

CHAPTER 2

NUCLEATION AND GROWTH KINETICS OF YAG FROM BaO/BaF₂/B₂O₃ FLUX

2.1. INTRODUCTION

Though crystal growth from solution has been widely used to obtain a variety of crystals, the nucleation and growth kinetics are understood only semi quantitatively, primary reason being the non availability of data based on experiments, which makes it difficult to assign numerical values for several factors in the expression. Particularly in the case of high temperature solution, it is difficult to determine various physical parameters such as viscosity, surface tension, density, volatility, solubility etc. The second important limitation is the present obscure state of knowledge about the atomic structure of the solution and interface kinetics. Little information available on the nature of solute-solvent interaction, the association and dissociation of ions and the formation of complex molecules makes it difficult to get concrete idea about the structure of the solution. Hence, any model of atomistic behaviour in the neighbourhood of a crystal-solution interface is highly speculative. Several monographs, reviews and books have been presented from time to time on nucleation and growth kinetics of the crystals from solution [80,81].

High temperature solution growth or flux growth has been found to be quite successful for the growth of

several garnet single crystals, which are having the general formula $A_3B_5O_{12}$,

where A is the rare earth ions such as Y^{3+} , Gd^{3+} etc, and B is the Fe^{3+} , Al^{3+} , Ga^{3+} etc.

Among the available flux systems $PbO/PbF_2/B_2O_3$ has been widely used for the growth of refractory oxides, particularly of garnets [82-85]. But this lead based flux system has few drawbacks, such as high volatility and corrosiveness. Hence, an alternate flux system $BaO/BaF_2/B_2O_3$ has been proposed as a solvent for rare earth garnets and orthoferrites by Hiskes et al [59]. The main advantages of this flux system are, very low volatility low rate of attack on platinum crucibles and low density compared with lead fluxes. This flux system has been used widely for seeded growth methods in which the crystal grows just below the surface of the solution in an open crucible. Elwell [57] has made an appraisal of $BaO/BaF_2/B_2O_3$ flux for the growth of Yttrium Aluminium Garnet crystals.

To understand the nature of the solvent systems, several systematic experimental studies have been made by various researchers. Coe and Elwell [55] determined the viscosity of the most successful lead based flux system for different compositions and different temperatures. To determine the viscosity of the solvent systems at high temperature an oscillating crucible viscometer has been designed and fabricated by Coe and Elwell [86]. Using this viscometer Elwell et al [60] have determined the viscosity of various compositions of $BaO/BaF_2/B_2O_3$ at

various temperatures. They have also determined the viscosity of $\text{BaO}/\text{BaF}_2/\text{B}_2\text{O}_3$ solution with various percentage of YAG at various temperatures. Volatility of lead flux has been presented by Coe and Elwell [54]. Timofeeva and Kavapil [22] have made an extensive study on solubility of YAG in lead based flux system. Solubility of YAG in typical compositions of $0.62\text{BaO} - 0.38\text{B}_2\text{O}_3$, $0.50\text{BaO} - 0.41\text{B}_2\text{O}_3 - 0.09\text{BaF}_2$ and $0.41\text{BaO} - 0.41\text{B}_2\text{O}_3 - 0.18\text{BaF}_2$ have been presented by Capper and Elwell [57]. They have also determined the density of the solution, volatility, and growth rate of YAG in $\text{BaO}/\text{BaF}_2/\text{B}_2\text{O}_3$ flux system.

Though several experimental reports on the growth parameters of YAG are available, so far no attempt has been made to investigate the growth kinetics of YAG from high temperature solution. In this chapter, the nucleation mechanism of YAG when it is grown from barium based flux system has been developed by using the classical heterogeneous nucleation theory. Thermodynamic considerations have been given to the chosen system to derive the expression for the interfacial tension of YAG-flux interface. Diffusion theory of crystal growth has been used to determine the growth rate and hence the size of the YAG clusters from $\text{BaO}/\text{BaF}_2/\text{B}_2\text{O}_3$ flux system has been investigated as a function of time and temperature. Numerical analysis of our theoretical prediction has been made using available diffusion and solubility data in the literature.

2.2. NUCLEATION OF YAG FROM $\text{BaO}/\text{BaF}_2/\text{B}_2\text{O}_3$ FLUX SYSTEM

The initial stage of crystallisation in a supersaturated liquid is the formation of nuclei of the crystalline phase by joining few atoms or molecules together.

The formation of new and more stable phase capable of developing spontaneously into gross fragments of the stable phase may be termed as nucleation. Nucleation, like ordinary chemical kinetics, involves an activation process leading to the formation of unstable intermediate states known as 'embryo' [87]. At this stage the embryo may continue to grow or tend to dissolve. Once the embryo attains a critical size, it will further grow. A nucleus differs from an equal number of normal molecules in possessing an excess of surface energy sufficient to produce the aggregate as a new phase. This energy is calculable with the aid of Gibbs general formula. The formation of nuclei may either be homogeneous, where the atoms or molecules build themselves in the interior of the present system or heterogeneous where the molecules or atoms build up on foreign particle or surface of the container or any other imperfection. It is generally agreed that in high temperature solution growth the nucleation is heterogeneous one. Wanklyn et al [88] proposed that there are preferred nucleation sites on platinum surface.

The theory of the nucleation process combines kinetics and thermodynamics in an interesting way and has attracted considerable attention [89].

