CHAPTER 2
LITERATURE REVIEW

2.1 Rochelle Salt Crystals Grown in Solution

The isotopic effects in partially deuterated piezoelectric crystals of Rochelle salt was discussed by R.R. Levitskii et al. (2004). They developed a theory for dielectric, piezoelectric, and elastic properties of partially deuterated (quenched disorder) crystals of Rochelle salt by taking into account the piezoelectric coupling. The study of paraelectric phase of Rochelle salt at 105 K was investigated by Mitrović et al. (1987). The investigation based on data collected at 105 K, provides very accurate structural information for the low temperature paraelectric form. Unlike the ferroelectric form, there is only one tartrate molecule in the asymmetric unit, and the structure displays no disorder to large anisotropic atomic displacements. The crystal structure and crystal data are provided in

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\text{Crystal data} \\
\text{K}^+\text{Na}^+\text{C}_4\text{H}_4\text{O}_6^{2-}\cdot4\text{H}_2\text{O} \\
\text{Mr} = 282.23 \\
\text{Orthorhombic, P2}_1\text{2}_1\text{2} \\
a = 11.7859 (6) \text{ Å} \\
b = 14.1972 (7) \text{ Å} \\
c = 6.1875 (3) \text{ Å} \\
V = 1035.33 (9) \text{ Å}^3 \\
Z = 4
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Fig 2.1 Crystal structure data of Rochelle salt

Fig 2.1. Raman spectroscopy and dielectric constants of ferroelectric Rochelle salt and calcium tartrate was discussed in detail by W Taylor et al. (1984).

2.2 Metal tartrate crystals grown in gel medium

Magnetic susceptibility study of ferroelectric Rubidium and ammonium hydrogen tartrate crystals was done by C.C. Desai et al. (1988). The Vibrational Studies of Gel Grown Ferroelectric RbHC₄H₄O₆ and SrC₄H₄O₆.4H₂O Crystal was dealt in detail by S. Selvasekarapandian et al. (1999). Single crystals of Rubidium Hydrogen Tartrate (RbHT) and Strontium Tartrate Tetrahydrate (SrTT) have been grown by a gel technique using a chemical reaction method. A controlled reaction has been employed between tartaric acid and feed solution (RbCl for RbHT and Sr(NO₃)₂) at room temperature. The laser Raman and FT-IR spectra of these crystals were recorded in the frequency range 100 - 4000cm⁻¹. The presence of tartrate ion, monohydrogen tartrate ion, water molecules and external mode vibrational frequencies were identified and discussed. The doublet and broad nature of tartrate ion vibrational frequencies have also been observed and analyzed. Characterization of pure and doped potassium hydrogen tartrate single crystals grown in silica gel was discussed in detail by Quasim et al. (2009). Growth of pure-, sodium- and lithium- doped potassium hydrogen tartrate single crystals by gel technique was reported. Growth conditions conducive for the growth of single crystals are worked out. The crystals were characterized by using powder XRD, SEM, FTIR, AES, EDAX, CH analysis and thermoanalytical techniques. The stoichiometric composition for the grown crystals were established as KHC₄H₄O₆.H₂O, (K)₀.₉₈(Na)₀.₀₂HC₄H₄O₆.H₂O and (K)₀.₉₄(Li)₀.₀₆HC₄H₄O₆.H₂O. Doping of sodium and lithium in the pure potassium hydrogen tartrate single crystals was found to influence the size, perfection, morphology, crystal structure and the thermal stability of crystals.
Characterization and thermal and electromagnetic behavior of gadolinium-doped calcium tartrate crystals grown by the solution technique was done by M.E. Toress et al. (1995). Mixed crystals of Calcium-Barium Tartrate were grown by a single diffusion method by D.K. Sawant et al. (2011). The optimum conditions were established by varying various parameters such as pH of gel solution, gel concentrations, gel setting time, concentration of reactants etc. Crystals having different morphologies were obtained. Whitish semitransparent, pale yellow, rhombohedral shaped, needle shaped crystals of Calcium-Barium Tartrate were obtained. Some of them were transparent diamond shaped, some are twined. Maximum sizes of the grown crystals are 5mm×3mm and thickness about 2 to 3 mm. The crystals grown were characterized by Thermogravimetry (TGA), Differential thermal analysis (DTA) and Derivative thermogravity (DTG). The results of these observations are described and discussed.

