

<i>Cryst. Res. Technol.</i>	34	1999	4	503–508
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Determination of Nucleation Parameters of YBCO from High Temperature Solution

The growth kinetics of YBCO single crystal from high temperature solution of YBCO-BaO/CuO solute-solvent system has been studied. Based on regular solution model and classical nucleation theory the thermodynamical data investigated for the system are used to determine the nucleation parameters, interfacial energy, metastable zone-width (supercooling temperature), free energy change, critical nucleation radius etc. which leads to the understanding of the nucleation phenomena of YBCO.

keywords: YBCO, Superconductor, Interfacial energy, Metastable zone width.

1. Introduction

The most promising technique to grow single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ (YBCO) is the high temperature solution using BaO-CuO as flux (HIDAKA et al.; HAYASHI et al.; ASSMUS et al.; ELWELL et al.). A satisfactory flux should have high solubility for the solvent and an appreciable change of solubility with temperature. The widely used flux is the BaO-CuO mixed in the molar ratio 0.28 : 0.72 (DEMBINSKI et al.; OKA et al.; CHEN et al.). The use of this self flux avoids additional contamination into the YBCO crystals from flux materials (KAISER et al.; WANKLYN et al.). The quasi-binary phase diagram of the solute-solvent system is very essential to grow YBCO crystal by flux technique. In most flux growth experiments no seed crystals are used. Spontaneous nucleation occurs by cooling through the metastable region below the liquidus line. In this metastable region where the solution is supersaturated the nucleus of critical size is formed before the growth of crystal. It has been considered difficult to grow large size YBCO crystals from BaO-CuO flux, because the solubility range of YBCO in BaO-CuO flux is very narrow (0-19 mole%) at the peritectic temperature (KRAUNS et al.). In spite of this, there are many efforts have been carried out to grow large size YBCO single crystals by Solute Rich Liquid Crystal Pulling (SRL-CP) method by many groups (HAMADA et al.; EGAMI et al.; NAMIKAWA et al.). All these techniques require the knowledge of the essential growth parameters like, interfacial energy, metastable zone-width, critical nucleation radius and Gibbs free energy etc. for the system. Up to now, there has been no reports in the literature regarding these key parameters. Here, an attempt has been made to estimate these parameters theoretically. In the present work interfacial energy, metastable zone-width and other nucleation parameters of YBCO crystal growth in BaO-CuO solvent have been calculated by employing the solubility data reported in (EMELCHENKO et al.). According to the assumption of regular solution model the nucleation process is considered to be homogeneous in nature and in the nucleation process solid and liquid phases coexist together. The nucleation process and growth mechanism

involved in the growth of YBCO from high temperature solution growth is similar to the low temperature solution growth system. In this paper the regular solution model has been adopted to calculate the nucleation parameters of YBCO for the first time.

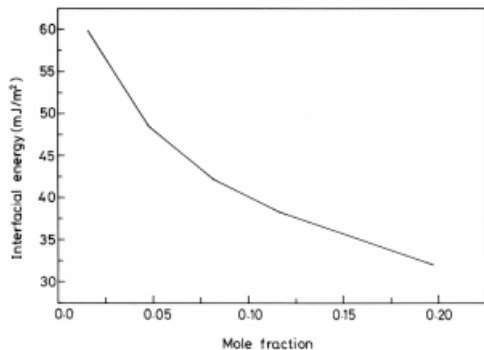


Figure 1: The variation of interfacial energy σ with mole fraction x_m of YBCO in BaO-CuO flux.

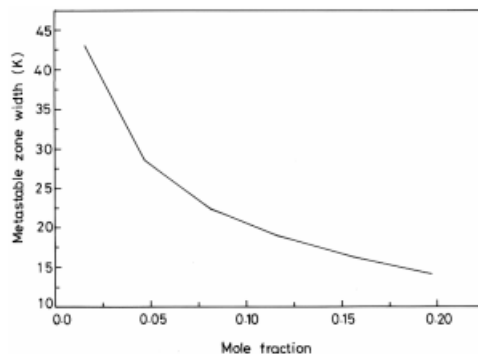


Figure 2: The variation of metastable zone-width ΔT_c with mole fraction x_m of YBCO in BaO-CuO flux.

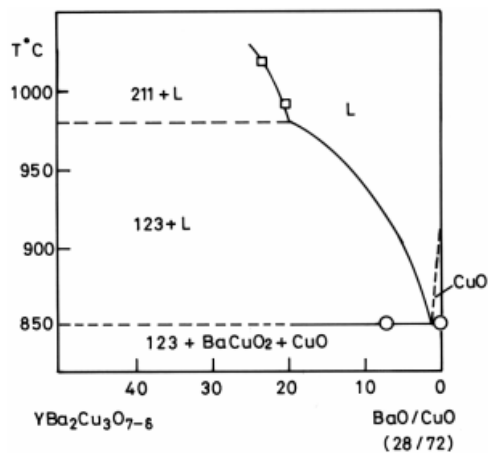


Figure 3: Solubility versus temperature data of YBCO in BaO-CuO solution taken from (EMELCHENKO et al.)

