

A Study on Crystal growth and characterization of terbium gadolinium

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Abstract- — In this paper we are presented a Crystal growth and characterization of terbium gadolinium and mixed terbium gadolinium fumarate heptahydrate. Crystal growth includes the systematic study of the growth and properties of the crystals. It can be both natural as well as artificial. A number of crystals of different variety in the crust of earth are grown in Mother Nature by freezing the molten state. These crystals include diamond, quartz and some precious stones. Some other crystals such as the ice crystals can be formed directly from a gas (water vapours) without passing through a liquid state. During the eruption of gases around volcanoes some mineral substances in the form of sulphur and ammonium chloride crystals are formed. The crystal growth is certainly an interdisciplinary subject. It covers the collaboration of the people from physics, chemistry, materials science, metallurgy, chemical engineering, crystallography, mineralogy, etc. Since the growth processes for the crystallization of salt and sugar has been practicing since 1500 BC, therefore, the growth can be treated as an ancient scientific activity. Their large-scale applications for devices have been realized only from the last quarter of 19th century.

Index Terms— terbium, Crystal, gadolinium, growth etc

I. INTRODUCTION

In recent years, the different growth and characterization techniques have advanced much. The formations of some materials of different sizes which are technologically important have been found. As such, the growth covers the crystals from bulk to small and even to fine, ultrafine, and nano-scale sizes. The concept of size becomes even more important with the progress achieved in nanotechnology in which the size effect explains the changes in the physical properties of crystalline materials. The process of characterization has become an important part of crystal growth for

knowing their properties. Therefore, the characteristics of the materials can be found by using different characterization techniques, as only one characterization does not give the complete understanding of the materials. The crystalline solids may be categorised into single crystals and polycrystalline solids. The crystals, in which the atomic arrays are periodic in three dimensions with repeated distances are called the single crystals. The materials consisting of an aggregate number of small crystallites with random orientations separated by well defined boundaries are polycrystalline in nature. It is rather more difficult to grow a single crystal than a poly-crystalline material and for this an extra effort is justified to achieve the outstanding advantages of single crystals. The reason for growing single crystals lies in the fact that many physical properties of solids are complicated or obscured by the effect of grain boundaries. Therefore, there has been always a requirement of good quality crystals for various applications. Good quality single crystals are essential for a variety of scientific and commercial purposes. In the modern world, there is a great demand for good quality single crystals in every branch of science and technology because many sophisticated instruments use different types of crystals, either as sensors or detectors.

After the crystal growth with tailored physics and chemistry it becomes necessary to do their characterization with more advanced instruments such that their conversion into useful devices play vital role in science and technology. In the present study, the growth of pure and mixed rare-earth coordination compounds (rare-earth fumarate single crystals) was carried out by a simple gel diffusion technique. The grown crystals were then characterized by various characterization techniques and some of their physical properties were studied.

Before highlighting the significance of rare-earth fumarates it is worthwhile to throw some light on the significance of co-ordination compounds.

Matter consisting of one or more elements and their chemical compounds, can exist in nature in solid, liquid or gaseous states. The crystalline solids have a regular and periodic arrangement of atoms or molecules. The energy released during the formation of an ordered structure is more than that of the energy released during the formation of disordered structure. The crystalline state is, therefore, a low energy state and is preferred by most of the solids. Crystals are the vital pillars of the world of modern technology [1, 2]. For the technological importance the crystals with quality, purity, and defect-free nature is a prerequisite. It has attracted human civilization from prehistoric times owing to their beauty and rarity. The crystals have much importance in photonic industry, electronic industry or optical fibre communications. The ability to grow good quality crystals has become an essential criterion for the competitiveness of nations. The dimensions of the crystals cover a wide range from micrometer up to millimetre in ceramics and thin film arrangements and centimetre scale in electronics and optics and in special cases up to meter scale in silicon single crystals, natural ice and quartz crystals. Crystal growth includes the systematic study of the growth and properties of the crystals. It can be both natural as well as artificial. A number of crystals of different variety in the crust of earth are grown in Mother Nature by freezing the molten state. These crystals include diamond, quartz and some precious stones. Some other crystals such as the ice crystals can be formed directly from a gas (water vapours) without passing through a liquid state. During the eruption of gases around volcanoes some mineral substances in the form of sulphur and ammonium chloride crystals are formed. The crystal growth is certainly an interdisciplinary subject. It covers the collaboration of the people from physics, chemistry, materials science, metallurgy, chemical engineering, crystallography, mineralogy, etc. Since the growth processes for the crystallization of salt and sugar has been practicing since 1500 BC, therefore, the growth can be treated as an ancient scientific activity. Their large-scale applications for devices have been realized only from the last quarter of 19th century. Today, the crystal growth has become a well