Sahaya Shajan et al. (2004) has grown Calcium tartrate single crystals using silica gel as the growth medium. Calcium formate mixed with formic acid was taken as the supernatant solution. It was observed that the nucleation density was reduced and the size of the crystals was improved to a large extent compared to the conventional way of growing calcium tartrate crystals with calcium chloride. The role played by formate–formic acid on the growth of crystals is discussed. The grown crystals were characterized by atomic absorption spectroscopy (AAS), X ray diffraction analysis (XRD), microhardness measurement, Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG) and differential thermal analysis (DTA). The results obtained are compared with the previous work.

Single crystal growth of pure and sodium modified copper tartrate crystals bearing composition (Cu)x(Na)y C4H4O6 nH2O (where x = 1, 0.77, 0.65; y = 0, 0.23, 0.35) is achieved using gel technique by Quasim et al. (2008). The optimum conditions required for the growth of these crystals are worked out. The morphological development of these crystals is studied using optical and scanning
electron microscopy. The dominant habit faces of the grown copper tartrate crystals are (001) and (111). Calculation of the cell parameters using CRYSFIRE software suggests that the pure copper tartrate crystal belongs to orthorhombic system with space group P2₁/c whereas the modified copper tartrate falls under tetragonal system with the space group P4₂/nbc. The external morphological development is shown to remain unaffected in the modified copper tartrate. The stoichiometric composition of the crystals is established by EDAX analysis, CH analysis, FTIR spectroscopy and thermoanalytical techniques. Thermal analysis of the grown crystals suggests that pure copper tartrate is thermally stable upto 42.84°C whereas the modified copper tartrate crystals are stable only upto 33.11°C and 25.11°C. Calculation of the percentage weight loss from the thermogram supplemented by EDAX/CH analysis and FTIR spectroscopy suggest that the chemical formula of pure copper tartrate crystal is CuC₄H₄O₆ 3H₂O whereas the chemical formula for the modified copper tartrate crystals is (Cu)₀.₇₇(Na)₀.₂₃C₄H₄O₆ 3H₂O and (Cu)₀.₆₅(Na)₀.₃₅ C₄H₄O₆ H₂O.

Growth of lanthanum tartrate crystals in silica Gel was reported by P. N. KOTRU et al. (1986) in detail. The spherulitic, dendritic and single-crystal growth of hydrated lanthanum tartrate by controlled diffusion in silica gels is reported. The influence of growth parameters, e.g. reactant concentrations, gel pH, gel ageing, on the size and nucleation density of crystals has been studied. Operative mechanisms of crystallization, results of growth kinetics and morphology of crystals are discussed. The adsorption property of the gel is found to play a vital role during the crystallization of lanthanum tartrate crystals. Parabolic kinetics, characteristic of a one-dimensional diffusion-controlled process, for single crystals is observed to be obeyed in case of variation of upper reactant concentration. Studies on gel-grown pure and strontium-modified lanthanum tartrate crystals was carried out by A. Firdous et al. (2009). Crystals of pure and strontium-modified lanthanum tartrate bearing composition (La)₁₋ₓ (Sr)ₓ C₄H₄O₆ nH₂O (where x = 0, 0.04, 0.10, 0.15; n = 5, 5, 6, 8) were obtained using gel method. The materials were
studied using CH analysis, X-ray powder diffraction, FTIR, EDAX and thermo analytical techniques. X-ray powder diffraction results analyzed by using suitable software suggest that while unmodified lanthanum tartrate has a monoclinic structure with the space group P2₁, the entry of strontium into its lattice changes the system to orthorhombic with the space group P2₁2₁2₁. The unit cell volume is observed to decrease with increase in the concentration of strontium in lanthanum tartrate. Thermal analysis suggests that pure lanthanum tartrate starts decomposing at 41.31°C whereas the strontium-modified lanthanum tartrate brings about better thermal stability which increases with an increase in strontium concentration.

