Synthesis, Thermal Stability, Structural Features and Electromagnetic Properties of $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ ($0 \leq x \leq 0.4$)

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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, $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$, and it was found that these properties varied remarkably at $x \approx 0.1$. Compositions $0 \leq x < 0.1$ remained stable only in a narrow low T- high Po_2 region and their modulation period changed stepwisely, 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 / $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ / Substitution / Modulation / Superconductivity

The "2201" phase in the Bi_2O_3-SrO-CuO 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 $Bi_{2+x}Sr_{2-x}Cu_{1+y}O_z$ and that for $0 \leq x \leq 0.1$ three kinds of phases including the Bi-poorest end of the above mentioned solid solution, $Bi_{17}Sr_{16}Cu_7O_z$, and $Sr_{14}Cu_{24}O_{41}$ coexisted. 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 $Po_2 = 30$ atm, which was an over-doped metal that became a superconductor when annealed in 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 $Po_2 = 1$ atm and 800°C.

All the samples were prepared by an ordinary ceramic method from Bi_2O_3, $SrCO_3$, and 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 $Bi_2Sr_2CuO_{6+\delta}$ was successfully obtained by firing the starting mixture in flowing 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 $Po_2 = 30$ atm and post-annealed in flowing N_2. We note here that small amounts of $Bi_{17}Sr_{16}Cu_7O_z$ and others were detected after a further treatment at 820˚C, showing the stability of $Bi_2Sr_2CuO_{6+\delta}$

SOLID STATE CHEMISTRY — Quantum Spin Fluids—

Scope of research

Quantum oxide systems such as high-T_c superconducting cuprates, $La_{2-x}Sr_xCuO_4$ and a spin-ladder, $(Sr,Ca)_{14}Cu_{24}O_{41}$ 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 exitations in quantum spin systems: interplay between spin and charge flow in doped spin systems: neutronscattering by using triple-axis as well as time-of-flight techniques.

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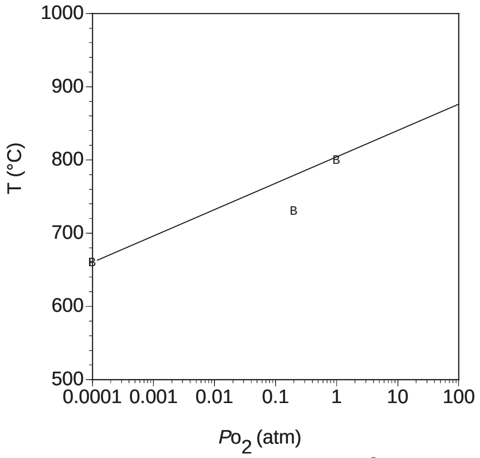

Figure 1. Temperature-oxygen pressure diagram with a border line below which the cation-stoichiometric composition remains stable. The closed squares are the present data and the open square is from ref. 2.

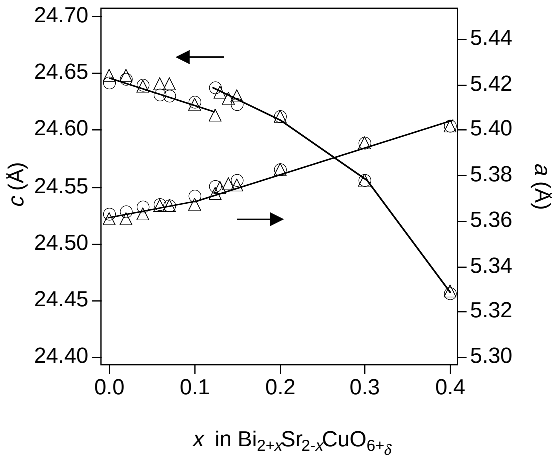

Figure 2. Composition dependence of the subcell lattice parameters. The triangles are for the samples prepared at 800°C in O_2, and the circles are for those prepared at 730°C in the air.

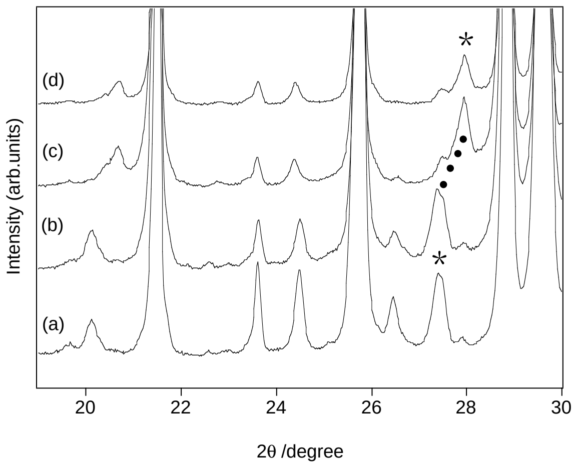

Figure 3. Partial enlargements of the XRD patterns of $Bi_2Sr_2CuO_{6+\delta}$ as-prepared in O_2 at 800°C (a), post-annealed in Ar at 200°C (b), 400°C (c), and 600°C (d).

being limited to $T \leq 800$˚C at $Po_2 = 1$ atm.

We tested the synthesis at a lower oxygen pressure as follows. Shown in Fig. 1 is a Po_2-T diagram with a border line below which the cation-stoichiometric composition remains stable.

Monophasic samples with higher Bi contents of $0 < x \leq 0.4$ were also prepared at both (T/˚C, Po_2/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 $x \approx 0.1$ and, at the same time, the slope, d*a*/d*x*, became sharper for $0.1 \leq x$. This anomaly concerning the lattice parameters is one of the several features that separate the composition range of $0 \leq x \leq 0.4$ into two with a border line at $x \approx 0.1$.

In parallel to this, the thermal stability examined at $Po_2 = 0.2$ atm and 1 atm also showed a gap at $x \approx 0.1$. 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_m and c_m of the vector $q = b_m b^* + c_m c^*$ showed an interesting stepwise composition dependence again at $x \approx 0.1$. These coefficients were evaluated from the XRD data using the following equation

$$1/d_{hklm}^2 = h^2/a^2 + (k+mb_m)^2/b^2 + (l+mc_m)^2/c^2, \quad (1)$$

where d_{hklm} stands for the *d* value of a superlattice peak (hkl, $\pm m$). We obtained a set of parameters ($a=b$ /Å, c /Å, b_m,c_m) = (5.361, 24.65, 0.205, 0.455) from the XRD pattern for the $x = 0$ sample prepared at 800°C and $Po_2 = 1$ atm.

Through a cyclic treatment of the former sample at 730°C in the air and at 800°C in flowing O_2 we noticed that the change was quite reversible. We further noticed that b_m and c_m were changed stepwisely, not continuously, from (b_m, c_m) = (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 O_2 and the other annealed in Ar at 600°C. The modulation wavelength varied from $\lambda = 4.9b$ for the as-prepared sample to $\lambda = 5.5b$ for the annealed one, which are consistent with the XRD results of $\lambda = 4.88b$ ($= b/0.205$) and $5.41b$ ($= b/0.185$), respectively.

From the resistance and magnetization measurements it has heen revealed that it is only the portion with (b_m, c_m) = (0.185, 0.288) that is superconducting but the portion with (b_m, c_m) = (0.205, 0.455) is an over-doped metal.

References

1. Y. Ikeda, H. Ito, S. Shimomura, Y. Oue, K. Inaba, Z. Hiroi, M. Takano, Physica C, **159**, 93 (1989).
2. M. Kato, K. Yoshimura, K. Kosuge, Physica C, **177**, 52 (1991).