CHAPTER 2

NUCLEATION STUDIES ON PURE AND DOPED TGS CRYSTALS

2.1 INTRODUCTION

The creation of a new phase in the body of the mother phase, be it gas, liquid, or solid, is one of the most fundamental aspects of phase transitions in general and of crystal growth in particular. The potential barrier which a system must overcome in order to create a (crystalline) nucleus in the ideally homogeneous mother phase and which determines the rate of nucleation is defined, in homogenous nucleation, by the interface energy. TGS crystals are at present the only ferroelectric crystals which can be grown easily in bulk form needed for IR imaging applications; for which (010) plates of size (1x1) cm² are required. There are problems associated with the growth of bulk transparent TGS crystals by traditional technique, due primarily to formation of spurious nucleation and irregular growth rate. The level of solution stability depends on many different conditions such as purity of raw materials, methods of preliminary treatment of solutions, crystallizer design, hydrodynamic conditions, rates of temperature reduction, etc. The study on induction period is important because, the growth process for large perfect crystals can be successful only if induction period is more than the time required for crystal growth (Zaitseva et al 1995). Many authors have investigated the solubility of pure and doped TGS (Kroes and Reiss 1984, Wang and Fang 1992, Nitsche 1958, and Davey et al 1975) and there is a wide variation in the values given by different investigators. However, reports on the nucleation parameters such as the induction period
and interfacial energy are very scarce. Wang et al 1992 have studied the solution status of TGS and TGSP crystals. The purpose of the present investigation on nucleation is mainly to determine the induction period of pure and amino acid doped (L-alanine, L-valine) TGS solutions under those conditions which are present during the growth of large TGS crystals. A quantitative experimental investigation of nucleation is extremely complicated. This is due primarily to the small sizes of the nuclei; which as yet makes it impossible to observe them directly and measure the condensation parameters. Induction period is difficult to be determined experimentally since the critical nucleus has not been detected by any means till now. It is possible to observe nucleation only after the nucleus has grown to sufficient size taking the solute out of solution making them either visible or making some other related property detectable. This time which is usually recorded as experimental induction period is usually much closer to the actual induction time and therefore does not cause any serious error in the calculations.

2.2 INDUCTION PERIOD

The classical nucleation theory makes two predictions, one with respect to the increase of the "Stationary nucleation rate" with supersaturation and the other with respect to the "time lag" (Katz et al 1967, Katz 1970, Katz 1977). A period of time usually elapses between the achievement of supersaturation, or supercooling, and the appearance of crystals in a given system. This time lag is known as the "induction period". The induction period can be affected by the level of supersaturation, the temperature, the state of agitation, the viscosity of the system, the presence of impurities and so on. Induction periods may be measured visually, that is by recording the time between the system attaining the supersaturation and appearance of first nucleus, e.g. as bright twinkling particles in a beam of light. On the other hand, concentration changes may be recorded over a period of time by turbidity, conductivity or refractive index measurements.
The induction period may be considered as the combination of several parts. For example, a certain relaxation time $t_r$ is required for the system to achieve a quasi steady-state distribution of molecular clusters. Time is also required for the formation of a stable nucleus $t_n$ and for the nucleus to grow to a detectable size, $t_g$. So the induction period $\tau$, may be written as

$$\tau = t_r + t_n + t_g$$

(2.1)

It is difficult, if not impossible, to isolate and measure the individual quantities, but the nucleus formation time, $t_n$, is often assumed to be the largest, although this may not always be true. The nucleus growth time, $t_g$ may be quite small, especially in aqueous solutions of inorganic salts. The relaxation time, $t_r$, depends to great extent on the system viscosity and, hence, diffusivity. Nielsen et al (1964) predicted the relaxation time $t_r = 10^{-13}$ $D^{-1}$, where $D$ is the diffusivity, so in an aqueous solution of an electrolyte with $D = 10^{-5}$ Cm$^2$/sec, the relaxation time would be $10^{-8}$ sec. However, in highly viscous system values of $D$ can be extremely low and $t_r$ very high.