Heterogeneous nucleation has been frequently treated in terms of a spherical cap shape nucleus. Hence, in the present case it is assumed that YAG embryo is forming on a plane and non deformable substrate, which is surrounded by the solution containing $\text{BaO-BaF}_2\text{-B}_2\text{O}_3$ flux and YAG. Schematic diagram of the heterogeneous cap shape embryo is shown in Figure 2.1. The free energy of formation

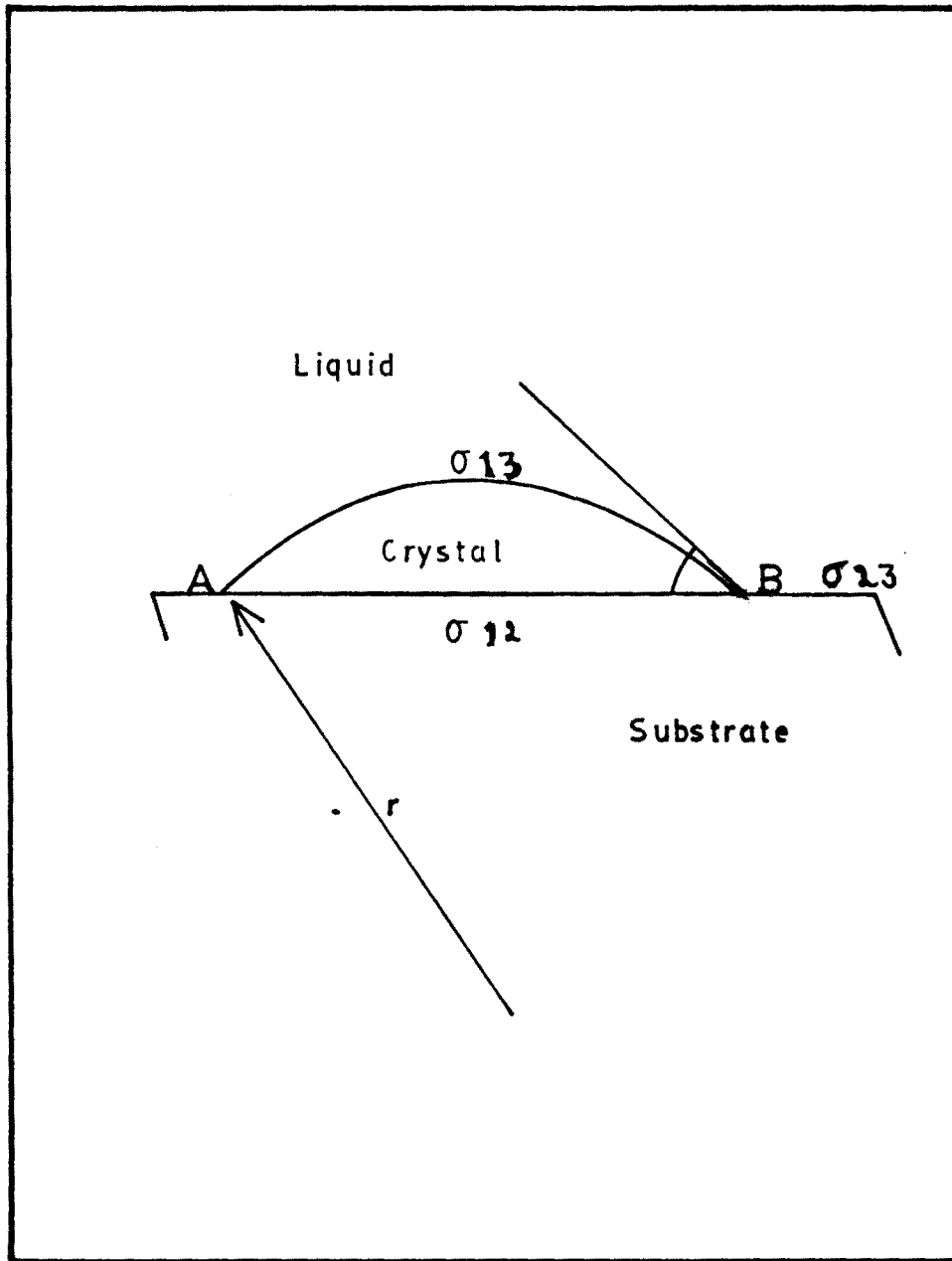


Fig. 2.1

SCHEMATIC DIAGRAM OF THE CAP SHAPE
EMBRYO FORMED ON THE SUBSTRATE

of YAG nucleus is

$$\Delta G = \Delta G_v + \Delta G_s \quad (2.1)$$

where ΔG_v is the excess volume free energy of formation which is a negative quantity and ΔG_s is the excess surface free energy, which is a positive quantity.

Equation (2.1) can be rewritten as

$$\begin{aligned} \Delta G_{\text{Het}} = & \frac{4}{3} \pi r^3 \Delta G_v \left[\frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right] \\ & + 4 \pi r^2 \left(\frac{1 - \cos \theta}{2} \right) \sigma_{13} + \pi r^2 \sin^2 \theta (\sigma_{12} - \sigma_{23}) \end{aligned} \quad (2.2)$$

where r is the radius of curvature of the embryo,
 θ is the contact angle,

σ_{12} , σ_{23} and σ_{13} are the interfacial tension between
 YAG_(solid) and substrate, substrate and solution
 and YAG_(solid) and solution respectively
 and ΔG_v is the free energy change between YAG solid
 and YAG solution, which may be represented as

$$\Delta G_v = \frac{\Delta \mu_{\text{YAG}}}{V} \quad (2.3)$$

where μ_{YAG} is the chemical potential of YAG.

and V is the molar volume of YAG.

