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CRYSTAL GROWTH OF THE $YBa_2Cu_3O_{7-\gamma}$ SUPERCONDUCTORS

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1. Introduction

Recent discovery of HTS led among others to the enormous amount of research work on powder sintered polycrystalline samples. Low density as well as the weak link between grains urged developing other methods for the preparation of ceramic superconductors. One of the most important ways appeared to be preparation of single crystals. The study of physical phenomena on single crystals is also very important to achieve a theoretical understanding of high temperature superconductivity, to optimize material properties for various applications and hopefully to get higher values of the superconducting transition temperature than the current maximum being about 120 K. Successful material processing, however, presupposes also a good knowledge of phase equilibria in a given system. The aim of this review is to give survey about the determination of phase relationships within the Y-Ba-Cu-O system and techniques for crystal growth of the YBCO superconductors. Since many various methods of YBCO single crystal growth were approved only two ways have been found to achieve crystals of a sufficient quality. There is solid state reaction leading to the achievement of small crystallites and crystal growth from high temperature solutions using nonstoichiometric melts. The latter one is currently the most promising way how to obtain the high quality bulk YBCO crystals and/or other related phases. Fully understanding of crystal growth processing is, however, necessary.

2. Fundamental Principles

[illegible] crystal growth from high temperature solution can be seen in Fig 1, where a typical eutectic phase diagram is given. Liquidus curve (drawn by full line in Fig.1) represents thermodynamic boundary between solvent and solvent + solute regions. The region of

[illegible] solution exists between the [illegible] liquidus one and that one drawn by dashed line. Existence of this metastable region, called also Ostwald-Miers region is a consequence of the necessity to form a nucleus of the critical size before the precipitation of a crystal. The broad of metastable region favoring growth of large crystals depends above all on the properties of the melt and the experimental arrangement. There exist three fundamental growing modes, corresponding to various techniques producing supersaturation:

(i) Solvent evaporation at a constant temperature during the growth. It results in homogeneous concentration of dopants, or impurities, homogeneous density of equilibrium effects, no variation of the composition in the case of solid solutions and possibility to grow materials with a specified valence state. Evaporation rate can be controlled by the temperature, gas flow removing the solvent vapors, free surface area of the melt, etc. The main disadvantage arises from the solvent vapors being very corrosive and attacking the insulation ceramic materials as well as heating elements.

(ii) Slow cooling with spontaneous uncontrolled nucleation requiring a small vertical temperature gradient keeping the bottom of the crucible at lover temperature then upper part. A continuous changing of the temperature during the growth can lead due to the difference in the solubility of the individual components to inhomogeneities and concentration gradients in the grown crystals. The dimensions of the crystals can be enlarged by limiting the number of spontaneously nucleated crystals, using e.g. temperature oscillations during the decreasing temperature. Another method restricting the nunber of nucleation centers is to spot cool the crucible bottom by an air jet or more simply by a ceramic or platinum rod. Nevertheless, due to the temperature gradient, where the top of the melt is hotter than the bottom, the natural convection is mininized and the tendency to a layering of the solution appears. In this case a stirring technique, e.g. Accelerated Rotation Crucible Technique (ACRT) should be applied.

(iii)Transport techniques like transport in a temperature gradient with an advantage of isothermal growth. In a such case a nutrient is held at higher temperature near the bottom of the crucible and the seed below the liquid level at the lower temperature. Mass transport from the dissolved nutrient to the seed is assured either by the natural convection and diffusion through the boundary layer or by stirring.

3. Experimental Arrangement

An important problem in the growth of YBCO crystals is the choice of suitable materials. Platinum crucibles, usually used for the growth of oxide materials, are heavily attacked by BaO-CuO based melts. This corrosion can be decreased using e.g. Au crucibles as reported by Kaiser[1]. Several other crucible materials have ever been suggested and approved like MgO, ZrO_2 or ThO_2. The most widely used crucible material is alumina as high purity and density as possible in order to avoid Al contamination of the crystals. Al enters the YBCO structure particularly at higher temperature and slower cooling rate. Al ions have

significant effect on reducing T_c and increasing tetragonality.

The general procedure for growth of YBCO crystals consists of mixing starting materials, compacting them into pellets, heating to a maximum temperature for several hours and cooling at a suitable rate to room temperature. Three techniques which have the advantage of separation of grown crystals from the melt have been successfully tested as follows:

(i)Cavity method[2] based on a formation of cavities in the melt most probably due to the oxygen evolution at higher temperature than 1000°C. The crystals grown in the melt are separated from the melt by its contraction during the solidification and cooling to room temperature. They must be recovered mechanically by breaking all the mass together with the crucible. Therefore it is advantageous to use ceramic crucibles like alumina for this method.

