

# Investigations on nucleation thermodynamical parameters of $\text{NdBa}_2\text{Cu}_3\text{O}_{7-d}$ (Nd123) crystallization by high temperature solution growth<sup>†</sup>

D P PAUL<sup>‡</sup>, R JAYAVEL, C SUBRAMANIAN and P RAMASAMY\*

Crystal Growth Centre, Anna University, Chennai 600 025, India

<sup>‡</sup>Department of Physics, University of Chittagong, Chittagong 1331, Bangladesh

**Abstract.** Investigations on nucleation thermodynamical parameters are very essential for the successful growth of good quality single crystals from high temperature solution. A theoretical estimation of the nucleation thermodynamical parameters like interfacial energy between the solid Nd123 and its flux BaO–CuO, metastable zone-width, Gibbs free energy, critical energy barrier for nucleation and critical nucleation radius have been calculated from the knowledge of solubility data and by applying the classical nucleation theory. Results are discussed to understand the growth kinetics of Nd123 crystals.

**Keywords.** High temperature solution; nucleation parameters; interfacial energy; metastable zone width.

## 1. Introduction

For basic study and applications, large size single crystals of high  $T_c$  superconductors are very important. In this regard, high  $T_c$  Nd123 superconductor exhibits sharper transition and large current density ( $J_c$ ) than those of Y123 which have the same crystal structure (Yoo *et al* 1994; Kambara *et al* 1997). Single crystal of Nd123 is generally grown from high temperature solution (flux method) due to its incongruent melting behaviour. In flux growth experiments spontaneous nucleation occurs by cooling through the metastable region below the liquidus. This metastable temperature range, called Ostwald–Mier region, where the solution is supersaturated and the nucleation process of the birth of critical and super critical nuclei occur before growth of the solute crystal. BaO–CuO is widely used as a flux for crystallization of Nd123 compounds (Nakamura *et al* 1996; Sawada *et al* 1996). The growth of large size Nd123 crystals have been difficult due to the inherent properties of the flux employed. In spite of this, lot of effort has been made to grow large size single crystals of Nd123 from high temperature solution by top seeded solution growth (TSSG) techniques by many groups (Krauns *et al* 1994; Nakamura *et al* 1996). In all the high temperature solution growth techniques require the knowledge of the essential nucleation thermodynamical parameters like interfacial energy, metastable zone width (supercooling temperature) and other nucleation thermodynamical parameters for the successful

growth of good quality single crystals. Of course, the experimental determination of these parameters is very difficult for high temperature solution growth. In this paper an attempt has been made to calculate these parameters theoretically to understand the role of these nucleation thermodynamical parameters for the crystallization of Nd123 from BaO–CuO flux. We considered the nucleation process as homogeneous and in the nucleation process solid (crystal) phase coexists with the liquid (solution) phase. The coexistence of Nd123 solid phase with the liquid phase was experimentally confirmed by Dimesso *et al* (1996).

## 2. Nucleation thermodynamical parameters

### 2.1 Interfacial energy

The interfacial energy,  $S$  of the interface between the growing crystal and the surrounding mother phase is a crucial parameter of the nucleation and growth of crystals. The concept of interfacial energy is very important for the nucleation and growth of high  $T_c$  single crystals. The interfacial energy can be determined experimentally from data on nucleation and growth kinetics, and from contact angle measurements. But such a determination is time consuming, laborious and very difficult for high temperature solution growth of incongruent melting compounds. Consequently, estimation of interfacial energy from physico-chemical data has drawn considerable attention (Kaweit *et al* 1961; Bennema and Van der Erden 1987). Bennema and Sohnel (1990) based on the regular solution theory have derived an expression for the linear dependence of  $S$  on solubility as

\*Author for correspondence

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$$S = (kT/d^2)[0.173 - 0.248(\ln x_m)]. \quad (1)$$

This expression has shown better agreement with experimental values of high temperature solution growth (Joseph Kumar *et al* 1996). In the present work this expression is used to calculate the interfacial energy of Nd123 single crystal growth in BaO–CuO flux. Solubility data have been evaluated from the Nd123–BaO–CuO solute solvent phase diagram (figure 1) (Kuroda *et al* 1996).