Using Young's equation for contact angle θ following expression can be arrived

$$\sigma_{23} = \sigma_{12} + \sigma_{13} \cos \theta \quad (2.4)$$

Equation (2.2) is differentiated with respect to r and equated to zero to determine the critical size of the nucleus

The radius of critical nucleus becomes

$$r_c^* = \frac{-2 \sigma_{13}}{\Delta G_v} \quad (2.5)$$

Substituting the values of r_c^* in equation (2.2) one gets critical free energy as

$$\Delta G_{\text{Het}}^* = \frac{16 \pi \sigma_{13}^3}{(3 \Delta G_v)^2} \phi(\theta) \quad (2.6)$$

The number of YAG molecules in the critical nucleus can be determined as

$$i_c^* = \frac{32 \pi \sigma_{13}^3 \phi(\theta)}{3V(\Delta G_v)^3} \quad (2.7)$$

$$\text{where } \phi(\theta) = \frac{(1 - \cos\theta)^2 (2 + \cos\theta)}{4} \quad (2.8)$$

2.3. NUMERICAL EVALUATION AND RESULTS

The driving force for the formation of YAG nucleus from the chosen molten flux system has been evaluated by using the solubility values presented by Capper and Elwell [57] for 0.41 BaO/0.18 BaF₂/0.41 B₂O₃ system and is shown in Figure 2.2. The solubility values corresponding to the temperature 1573K is fixed as equilibrium concentration C^* and change in free energy of YAG molecule inside and outside the nucleus has been evaluated for various concentrations of YAG using the expression

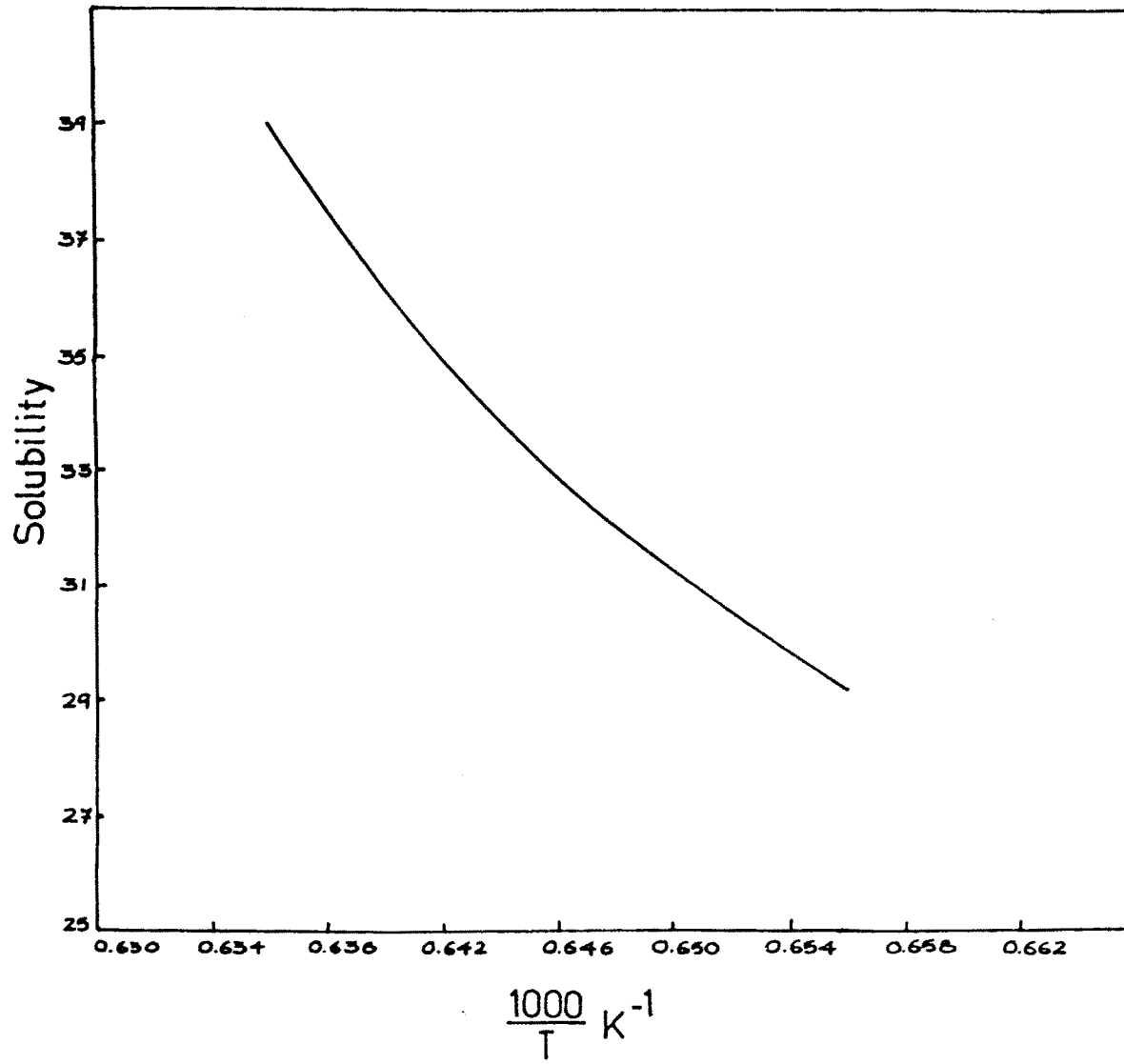


Fig. 2.2

SOLUBILITY OF YAG IN 0.41 BaO/0.18 BaF₂/0.41 B₂O₃
 AS A FUNCTION OF TEMPERATURE

$$\Delta\mu_{\text{YAG}} = kT \ln C/C^* \quad (2.9)$$

Numerical evaluations of equation (2.6) and (2.7) for the critical free energy and the total number of YAG molecules in the critical nucleus respectively have been made for different concentrations, contact angles and interfacial tensions. The exact values of contact angle may differ from surface to surface and there is some uncertainty in determining the interfacial tension. Therefore numerical values have been made for the entire possible range of contact angle and interfacial tension. Figure 2.3 shows a plot of critical size of YAG nucleus as a function of supersaturation in the flux for various values of interfacial tension by keeping the contact angle ($\theta = 135^\circ$).