advanced technique and does not remain the phenomena confined to nature only. Moreover, the crystals that do not grow in nature can be grown in laboratory for scientific and technological use. Now as far as Gibb's phase equilibrium concept is concerned, some driving force is required for the growth of crystals to occur. The conditions of a system change in accordance with the laws of thermodynamics in such a manner that the free energy in the whole of the system decreases. A decrease in free energy (driving force) associated with the crystallization process works to promote the ordered arrangement of atoms or molecules in the form of the growth of crystals. Basically, crystal growth is a delicate process of re-arranging the units of a substance such as atoms, molecules, ions or molecular assemblies into a regular three dimensional periodic arrays. However, the arrangement of perfect regularity has never been found in real crystals because of the presence of different kinds of local disorder and long-range imperfections such as dislocations. The field of crystal growth being an inter-disciplinary subject involves a variety of research fields. It is a three tier process i.e. (i) to grow good quality single crystals (ii) to study their physical and structural characteristics and (iii) to find their applications in science and technology. For the history of crystal growth, one can get the useful information from the works of Scheel [3, 4].

II. DIELECTRIC AND CONDUCTING BEHAVIOUR OF TERBIUM, GADOLINIUM AND MIXED GADOLINIUM-TERBIUM FUMARATE HEPTAHYDRATE SINGLE CRYSTALS

Metal-organic compounds are highly being considered as an alternative to inorganics for many reasons. They are cheaper and their structure can be easily modified through chemistry, thus making them highly versatile. The single crystal growth of metal-organic compounds with unusual dielectric, ferroelectric and second order non-linear optical (NLO) properties is currently considered as one of the vital issues. In the class of metal-organic coordination compounds the rare-earth coordination compounds are potential candidates which besides showing dielectric and ferroelectric properties are also thermally stable [204] and also have the ability to incorporate both photoluminescent centers and

magnetic properties [205]. Study of dielectric characteristics indicates the response of the material to an electric field. Different polarizations may result into the variation in dielectric constant ϵ' and dielectric loss ($\tan\delta$) of a material. Study of variations in dielectric constant ϵ' with respect to the temperature is very useful in the study of phase transition taking place in the materials. Bhat et al [206, 207] have reported dielectric studies of some rare-earth coordination compounds. Torres et al [78] have observed two phase transitions in the cadmium tartrate crystals, one due to structural changes and the other due to loss of water molecules. Since, the title compounds belong to the centro-symmetric space group $P21/n$, therefore, their dielectric anomaly due to the structural changes is ruled out at the very outset. The dielectric anomaly found in the compounds under report

has been attributed to their dehydration. Dielectric properties of some inorganic fumarate compounds have also been reported in the literature [208, 209]. During the last few years, a number of efforts were made by the researchers to find out new solids with high ionic conductivity for industrial applications, such as solid state batteries, fuel cells, sensors, etc [91]. As reported in the literature, the proton conduction of these solids may play a role in a number of processes. The direct application of solid-state proton conduction occurs in the situations where there is a requirement to transmit hydrogen across some intervening barrier. This occurs in fuel-cell technology as already mentioned in general introduction paper-1. The properties which are relevant to the function in fuel cells is reported in the literature [94]. The proton is the only ion which may be expected to form and be mobile in molecular organic solids, and hence may play an important role in intra molecular biological processes. Correspondingly, a number of specific biological processes appear to depend on proton transfers [95-97] for example, photosynthesis, where a primary process involves proton liberation and migration across a membrane, certain enzymatic processes etc. In order to understand the dielectric characteristics and the temperature and frequency dependence of ac conductivity of gel grown pure and mixed rare-earth fumarate crystals, measurements of the concerned parameters were taken and the results obtained thereof are presented in this paper.

