CHAPTER II

EXPERIMENTAL DETAILS
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EXPERIMENTAL DETAILS

This chapter describes the methods of growth of various ferroelectric crystals in the present investigation and the experimental techniques that have been used for characterisation.

2.1 CRYSTAL GROWTH

Growth of crystals is possible from any of the three phase namely i) solution phase ii) melt phase and iii) vapour phase and the selection of method of crystal growth is mainly confronted by two constraints, the nature of the method and the properties of the materials [1]. In the present work, three crystal growth techniques i) gel method ii) flux method and iii) slow evaporation solution method are adopted for the growth of crystals. Gel technique is an excellent technique to grow crystals, particularly, for low solubility compounds. Flux method is used for the very high melting point compounds.

2.2 CRYSTAL GROWTH IN GELS

Growth of crystals by gel technique has gained considerable momentum on account of its simplicity, feasibility and versatility. Crystals of substances with high/low solubility and a low thermal stability are difficult to grow from solutions, but large size and very good quality crystals of these compounds can be grown by gel method. A gel is a two component system semisolid in nature and rich in liquid. It consists fine pores through which diffusion can takes place. It can be observed experimentally that reactants diffuse through gels as through water. The process of forming a gel is called gelation and it is accompanied by a large increase in viscosity. The change is gradual and not a sudden one. In gel technique, crystal growth is achieved by controlling the diffusion and the rate of mixing of soluble species to form insoluble salt.

Two types of gels are available namely elastic and non elastic gels. The solid framework that immobilizes the liquid may be composed of long chain
molecules together, at only a few points, in which case the gel is called an elastic gel. Alternately, the framework may be more like a three-dimensional network, in which case the gel is called a non-elastic gel.

Varieties of gels namely, silica gel, agar-agar, soft soaps from potassium salts of higher fatty acids, number of oleates and stearates, polyvinyl alcohol and various hydroxides in water are available. Of all the above, silica gels have been used to grow the crystals in the present investigation.

Gelling mechanism and structure of silica gel

Monosilicic acid may be formed as sodium metasilicate goes into the aqueous solution according to the following dynamic equilibrium process.

\[
Na_2SiO_3 + 3H_2O \rightleftharpoons H_4SiO_4 + 2NaOH
\]

Under suitable pH conditions this acid is polymerized with the liberation of water as follows

\[
\begin{align*}
&\text{OH} \quad \text{OH} \quad \text{OH} \\
&\text{HO} \quad \text{Si} \quad \text{OH} + \text{HO} \quad \text{Si} \quad \text{OH} \quad \text{OH} \\
&\text{OH} \quad \text{OH} \quad \text{OH} \\
\end{align*}
\]

The above change occurs continuous until a three-dimensional network of Si ---- O links is established as shown below.
As polymerization process continues, water accumulates on top of the gel surface, a phenomenon known as syneresis [2]. In the process of gelation, pH plays a vital role. There is no well defined relation for the period of gelation. It is known that two other ions namely H$_3$SiO$_4$ and H$_2$SiO$_4^{2-}$ are produced in relative amounts depending on the hydrogen ion concentration. Of the two, H$_2$SiO$_4^{2-}$ is associated with higher pH values. It is more reactive and its higher charge leads to a greater degree of repulsion. H$_3$SiO$_4^-$ is favored by moderately low pH values and is responsible for the initial formation of long chain polymerisation products. In most of the cases, the pH range 3 - 5 is favoured for growth of the good quality crystals.

**Nucleation control**

It is necessary to suppress the fast nucleation process until a few crystals are formed because it is detrimental to the crystal size and perfection [2,3]. There are many methods for controlling the nucleation which is achieved by,

i) changing the gel parameters like pH value, density and gel aging [4]

ii) concentration programming [2,4,5] and

iii) introducing an intermediate neutral gel between the reactants which will slow down the reaction and hence reduce the number of nuclei [6-8].
Methods of gel growth

Growth of crystals in gel can be done by adopting any one of the following method [2].

i) chemical reaction method
ii) chemical reduction method
iii) solubility reduction method

In the present investigation, chemical reaction method is employed for the growth of crystals.

i) Chemical reaction method

It has a special advantage of growing crystals which are insoluble in water and which decompose before melting. Chemical reaction method consists of incorporating one reagent in the gelling mixture and then diffusing another reactant in to the gel leads to high supersaturation and initiates nucleation and crystal growth [2]. This may be done by using test tubes (Fig.2.1).