Another plot has been drawn between the critical free energy of YAG nucleus and concentration, for different σ (and $\theta = 135^\circ$) which is shown in Figure 2.4. The size and free energy of formation are plotted as a function of supersaturation for three different contact angles taking $\sigma = 400 \text{ mJ/m}^2$. This is presented in Figure 2.5.

2.3.1. Evaluation of Interfacial tension

To determine the magnitude of interfacial tension between the crystalline YAG and the solution the author has used the regular solution model [90] proposed by Reiss and Shugard.

According to the chosen model N_s molecules of YAG and N_1 molecules of solvent are randomly distributed over

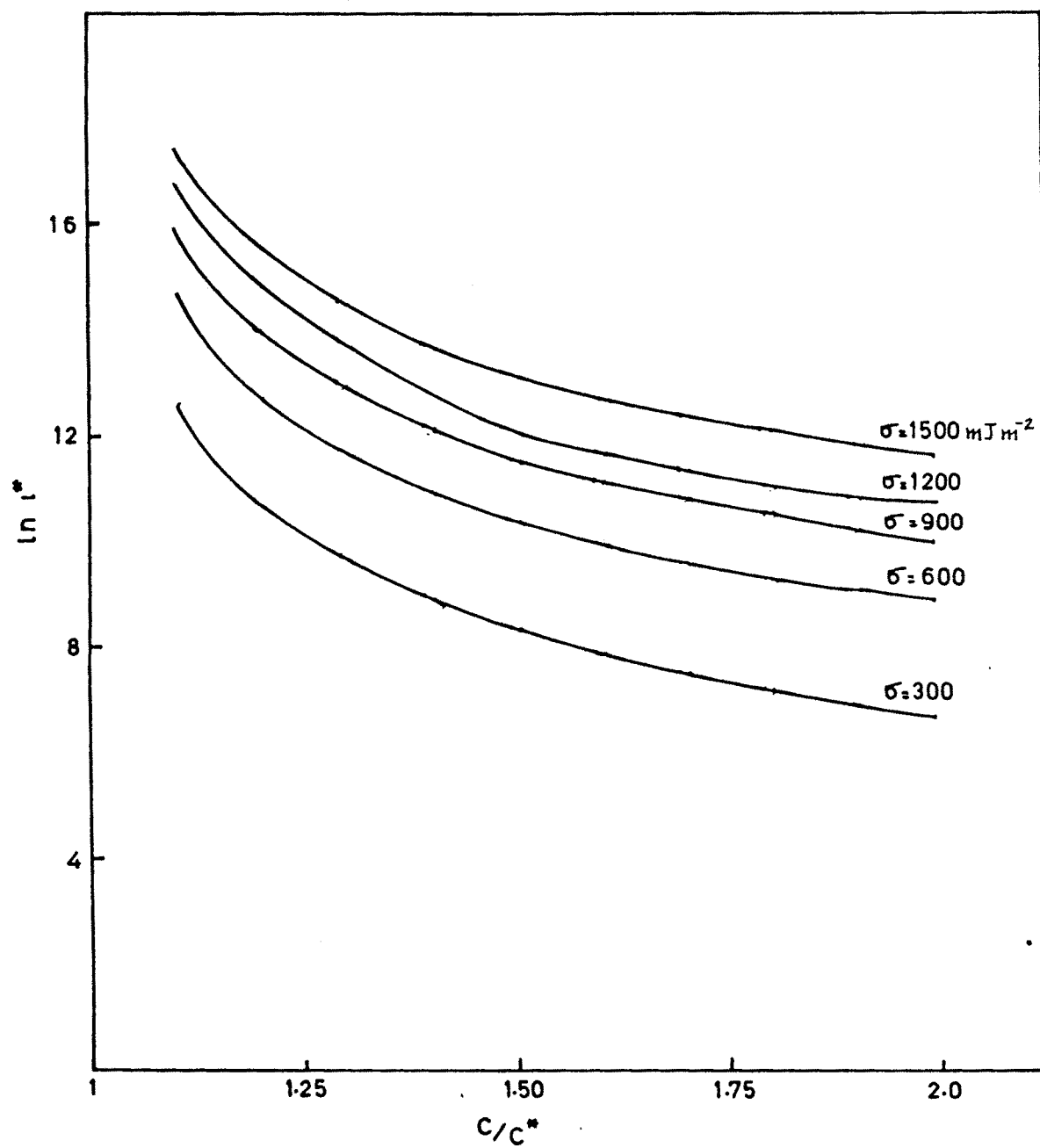


Fig.2.3

CRITICAL SIZE OF YAG NUCLEUS AS A FUNCTION OF SUPERSATURATION

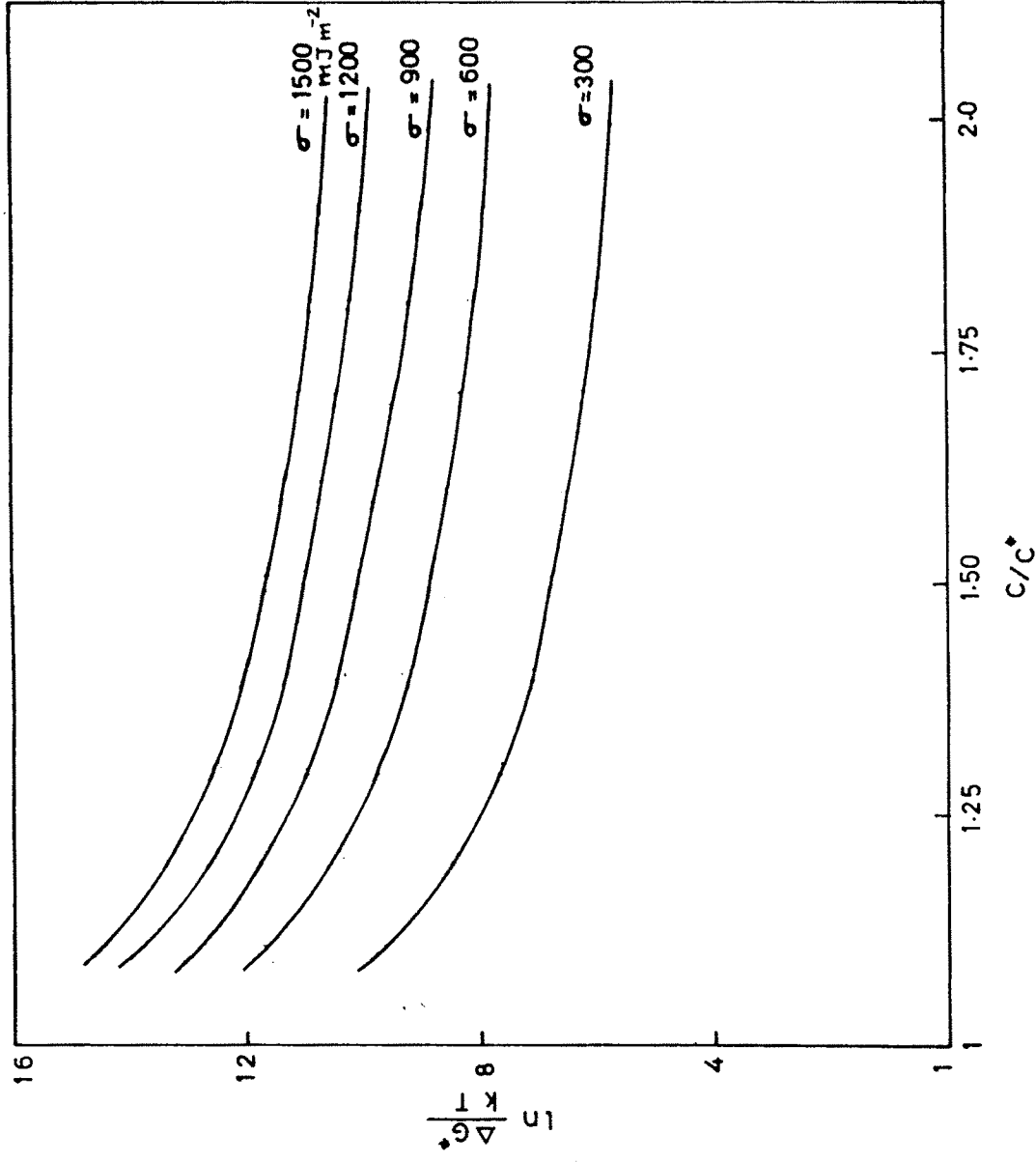


Fig. 2.4

THE CRITICAL FREE ENERGY OF YAG NUCLEUS AS A FUNCTION OF CONCENTRATION FOR DIFFERENT σ

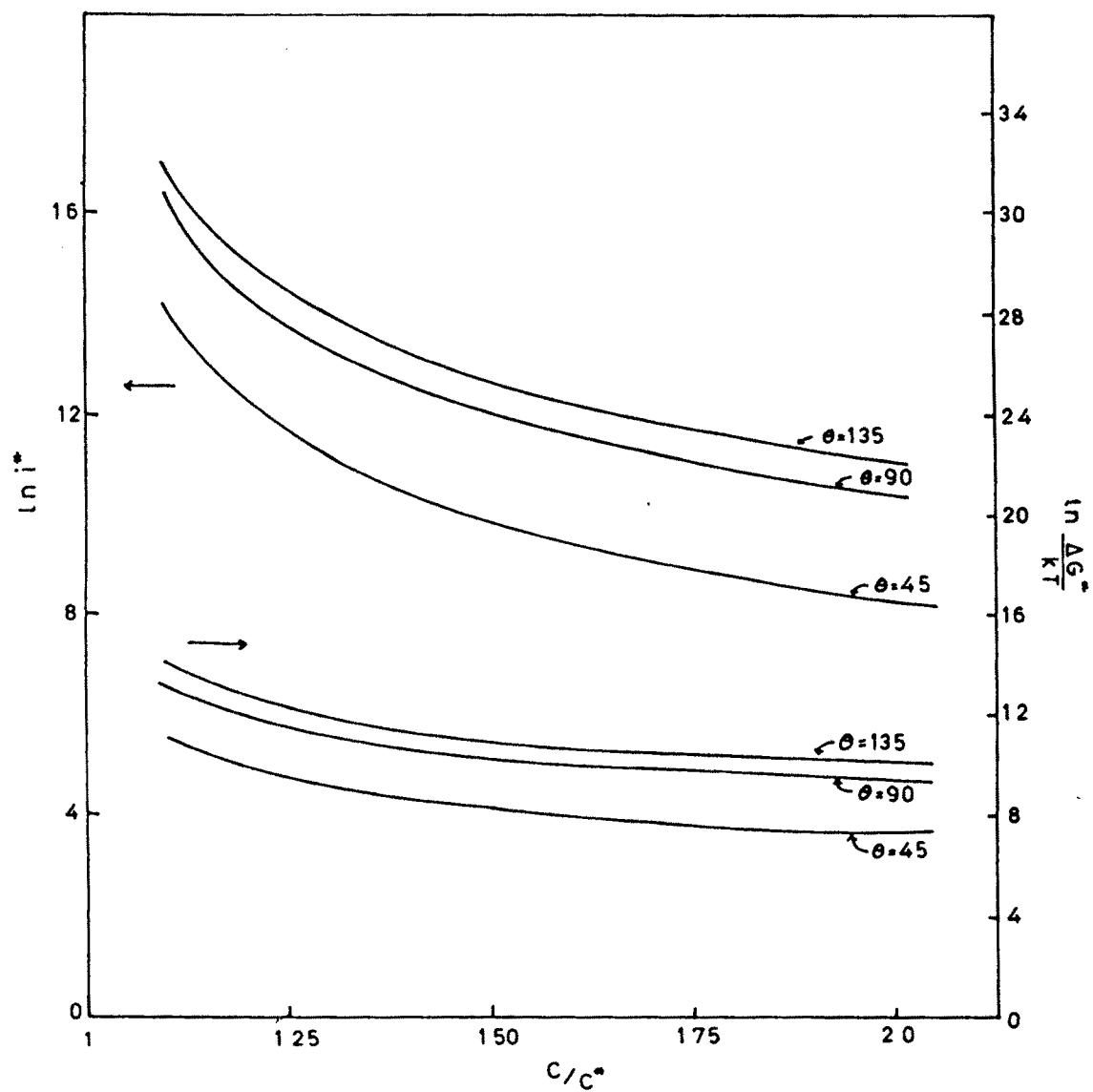


Fig.2.5

THE SIZE AND FREE ENERGY OF FORMATION AS A FUNCTION OF
CONCENTRATION FOR DIFFERENT σ

the $M = N_s + N_1$ lattice sites in the system. Recently Dhanasekaran et al [91] have shown that the number of lattice sites can be assumed to be greater than $N_s + N_1$ to obtain one more independent variable. In order to avoid mathematical complexity it has been assumed that $M=N_s+ N_1$. The Helmholtz free energy of the system can be written by using Bragg-Williams approximation as