III. GROWTH AND CHARACTERIZATION OF TERBIUM, GADOLINIUM AND MIXED GADOLINIUM-TERBIUM FUMARATE HEPTAHYDRATE SINGLE CRYSTALS

The methods of growth for obtaining single crystals may be classified according to their phase transition i.e., liquid phase, solid phase and the vapor phase. Though there are so many methods for growth of crystals, no method can be called as an ideal method. Crystal growth in gels is used for growing single crystals of the materials that show poor solubility in water. This technique has been recognized as an alternative to solution-growth method. The gel growth technique has gained considerable importance due to its simplicity and effectiveness in growing single crystals of various compounds. Despite the limitation in the sizes of the gel grown crystals, the main advantage of the gel diffusion technique is that in this method the crystals normally grow at low temperatures, therefore, there is a minimum concentration of equilibrium defects in the crystals. The gel also prevents the convection currents or turbulences and being chemically inert provides a three dimensional crucible. Moreover, due to the transparency of the gel medium, the growth of crystals can also be monitored regularly in this technique. On the other hand, high temperature techniques are usually expensive and may not be within the reach of every laboratory. A variety of crystals required for the purpose of research and application have been grown in silica gels. Fumarates being insoluble in water and decompose before melting, therefore, for the growth of terbium fumarate, gadolinium fumarate and their mixed fumarate heptahydrate single crystals we have adopted the single gel diffusion technique. During the single diffusion, one reagent is incorporated in gelling mixture (lower reactant) and another is diffused into the gel (upper reactant), leading to high supersaturation followed by nucleation and the crystal growth. While as in the double diffusion technique, the gel is used to separate the solution containing the reagents by placing the gel in the bent portion of a U-tube and the reagents in its arms. So far as the crystallization of these coordination compounds is concerned, the high affinity of rare-earth elements for oxygen donor atoms make carboxylates excellent candidates as bridging ligands

for preparing stable materials which favours the formation of cluster like solids. The literature survey shows that there are interests in the research of coordination compounds from fumaric acid describing the studies about crystallinity, luminescence, and magnetic properties. The thermal decomposition of fumarate with the following metal ions have also been reported in the literature: gadolinium, ytterbium, transition metals (II), copper. As for as, the rare-earth coordination compounds are concerned, they are the potential candidates which besides showing ferroelectric properties are also thermally stable. Moreover, these types of compounds can be readily characterized by X-ray crystallography methods, which facilitates establishment of structure-property relationships. The significance of the growth of mixed crystals is that their characteristics are different from that of the crystals of single components grown separately. For example, the variations in the hardness of pure and mixed KBr and KI system are reported in the literature. The physico-chemical characteristics of mixed crystals have brought significant changes in comparison with those of the pure crystals. The structural transitions, variation in thermal stability and modifications in external morphology of mixed crystals are also reported in the literature. In the present work, fumaric acid (HOOC-CH=CH-COOH) having relatively small central moiety was used as a ligand for the growth of terbium fumarate, gadolinium fumarate and mixed Gd-Tb fumarate heptahydrate single crystals. The growth of solid state compounds of rare-earth fumarates by gel diffusion method and hydrothermal methods are also reported in the literature. For the materials characterization of the crystals grown in the present study, we report the results obtained by X-ray diffraction, FT-IR spectroscopy, elemental analysis (CHN and EDAX), thermo-analytical techniques such as thermogravimetry (TG) and differential thermal analysis (DTA). An attempt has also been made to relate the results on nucleation kinetics with the classical nucleation theory.

VI. THERMAL BEHAVIOUR OF TERBIUM, GADOLINIUM AND MIXED GD-TB FUMARATE HEPTAHYDRATE SINGLE CRYSTALS

Thermal methods, generally referred to as thermo-analytical techniques give a deeper insight into the mechanisms involved in changes in a given material besides leading to novel intermediate and end products in large number of cases. There has been some discussion on whether thermal analysis can really be regarded as an analytical method. It was concluded that thermal analysis could be fitted into general systems on theory model of chemical analysis [232] and is based on three elements i.e, the sample, the reagent and the signal, by considering heat as a reagent. Thermal studies are also very important to throw light on the thermal stability of the substances. Thermal analysis is the measurement of changes in physical properties of a substance as a function of temperature when the substance is subjected to a controlled temperature programme [233-235]. Important information regarding the phase transformations taking place in a material is also provided by the thermo-analytical techniques. Thermal methods of analysis are now being used in a very large range of scientific investigations. These techniques also provide a wide range application in materials like building materials, ceramics, cements, glass, minerals, soils, catalysts, explosives, plastics and rubber, textiles, oils, soaps, waxes, food, petroleum, and biological samples [236]. In this paper, the comparative study of thermal behaviour of single crystals of terbium fumarate, gadolinium fumarate and mixed Gd-Tb fumarate heptahydrate crystals is reported. The non-isothermal decomposition kinetics of these compounds is also discussed.