(ii)Melt transport method[1] utilizing wetting and creeping of the liquid solutions on metals like gold and platinum so that quasi free crystals can be obtained. Moreover the lower homogenization temperature in comparison to that used at the case of previous method of about 1000°C is sufficient. The melt is spontaneously transported over the crucible walls, therefore another external crucible must be used. Single crystals are particularly grown on outer surface of the internal crucible or in external crucible perpendicularly to its bottom and can be easily taken out.

(iii)Crystal growth from homogeneous melt[3] represents probably the best way for the growth of large crystals and their separation at the same time. It consists of achieving the proper concentration and temperature conditions for complete dissolution of solid phases, crystal growth procedure and removing the melt from the crystals by decanting or pouring the liquid through a sieve or by tilting the crucible. Achieving such conditions, however, requires a systematic study of phase relationships in the system and optimization of growth conditions.

4.Solvents

The choice of a suitable solvent for the crystal growth from high-temperature solutions is a complex problem involving both the physical and the chemical properties of the melt. From the physical properties the most important is the melting temperature, the viscosity, density and volatility. From the chemical properties it is the basicity or acidity of used oxides affecting the solubility of the crystallizing phase in the given melt. Many various solvents than BaO-CuO were tried for crystal growth of YBCO crystals. However, such factors as limited dissolution, formation of more stable phases with Y- or Ba- ions, the oxidation state of CuO etc, excluded their use and so the most suitable solvent seems to be BaO-CuO based melt.

5. Growth conditions

Temperature range for crystal growth is limited by the temperature of peritectic melting of YBCO being about 1000 °C and the temperature of eutectic melting of the melt at about 900°C. Hence it is very important to find the composition of the melt with the liquidus temperature just

below the temperature of peritectic melting of YBCO, i.e. to have the temperature range as large as possible. The data on solid-liquid phase equilibria are collected in phase diagrams. For crystal growth the most important diagrams are those including primary crystallization field of YBCO phase as the Y_2BaCuO_5-$Ba_3Cu_5O_8$ pseudo binary phase diagram already reported by several authors[4-7]. The most reliable results on this system are given by Oka et.al[7] which detail focused the measurement upon the area surrounded by CuO-$BaCuO_2$-YBCO triangle suggested to be favorable for growing the YBCO crystals in many reports. Their measurements were carried out along four radial directions starting from YBCO as the common end member, towards CuO, $Ba_3Cu_{12}O_{15}$, $Ba_3Cu_7O_{10}$ and $Ba_2Cu_5O_8$, respectively, as the opposite-end members. Phase relationships in the CuO-$BaCuO_2$-YBCO system at 950°C in air and at 975°C in oxygen were determined by Nevriva et.al[8] using the procedure based on the separation of the melt from an equilibrium sample and the consequent analysis of its solid residue. The optimum compositions for crystal growth following from our systematic study of phase equilibria in this system are in agreement with the results of crystal growth experiments[9-10]. The region of melt compositions giving the best results is shown in Fig.2 (see the region indicated by dashed line with points corresponding to the melt composition under-studied). Our results exhibit a shift of the optimum melt composition to the higher content of CuO comparing the data reviewed by Scheel and Licci[11]. It is probably due to composition changes as consequence of the following chemical reactions:
(i)The reactions between the crucible and the melt.
(ii)The reactions of BaO component with CO_2 always present in air.
(iii)The equilibrium interaction between the melt and oxygen in air.

The above discussed facts explain either the mutual inconsistency of reported results or the necessity to optimize crystal growth conditions in the framework of the ambient atmosphere, crucible material, temperature regime and melt composition.

REFERENCES

[1.] D.L. Kaiser, F. Holtzberg, M.F. Chisholm and T.K. Worthington, J. Crystal Growth 85, (1987) 593.

[2.] H. Katayama Yoshida, I.Okabe, T. Takahashi, T. Sasaki, T. Hirooka, T. Suzuki, T. Ciszek and K. Oki, Jap. J. Appl. Phys.26, (1987) L2007.

[3.] F. Licci, H.J. Scheel and T. Besagni, Physica C 153-155, (1988) 431.

[4.] R.A. Laudise, L.F. Schneemeyer and R.L. Barns, J. Crystal Growth 85,(1987) 569.