Kinetics and mechanism of thermal decomposition of strontium tartrate crystals was dealt in detail by S.K. Arora et al. (2004). Thermo gravimetric and differential thermal analysis have been used for thermal characterization of the gel-grown crystals of strontium tartrate by measuring the changes in their physicochemical properties as a function of increasing temperature with time. The material turns out to be trihydrated. The obtained experimental data show that the material is thermally stable up to 393 K, beyond which it exhibits marked tendency to decompose. The decomposition process occurs in four stages until, ultimately, strontium carbonate is obtained at 678 K. The energies of the reactions involved and the mechanism of decomposition at each stage have been examined. The values of kinetic parameters, e.g. order of reaction, activation energy and the frequency factor are also evaluated. The results have been adequately interpreted in the light of existing theories. Magnetic moment measurements of gadolinium, holmium and ytterbium tartrate trihydrate crystals by Basharat Want et al. (2008) gives a detailed account of magnetic moment and susceptibility of single crystals of rare earth tartrates of the type R(C₄H₄O₆)(C₄H₅O₆)·3H₂O (where R = Gd, Ho, and Yb), using a vibration sample magnetometer are reported. The experimental values of molar susceptibilities for Gd (C₄H₄O₆) (C₄H₅O₆)·3H₂O, Ho(C₄H₄O₆) (C₄H₅O₆)·3H₂O, and Yb(C₄H₄O₆) (C₄H₅O₆)·3H₂O are 2.58×10⁻², 4.66×10⁻², and
8.03×10^{-3} (in cgs em units), respectively. The calculated effective magnetic moments are in good agreement with the theoretical predictions on rare earth ions.

Laser Raman and Infrared Spectra of Dipotassium Tartrate Hemihydrate from solution by R. Bhattachajee et al. (1989) gives a systematic analysis of the 1R and Raman spectra of dipotassium tartrate hemihydrate (K$_2$C$_4$H$_4$O$_6$ 4H$_2$O) in terms of the standard frequency correlations, deuteration shift and typical nature (with respect to intensity and width) of bands due to different modes is reported. The bands due to the internal modes (excluding some skeletal modes) of the C$_4$H$_6$O$_6^{2-}$ ion appear as doublets. The Laser Raman and Infra red spectra of Di-Potassium Tartrate Hemi-hydrate by G. P. Srivastava et al.(1982) gives a detailed analysis of the Raman and infrared spectra of dipotassium tartrate hemi-hydrate grown from solution. It has been inferred that the C$_4$H$_4$O$_6^{2-}$ ion and H$_2$O molecule in a DKT crystal occupy points of C$_1$ site symmetry. Various units of C$_4$H$_4$O$_6^{2-}$ ion /(H$_2$O molecule) located at crystallographically distinguishable positions in this crystal do not appear to be different in their structure or the force fields governing their vibrational dynamics. Laser Raman and Infrared Spectra of Tartaric Acid Crystals has been explained in detail by R. Bhattacharjee et al.(1989). In this paper they have reported a detailed analysis of the observed IR and Raman spectra of TA based on standard frequency correlations, deuteration shift and typical characteristics (with respect to intensity and width) of bands due to different modes. Our assignments are also supported by the spectra of TA in aqueous solution. This study should therefore help not only in identifying the bands of TA but also indistingguishing the bands due to OH stretching modes of vibration. EPR study of Mn$^{2+}$ doped ammonium tartrate single crystals is carried out at room temperature by Ram Kripala et al. (2008) in detail.

Structural and dielectric characterization of cadmium tartrate was discussed in detail by M. E. Torres et al.(1998). Polycrystalline samples of dimeric cadmium tartrate were studied using impedance measurements and x-ray powder diffraction.
The dependence of the real part of the dielectric constant on temperature showed a sharp peak at about 65 °C, revealing a structural phase transition, while the other broad peak in the temperature range (70°C To 85 °C) was due to the loss of water molecules. The x-ray powder diffraction patterns at three temperatures 25°C, 60°C, and 70 °C are consistent with three non equivalent space groups. The Growth of Cadmium Tartrate crystals by gel technique was investigated by N. S. Patil et al.(2011). Cadmium Tartrate crystals were grown by simple gel technique using single diffusion method. The optimum conditions were established by varying various parameters such as pH concentration, setting time, ageing time and concentration of reactants of gel solution. Crystals having different morphology & habits were obtained. Prismatic dendritic crystals of Cadmium Tartrate & prismatic diamond shape shining & yellowish coloured single crystal were obtained. Some of them were transparent & some of translucent & few others were opaque. The crystals were characterized using XRD, FT-IR & UV. The structural and optical properties of calcium cadmium tartrate was found out by D. K. Sawant et al.(2011). Calcium Cadmium tartrate single crystals were grown in silica gel at ambient temperature. Effect of various parameters like gel pH, and gel aging, gel density and concentration of reactants on the growth of these crystals were studies. Crystals having different morphologies and habits were obtained. Transparent, pyramidal shaped like diamonds crystals of Calcium Cadmium tartrate were obtained. Some of them were faint yellowish, milky white, due to fast growth rate attached crystals are obtained; faces are well developed and polished. The crystals grown were characterized by PL, SEM, and UV. XRD studies reveal that the crystal lattice of the Calcium Cadmium is orthorhombic and crystalline perfection of the crystals is extremely good. Photoluminescence spectrum shows Cyan, green and orange emissions. SEM image showed plate like morphology and further plate like growth was observed on some plates.

