

Estimation of Nucleation Thermodynamical Parameters of $\text{La}_2\text{Sr}_2\text{CuO}_4$ (LSCO) and $\text{YBa}_2\text{Cu}_2\text{O}_{7-\delta}$ (YBCO) Crystallizing from High Temperature Solution

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Received 17 March 2016; accepted 2 May 2016; published 5 May 2016

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Abstract

The growth kinetics of LSCO and YBCO single crystals from high temperature solution of LSCO-CuO solute-solvent and YBCO-CuO solute-solvent systems has been investigated. Based on regular solution model and classical nucleation theory, the thermodynamical data investigated for the systems are used to determine the nucleation parameters: interfacial free energy, metastable zone-width, volume free energy, critical energy barrier for nucleation and radius of critical nucleus for LSCO and YBCO which leads to the understanding of the nucleation phenomena of LSCO and YBCO.

Keywords

LSCO, YBCO, Interfacial Energy, Metastable Zone-Width

1. Introduction

The important renewable method of growing single crystals of $\text{La}_2\text{Sr}_2\text{CuO}_4$ (LSCO) and $\text{YBa}_2\text{Cu}_2\text{O}_{7-\delta}$ (YBCO) is the high temperature solution using LSCO-CuO [1]-[3] and BaO-CuO [4]-[6] as flux respectively. A satisfactory flux should have high solubility for the solvent and an appreciable change of solubility with temperature. The widely used flux is the LSCO-CuO mixed in the ratio 0.23:0.77 for LSCO [7] and BaO-CuO mixed in the ratio 0.28:0.72 for YBCO [8]. The binary phase diagram of the solute-solvent system is very essential to grow LSCO and YBCO crystals from flux technique. The high temperature solution growth techniques require the knowledge of the essential nucleation thermodynamical parameters like interfacial energy, metastable zone-

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width, volume free energy, critical energy barrier for nucleation and radius of crystal nucleus for the growth of good quality bulk single crystals. Up to now, there have been no reports in the literature regarding these key parameters. Here an attempt has been made to estimate these parameters theoretically to understand the role of these nucleation parameters for the crystallization of LSCO from LSCO-CuO flux and YBCO from BaO-CuO flux. 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. In this paper the regular solution model has been adopted to calculate the nucleation parameters of LSCO and YBCO for the first time.

2. Nucleation Thermodynamical Parameters

2.1. Interfacial Energy

The interfacial energy σ is the interface between the growing crystal and the surrounding mother phase in important role in the nucleation of crystals. It is well known that for all crystal-solution interfaces, it is difficult to predict theoretically the interfacial energy with sufficient accuracy. Also, it is more difficult to determine σ by direct unambiguous experiments from high temperature solution growth. Nielson and Sohnel [9] 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 [10]-[12]. Quite recently, many workers have reported theoretical derivations of more refined expressions for the linear dependence between interfacial energy and solubility [13]. The interfacial energy can be determined experimentally from data on nucleation and growth kinetics, and from contact angle measurements. Consequently, estimation of interfacial energy from physico-chemical data has drawn considerable attention [14]. Bennema and Sohnel [15] 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 LSCO crystal from the solubility data of the LSCO-CuO binary phase diagram (Figure 1) and of YBCO crystal of BaO-CuO quasi-binary phase diagram (Figure 2).

2.2. Metastable Zone-Width

Crystallization involves two distinct steps: nucleation, which is the birth of a nucleus and crystal growth which

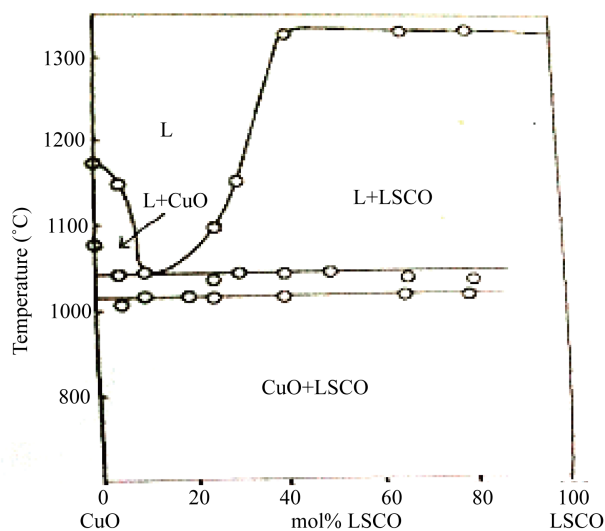


Figure 1. Binary phase diagram of LSCO-CuO.

