Phase relationships and physical properties of Pb-doped and undoped 2212 superconductors

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In the system Bi$_2$O$_3$-SrO-CaO-CuO the phase relations were determined to elucidate the solid solution range of the Bi$_2$Sr$_2$CaCu$_2$O$_8$ phase. For the «2212» phase two separate single-phase fields exist: (a) N phase: deficient in (Sr+Ca), orthorhombic, superconducting and (b) B phase: (Sr+Ca) -stoichiometric, orthorhombic, not superconducting. Both phases occur in the same space group, Amaa or A2a, but with different wave vector modulations: (a) N : a=5.393Å, b=5.404Å, c=30.781Å, q=0.218+0.36c and (b) B : a=5.397Å, b=5.410Å, c=30.822Å, q=0.21b. The solubility limit of Pb$^{2+}$ for Bi$^{3+}$ in the solid solution Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_8$ with 0≤x≤1 is reached at x=0.35±0.03.

Key words: 2212-superconductor, phase relationships, Pb-solubility limit

Relaciones de fase y propiedades físicas de superconductores: 2212 puros y dopados con Pb

La relación de fases en el sistema Bi$_2$O$_3$-SrO-CaO-CuO fue determinada para dilucidar el rango de solución sólida de la fase Bi$_2$Sr$_2$CaCu$_2$O$_8$. Para la fase «2212» existen dos campos monofásicos: (a) Fase N: deficiente en (Sr+Ca), ortorrómbica, superconductora y (b) Fase B: aproximadamente estequiométrica en (Sr+Ca), ortorróbica, no superconductora. Ambas fases pertenecen al mismo grupo espacial, Amaa o A2aa, pero con diferentes módulos de vector de onda: (a) N : a=5.393Å, b=5.404Å, c=30.781Å, q=0.218+0.36c y (b) B : a=5.397Å, b=5.410Å, c=30.822Å, q=0.21b. El límite de solubilidad del Pb$^{2+}$ por Bi$^{3+}$ en la solución sólida Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_8$ con 0≤x≤1 es alcanzado a x=0.35±0.03.

Palabras clave: Superconductor 2212, relaciones de fase, límite de solubilidad del Plomo

1. INTRODUCTION

In the quaternary system Bi$_2$O$_3$-SrO-CaO-CuO three superconducting phases exist, described by the homologous series Bi$_2$Sr$_2$Ca$_{2-n}$Cu$_n$O$_{8+2n}$ with n=1,2,3. They are often defined by the atomic ratio of the elements Bi:Sr:Ca:Cu, by their superconducting transition temperatures or by their c-axis length: 2201 or 8K or 24Å phase, 2212 or 80K or 30Å phase and 2223 or 110K or 36Å phase.

Successful fabrication of these materials requires the knowledge of the equilibrium phase diagram of the quaternary system Bi$_2$O$_3$-SrO-CaO-CuO in order to determine the stability range of the superconducting phases. The phase relations in the subsystem Bi$_2$O$_3$-SrO-CaO-CuO have been determined and the superconducting «2201» phase, also called Raveau-phase, is stable over a wide compositional range but with a deficiency in SrO content (2,3,4). The stoichiometric «2201» phase does not show superconducting behaviour and its compositional range is very narrow: Sections of the quaternary system are investigated showing that the superconducting «2212» phase also occurs only with a deficiency in the SrO content (2,3,4). An entire description of the compositional regions of the «2212» and the «2223» phase are not performed up to now. It is well-known, however, that the addition of PbO facilitates the formation of these phases, but only a little work has been done to determine the compositional range of the Pb-doped «2212» phase.

The aim of this work is to establish the solid solution range of the «2212» phase as well as the solubility limit of Pb in the Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_8$ solid solution with 0≤x≤1.

2. EXPERIMENTAL METHOD

In order to determine the solid solution range of the Bi$_2$Sr$_2$CaCu$_2$O$_8$ phase in the four-component system it is essential to investigate the compositions of the coexisting phases in four-phase equilibria. Therefore the bulk compositions of the samples were devised accordingly. The preparation of the samples and the physical analysis are given in detail elsewhere (5).

The microstructure of the samples was investigated by SEM (CAMBRIDGE 180). The chemical composition of all phases of each sample were determined by EPMA (ARL-SEM electron microprobe) using Bi$_2$O$_3$, PbO, CaSrSiO$_3$-glass and CuO as standards. It should be noted that throughout this manuscript the formulae of all solid solutions are normalized to the conditions Bi=2 or Bi+Pb=2.
3. RESULTS AND DISCUSSION

In fig. 1 the results of the microprobe analysis of the coexisting phases of the series Bi$_2$Sr$_2$Ca$_x$Cu$_y$O$_{2n+2}$ with $n=1,2,3$ are plotted in a Bi$_2$O$_3$-(Sr+Ca)O-CoO diagram. It reveals several compositional ranges marked by A, B, N and C.