The basic growth procedure is to allow the solutions of two required water soluble material to react inside the gel by way of diffusion. For example, if AX and BY are two water soluble compounds, one is incorporated into the gel and the other is placed on the gel surface. Reaction takes place inside the gel leading the crystallization of the insoluble product say AY and the other product BX must be water soluble.

\[ AX + BY \rightarrow AY + BX \]

ii) Chemical reduction method

This method enables the crystal growth of metals like gold, copper, cobalt, nickel, etc. in gel at room temperature. In the growth of copper crystals, the gel is
Figure 2.1 Chemical Reaction method
(Test tube system)
impregnated with CuSO₄. After gelation, reducing agents such as hydroxylamine hydrochloride or hypophosphorous acid is taken over the gel set and diffusion takes place. Chemical reduction of CuSO₄ into copper yields tetrahedral copper crystals inside the gel [9].

iii) Solubility reduction method

Strongly acidic electrolytes with good solubility in water such as KDP and ADP can be crystallised in gel by this method [10,11]. In such cases the material itself can be used for the purpose of gel setting in the place of an acid. After gel set, suitable solvent like ethanal, methonal, etc., can be used as the outer reactant. Diffusion of the above inside the gel reduces the solubility of the impregnated material, leading to supersaturation and finally the crystal growth.

Advantages of gel method
i) The gel acts an ideal medium (i.e., three dimensional media) for the diffusion of reacting ions / solvents
ii) gel grown crystals are found to be comparatively less defective
iii) It remains chemically inert and does not involve in the chemical reactions during crystallization
iv) It holds the crystals in fixed positions without overlapping, irrespective of internal disturbances
v) crystals can be grown at room temperature
vi) nucleation can be controlled effectively by varying the gel density and by adopting other suitable processes
vii) observation of nucleation, measurement of growth rate and study of morphological changes can be made effectively

2.3 GROWTH FROM SOLUTION METHOD

The growth from solutions takes place in two stages: i) nucleation and ii) growth. Therefore, the first requirement is that of a suitable solvent which can dissolve the solute to an appreciable extent. This may be possible either under
normal conditions (atmospheric pressure and room temperature) or high pressures / temperatures. The solvent may be water or melt of solvent. Crystal growth from solution method are broadly classified into two types: i) Low temperature solution growth and ii) high temperature solution growth [12].

2.4 LOW TEMPERATURE SOLUTION GROWTH

In the solution method, nucleation can be carried out from highly supersaturated solutions, so that it can occur spontaneously; but conditions should be such that the solution becomes metastable after a few nuclei have been formed. By metastable condition, we mean a very small supersaturation, which prevents formation of many nuclei. The growth can then occur over the few seed nuclei already formed. As the growth proceeds, the supersaturation decreases. In order to maintain a reasonable growth rate, the supersaturation has to be kept constant. The principle method used to produce supersaturation are i) slow evaporation of the solvent ii) lowering the temperature iii) adding solute iv) adding another solvent [13]. In the present work slow evaporation method is used for growing the crystals.

2.5 HIGH TEMPERATURE SOLUTION GROWTH

The technique of high temperature solution growth may be divided into two categories i) hydrothermal method and ii) flux method.

2.5.1 Hydrothermal method

If the solubility of the solute in water is not high, growth from aqueous solutions becomes inconvenient. Since the solubility generally increases with increasing temperature, the temperature of operation may be increased beyond 100°C. Growth under conditions of high temperatures and high pressures is called hydrothermal growth.
2.5.2 Flux method

In the absence of proper solvents, growth may be carried out from melts of solids, which do not react with the solute. In order to grow materials with high melting points, some ‘flux’ materials may be added, which bring down the melting point. Flux growth is defined as the use of a liquid inorganic compound at elevated temperature as solvent for crystallisation. The growth from melt is perhaps reserved for growth from a one component system where no solvent is present. Molten or fused inorganic salts and oxides are often powerful solvents for refractory materials. Consequently they can often serve as media for crystal growth. Such solvents are often called fluxes by analogy with soldering, brazing and other metal joining processes where the flux dissolves oxide films [14].

Substances that are used as fluxes should have the following characteristics. i) Be a good reversible one ii) not form solid solutions with the materials being grown iii) low viscosity iv) easy to remove after growth v) compatible with the crucible vi) not reacting with furnace atmosphere vii) readily obtainable in pure state viii) cheap and nontoxic.