### 2.2.1 Induction period and the rate of nucleation

The induction time is undoubtedly related in some way to the size (Li et al 1976) and complexity of the critical nucleus. Despite its complexity, the induction period has frequently been used as a measure of the nucleation rate. A number of authors (Kashchiev et al 1991, Sohnel 1983, Bennema and Sohnel 1990, Mersmann 1990, Sangwal 1989, Sohnel 1982) have made simplifying assumption that the induction period is essentially devoted to nucleus formation and can therefore be considered inversely proportional to the rate of nucleation

$$\tau \propto J^{-1}$$

(2.2)
from which the classical nucleation relationship gives

$$\log \left( \frac{1}{\tau} \right) \propto \frac{\sigma^3}{T^3 (\log S)^2} \quad (2.3)$$

For a given temperature, a plot of $\log \tau$ versus $(\log S)^{-2}$ should be a straight line and a value of $\sigma$, the surface energy, can be calculated using the above graph.

Nie
tson and Sohnel 1971 determined surface tensions of many electrolyte crystal - aqueous solutions systems from a measurement of induction periods in precipitation experiments. The interfacial tension and induction period $t_i$ were interrelated by the expression:

$$\gamma = kT \left[ \frac{5\ln (2x_m^{1/2}D_v^{2/3} t_i) \ln S^2}{2\beta v^2} \right]^{1/3} \quad (2.4)$$

Where $t_i$ is the experimentally determined induction period, $S$ is the supersaturation ratio, $D$ is the diffusion coefficient, $v$ is the mean ionic volume, $\beta$ is a dimensionless factor depending on the shape of the nucleus, $x_m$ is the initial mole fraction of solute.

Kashchiev et al 1991 made an analysis providing a general formula for the induction time $t_i$ in new phase formation, which is valid for any number of nuclei taking part in the process and which reduces to the known expressions for $t_i$ derived in the scope of either the mononuclear or polynuclear mechanism. The expression for $t_i$ is given as follows:

$$t_i = \frac{1}{JV} + \left( \frac{\alpha}{a_n J G^{n-1}} \right)^{1/n} \quad (2.5)$$

Where $t_i$ is the induction time, $J$ is the rate of nucleation, $V$ is the volume of the parent phase, $G$ is the growth rate, $a_n$ is the shape factor.
2.3 MEASUREMENT OF INDUCTION PERIOD

Depending upon the solubility of the material one has to choose the appropriate techniques available for determining the induction period. For insoluble materials conductivity method and turbidity method can be used. Dilatometer and direct vision method are suitable for well soluble substances.

Conductivity method

A 250 ml beaker is normally used as the nucleation cell. Equal volume of equimolar concentration solutions of the reactants which form an insoluble precipitates are taken in two separate glass vessels. They are kept in the thermostat at chosen operating temperature. When equilibrium temperature is reached the two reactant solutions are simultaneously poured into the nucleating cell. The electrical conductivity of the solution is measured. At low initial supersaturation, the conductivity seems to remain constant with time and no crystal seems to precipitate. At some higher supersaturations, it seems that sometimes it is constant and then decreases, then passes through an inflection point and approaches the value for the saturated solution. The first constant supersaturation can be treated as induction period.

Turbidity method

In this method the nucleation cell is illuminated with powerful source of light. When two reactants are mixed in the nucleation cell the solution is transparent initially. Once the nucleation starts, the solution will become turbid. The time elapsed between the time of mixing and the occurrence of turbidity gives the induction period.
Dilatometer method

This method is very useful for highly soluble substances. The apparatus consists of a cylindrical glass bulb. The top end is fused to a capillary tube of tiny bore. The supersaturated solution at higher temperature is taken in the dilatometer up to certain mark. A drop of pure oil is taken over the liquid meniscus to avoid evaporation. When the equilibrium temperature is reached the meniscus reading is noted at regular intervals of time using cathetometer. During the induction period the height of the liquid remains constant and started increasing with the onset of nucleation.