The ideal stoichiometric compositions of the 2201-, 2212- and 2223 phases, marked by solid squares, are connected by the dashed line. The solid lines are tie-lines of coexisting crystals measured in different samples. Due to the overlap of data points only a significant part of the results is presented. The obvious deviations from the ideal compositions can be described by three independent parameters $x, y, z$. The parameter $x$ is defined as the Ca/(Ca+Sr) ratio. The parameter $y$ is defined as $y = (2Cu/Bi)$. This ratio corresponds to the number of copper atoms in the formula Bi$_2$(Sr,Ca)$_{1-y}$CuO$_{4+2y}$, i.e. $y = 1$ for 2201, $y = 2$ for 2212 and $y = 3$ for the 2223 ideal composition. The parameter $z$ is defined as $z = (Cu-(Sr+Ca))$, describing the excess or deficiency of the earth alkali.

These definitions lead to the general formula: Bi$_2$(Sr$_{1-x}$Ca$_x$)$_1$Y$_{1-y}$CuO$_{4+2y}$. The different compositional ranges can be demarcated by these parameters as:

$$A \text{ phase: } 0.05 \leq x \leq 0.08, 0.95 \leq y \leq 1.08, -0.25 \leq z \leq -0.06,$$

$$R \text{ phase: } 0.08 \leq x \leq 0.71, 0.92 \leq y \leq 1.35, 0.15 \leq z \leq 0.50,$$

$$B \text{ phase: } 0.03 \leq x \leq 0.55, 1.70 \leq y \leq 2.11, -0.17 \leq z \leq 0.10,$$

$$N \text{ phase: } 0.29 \leq x \leq 0.72, 1.72 \leq y \leq 2.26, 10.10 \leq z \leq 0.32,$$

$$C \text{ phase: } 0.42 \leq x \leq 0.50, 2.25 \leq y \leq 2.91, 0.02 \leq z \leq 0.04.$$

$A$ corresponds to the monoclinic, non-superconducting 2201-phase (3) and $R$ to the orthorhombic, superconducting 2201-phase (4), deficient in (Sr+Ca). The separation of these phases is confirmed by the existence of tie-lines (fig.1). The compositional ranges determined for $A$ and $R$ are in very good agreement with the work of Roth et al. (4) and Sedmidubsky et al. (7).

The separation of the 2212 phase in a non-superconducting $B$ and superconducting $N$ phase is in the same way confirmed by tie-lines. The coexistence of $B$ and $N$ in the same sample proves that these phases are not members of a unique 2212 solid solution series. The $B$ phase can be considered as almost stoichiometric. Whereas the $N$ phase is characterized by a deficiency of (Sr+Ca) This single phase region of $N$ is in good agreement with the work of Hong et al. (8) and Rubin et al. (9). To elucidate the separation more clearly the data of the $B$ and $N$ phase are plotted in a $x$-$z$ diagram showing the effect of the variable $x$, i.e. the Ca/(Ca+Sr) ratio (fig.2). The almost horizontal tie-lines demonstrate that $x$ is nearly identical in coexisting $B$ and $N$ phases.

The different behaviour of both 2212 modifications is also manifested in different physical properties (10). In fig. 3 the temperature dependent resistance of two samples of the $B$ and $N$ phase are plotted. The $B$ phase itself exhibits the typical temperature dependence of a semiconductor and reveals no superconducting behaviour down to 7.5K. The dip in the curve below 60K is due to a small amount of superconducting $R$ phase. The coexistence of these two phases is already corroborated by the tie-line in figure 1.

In contrast, the $N$ phase is showing the typical temperature dependence of superconductive with a sharp transition to the superconducting regime $T_c$ at 97.2K, $T_c$ at 93.5K. This sample is almost pure $N$ and the $R$ (T)-measurements confirm that the $N$-phase is the well known 30A superconductor extensively investigated in recent years.

The establishment of two different 2212 modifications is also evident from X-ray powder diagrams. The patterns of the two modifications show significant differences in their peak intensities. In fig. 4 the diagrams of three different sample compositions are shown containing the nearly pure $B$ phase (i), an approximately equal mixture of $B$ and $N$ phase (ii) and the nearly pure $N$ phase (iii). A peak profile analysis discovered a splitting of all reflections in the sample with an equal mixture of $B$ and $N$. This is due to different lattice constants of the two phases thus revealing the different chemistry of these phases as seen in fig. 1 and 2. Figure 5 (i) shows the 008 reflection of the nearly pure $B$ phase (i)
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Fig. 3: Resistivity curves of B and N phase. The temperature-dependent resistivities are each normalized by their values at 300K.

