

Pb Solubility of the High-temperature Superconducting Phase $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$

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Abstract

For the nominal composition of $\text{Bi}_{2.27-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$ the lead content was varied from $x=0.05$ to 0.45 . The compositions were examined between 830°C and 890°C which is supposed to be the temperature range over which the so-called 2223 phase ($\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$) is stable.

Only compositions between $x=0.18$ to 0.36 could be synthesized in a single phase state. For $x>0.36$ a lead containing phase with a stoichiometry of $\text{Pb}_4(\text{Sr,Ca})_5\text{CuO}_d$ is formed, for $x<0.18$ mainly $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ and cuprates are the equilibrium phases.

The temperature range for the 2223 phase was found to be 830°C to 890°C but the 2223 phase has extremely varying cation ratios over this temperature range. Former single phase 2223 samples turn to multi phase samples when annealed at slightly higher or lower temperatures. A decrease in the Pb solubility with increasing temperature was found for the 2223 phase.

1. Introduction

In the system BiO-SrO-CaO-CuO three superconducting phases are known: $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (2201), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2212) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223). 2212 is easily prepared over a large composition range with different T_c 's. But $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ which is of special interest due to its high critical temperature of 110 K is still very difficult to prepare in a single phase state though Majewski et al. [1] reported a way. They prepared samples containing up to 90 to 95 vol. % 2223 pha-

se with a starting composition significantly Bi-richer than the exact 2223 composition, but at much higher sintering temperatures than recommended for leaded compositions. It is fairly well-known that the 2223 phase formation is promoted by partial substitution of Bi by Pb [2]. But there still exist major problems for single phase material preparation. Numerous attempts have been made to synthesize the lead substituted 2223 phase in a single phase state [3 to 7] but most of the time it was done in an empirical way to find out the best starting composition, temperature, pressure and atmosphere. But this is not very satisfactory since many disagreements exist between the authors.

For the lead free system Majewski et al. [8] and more recently R. Müller et al. [9] presented the phase equilibria in the BiO-SrO-CaO-CuO system at different temperatures in air with special regard to the single phase region of the 2212 and 2201 phase. In [9] the single phase regions of 2212 and 2201 are very precisely worked out for 830°C.

In [8] the single phase region of 2212 for various temperatures and the associated T_c 's are reported.

In contrast to the very exact knowledge of the homogeneity range of the 2212 phase only few informations of the homogeneity range of the 2223 phase are found in the literature. This lack of information may be due to the extremely complicated circumstances. Only a few attempts have been made to examine the phase equilibria and to find a single phase region for the 2223 phase. Endo et al. [3] studied the region in the vicinity of the ideal stoichiometry 2223 and found remarkably differences in the phase formation and small differences in T_c . They found that $T_c(0)$ is affected by small composition variations, and if Ca and Cu is in excess to the ideal stoichiometry T_c may be lowered to around 95 K.

A more detailed study is given by Strobel et al. [10] who considered a temperature-concentration cut through the system along the composition line $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+x}$ from 825 to 1100°C under the assumption that Pb forms no phases independent on Bi.

They say that the 2223 phase exists, as a dominant phase between around 835°C and 875°C for $3 < n < 4$. The presence of Pb lowers the

transition lines of the superconducting phases to about 10 to 15°C. None of these studies provides a complete description of the single phase region of 2223 and of the dependence on Pb content.

Knowing the homogeneity range in dependence on temperature and lead content would be very helpful for preparation of high-quality material. There is still no explanation why partial substitution of Bi by Pb helps to prepare the 2223 phase. The positive effect of Pb might be due to a widening of the homogeneity range or a stabilization of the 2223 phase. To get more insight in the complicated circumstances the lead content was systematically varied starting from the nominal composition of $\text{Bi}_{1.91}\text{Pb}_{0.36}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$. This composition with a common substitution degree was found to be relatively easily prepared in a single phase state.