$$A = \frac{C}{2M} [N_s \phi_s + N_1 \phi_1 + N_s N_1 (\phi_s + \phi_1 + 2\phi')] + kT N_s \ln x + kT N_1 \ln (1-x), \quad (2.10)$$

where C is the coordination number, ϕ' is the energy loss upon the formation of a solvent-solute bond and x is the mole fraction of YAG in the solution.

The chemical potential of the solute and solvent molecules are

$$\mu_s = \left(\frac{\partial A}{\partial N_s} \right)_{T, N_1} = \frac{C}{2} [2\phi' x - \phi' x^2 + 2\phi_{s1} - \phi_1] + kT \ln x \quad (2.11)$$

$$\mu_1 = \left(\frac{\partial A}{\partial N_1} \right)_{T, N_s} = \frac{C}{2} [2\phi' (1-x) - \phi' (1-x)^2 + 2\phi_{s1} - \phi_s] + kT \ln (1-x) \quad (2.12)$$

where $\phi_{s1} = \frac{1}{2} [(\phi_s + \phi_1) - \phi']$,

ϕ_s being the energy of interaction between two solute molecules on neighbouring sites and ϕ_1 being the

corresponding energy between the solvent molecules in neighbouring sites. In order to derive an expression for the interfacial tension between YAG crystals and flux containing YAG molecules, the lattice planes are labelled positively beginning with 0 into one phase and negatively beginning with -1 into the other phase so that the interface is located between -1 and 0.

The simplest way to calculate the excess free energy associated with the interface is as follows. If the flux system were uniform at the mole fraction x , throughout, then the energy between planes -1 and 0 would be