Fig. 4: X-ray powder diagrams of (i) almost pure B phase, (ii) a mixture of B and N phases, (iii) almost pure N phase.

Fig. 5: 008 reflection of (i) almost pure B phase, (ii) a mixture of B and N phases, (iii) almost pure N phase. Dots: experimental points, solid lines: calculated Gaussian peak profiles. The + signs refer to reflection indices of the $5b$-superstructure.

Together with two small $5b$-superstructure reflections. In figure 5 (ii) the reflections of the B and N phase are superimposed indicating that in this sample the semiconducting B phase coexists with the superconducting N phase. Figure 5 (iii) shows the 008 reflection of the nearly pure N phase together with small superstructure reflections.

With the information of the phase relationships large single crystals of the B as well as of the N phase were grown from the melt. From X-ray precession photographs of layer 0kl the most important different feature of both 30A modifications is presented. The single crystal of the non-superconducting B phase shows a

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modulation along (010) resulting in a modulation vector of \( q = 0.21b^* \) corresponding to a 5b-superstructure (Fig. 6 (i)). The \( N \) crystal with a transition temperature of \( T_s = 83K \) exhibits a modulation along (010) and an additional modulation along (001) resulting in a modulation vector \( q = 0.21b^* + 0.36c^* \). This is clearly seen by the reflections in the vicinity of reflection (040) marked by arrows in (i). Mo Kα radiation, 2θ-filter, 40mA, 40kV, \( \phi \)-rotation (i), (ii). The splitting of the reflections in (i) occurs from a second crystal with an intergrowth parallel (001) and an azimuthal spread of the \( a \)- and \( b \)-axis of 10°. This separation into a superconducting and a non-superconducting modification as verified for the 24Å and 30Å phases is not observed for the 36Å phase, marked in figure 1 by C. The compatibility relations regarding the here defined phases in the quaternary system are described elsewhere (10).

In order to determine the solubility limit of Pb in the 2212 phase a series of samples with the formula \( Bi_{2-m}Pb_mB_{2}CaCu_{2}O_{8+\delta} \) with \( 0 < m < 1 \) was synthesized. In fig. 7, the atomic composition of the \( Bi_{2-m}Pb_mB_{2}CaCu_{2}O_{8+\delta} \) phase measured by EPMA is plotted as a function of the nominal Pb content \( m_{\text{Pb}} \). The slopes of the Bi- and Pb-curves prove a 1:1 substitution of Bi by Pb up to the solubility limit of \( x = 0.35 \pm 0.03 \); where \( x \) refers to the actual chemical composition. For higher Pb concentrations in the samples, the Pb content incorporated in the (Bi,Pb)-2212 crystals is constant. The number of Cu and Ca atoms remain constant throughout the whole range of \( m \)-values, but both atoms are significantly deficient compared to their stoichiometric proportion. For Sr, the insignificant increase for \( m = 0.0 \) up to \( m = 0.4 \) is followed by a strong decrease from 2.0 to about 1.8 atoms in the range of \( 0.4 < m < 0.8 \). This decrease appears to be due to the formation of the Pb,Sr-rich phase \( (Sr_{0.3}Ca_{0.7})_2(Pb_{0.8}Bi_{0.2})_2O_{8+\delta} \) which acts as a Sr-sink. The amount for this phase increases rapidly with increasing Pb-content \( m \) of the samples. In this series, the lower limit of the Sr-amount for the existence of the Pb-saturated Bi-2212 compound appears to be \( Sr = 1.8 \), which is reached at \( m = 0.8 \).

The data points of this series plotted in a (BiO1.5+PbO)-
(SrO+CaO)-CuO diagram are situated in the compositional range of the Pb-free N phase. This is confirmed by X-ray powder data revealing also the incorporation of Pb for Bi by the decrease of the a- and b-axis and the simultaneous increase of the c-axis up to the solubility limit (12).

4. CONCLUSIONS

For the 24Å phases A and R, for the 30Å phases B and N, and for the 36Å phase C the solid solution ranges have been determined by the investigation of the phase equilibria using the EPMA method. The two modifications B and N have been further investigated by X-ray diffraction and resistivity measurements showing that the phases have different wave vector modulations B: \( q = 0.21b^0 + 0.36c^0 \) and that B is the non-superconducting and N the superconducting modification. The substitution of Pb\(^{2+}\) for Bi\(^{3+}\) in the solid solution Bi\(_{2-n}\)Pb\(_n\)Sr\(_2\)Ca\(_2\)Cu\(_4\)O\(_{8+δ}\) with 0≤n≤1 has been investigated. Up to the solubility limit of x=0.35±0.03 Bi is 1:1 substituted by Pb.

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