Stabilization of the high temperature phase in Bi–Ca–Sr–Cu–O system

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Abstract. Since the discovery of Bi-containing high- T_c superconductors, difficulties in obtaining monophasic samples have been known. The study of phase formation in the system $\text{Bi}_2\text{Sr}_{(3-x)}\text{Ca}_x\text{Cu}_2\text{O}_y$, where $0.5 < x < 2.5$ and conditions for raising HT phase (110 K) content by loading a superstoichiometric excess of Ca and Cu ions into the initial composition as well as by a substitution of lead for a part of bismuth is the object of the present paper.

Keywords. Heat treatment conditions; superconductivity; bismuthates.

1. Introduction

Since the discovery of Bi-containing high- T_c superconductors difficulties in obtaining monophasic samples have been known. At present two structural phases (i) a low temperature (LT) 2212 ($T_c = 85$ K) and (ii) a high temperature (HT) 2223 (110 K), are determined (Statt and Wanc 1988), however, samples contain a mixture of phases and two-step transitions can be observed on the curves (T) and $X(T)$.

The present paper deals with the system $\text{Bi}_2\text{Sr}_{(3-x)}\text{Ca}_x\text{Cu}_2\text{O}_y$, where $0.5 < x < 2.5$, and analysis of the conditions for raising the HT-phase content by loading a superstoichiometric excess of Ca and Cu ions into the initial composition as well as by a substitution of lead for a part of bismuth.

2. Experiment

A standard ceramic technology route was applied for preparation of the samples. The initial compounds Bi_2O_3 , SrCO_3 , CaCO_3 , CuO and PbO were weighed in a certain ratio, mixed, annealed in air at 815–830 °C for 12–24 hr, pressed into pellets and sintered in air at room temperatures from 845 °C to premelting ones for 12–360 hr. The samples were either quenched in air or cooled together in the furnace.

To optimize the heat treatment conditions the process of the SC phase formation was studied using DTA, TG and X-ray diffraction analyses.

Changes in phase composition of the samples were controlled by a relative change in the peak intensity on the diffraction patterns, electron microprobe analysis and variation of the magnetization. X-ray fluorescence method was used to control the ceramic composition.

3. Discussion

According to the data, in the samples studied with x values from 0.9 to 2.1 after annealing for 24–28 hr at 860–875 °C, practically monophasic samples of 2212 are obtained which show $T_c = 80$ –85 K by resistivity measurements.

Stage-by-stage control of metallic ion content in the process of heat treatment

showed that with an increase of the annealing time, up to 20% of Cu and 8% of Ca ions volatilize, which is in agreement with the data by Hakuzaku *et al* (1989).

As a consequence, it was interesting to investigate the systems in which Ca and Cu contents exceed the stoichiometric ones.

According to the X-ray diffraction analysis data as well as electron-probe microanalysis, resistivity and magnetic measurements, the phases 2212 and Ca_2CuO_3 are formed in the systems 2224, 2246, 2268, 4457 under the above said temperature conditions during 24–48 hr; with time their amount increases and then the phase 2223 appears. This phase content increase is accompanied by the lowering of the 2212 phase content (figure 1).

The amount of decrease of the phase 2212 and Ca_2CuO_3 with the advent of 2223 phase testifies to the fact that the HT phase formation proceeds according to the reaction:

and is controlled by the rate of Ca and Cu diffusion—noticeable amounts of the phase 2223 are formed as a result of very long-term annealing. The highest content of the HT phase has been obtained in the powders of the system 2224. Application of a step-by-step annealing at 790, 815, 845 and 860 C for 200–250 hr with an intermediate grinding made it possible to bring the phase 2223 content up to 80% in the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ powder.

Pellets of such a powder prepared at a heat treatment for 200 hr have $T_c = 110$ K (according to resistivity measurements).

Aiming to raise the 2223 phase content and in accordance with the data by Escudero *et al* (1988) and Maeda *et al* (1989) the effect of lead addition on the kinetics of phase formation was studied for the systems with the nominal composition 4334, 2224 and 4457.

The introduction of lead essentially accelerates the process of the superconducting phase formation (figures 2,3).

In the presence of Pb the phase 2223 formation starts as early as 48 hr after annealing. Increase of the annealing time to 70–100 hr results in the formation of 50–60% of the phase 2223.

Figure 1. Change of phase composition of the samples $\text{BiSr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ vs time of annealing at 860 C (1) phase 2212; (2) phase 2223.

Figure 2. Change in magnetization of samples. (1) $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_y$; (2) $\text{Bi}_{3.2}\text{Pb}_{0.8}\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_y$; (3) $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$; (4) $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_y$.

Figure 3. Change of the phase composition of $\text{Bi}_{2.8}\text{Pb}_{1.2}\text{Sr}_4\text{Ca}_5\text{Cu}_7\text{O}_y$ vs time of annealing. (1) phase 2212; (2) phase 2223.

According to the X-ray diffraction analysis data, appearance of Ca_2PbO_4 phase is observed when the phase 2223 is formed; the values become smaller with increase of the 2223 phase content.

It is apparent that introduction of lead into the compositions with a superstoichiometric content of Ca and Cu promotes diffusion processes that lead to an interaction of the phase 2212 with the excess of Ca and Cu and formation of the phase 2223 due to construction of additional layers CaO and CuO in a crystallographic cell.

References

- Escudero K, Chavira E, Leon L M and Rios-Jara D 1988 *Phys. Rev.* **B38** 9272
- Hakuzaku Y, Kittaka K and Ogushi T 1989 *Jpn J. Appl. Phys.* **28** L402
- Maeda A, Noda K, Tanaka S and Uchinokura K 1989 *Jpn. J. Appl. Phys.* **28** L576
- Statt B W and Wanc Z 1988 *Physica* **C156** 251