Visual observation method

The supersaturated solution is taken in the cell at a higher temperature (10°C above the experimental temperature) and is kept in the thermostat. As soon as the temperature of the solution reaches the temperature of the bath, the time is recorded. Once the nucleation starts, it grows suddenly and bright sparkling particles are seen. The time that elapses between the attainment of supersaturation and the observation of the bright particles gives the induction period.

Studies on the induction period are important not only from the point of view of practical information on the crystallization process but also because they can yield information about the crystallization mechanism, the nature of the various stages of crystallization process, and about some of the physical properties of crystalline substances. In the present investigation induction period measurements were used to calculate the interfacial energy.
2.4 NUCLEATION OF PURE AND DOPED TGS SOLUTIONS


The theories of homogenous nucleation developed by Volmer and Weber 1926, Becker and Doering 1930 and Turnbull and Fisher 1949 form the basis of nucleation studies. Spontaneous formation of crystal nuclei was reported by (Mersmann 1990, Sangwal 1989, Bennema and Sohnel 1990) to take place at temperature below the saturation temperature if sufficient waiting time was allowed. The classical nucleation theories assume ideal steady state conditions which are only attained when the saturation is very slowly and homogeneously increased to its critical value and predict immediate nucleation once a system is supersaturated. However, in most cases there is a time lag or induction period between the achievement of supersaturation and the onset of nucleation. Accurate prediction of nucleation rates is very difficult. Nielson and Sohnel 1971 studied the homogenous nucleation of sparingly soluble electrolytes by means of a rapid flow technique. It is possible to measure induction periods with reasonable accuracy and several investigators (Zaitseva et al 1995, Bennema and Sohnel 1990, Sangwal 1989) have used such values as a measure of the nucleation rate assuming that the nucleation rate is inversely proportional to the induction period.
2.5 THEORY

The basic relationship of equilibrium between solid and its solution which connects the solubility expressed as the chemical potential to the particle size is the Thomson equation,

\[
\mu_r - \mu_\infty = -\frac{2\sigma}{r} \tag{2.6}
\]

When the crystal attains a radius \( r \), it will be in equilibrium with the solutions and under these conditions the chemical potentials of the two coexisting phases are equal. The free energy of formation of the nucleus of the new phase of radius \( r \) in equilibrium with its solution is expressed as

\[
\Delta G = \frac{16\pi\sigma^3 v^2}{3(\mu_r - \mu_\infty)^2} \tag{2.7}
\]

The frequency of formation of these crystal nuclei from their respective supersaturated solutions has been given as

\[
J = K \exp\left(\frac{-U_1}{kT}\right) \exp\left(\frac{-\Delta G}{kT}\right) \tag{2.8}
\]

Where \( U_1 \) is the energy of activation for the molar transition from phase 1 (solution) to phase 2 (Crystal).

For a given volume of solution the frequency of formation of nuclei is inversely proportional to the induction period.

\[
\ln \tau = \ln K^{-1} + \frac{U_1}{kT} + \frac{\Delta G}{kT} \tag{2.9}
\]

For an isotherm, the term \( \frac{U_1}{kT} \) is a constant and Equation (2.9) is written as
\[ \ln \tau = B + \frac{\Delta G}{kT} \tag{2.10} \]

Where \( B \) is a constant. The energy of formation \( G \) can be evaluated from the change in chemical potential (Shanmugham et al 1984)

\[ \mu_1 \cdot \mu_{10} = \mu_r \cdot \mu_\infty = kT \ln \left( \frac{x}{x_0} \right) \tag{2.11} \]

where \( \mu_1 \) is the chemical potential of supersaturated solution, \( \mu_{10} \) is the chemical potential of saturated solution. \( \mu_r \) is the chemical potential of nucleus of radius \( r \), \( \mu_\infty \) is the chemical potential of nucleus of infinite radius.