2. Experimental

Samples were prepared by the conventional solid state synthesis route starting from 99.9 % pure oxides (Bi_2O_3 , PbO , CuO) and carbonates (CaCO_3 , SrCO_3). The powders were weighed and intimately mixed in an agate mortar. The calcination was performed in three steps: 12 h at 750°C, 24 h at 780°C and 12 h at 800°C. After calcination the powders were again grind, pressed into small cylindrical rods and sintered for 60 h in air at 850°C. The sintering step was four times repeated after an intermediate grinding and pressing step resulting in a total sintering time of 300 h. These long reaction times in connection with intermediate grinding and pressing are necessary to assure the completeness of the reaction. After this 300 h reaction time all compositions were annealed at 830 for 200 h, at 860°C, 865°C, 870°C for 60 h, at 880°C 12 h and at 890°C for 2 h. The increasing amount of liquid with increasing temperature makes it necessary to decrease the annealing time since the liquid reacts very easily with the alumina crucible. But this decrease in reaction time with increasing temperature is no drawback for the examinations since all samples were first five times reacted at 850°C to make sure that

the most limiting step for reaching the equilibrium state, the 2223 formation, is completed before annealing at various temperatures.

Starting from the nominal composition of $\text{Bi}_{2.27-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$ samples with $x=0.05, 0.18, 0.27, 0.36$ and 0.45 were prepared.

Phase identification was performed by optical microscopy, X-ray diffraction using Cu-K_α and EDX analyses.

For the composition $\text{Bi}_2\text{Pb}_{0.27}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$ representing a composition in the middle of the homogeneity range the lead content of the 2223 crystallites was measured at all considered temperatures. Microprobe analysis was necessary to accurately monitor the Pb content.

3. Results

3.1. Homogeneity Range

In Table 1 all found phase equilibria are listed in connection with a symbol corresponding to a certain region in Fig. 1. Figure 1 shows the homogeneity region and existence regions for 2223 in the section under consideration. For the sake of clarity only regions are drawn, no real phase diagram is constructed due to the enormous complexity of five component systems.

Between $x=0.18$ and 0.36 a single phase region of 2223 is found. Figure 2 shows a Scanning Electron Microscope photograph (BSE) of a sample with the nominal composition of $\text{Bi}_2\text{Pb}_{0.27}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$. The sample is located in the middle of the single phase region and no other phase than 2223 is detected.

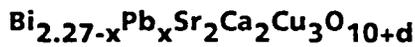
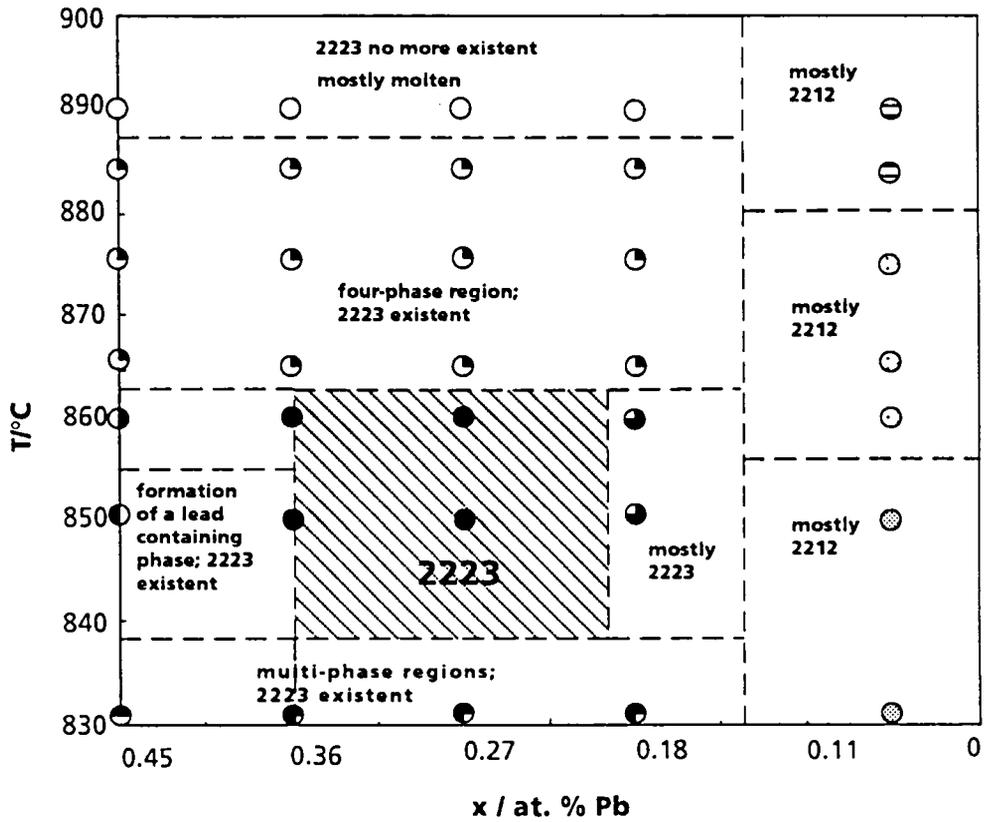


