalline materials.

The size and shape of the crystal plays an important factor during industrial crystallization, since the undesirable habits such as plate-like or needle-like causes the problems of separating, washing or drying [87]. Also, the physical properties such as packing density, agglomeration and re-dissolution mainly depend on the shape of the crystal [55]. Moreover, growth of large size single crystals has been a subject of perennial concern in order to use them for device application. Seeded free evaporation method [88, 89] can be expected to be useful in growing high quality large size single crystals of Epsomite group materials.

Formation of hybrid Epsomite group crystals by doping them with II-VI compounds, rare earths and transition metals can be considered as a better direction for further research. However, here arise a question regarding the solubility in water of the dopant material, since the Epsomite group crystals are grown from their aqueous solutions. For example, ZnS and CdS are II-VI compounds which are insoluble in water. Mahadevan and his co-workers [90 - 95] could grow successfully the

ZnS/CdS doped KDP/ADP single crystals from aqueous solutions of KDP/ADP mixed with aqueous solutions of slightly water soluble ZnS/CdS nanomaterials. Adoption of this method is expected to be useful in the case of Epsomite group crystals also.

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.

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