$$\Sigma_1 = gp [x^2 \phi_s + x(1-x)(\phi_s + \phi_1 + 2\phi') + (1-x)^2 \phi_1] \quad (2.13)$$

where g is the number of bonds per molecule and p is the number of molecules per plane. Similarly if the system were uniform in the solid with YAG molecules

$$\Sigma_s = gp (\phi_s). \quad (2.14)$$

When the interface actually exists, the energy between the planes 0 and -1 is given by

$$\Sigma_{1s} = gp [x \phi_s + \frac{1}{2} (1-x) (\phi_s + \phi_1 + 2\phi')] \quad (2.15)$$

The energy change in the process of creating the interface may be written as

$$\Sigma = 2 \Sigma_{1s} - \Sigma_s - \Sigma_1. \quad (2.16)$$

If the area per atom in the surface is 'a' then, the total interfacial area of the reassembled system is equal to

53 MF

2pa. The surface energy per unit area is 800080

$$\sigma = \frac{g}{a} [\phi' (1-x)^2] \quad (2.17)$$

$$\text{where } a = \sqrt{3} (v/2)^{2/3}, \quad 800080 \quad (2.18)$$

V being the volume of YAG molecule in the lattice. If the numerical values of interaction terms are available one can evaluate the interfacial tension. Due to the non-availability of the numerical value of the interaction term, ϕ' to evaluate the exact values of interfacial tension, the different possible values of σ have been used to determine the nucleation parameters.