A detailed explanation of Infrared spectroscopic and thermal studies of gel grown spherulitic crystals of iron tartrate is done by Sherly Joseph et al.(1997). In
the investigation of Characterization of gel grown iron-manganese-cobalt ternary levo-tartrate crystals by S. J. Joshi et al. (2010), crystals of different compositions have been grown by single-diffusion gel growth technique in silica hydrogel medium. The metallic composition in the crystals was estimated by EDAX. The coloration of the crystals changed with composition of metallic content. The powder XRD study suggested the crystalline nature and indicated the presence of some extra phases. The grown crystals were characterized by FT-IR spectroscopy, TGA, dielectric and Vibrating Sample Magnetometer (VSM) studies. The FT-IR study suggested the presence of O-H, C=O, C-O and metal-oxygen bonds. The effect of composition of metallic content was observed in certain absorption regions in FT-IR spectra. The thermal stability of the crystals was studied by thermogravimetry and the kinetic and thermodynamic parameters of dehydration were calculated. The effect of composition of ternary levo-tartrate was observed in dielectric study. The dielectric study was carried out in the frequency range of applied field from 500 Hz to 1 MHz. The variations in dielectric constant, dielectric loss, a.c. resistivity and a.c. conductivity with frequency of applied field were studied. VSM study suggested that all crystals were of paramagnetic nature.

In the present investigation a detailed investigation of the Laser Raman spectrum, Fourier transform infrared spectrum and Powder X-ray diffraction spectrum, thermal analysis, dielectric studies and antimicrobial activities of the pure and Cu(NO₃)₂ 3H₂O doped Rochelle salt (NaKC₄H₄O₆ 4H₂O) crystals have been done. The gel growth of pure, Cu²⁺,Fe²⁺ doped Potassium hydrogen tartrate crystals have been done. EDAX study has been made to find the effect of dopant and the functional group analysis has been made from FTIR studies. The structural analysis and the lattice parameters have been found out from powder XRD studies. The magnetic properties such as magnetic susceptibility and magnetic moment of the pure and doped samples have been found out. From the thermal analysis the decomposition process of the samples have been given. A detailed analysis of sodium potassium bi-tartrate crystals grown from gel has been done for the first
time. The functional group analysis, structural analysis, magnetic properties and thermal analysis have been made and discussed in detail. In the present investigation di-potassium tartrate has been grown from gel for the first time. A detailed characterization studies like FTIR, Powder XRD, Magnetic properties and thermal analysis and dielectric studies have been made.

In the present study, pure and copper doped iron tartrate crystals grown from gel. The grown crystals were characterized by FTIR, Powder XRD, Magnetic properties test, TGA and DSC analysis. A detailed comparative studies have been made between pure and doped crystals. A detailed analysis about pure, Cu$^{2+}$,Fe$^{2+}$ and Mg$^{2+}$ doped cadmium tartrate crystals have been done. The EDAX study has been made to confirm the effect of dopant on the pure crystal. Studies including FTIR, Powder XRD, magnetic moment, thermal and dielectric analysis have been made. A detailed comparison has been made between pure and doped crystals. Gel growth of cobalt tartrate crystals have been done by chemical reaction method and characterization such as FTIR, Powder XRD, magnetic analysis, thermal studies and dielectric properties of the grown crystals have been made.