Fig. 1. Homogeneity region and existence regions of 2223

- single phase 2223
- ⊖ $\text{Pb}_4(\text{Sr,Ca})_5\text{CuO}_d + 2212 + 2223 + \text{CuO}$
- $\text{CuO} + 2223 + 2212$
- ⊗ $2212 + (\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41-x} + \text{Ca}_2\text{CuO}_3 + \text{CuO}$
- ⊕ $\text{Pb}_4(\text{Sr,Ca})_5\text{CuO}_d + (\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41-x} + 2223 + \text{liquid} + \text{CuO}$
- $\text{CuO} + 2223 + 2212$
- ⊕ $\text{Pb}_4(\text{Sr,Ca})_5\text{CuO}_d + (\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41-x} + 2223 + \text{liquid}$
- ⊙ $2212 + (\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41-x} + \text{Ca}_2\text{CuO}_3 + 2223$
- ⊕ $2223 + (\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41-x} + \text{Ca}_2\text{CuO}_3 + \text{liquid}$
- ⊖ $2212 + (\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41-x} + \text{Ca}_2\text{CuO}_3 + 2223 + \text{liquid}$
- $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41-x} + \text{Ca}_2\text{CuO}_3 + 2212 + \text{liquid}$

Table 1. All analysed phases with symbols corresponding to Fig.1

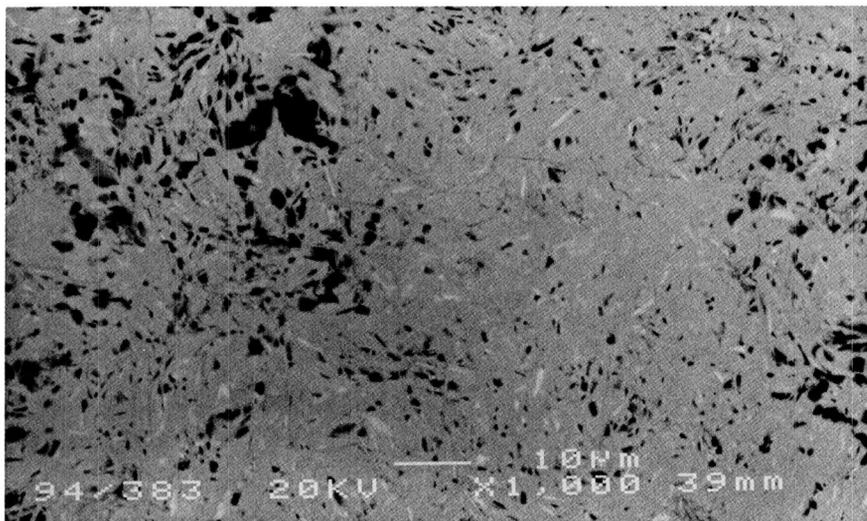


Fig. 2. BSE image of $\text{Bi}_2\text{Pb}_{0.27}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$ at 850°C

For $x > 0.36$ 2223 is in equilibrium with numerous other phases among which a lead containing phase ($\text{Pb}_4(\text{Sr},\text{Ca})_5\text{CuO}_d$) indicates that the maximum Pb-solubility is exceeded. For $x < 0.18$ only small amounts of 2223 are detected. Phase equilibria with predominantly 2212 are stable over the whole temperature range.