2.4. GROWTH OF YAG CLUSTERS

Assuming the growth of YAG clusters by the diffusion mechanism, the size of the cluster has been evaluated using the steady state diffusion equations. For a spherically symmetrical diffusion field, the growth of YAG crystal is governed by the equation

$$\frac{d}{dt} \left(\frac{4}{3} \pi R^3 \right) = 4 \pi R^2 D \left(\frac{\partial C}{\partial r} \right)_{r=R} \quad (2.19)$$

where R is the size of the crystal and D is the Diffusion coefficient of YAG in BaO/BaF₂/B₂O₃ flux containing YAG

To solve this equation we should know C (r,t). By using the following boundary conditions

$$\begin{aligned} C(r,0) &= C_{\infty} \\ C(R_0,t) &= C_{\infty} \quad \text{and} \\ C(R,t) &= C^* \end{aligned} \quad (2.20)$$

where R_0 is the radius of the critical YAG nucleus. Equation (2.19) becomes

$$\int_{R_0}^R 4\pi r^2 (C - C^*) dr = \int_0^t 4\pi R^2 D v \left(\frac{\partial C}{\partial r} \right)_{r=R} dt. \quad (2.21)$$

Assuming that the growth rate is very low, one can obtain from equation (2.21), the size,

$$R = [2Dv (C_\infty - C^*)]^{1/2} t^{1/2} \quad (2.22)$$

and the growth rate,

$$R^* = \frac{dR}{dt} = \left[\frac{Dv(C_\infty - C^*)}{2t} \right]^{1/2}. \quad (2.23)$$

The diffusion coefficient 'D' of YAG is calculated from the available experimental data on viscosity [60] for different temperatures using the Stokes - Einstein equation, as

$$D = \frac{kT}{3\pi\eta a_0} \quad (2.24)$$

where η is the viscosity, a_0 is the hard sphere diameter and T is the process temperature.

The theory of liquids has not yet advanced to a point where quantitative conclusions can be drawn regarding the behaviour of complex liquids. The hard sphere or rigid sphere model [92] has been used to get semi quantitative information on cluster formation. According to this interpretation the expansion coefficient α and surface tension σ may be used to get the diameter of the rigid spheres of which the liquid is considered to be

composed of. It has been fixed the hard sphere diameter value of $0.41 \text{ BaO}/0.18 \text{ BaF}_2/0.41 \text{ B}_2\text{O}_3$ as 2.4 \AA as reported by Elwell et al [60].

Numerical results of growth rate of YAG when it is grown from $\text{BaO-BaF}_2\text{-B}_2\text{O}_3$ flux as a function of temperature for different time intervals is plotted in Figure 2.6. The size of the YAG clusters as a function of time for different temperatures in $\text{BaO-BaF}_2\text{-B}_2\text{O}_3$ flux system is presented in Figure 2.7. The theoretically predicted growth rate is compared with experimental observations [56,93]. It was observed that the theoretically predicted growth rate is higher than the experimentally determined values. This may be attributed to the non consideration of surface kinetics such as adsorption, incorporation of YAG molecules into step and kink sites etc. Moreover the experimental growth rate determination was performed mostly using top seeded growth technique.

2.5. SUMMARY AND CONCLUSION

Nucleation and growth phenomena of YAG are considered for the present investigation when YAG crystal is grown from $\text{BaO-BaF}_2/\text{B}_2\text{O}_3$ flux containing different concentration of YAG molecules. The heterogeneous nucleation mechanism of YAG is determined using classical nucleation theory, and hence the critical parameters of the nucleus such as size and free energy of formation of YAG nucleus are numerically evaluated. Thermodynamical consideration has been given to the chosen system and hence the chemical potential of the solute and the solvent molecules are derived and expression for determining the excess free energy associated with the formation of nucleus-solution interface has been evaluated in terms of the interaction