[5.] R.W. Mc Callum, R.N. Shelton, M.A. Nock, J.D.Swenson, M.A. Demenko, K.A. Gschneider, E.D. Gibson and A.R. Moodenbaugh (Ames Lab.), Microstructure and Superconductivity in High T Materials, preprint [Prepared for publication

[6.] Z. Jishan, J. Xiaoping, H. Jiangnu, J. Ming, Y. Yang, Z. Zhia, G. Yanlong, T. Yajun, O. Guiwen and H. Zhuangqi, Supercond. Sci. Tech. 1,(1988) 107.

[7.] K. Oka, K. Nakane, M. Ito, M. Saito and H. Unoki, Jap. J. Appl. Phys. 27,(1988) L 1065.

[8.] M. Nevriva, P. Holba, S. Durcok, D. Zemanova, E. Pollert and A Triska, Physica C 157, (1989) 334, 265.

[9.] M. Nevriva, P. Holba, S. Durcok, D. Zemanova, E. Pollert and A. Triska, Proc. ICF'5, Bombay, 1988.

[10.] M. Nevriva, Experimental Workshop on High Temperature Superconductors, Trieste, 1989.

[11.] H.J. Scheel and F. Licci, MRS Bulletin October, (1988) 56.

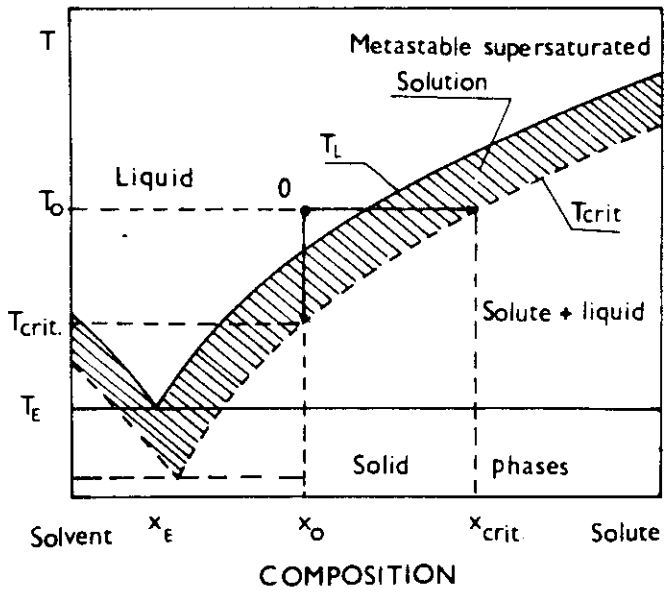

Fig. 1. Hypothetic pseudobinary phase diagram of solvent-solute system.

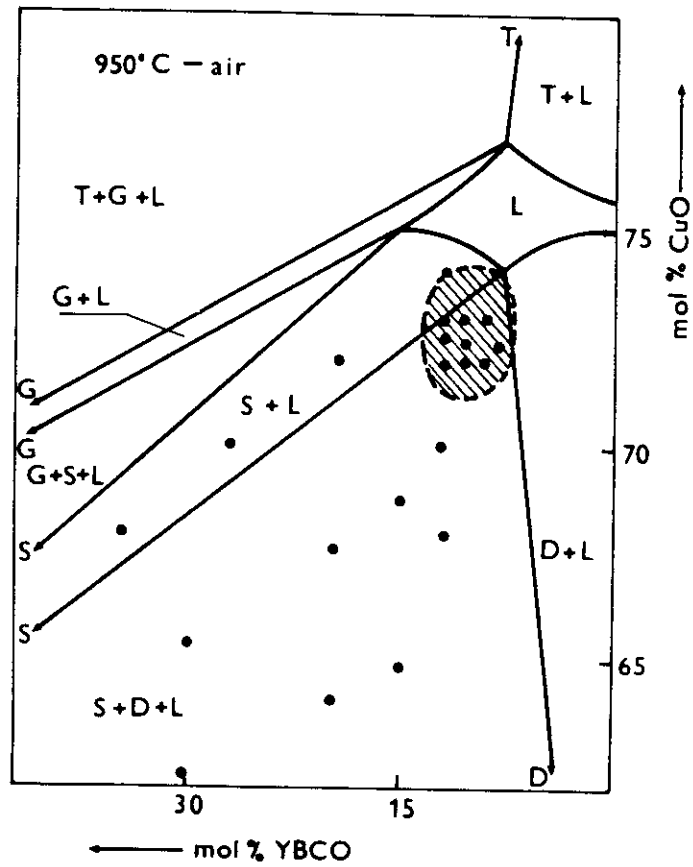

Fig. 2 . Graphically represented composition of melts that used during our systematic study [9 - 10].