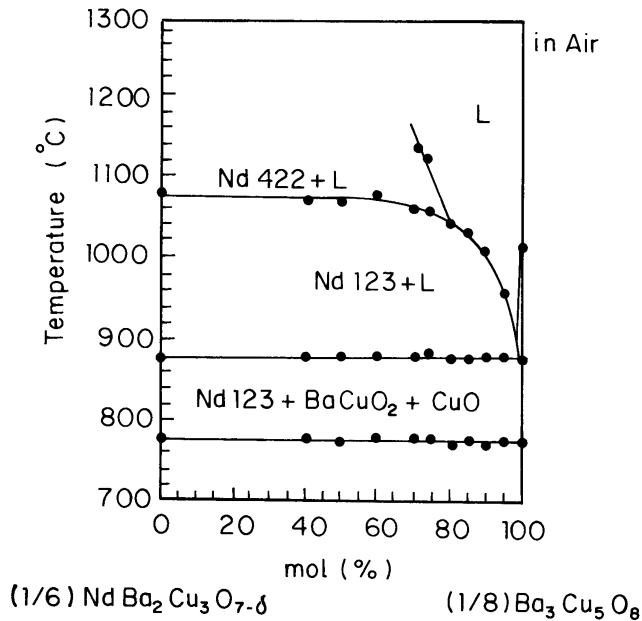
## 2.2 Metastable zone width

Crystallization involves two distinct steps: nucleation, which is the birth of a nucleus and crystal growth which involves the subsequent growth of the existing nucleus. In order to realize these, the system must be supersaturated. A supersaturated solution is thermodynamically in a non-equilibrium state and is known as metastable state. This state relaxes into a thermodynamically stable state with the formation of nuclei of a new phase. Classical theories, describing homogeneous nucleation as a relaxation process from a metastable state, were developed by Volmer, Weber, Becker and Zeldovich (Abraham 1974).

The relative supersaturation of a solution at a temperature  $T$  is

$$S = 1 + \frac{\Delta H_s \Delta T}{RT^2}. \quad (2)$$

The value of  $\Delta H_s$  is reported from the Nd123 solute and BaO–CuO solvent system (Kambara *et al* 1997).



**Figure 1.** Solubility versus temperature of Nd123 solute in BaO–CuO solvent (Kuroda *et al* 1996).

Fluctuations within the supersaturated solution cause the formation of small clusters of molecules, known as embryos. The driving force for the nucleation from the supersaturated solution is

$$\Delta G_v = \frac{-kT}{v} \ln S. \quad (3)$$

The Gibbs free energy change associated with the formation of Nd123 nucleus can be written as,

$$\Delta G = \Delta G_s + \Delta G_v. \quad (4)$$

For a spherical nucleus,

$$\Delta G = 4\pi r^2 s + 4/3 \pi r^3 \Delta G_v. \quad (5)$$

The critical radius and the critical energy barrier associated with the critical nucleation are related as,

$$r^* = \frac{-2s}{\Delta G_v}, \quad \Delta G^* = \frac{16\pi s^3}{3\Delta G_v^2}. \quad (6)$$

If there is  $m$  number of molecules per unit volume, the number of nuclei of critical size  $r^*$  is,

$$m^* = m \exp(-\Delta G^*/kT). \quad (7)$$

Then the rate of nucleation is expressed as,

$$J = m^* Z^* A^*, \quad (8)$$

where,  $Z^*$  is the frequency of attachment of a single molecule to a unit area of nuclei and  $A$  is the area of critical nucleus.

Hence,

$$J = Z^* A^* m \exp(-\Delta G^*/kT), \quad (9)$$

where the pre-exponential factor varies very slowly as compared to the exponential term. For the case of nucleation from high temperature solution the pre-exponential factor is usually taken as  $10^{30}$  (Walton 1969).

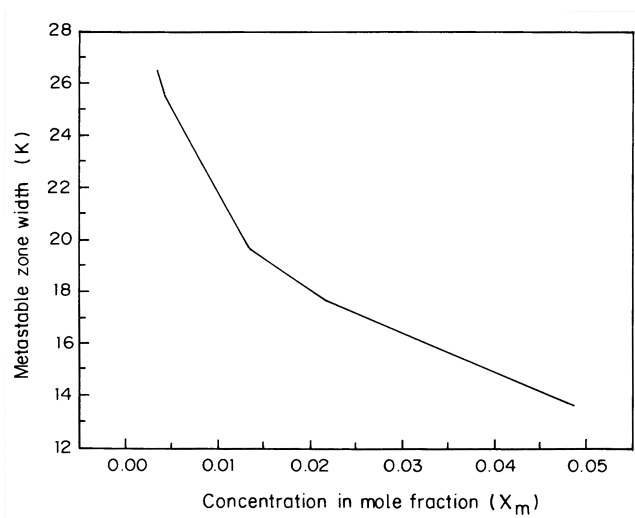
The critical supercooling  $\Delta T_c$ , required to grow one nucleus per unit volume in one sec which is called the metastable zone width and the other nucleation parameters of Nd123 in BaO–CuO flux are calculated from the above equations using the condition for critical energy formation.

## 3. Results and discussion

The interfacial energy, metastable zone-width, critical energy barrier, critical nucleation radius etc of Nd123 crystal in BaO–CuO flux are calculated for different mole fractions using the above formalism and presented in table 1.