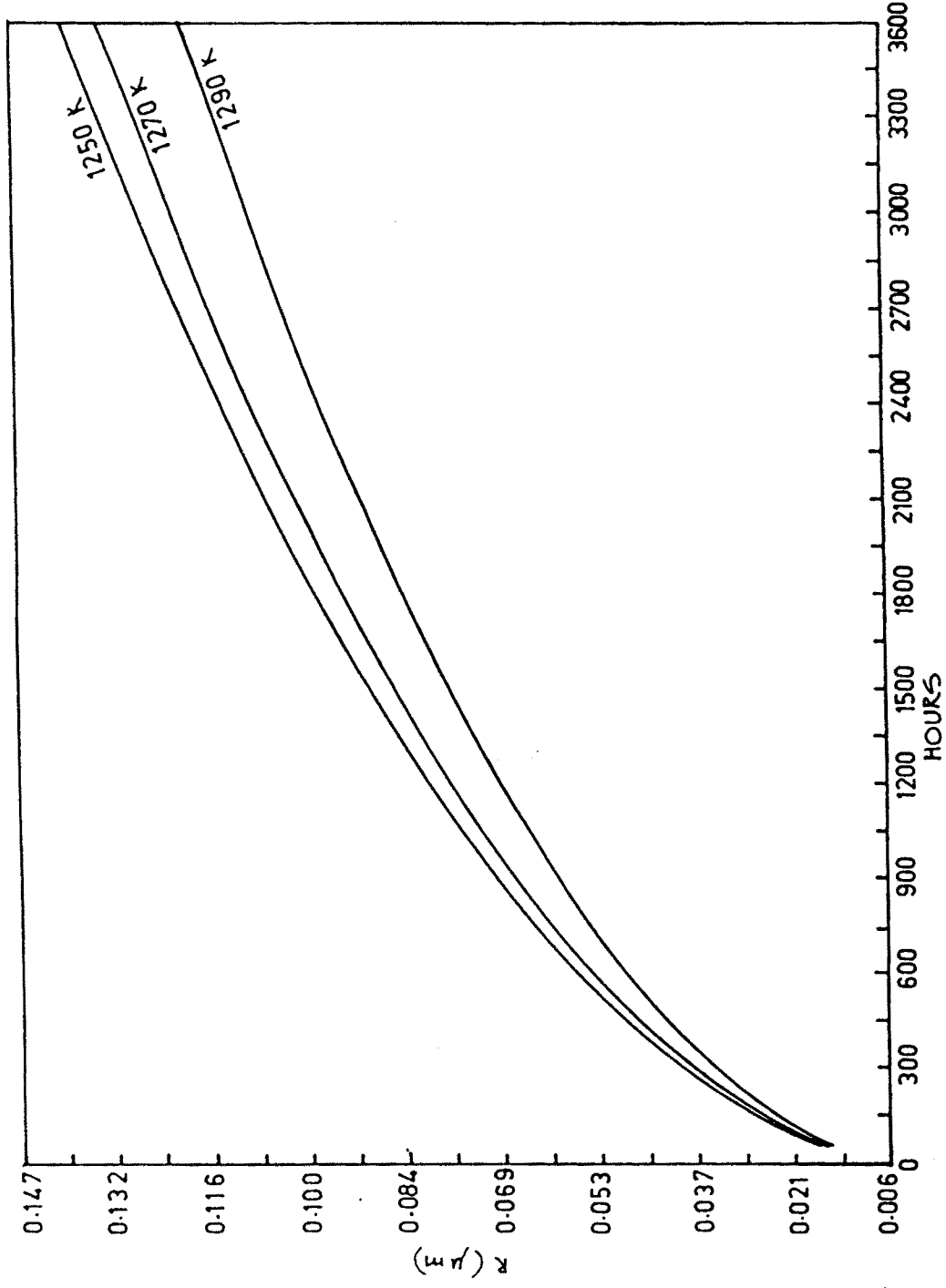


Fig. 2.6.

NUMERICAL VALUES OF THE SIZE OF THE YAG CLUSTER
AS A FUNCTION OF TIME

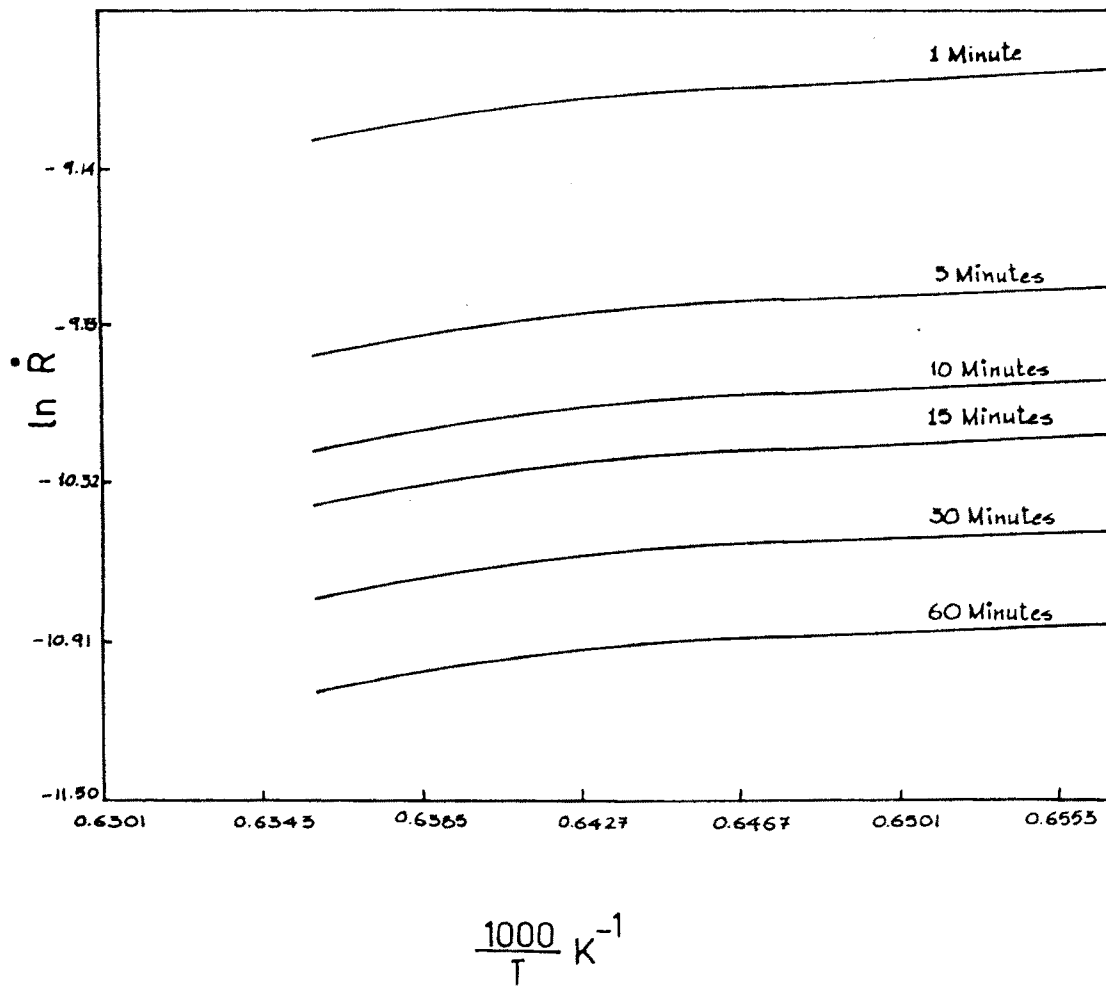


Fig. 2.7
 GROWTH RATE OF THE CLUSTER AS A FUNCTION OF
 TEMPERATURE FOR DIFFERENT TIME

energies between the solute and solvent molecules. Assuming a spherical diffusion boundary around the growing island, the size of YAG cluster and its growth rate have been determined. The deviation of calculated growth rate from the experimental value is attributed to the nonconsideration of surface kinetics.