Title: Synthesis, Thermal Stability, Structural Features and Electromagnetic Properties of Bi$_{2+x}$Sr$_{2-x}$CuO$_{6+d}$ (0£x£0.4)

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The thermal stability and structural modulation were studied systematically in a wide range of $0 \leq x \leq 0.4$ for the 2201 phase in the Bi-Sr-Cu-O system, $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+\delta}$, and it was found that these properties varied remarkably at $x = 0.1$. Compositions $0 \leq x \leq 0.1$ remained stable only in a narrow low $T$-high $P_0$ region and their modulation period changed stepwise, not continuously, and reversibly between 4.9b (oxidized) and 5.5b (reduced) when the oxygen content was changed only by 0.65%. In relation to this we propose for $0 \leq x < 0.1$ specifically that the change in oxygen content induces the exchange of small amounts of Bi and Sr ions between the "BiO" and "SrO" sheets. The superconductivity of the cation-stoichiometric composition ($x = 0$) was also studied as a function of oxygen content.

Keywords: Phase diagram / $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+\delta}$ / Substitution / Modulation / Superconductivity

The "2201" phase in the Bi-Sr-Cu-O system is known to adapt itself to various Bi:Sr:Cu ratios. Our previous phase diagramic study done at 840°C in the air [1] showed that the monophasic range was $0.1 < x < 0.6$ and $0 < y < x/2$ for $\text{Bi}_{2-x}\text{Sr}_x\text{Cu}_6\text{O}_{12+y}$ and that for $0 < x < 0.1$ three kinds of phases including the Bi-poorest end of the above mentioned solid solution, $\text{Bi}_x\text{Sr}_y\text{Cu}_6\text{O}_{12+y}$, and $\text{Sr}_x\text{Cu}_6\text{O}_{12+y}$ co-existed. More recently it has been reported that the solubility range is extended toward $x = 0$ at high oxygen pressures. Kato et al. successfully obtained a cation-stoichiometric sample with $x = 0$ at 840°C and $P_0 = 30$ atm, which was an over-doped metal that became a superconductor when annealed in $\text{N}_2$ [2].

In this report we will shed a new light on the relation among Bi content, oxygen content, thermal stability, and structural features of the 2201 phase by comparing behaviors of monophasic samples with $0 \leq x \leq 0.4$ systematically which were all prepared under conventional conditions like $P_0 = 1$ atm and 800°C. All the samples were prepared by an ordinary ceramic method from $\text{Bi}_2\text{O}_3$, $\text{SrCO}_3$, and $\text{CuO}$, each with a purity of 99.9%. Appropriate mixtures of these starting materials were pressed into pellets and heated at 600°C-840°C for 20h-120h in total with intermittent grinding, mixing and pelletizing processes. Three different atmospheres including an oxygen stream of 1 atm, the air, and an Ar stream of 1 atm were used. Certain samples were post-annealed in the Ar atmosphere at different temperatures between 200-700°C for 12-240h depending upon the temperature.

Cation-stoichiometric $\text{Bi}_x\text{Sr}_y\text{Cu}_6\text{O}_{12+y}$ was successfully obtained by firing the starting mixture in flowing $\text{O}_2$ first at 720°C and finally at 800°C. The tetragonal cell parameters of $a = 5.361$ Å, $c = 24.65$ Å calculated from the X-ray diffraction peaks were almost identical to those ($a = 5.37$ Å, $c = 24.65$ Å) of Kato et al.’s sample with $\delta = 0.2$ which was synthesized under $P_0 = 30$ atm and post-annealed in flowing $\text{N}_2$. We note here that small amounts of $\text{Bi}_{1-x}\text{Sr}_x\text{Cu}_6\text{O}_{12+y}$ and others were detected after a further treatment at 820°C, showing the stability of $\text{Bi}_2\text{Sr}_2\text{CuO}_{4+\delta}$.

### SOLID STATE CHEMISTRY — Quantum Spin Fluids—

**Scope of research**

Quantum oxide systems such as high-$T_c$ superconducting cuprates, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and a spin-ladder, $(\text{Sr,Ca})_x\text{Cu}_2\text{O}_4$ are synthesized in the form of single crystals using traveling-solvent-floating-zone and laser abrasion techniques. Detailed equilibrium phase diagram of Bi cuprate systems is investigated. Main subjects and techniques are: mechanism of high-$T_c$ superconductivity: origin of quantum phase separation in strongly correlated electron systems: spin excitations in quantum spin systems: interplay between spin and charge flow in doped spin systems: neutronsscattering by using triple-axis as well as time-of-flight techniques.
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In the air and at 800°C annealed at 400°C treatments as can be seen most typically for the sample  

Monophasic samples with higher Bi contents of 0 < x ≤ 0.4 were also prepared at both (T°C, Po2/atm) = (800, 1) and (730, 0.2). The composition dependences of the lattice parameters, a and c, are plotted in Fig. 3. As Bi content increases from x = 0 to 0.4, the c parameter decreased by 0.8%, while a increased by 0.6%. In further detail, the c parameter showed a small jump at x = 0.1 and, at the same time, the slope, da/dx, became sharper for 0.1 ≤ x. This anomaly concerning the lattice parameters is one of the several features that separate the composition range of 0 ≤ x ≤ 0.4 into two with a border line at x = 0.1.

In parallel to this, the thermal stability examined at Po2 = 0.2 atm and 1 atm also showed a gap at x = 0.1. Saying typically, the decomposition temperature was as high as 880°C for x = 0.125 in the air but it dropped to ~780°C for x = 0.10 in the same atmosphere.

It is well-known that the 2201 structure is incommensurately modulated with its wave vector, q, lying in the b* c* plane. We found the same type of modulation in all the present samples by means of XRD and TEM. The coefficients b and c of the vector q = b b* + c c* showed an interesting stepwise composition dependence again at x = 0.1. These coefficients were evaluated from the XRD data using the following equation

\[ 1/d_{hkl}^2 = 4\pi^2/(k+mb)^2 (l+mc)^2, \]

where \( d_{hkl} \) stands for the d value of a superlattice peak (hkl, ±m). We obtained a set of parameters (a=b /Å, c /Å, b, c) = (5.361, 24.65, 0.205, 0.455) from the XRD pattern for the x = 0 sample prepared at 800°C and Po2 = 1 atm.

Through a cyclic treatment of the former sample at 730°C in the air and at 800°C in flowing O2, we noticed that the change was quite reversible. We further noticed that b and c were changed stepwisely, not continuously, from (b, c) = (0.205, 0.455) to (0.185, 0.288) by reducing treatments as can be seen most typically for the sample annealed at 400°C in Ar (see Fig. 3). These two types are mixed in samples annealed under intermediate conditions like 730°C in the air. There seems no doubt that a slight change in oxygen content switches the modulation mode from one to the other, without changing the a and c parameters remarkably.

We conducted TEM observations on the two typical samples with x = 0, one as-prepared in O2 and the other annealed in Ar at 200°C (b), 400°C (c), and 600°C (d).

![Figure 1. Temperature-oxygen pressure diagram with a border line below which the cation-stoichiometric composition remains stable. The closed squares are the present data and the open square is from ref. 2.](image1)

![Figure 2. Composition dependence of the subcell lattice parameters. The triangles are for the samples prepared at 800°C in O2, and the circles are for those prepared at 730°C in the air.](image2)

![Figure 3. Partial enlargements of the XRD patterns of Bi2Sr2CuO6+x as-prepared in O2 at 800°C (a), post-annealed in Ar at 200°C (b), 400°C (c), and 600°C (d).](image3)

**References**