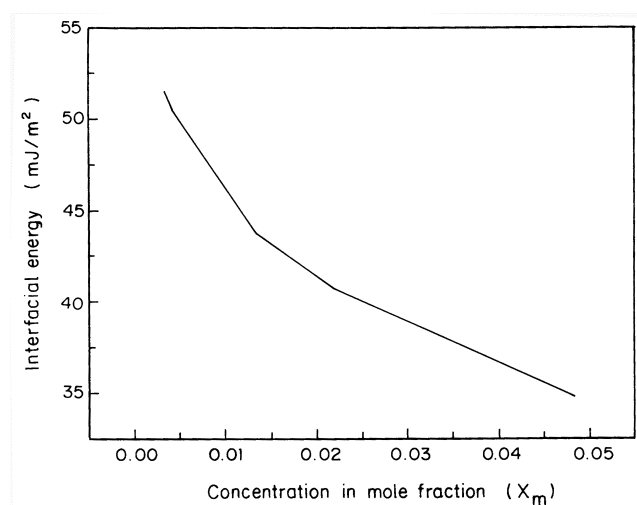
**Table 1.** Variations of solubility in mole fraction, interfacial energy, metastable zone width, volume free energy, critical energy barrier and critical nucleation radius of Nd123 in BaO–CuO flux with heat of solution 282 kJ/mol.

Temperature, $T$ (K)	Mole fraction ( $x_m$ )	Interfacial energy ( $s$ ) (mJ/m <sup>2</sup> )	Metastable zone width ( $\Delta T_c$ ) K	Free energy change ( $\Delta G_v$ ) ( $\times 10^6$ J/m <sup>3</sup> )	Critical energy barrier ( $\Delta G^*$ ) <sup>3</sup> ( $\times 10^{-16}$ mJ/m <sup>3</sup> )	Critical nucleation radius ( $r^*$ ) nm
1341.2	0.04833	34.81	13.7	– 23.51	12.78	2.96
1293.2	0.02166	40.79	17.7	– 30.38	12.33	2.69
1253.2	0.01333	43.77	19.9	– 34.29	11.95	2.55
1233.2	0.00833	47.11	22.7	– 38.60	11.75	2.44
1173.2	0.00417	50.47	25.6	– 43.89	11.18	2.30
1153.2	0.00333	51.42	26.5	– 45.52	10.99	2.60

**Figure 2.** Shows the variation of interfacial energy  $s$  with mole fractions of Nd123 BaO–CuO flux.

The variation of interfacial energy with concentration in mole fractions of Nd123 is shown in figure 2. From the figure it can be seen that the interfacial energy decreases gradually with the rise of mole fractions of solute in the solution, which may be due to the inherent property of the flux and the trend of the graph agrees with the experimental observation of high temperature solution growth (Joseph Kumar *et al* 1996).

The calculated values of metastable zone-widths for the system at different mole fractions of the solute Nd123 in the solution is shown in figure 3. From the figure it can be concluded that the metastable zone-width is narrow at higher concentrations, i.e. at higher temperature and wide at lower concentrations, i.e. at lower temperature of the solution. This is very much conformable with the expected prediction. Because, the degree of probability of nucleation depends on the intermolecular distances of the solute particles in the solution and therefore on its concentration. Our theoretically predicted values of metastable zone-width (13°C–20°C) for the mole fractions (0.04833–0.01333) can be compared to the supercooling temperature given for the growth of Nd123 crystal by TSSG technique (Krauns *et al* 1994; Nakamura *et al* 1996).

**Figure 3.** Shows the variation of metastable zone-width  $\Delta T_c$  with mole fractions of Nd123 in BaO–CuO flux.

We considered the homogeneous nucleation, so the metastable zone widths reported in the present work for the BaO–CuO flux may be the maximum possible values. There are a number of factors, such as presence of impurities in the solute, mechanical and thermal shocks, stirring and scratches in the crucible wall which may affect the metastable zone width. Despite this, the present work provides a comprehensive picture for the better understanding of the growth kinetics of Nd123 crystals grown from BaO–CuO flux. Moreover, the uncertainty in determining the above thermodynamical nucleation parameters from high temperature solution growth of Nd123 crystals creates interest in determining the above parameters.

### List of symbols

- $d$ , Mean molar ionic diameter in crystal ( $m$ ) =  $\{(6/p)v\}^{1/3}$ ;
- $\Delta G_v$ , excess volume free energy change (J/m<sup>3</sup>);
- $\Delta G_s$ , excess surface free energy change (J/m<sup>2</sup>);
- $\Delta G$ , Gibbs free energy change (mJ/m<sup>3</sup>);
- $\Delta H_s$ , enthalpy of solution (J/mol);
- $k$ , Boltzmann constant (J/K);

$M$ , molecular weight (kg);  
 $n$ , number of ions in formula unit;  
 $N_A$ , Avogadro's number ( $\text{kmol}^{-1}$ );  
 $R$ , gas constant (J/K mol);  
 $S$ , supersaturation ratio;  
 $T$ , absolute temperature (K);  
 $\Delta T$ , supercooling (K);  
 $v$ , mean molar ionic volume ( $\text{m}^3$ ) =  $M/rN_A n$ ;  
 $x_m$ , mole fraction of solute in solution;  
 $\sigma$ , interfacial energy ( $\text{mJ/m}^2$ );  
 $\rho$ , density ( $\text{kg/m}^3$ ).

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