Annealing of samples at temperatures between 865 and 885°C results in no differences concerning the phase equilibria for $x = 0.45$ to 0.18 all compositions are located within a four phase region (Table 1). Figure 3 shows a BSE image of a sample at 880°C lying in the four-phase region.

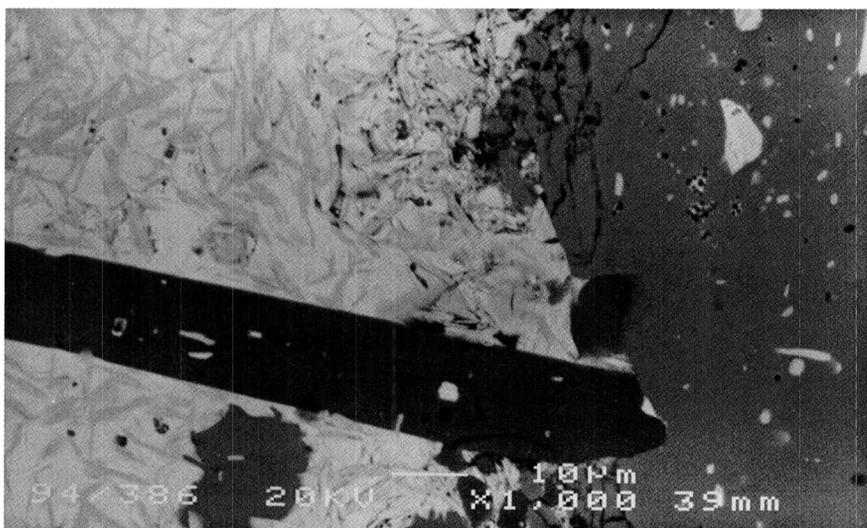
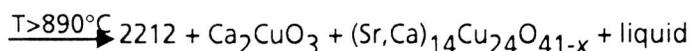
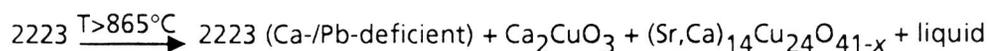


Fig. 3. BSE image of $\text{Bi}_2\text{Pb}_{0.27}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$ at 880°C (white: liquid, light grey: 2223, grey: Ca_2CuO_3 , dark grey: $(\text{Sr},\text{Ca})_{14}\text{Cu}_{24}\text{O}_{41-x}$)

Samples with $x=0.45$ to 0.18 contain no 2223 at temperatures higher than $890\text{ }^{\circ}\text{C}$. We can state the following reaction scheme:



The 2223 compositions formed with increasing temperature have no more a stoichiometry of $(\text{Bi,Pb})_{2.27}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$ and are located outside the plane under consideration. With increasing temperature the Sr content goes up and the Ca content down, moreover the Cu to (Bi,Sr,Ca,Pb) ratio goes up indicating a cation deficiency for higher temperatures.

Up to 890°C no significant changes in phase equilibria were found (Fig. 1). The decomposition of the 2223 phase happens within a temperature range of about 5 degrees. At 885°C 2223 is still detected whereas at 890°C there is no more 2223. No difference between compositions with differing Pb content could be found.

Samples with $x < 0.18$ show a completely different behavior. Over the whole temperature range 2212 is the predominating phase with small amounts of cuprates and liquid (at temperatures higher than 875°C) (Fig. 1 and Table 1). At 890°C significantly less liquid compared to compositions with $x > 0.18$ is formed indicating the transition to another phase region.