Applying equations (2.7) and (2.11) in equations (2.10)

\[ \ln \tau = B + \frac{16\pi \sigma^3 v^2}{3k^3 T^3 \ln^2 (x/x_0)} \]
\[ = B + \frac{16\pi \sigma^3 v^2 N}{3R^3 \tau^3 \ln^2 (x/x_0)} \tag{2.12} \]

Equation (2.12) suggests a straight line for \( \ln \tau \) against \( 1/\ln^2(x/x_0) \) with the slope given by

\[ m = \frac{16\pi \sigma^3 v^2 N}{3R^3 \tau^3} \tag{2.13} \]

The interfacial energy of the solid relative to its solution has been calculated from the slope of the line \( \ln \tau \) against \( 1/\ln^2(x/x_0) \) as

\[ \sigma = RT \left[ \frac{3m}{16\pi v^2 N} \right]^{1/3} \tag{2.14} \]
2.6 EXPERIMENTAL

A 100 ml glass beaker was used as nucleation cell. The nucleation cell was placed in a cryostat and the temperature was thermostatically controlled to an accuracy of ± 0.05° C. The solutions were stirred by means of a motor. A lamp placed at the rear of the cryostat was used to illuminate the nucleation cells. Recrystallized salt of TGS and millipore water were used in the present study. The dopants AR grade L-alanine and AR grade L-valine were used to study their effect on the induction period in the TGS saturated solutions at different temperatures. Aqueous solutions of pure and doped TGS were prepared by dissolving the required amount of TGS salt in 100 ml of millipore water at a temperature slightly higher than their respective saturation temperatures. The solution was continuously stirred for at least 24 hours before use. The induction periods of pure and doped solutions were measured by means of the isothermal method (Zaitseva et al 1995). When the temperature reached the desired value, it was held constant and the time was measured until the first crystal appeared in the bottom of the crystallizer.

2.7 ANALYSIS OF THE RESULTS

According to the classical theory of homogeneous formation of spherical (Volmer et al 1926).

\[
\ln \tau = -\ln B + \frac{16\pi\alpha^3 V^2 N_A}{3R^3 T^3 (\ln S)^2} \tag{2.15}
\]

Where \( V \) is the molar crystal volume, \( N_A \) is Avogadro’s number, \( R \) is the gas constant and \( S \) is the relative supersaturation. \( ln B \) depends weakly on temperature, so there is a linear dependence between \( ln \tau \) and \( (\ln S)^{-2} \) at \( T = \) constant. As shown in figures (2.1 2.2 2.3), when \( ln \tau \) is plotted against \( (\ln S)^{-2} \), these data give straight lines in accordance with equation (2.15). The interfacial energy values obtained from the slopes of these lines are in
Figure 2.1 Plot of $\ln \tau$ Vs $(\ln S)^2$ for pure TGS solution.
Figure 2.2  Plot of $\ln t$ Vs $(\ln S)^{-2}$ for L-alanine doped TGS solution
Figure 2.3 Plot of $\ln t$ Vs $(\ln S)^2$ for L-valine doped TGS solution
the range of 2-6 mJ/m² at 35°C for pure and amino (L-alanine and L-valine) respectively. Impurities can influence crystal growth rates in a variety of ways (Davey 1975). The soluble impurities may increase or decrease the induction time due to a change in the solubility of the salt being crystallized or due to adsorption on nuclei. They may also affect the induction period because of a chemical interaction between the impurity and the crystallizing substance. It has been reported that the presence of soluble impurities reduces the solubility and hence decreases the induction period (Nagalingam et al. 1981). It has been observed from the experimental results that the induction period τ reduces while doping with L-alanine and L-valine (Aravazhi et al. 1997 a). This is attributed to the increase in the rate of formation of nuclei while doping with amino acids.

2.8 CONCLUSION

The classical theory of homogeneous nucleation has been employed to study the nucleation of pure and doped TGS solutions and it has been found from the experimental observations that the induction period decreases with doping of amino acids. This is attributed to the increase in the rate of formation of nuclei while doping with amino acids and hence the role of dopants on the nucleation process has been studied.