VII. CONCLUSION

In the present work, the growth of terbium fumarate, gadolinium fumarate and mixed Gd-Tb fumarate heptahydrate single crystals was accomplished by an inexpensive silica gel diffusion technique. The effect of various growth parameters, such as gel concentration, gel age, gel pH, upper reactant concentration, lower reactant concentration and gel temperature on the nucleation rate of these crystals was studied. The results found thereof, were in good conformity with the classical nucleation theory. The optimized gel pH for the growth of well faceted crystals was found to be of the range $5.0 \leq \text{pH} < 6.0$. The qualitative and quantitative elemental analysis, employing EDAX and CHN techniques, confirm the

presence of heavier and lighter elements of the compounds. From CHN analyses, a molecular formula for terbium fumarate, gadolinium fumarate and mixed gadolinium-terbium fumarate could be established respectively as $Tb_2(C_4O_4H_2)_3 \cdot 7H_2O$, $Gd_2(C_4O_4H_2)_3 \cdot 7H_2O$ and $GdTb(C_4O_4H_2)_3 \cdot 7H_2O$. The crystallinity of these materials was confirmed by their X-ray diffraction analyses. The presence of all the functional groups associated with the fumarate ligand was confirmed by the FT-IR spectrum. Scanning electron microscopy suggested the monoclinic morphology of the crystals with two-dimensional spreading and piling up of layers. From single crystal XRD analysis, the crystal structure of terbium fumarate heptahydrate was found to be monoclinic bearing a space group $P2_1/n$, with the cell parameters: $a=9.4495 \text{ \AA}$, $b=14.6561 \text{ \AA}$, $c=14.7272 \text{ \AA}$ and $\alpha=\gamma=90^\circ$ and $\beta=91.318^\circ$. The cell parameters of gadolinium fumarate heptahydrate and mixed GdTb fumarate heptahydrate were found by using Crysfire software programme. For gadolinium fumarate heptahydrate, $a=9.491 \text{ \AA}$, $b=14.772 \text{ \AA}$, $c=14.813 \text{ \AA}$ and $\alpha=\gamma=90^\circ$ and $\beta=91.26^\circ$ and for mixed GdTb fumarate heptahydrate, $a=9.2705 \text{ \AA}$, $b=14.3701 \text{ \AA}$, $c=14.3602 \text{ \AA}$ and $\alpha=90^\circ$, $\beta=91.41^\circ$ and $\gamma=90^\circ$. The cell parameters of gadolinium fumarate and mixed gadolinium-terbium fumarate heptahydrates were seen to be nearly equal to the cell parameters of terbium fumarate heptahydrate as obtained from its single crystal X-ray diffraction. As such, the three compounds grown in the present work are isomorphous to each other. A phase matching search was also followed, which showed that samarium fumarate heptahydrate crystals are isomorphous to terbium fumarate heptahydrate and hence isomorphous to gadolinium fumarate heptahydrate and mixed GdTb heptahydrate. The molecular formula for each of the compounds was substantiated by their thermogravimetric analyses. The thermal stability of terbium fumarate and gadolinium fumarate crystals was found to be 110°C and that of the mixed GdTb fumarate crystals was 120°C . DTA/DTG peaks for each of the compounds corresponding to nearly the same temperature suggest an isomorphous phase transition. The dehydration of coordinated water molecules of these compounds correspond to the DTA peaks respectively at 132.63°C , 133.63°C and 149°C for terbium fumarate,

gadolinium fumarate and mixed terbium-gadolinium fumarate heptahydrates. The pure rare-earth fumarate crystals decompose in two steps of thermal decomposition with the formation of their corresponding oxides, while as the mixed rare-earth fumarate decomposes in three steps till the formation of its oxide. The decomposition peaks of the dehydrated compounds correspond to 481.5°C , 484.59°C and 493.45°C respectively for terbium fumarate, gadolinium fumarate and mixed gadolinium-terbium fumarate. This suggests that the molecular structure of these pure and mixed compounds could be same with the exemption that the mixed compound could be a bit harder than the pure fumarate crystals.

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