In the flux method, saturated solution is prepared by holding or soaking a crucible containing flux and the crystal constituents at a temperature slightly above the saturated temperature long enough to effect complete solution. Then the crucible is cooled at a rate of $d\theta/dt$ (degrees/hr) through a temperature range where the desired crystal is known to precipitate. The supersaturation will depend upon the values of the temperature coefficient of solubility $ds/d\theta$ in the chosen interval. Usually $d\theta/dt$ is adjusted so that $ds/dt$ is in the range .02 to .20 weight percent/hr. For most values of $ds/d\theta$, this results in $d\theta/dt$ varying between 10 to 20°/per day. Crystals usually nucleate in the coolest region of the crucible. Even when the most careful efforts are made to keep a crucible isothermal, some region remains slightly cooler and nucleation begins there. Attempts have also been made in some favorable cases to use seed crystals. Control of growth is usually restricted to external temperature regulation. In the present work, three
Figure 2.2 Three zone furnace system for growing the crystals in Flux method

1) Rotating ceramic tube 2) platinum wire 3) thermal insulation 4) heating element 5) thermocouples 6) crucible support 7) growing crystal 8) platinum crucible 9) ceramic tube 10) quartz tube
zone furnace system is used for growing the crystals in slow cooling flux method (Fig. 2.2).

**Advantages of flux method**

i) growth at temperature below the solute melting point  
ii) high quality crystals are obtainable  
iii) doping with suitable elements is easily achieved  
iv) solid solution crystals can be grown  
v) stoichiometric forms of crystals are obtainable

### 2.6 VIBRATIONAL STUDIES

Raman spectra of the samples investigated and reported in this thesis are recorded in the frequency range 50 - 4000 cm\(^{-1}\) mostly using a Dilor Z24 triple monochromator coupled with a spectra physics model 165 Ar\(^+\) laser. The Raman spectrometer consists of four major components i) the laser ii) the sample illuminator assembly iii) the triple monochromator and iv) the detector and recorder.

The Ar\(^+\) laser capable of giving very prominent lines at 514.5 nm and 488 nm is used as the exciting source for the Raman measurements. The laser beam is directed into the sample compartment by use of dielectrically coated mirrors of very high reflectance. The sample illuminator assembly has arrangements for holding the powder sample in capillary tube. Single crystal can be oriented with goniometer head. The polarization of the incident laser beam can be adjusted to record single crystal Raman spectra. The scattered laser beam is focused on the triple monochromator arrangement. Signals from the monochromator are received and amplified by the cooled photomultiplier tube. The high quality photomultiplier tube is used as detectors in Raman spectrometer. Two factors are of importance in the choice of a photomultiplier tube for the detection of weak signals. They are low dark current and high quantum efficiency.
Figure 2.3 Schematic diagram of Raman Spectrometer
efficiency is a measure of the ratio of the signal at the anode to the number of photons at the cathode. Cooling the tube greatly reduces thermion dark current (the dark current is the signal due to thermally excited electrons which leave the cathode of a phototube in the absence of light).

The Raman spectrometer block diagram with the essential parts is shown in Figure 2.3. In the recording system operated in the photon counting mode, the anode pulses of the PMT are fed to a pre-amplifier and converted into d.c. signal. This signal level is proportional to the pulse current which is displayed and recorded by the chart recorder. Spectra of few samples have been recorded in Ramanor HG2S Raman spectrometer.

The FT-IR spectra are measured using a Bruker IFS66U model spectrometer in the frequency ranges 40 - 400 cm\(^{-1}\) and 400 - 4000 cm\(^{-1}\). The Fourier Transform Infrared spectrometer is based on the blending of a Michelson interferometer with a sensitive infrared detector and a digital minicomputer. Polyethylene pellet method was used for the region 40 - 400 cm\(^{-1}\) and KBr pellet technique was used in the 400 - 4000 cm\(^{-1}\) region.

2.7 DIELECTRIC STUDIES

The capacitance, loss factor (tan \(\delta\)) and resistance of the grown crystals are measured using a Hewlet - Packard multifrequency LCR meter (model 4275A) and ANDO LCR meter (model AG - 4311). Data are recorded over the frequency range 100Hz - 10MHz. The crystal is mounted between the two flat silver electrodes in ordinary conducting cell. The crystal faces are polished and coated with silver paint to render good electrical contact between the crystal and the electrodes for the dielectric and electrical conductivity studies. For studying the temperature effect on dielectric constant, dielectric loss and conductivity, the crystal is placed in a resistance heated furnace and the temperature of the crystal
is measured using a chromel - alumel thermocouple with the temperature indicator.

The dielectric constant of the grown crystals are calculated using the formula,

\[ K = \frac{C d}{\varepsilon_0 A} \]

where,

- C - Capacitance of the sample
- d - Thickness of the sample
- \( \varepsilon_0 \) - Dielectric constant in free space
- A - Area of the sample
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