3.2. Lead Content

Microprobe analyses were performed for a composition with $x=0.27$ to document the changes in cation stoichiometry with temperature. This composition is located in the center of the homogeneity region.

850°C analysis results in the nominal composition since the sample is single phase. With increasing temperature the 2223 crystallites become Pb- and Ca-deficient.

Figure 4 shows the lead solubility of the 2223 crystallites in dependence of temperature represented by the ratio $\text{Bi}/(\text{Bi}+\text{Pb})$.

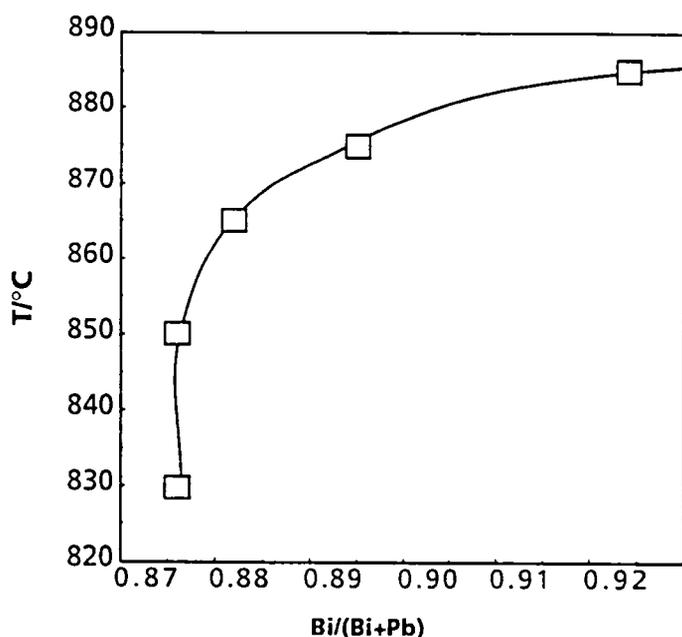


Figure 4. Pb-solubility of 2223 in dependence of temperature

4. Discussion

Regarding the homogeneity for a nominal composition of $\text{Bi}_{2.27-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$ it is remarkable that there is no lead free composition for this (Bi+Pb) content. This suggests a widening of the homogeneity range of 2223 by lead substitution. In fact, this is in accordance with the results for the lead free system where no 2223 in the vicinity of the idealized stoichiometry 2223 is found but compositions of about 2.5 223 gave high volume percentages of 2223 [1]. Thus we can regard the here presented homogeneity region as a section through the whole homogeneity region having the connection to the lead free system at Bi=2.5, i.e. out of the plane under consideration.

More experiments are necessary to assure this assumption. Nevertheless the results imply a widening of the homogeneity range to Bi-poorer compositions, compared to the lead free system with increasing Pb content.

In the considered section for compositions with $x < 0.18$ the borderline of

the homogeneity range is crossed and the compositions are in a different phase region.

The fact that the sample with $x=0.05$ shows almost no 2223 and significantly less liquid than all other compositions up to 890°C indicates a location of the sample in a different phase region. If one would assume that the compositions with $x<0.18$ are confronted with a higher kinetic barrier for 2223 formation due to less Pb than such with $x>0.18$, this barrier should be partly overcome with increasing temperature indicated by a growing 2223 content. At 890°C the samples should have comparable amounts of liquid as the compositions with $x>0.18$ since there is no kinetic barrier for liquid formation.

From these results it is possible to say that there is no continuous Pb substitution from $x=0$ to 0.36 possible for a (Bi,Pb) content of 2.27. Also for other 2223 compositions phase formation may depend on proper Pb content corresponding to a certain substitution degree. For the determination of the complete homogeneity range experiments with (Bi+Pb) content variations are in progress.

Since the lead content is also a function of temperature the 2223 preparation gets even more complicated. One has to establish for every temperature the homogeneity range as a function of Bi substitution.

5. Literature

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