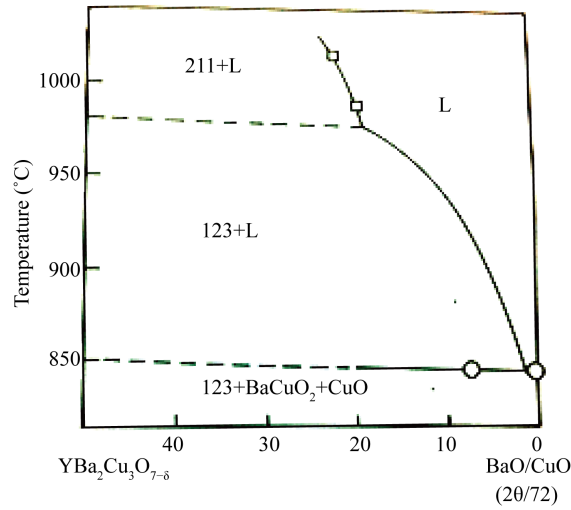


Figure 2. Quasi-binary phase diagram of YBCO-BaO/CuO.

involves the growth of the existing nucleus. In order to thermodynamically in a non-equilibrium state and is known as metastable state. This state comes to a thermodynamically stable state with small perturbation, which causes the formation of nuclei of a new phase. The formation of such nuclei is limited due to energy barrier 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 were developed by high and Pound [16], Nielson [17] and Zettlemoyer [18] describing nucleation as a relaxation process from a metastable state. The relative super saturation S of a solution at a temperature T is

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

where, x_m is the heat of solution; ΔT is the super cooling and R is the gas constant.

The relation between the solubility and the enthalpy of a real solution is given as

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

where, 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, the slope of which equal to ΔH_s . The value of $-\Delta H_s/R$ is calculated from the data of LSCO solute in LSCO-CuO solvent solubility curve (Figure 1) and YBCO solute in BaO-CuO (Figure 2).

2.3. Volume Free Energy

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 volume free energy change per unit volume; v is the specific volume of the solute molecule and k is the Boltzmann constant.

2.4. Critical Energy Barrier

The radius of critical nucleus, and critical energy barrier associated with the critical nucleation for spherical nucleus are related as

$$r^* = \frac{-2\sigma}{\Delta G_v}, \quad \Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_v^2} \quad (5)$$

3. Results and Discussion

The interfacial energy, metastable zone-width (supercooling temperature), volume free-energy, critical energy barrier and radius of critical nucleus of LSCO and YBCO has been calculated using the different formalism as discussed above and presented in **Table 1** and **Table 2**.

The variation of interfacial energy with temperature is shown in **Figure 3** for LSCO. From **Figure 3**, it can be observed that the interfacial energy increases, with the decrease of temperature of the solution and the trend exhibited with the experimental observation of high temperature solution growth of KTP crystals crystallizing from $K_6P_4O_{13}$ flux [19] and in the $NdBa_2Cu_3O_{7-\delta}$ (Nd123) system [20], the strong anisotropy in the interfacial energy may be due to the inherent property of LSCO in LSCO-CuO solute- solvent system. The variation of interfacial energy with temperature exhibits similar trend in case of YBCO in BaO-CuO solute-solvent system as shown in **Table 2** which is also similar the experimental observation of high temperature solution growth [21] [22].

The calculated value of metastable zone-width for LSCO at different temperatures is shown in **Table 1** and for YBCO at different temperature is shown in **Figure 4**. From **Table 1** for LSCO and **Figure 4** for YBCO, it can be concluded that the metastable zone-width is narrow at higher temperature and wide at lower temperature of the solute in the solution. This is very much conformable with the expected prediction. The degree of probability of nucleation depends on the intermolecular distances of the solute particles in the solution and therefore on its concentration. In the literature there is no specific value of metastable zone-width and crystallization tem-

Table 1. Nucleation Thermodynamical parameters of LSCO.

Temp. T (K)	Mole-fraction (x_m)	Interfacial energy σ (mJ/m ²)	Metastable zone-width ΔT_c (K)	Volume free-energy $\Delta G_v \times 10^6$ (J/m ³)	Critical energy $\Delta G^* \times 10^{-16}$ (mJ/m ³)	Radius of critical nucleus r^* (nm)
1530	0.395	16.88	15.8	-7.43	14.59	4.54
1510	0.383	16.97	15.9	-7.54	14.40	4.5
1490	0.368	17.16	16	-7.72	14.20	4.5
1470	0.349	17.45	16.4	-7.97	14.02	4.38
1450	0.327	17.85	16.8	-8.3	13.83	4.3
1430	0.302	18.38	17.5	-8.74	13.62	4.21
1410	0.276	18.98	18.3	-9.23	13.45	4.11
1390	0.249	19.69	19.3	-9.82	13.26	4.01
1370	0.221	20.51	20.6	-10.5	13.11	3.91
1350	0.193	21.45	21.8	-11.4	12.72	3.76

Table 2. Nucleation Thermodynamical parameters of YBCO.