2. Interfacial energy

The interfacial energy σ of the interface between the growing crystal and the surrounding mother phase plays an important role in the nucleation of crystals. It is well known that for all crystal- solution interface, it is difficult to predict theoretically the interface energy with sufficient accuracy. Also, it is more difficult to determine σ by direct unambiguous experiments from high temperature solution growth. NIELSON and SOHNEL reported the relationship between interfacial energy σ and solubility for the nucleation of electrolyte crystals in aqueous solution. Later, nucleation experiments have been employed to determine σ from supersaturated solutions and the relationship between interfacial energy and solubility have been given for low temperature solution growth system by many researchers (SOHNEL; SANGWAL; BENNEMA et al.). Theoretical estimation of interfacial energy from

physico-chemical data has drawn considerable attention. Quite recently many workers have reported theoretical derivations of more refined expressions for the linear dependence between interfacial energy and solubility (BENNEMA et al.; CHRISTOFFERSEN et al.; MERSMANN). Among these expressions the expression given by BENNEMA and SOHNEL has shown better agreement with experimental values of high temperature solution growth (JOSEPH et al.). BENNEMA and SOHNEL based on the regular solution theory have derived an expression for the relationship between the interfacial energy and solubility as

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

where x_m is the mole fraction of solute, T is the temperature in Kelvin, d is the inter ionic distance or ionic diameter and k is a Boltzmann constant. In the present work this expression is used to calculate the interfacial energy of YBCO crystal from the solubility data of the YBCO - BaO/CuO quasi-binary phase diagram (EMELCHENKO et al.) Fig.3.

3. Metastable zone-width:

Crystallization involves two distinct steps: nucleation, which is the birth of a nucleus and crystal growth which involves the growth of the existing nucleus. In order to realize these, the solution must be supersaturated. A supersaturated solution is thermodynamically in a non equilibrium state and is known as metastable state. This state comes to a thermodynamically stable state with small perturbations which causes the formation of nuclei of a new phase. The formation of such nuclei is limited due to energy barrier encountered in the process and happens only when the radii of the newly born nuclei are greater than or equal to a critical size. Initial stage of crystallization in supersaturated solution is the formation of nuclei of crystalline phase. Classical homogeneous theories describing nucleation as a relaxation process from a metastable state were developed by HIRTH and POUND, NIELSON and ZETTLEMOYER.

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

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

where, ΔH_s is the heat of solution, ΔT is the supercooling and R is the gas constant. The relation between the solubility and the enthalpy of a real solution is given as

$$\ln x_m = \frac{-\Delta H_s}{RT} + \frac{\Delta S_E}{R} \quad (3)$$

here, ΔS_E is the excess entropy of mixing. From the above equation it is apparent that a plot of $\ln x_m$ versus $1/T$ gives a straight line and the slope of which equals to $-\Delta H_s/R$. The value of ΔH_s is calculated from the data of YBCO solute in BaO-CuO solvent solubility curve (EMELCHENKO et al.) Fig 3. 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

$$\Delta G_v = \frac{-kT}{v} \ln S \quad (4)$$

where, ΔG_v is the excess free energy change per unit volume, v is the specific volume of the solute molecule and k is the Boltzmann constant. The Gibbs free energy change associated with the formation of YBCO for a spherical nucleus can be written as

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

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

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

The rate of homogeneous nucleation is expressed as (HIRTH et al.)

$$J = A \exp(-\Delta G^*/kT) \quad (7)$$

where, A is a pre-exponential factor which varies very slowly 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). The critical supercooling ΔT_c , required to grow one nucleus per unit volume in one second which is called the metastable zone width and the other nucleation parameters of YBCO are calculated from equation (6), (4) and (2) using the condition for critical energy of formation in equation (7).

4. Results and discussion

The interfacial energy, metastable zone-width and the other nucleation parameters of YBCO crystal growth in BaO-CuO flux are calculated for different mole fractions using the above formalism and presented in Table 1.

The variation of interfacial energy with mole fraction is shown in Fig.1. The interfacial energy increases with the decrease of mole fraction of the solution, which may be due to the inherent property of the flux and the trend exhibited in the graph is similar to the experimental observation of high temperature solution growth (JOSEPH et al.). The calculated values of metastable zone-width for YBCO - BaO/CuO solute - solvent system for different mole fractions is shown in Fig. 2. From the figure it is concluded that metastable zone-width is wide at low concentrations, i.e, at low temperature and narrow at high concentrations, i.e, at high temperature of the solute in the solution. This is as expected, 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 (14°C-22°C) used for the mole fractions from $x_m=0.19$ to 0.08 can be compared with the temperature difference between the growing crystal and the solid feeder material in (SRL-CP) YBCO growth experiments (EGAMI et al.; NAMIKAWA et al. and YAMADA et al.). But, the other nucleation parameters like, critical Gibbs free energy, critical nucleation radius are not affected very much with the increase or decrease of temperature of the solution. The present work provides a comprehensive picture for the better understanding of the growth kinetics of YBCO crystal from BaO-CuO flux. The uncertainty in determining the above nucleation parameters from high temperature solution growth of YBCO crystal creates interest in determining the above parameters.