Temp. T (K)	Mole-fraction (x_m)	Interfacial energy σ (mJ/m ²)	Metastable zone-width ΔT_c (K)	Volume free-energy $\Delta G_v \times 10^6$ (J/m ³)	Critical energy $\Delta G^* \times 10^{-16}$ (mJ/m ³)	Radius of critical nucleus r^* (nm)
1254.78	0.19737	31.97	14.08	-21.97	11.96	2.99
1241.68	0.15368	35.04	16.37	-24.68	11.83	2.84
1223.20	0.11579	38.33	19.01	-28.44	11.66	2.69
1198.20	0.08158	42.15	22.34	-33.14	11.42	2.54
1173.20	0.04737	48.28	28.46	-41.06	11.84	2.35
1123.20	0.01579	59.77	42.96	-57.80	10.71	2.07

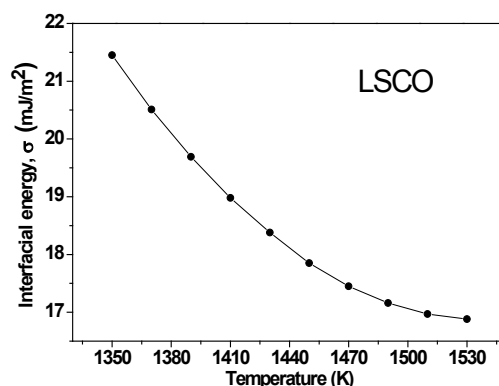


Figure 3. Variation of interfacial energy of LSCO with temperature.

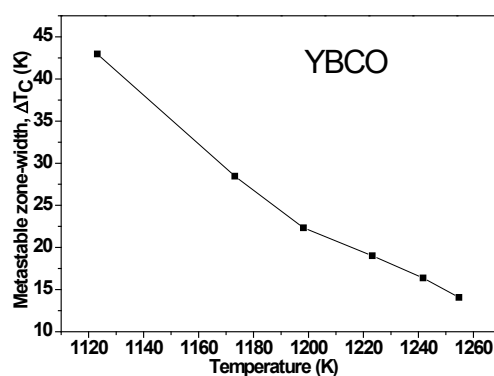


Figure 4. Variation of metastable zone-width of YBCO with temperature.

perature. Different laboratories reported different values of metastable zone-width and crystallizing temperature ranging from 1550 - 1350 K [21] [23]-[25] which is comparable to theoretically calculated values.

The calculated value of metastable zone-width for LSCO at different mole-fraction is shown in **Figure 5**. From **Figure 5**, it is concluded that metastable zone-width is wide at low concentrations *i.e.* at low temperature, and narrow at high concentration *i.e.* at higher temperature of the solute in the solution. The variation of interfacial energy with mole fraction is shown in **Table 1** and **Table 2** for LSCO and YBCO. It is observed that 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 trend exhibited in the graph is similar to the experimental observation of high temperature solution growth [22].

The change in free energy on the formation of a single YBCO molecule at equilibrium has been calculated using the available thermodynamical data. Using the regular solution model the thermodynamical potential of the components associated with the reaction has been calculated. The critical energy, ΔG^* has been evaluated by calculating the excess free energy. The critical energy of YBCO with temperature is shown in **Figure 6** and for LSCO in **Table 1**. It is noticed that critical energy decrease with increasing temperature which associated with the interface in terms of the energy of interactions between the molecules.

For the better understanding of the growth kinetics of LSCO and YBCO crystals, the other nucleation thermodynamical parameters of LSCO and YBCO such as volume free-energy, critical energy, radius of critical energy, energy of formation in the nucleus are calculated for various values of interfacial tension is given in **Table 1** and **Table 2**. The present work provides a comprehensive picture of LSCO crystal from crystallizing LSCO-CuO flux and YBCO crystal from crystallizing BaO-CuO flux. The uncertainty in determining the above nucleation parameters of LSCO and YBCO crystals from high temperature solution growth by experimental method creates interest in determining the above parameters.

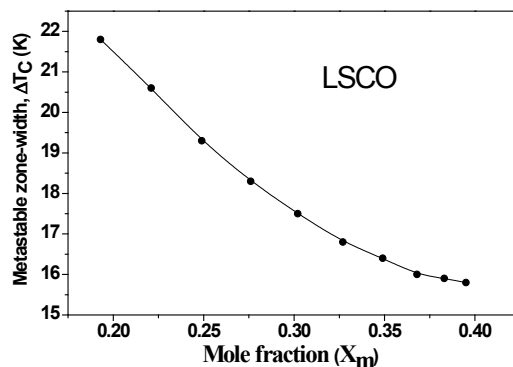


Figure 5. Variation of metastable zone-width of LSCO mole fraction (x_m).

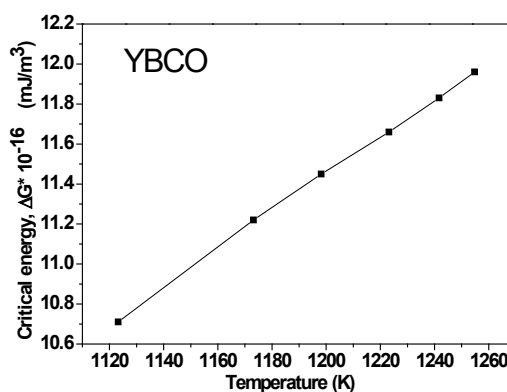


Figure 6. Variation of critical energy of YBCO with with temperature.

4. Conclusion

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

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