Temperature (K)	Mole Fraction (x_m)	Interfacial Energy σ (mJ/m ²)	Metastable zone -width ΔT_c (K)	Critical Free energy Change ΔG^* (mJ/m ³) $\times 10^{-16}$	Critical nucleation radius r^* (nm)
1254.78	0.19737	31.97	14.08	11.96	2.99
1241.68	0.15368	35.04	16.37	11.83	2.84
1223.20	0.11579	38.33	19.01	11.66	2.69
1198.20	0.08158	42.15	22.34	11.42	2.54
1173.20	0.04737	48.28	28.46	11.84	2.35
1123.20	0.01579	59.77	42.96	10.71	2.07

Table 1: Variation of solubility in mole fraction, interfacial energy, metastable zone- width and other nucleation parameters of YBCO in BaO-Cuo flux.

5. Conclusion

The nucleation parameters of YBCO crystal growth from the BaO-CuO flux at different crystallization temperatures have been calculated. As there are no sufficient data available in the literature the present theoretically estimated values will be useful for the growth of large size good quality single crystals of YBCO.

Acknowledgement:

D. P. Paul acknowledges the financial support of ICTP, Italy to conduct the research.

References

- ASSMUS, W., SCHMIDBAUER, W.: Super. Sci. Technol. **6** (1993) 555
 BENNEMA, P., GILMER, G. H.: in Crystal Growth, An Introduction. Ed. P.Hartman (North Holland, Amsterdam,1993) p.263.
 BENNEMA, P., SOHNELL, O., J. Crystal Growth **102** (1990) ???
 CHEN CHANG KANG, HU YONGLE, WANKLYN, B. M., HODBY, J. W.: Crystal Growth **129** (1993) 239
 CHRISTOFFERSEN, J., ROSTRUP, E., CHRISTOFFERSEN, M. R.: J.Crystal Growth **113** (1991) 599-605
 DEMBINSKI, K., GERVAIS, M., ODIR, P., COUTURES, J.P.: Less-Common Metals **164/165** (1990) 177
 EGAMI, M., YAMADA, Y., NAMIKAWA, Y., SHIOHARA, Y.: J. of Electronic materials, **24, 12** (1995) 1907
 ELWELL, D., SCHEEL, H. J.: Crystal Growth from High Temperature Solutions, Academic Press (London)
 EMELCHENKO, G. A, ABROSIMOV, N. V., BAZHENOV, A. V., MASALOV, V.M., ZHOKHOVH, A. A, KONONOVICH, P. A., LOGVENOV, G.YU., KHASANOV, S. S.: Materials Lett. **9** (1990) 96
 HAMADA, Y., SHIOHARA, Y.: Physica C **217** (1993)
 HAYASHI, S., OHNO, T., INOUE, T., KOMATSU, H.: J. Crystal Growth **91** (1988) 331
 HIDAKA, Y., ENOMOTO, Y., SUZUKI, M., ODA, M., MURAKAMI, T.: J.Crystal Growth **85** (1987) 581
 HIRTH, J. P., POUND, G. M.: Condensation and evaporation, nucleation and growth kinetics, Pergamon press, Oxford,1963
 JOSEPH KUMAR, F., GANESA MOORTHY, S., JAYARAMAN, D., SUBRAMANIAN, C.: J. Crystal Growth **160** (1996) 124-135
 KAISER, D. L., HELTZBERG, F., SCOTT, B. A., MCGUIRE, T. R.: Appl. Phys. Lett. **51** (1987) 1040
 KRAUNS, C., SUMIDA, M., TAGAMI, M., HAMADA, Y., SHIOHARA, Y.: Z. Phys. B **96** (1994) 207
 MERSMANN, A.: J. Crystal Growth **102** (1990) 841
 NAMIKAWA, Y., EGAMI, M., KOYAMA, S., SHIOHARA, Y.: Advances in Superconductivity VIII (Proceedings of ISS'95) (1996) 739-742

- NIELSON, A. E., SOHNEL, O.: J. Crystal Growth **11** (1971) 233
NIELSON, A. E.: Kinetics and Precipitation, Ed. R. Belcher and L. Gordon, Pergamon Press, New York, 1964
OKA, K., NAKENE, K., ITO, M., SAITO, M., UNOKI, H.: Japan J. Appl. Phys. **27** (1988) L1056
SANGWAL, K.: J. Crystal Growth **97** (1989) 393
SOHNEL, O.: J. Crystal Growth **57** (1982) 101
WANKLYN, B. M., CHEN CHANG KANG, WATTS, B. E., HAYCOCK, P., PRATT, F.: Solid State Commun. **66** (1988) 441
WALTON, A. G.: Nucleation, Ed. A. C. Zettlemoyer, Marcel Dekker, New York, 1969, p.241
ZETTMLOYER, A. C.: Nucleation, Ed. Dekker, New York, 1969

(received May 19, 1998; accepted June 30, 1998)

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