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New oxide superconductors in the Sr–Bi–Cu–O system

KEIJI MOROISHI*, AKIHISA INOUE, KUNIO MATSUZAKI,
TSUYOSHI MASUMOTO
Institute for Materials Research, Tohoku University, Sendai 980, Japan

New oxide superconductors in the Sr–Bi–Cu–O system were prepared by the conventional processing techniques consisting of mixing, pressing and sintering. The compositions of the superconductors are located in a range surrounded by CuO, $SrCu_2O_3$ and $Sr_{0.9}Bi_{1.1}O_{2.55}$. No distinct compositional change in the critical temperature, T_c, is observed and the value is 8 to 9 K at onset and 4 to 5 K at zero resistance. The zero resistance value increases on replacement of strontium by sodium or potassium which have different atomic valences and a nearly equal ionic radii compared to strontium, accompanied by an increase in the positive slope of electrical resistance and reaches a maximum value of 6.7 K for $Sr_{0.9}Na_{0.1}Bi_1Cu_2O_{4.45}$ and 5.9 K for $Sr_{0.9}K_{0.1}Bi_1Cu_2O_{4.45}$. The further increase in sodium and potassium content brings about the disappearance of superconductivity, along with an extreme increase in the negative slope of electrical resistance. The increase in T_c for the Sr–Bi–Cu oxides with the replacement by sodium or potassium is probably because the replacement gives rise to a change in the valence of copper atoms and/or the formation of an oxygen-deficient structure.

1. Introduction

Since the discoveries of the new type of oxide superconductors with high critical temperatures (T_c) of 30 to 95 K in the La–Ba–Cu–O[1] and Y–Ba–Cu–O[2, 3] systems, oxide superconductors have attracted extremely great interest owing to the expectation of the appearance of a superconductor with T_c in the vicinity of room temperature. Most recently, an oxide in the Y–Ba–Cu–Sr system has been reported to show zero resistance at 338 K, even though definite confirmation of the high-temperature superconductivity was not always carried out [4]. Additionally, some concepts have been proposed of the mechanism of the high T_c superconductivity for the lanthanide-based oxides, but the details of the mechanism are at present unsolved. Research to find a new oxide superconductor in different component systems is very important from the materials science and engineering points of view. It is expected to provide useful information for the construction of a more detailed mechanism of the high T_c superconductivity for the lanthanide-based oxides. We have found a new type of oxide superconductor with zero resistance at about 5 K in the Sr–Bi–Cu–O system. This paper attempts to clarify the compositional range and superconductivity of Sr–Bi–Cu–O superconductors and the change of T_c on replacement of strontium by the alkaloid group elements lithium, sodium or potassium.

2. Experimental procedure

Powders of $SrCO_3$ (96 wt %), Bi_2O_3 (99.9999 wt %) and CuO (98 wt %) were mixed in the desired proportions. The mixtures were presintered at 1073 K for 2 h in air and then crushed. The presintering and crushing treatment was repeated twice and then the mixtures were pressed at an applied pressure of 500 MPa for 20 min to produce pellets of 10 mm diameter and 1 to 2 mm thick. Subsequently, the pellets were sintered at 1073 K for 18 h in air and cooled to room temperature in the furnace. The structure of the synthesized oxides was examined by X-ray diffraction analysis with monochromatic Cu$K\alpha$ radiation. Resistance measurement was made by the four-point method over the temperature range 4.2 to 293 K. Electrical contact was made with the sample using conducting carbon paste. The temperature was measured using a calibrated platinum thermometer in the temperature range studied with an accuracy better than ± 0.1 K. Additionally, in order to clarify the effect of alkaloid elements (R = Li, Na and K) on the structure and superconductivity of $R_xSr_{1-x}Bi_1Cu_2O_{4.5-0.5x}$ ($x = 0.05$, 0.1 and 0.2), the R–Sr–Bi–Cu oxides were also synthesized through the same process using K_2CO_3 (99.5 wt %) and Na_2CO_3 (99.5 wt %).

3. Results and discussion

Fig. 1 shows the compositional dependence of electrical conductivity for Sr–Bi–Cu oxides. It is notable that the superconductors are formed in a wide range of strontium to bismuth ratio above 1 and below 40 mol % Sr and the deviation of composition from this range brings about the change from superconductor to insulator through semiconductor. As examples, Fig. 2 shows the temperature dependence of normalized

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*Permanent address: Research and Development Laboratories, Hoya Corporation, Akishima Tokyo 196, Japan.

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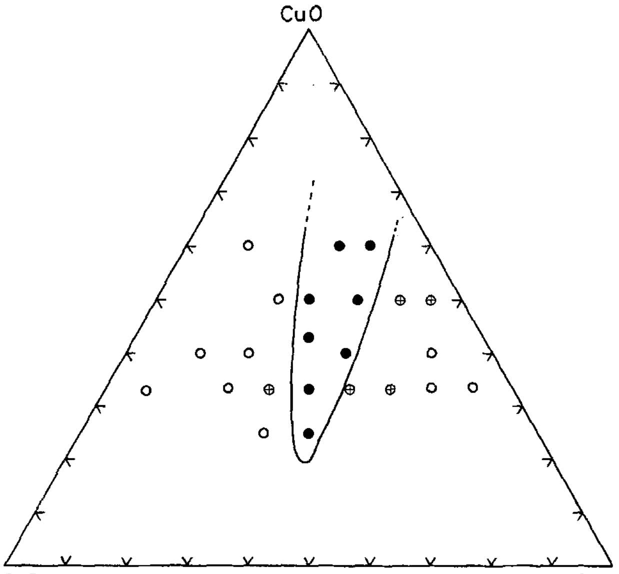

Figure 1 Compositional range for the formation of superconducting Bi–Sr–Cu oxides. (●) Superconductor, ⊕ semiconductor, ○ insulator.

electrical resistance, R/R_{293}, for superconducting $Sr_1Bi_1Cu_2O_{4.5}$ and $Sr_2Bi_1Cu_3O_{6.5}$ oxides. The oxygen concentrations represent nominal weighed values. The former oxide exhibits superconductivity with onset at 8.5 K and zero resistance at 5.0 K. The other Sr–Bi–Cu oxides with compositions marked by ● in Fig. 1 also showed the onset of superconductivity in the range 7.8 to 8.8 K, nearly the same as that for $Sr_1Bi_1Cu_2O_{4.5}$, and no distinct change in the onset T_c with composition was seen in spite of the significant change in composition.

Fig. 3 shows the X-ray diffraction patterns of $Sr_{0.8}Bi_{1.2}Cu_2O_{4.6}$, $Sr_1Bi_1Cu_2O_{4.5}$, $Sr_{1.6}Bi_{0.4}Cu_2O_{4.2}$ and $Sr_2Bi_1Cu_3O_{6.5}$ oxides. Although the diffraction patterns could not be definitely identified, one can notice the feature that the pattern of $Sr_1Bi_1Cu_2O_{4.5}$ exhibiting superconductivity has two sharp peaks at 29° and 30° and splitting of the peak at about 47°. If only the high intensity peaks are indexed, the superconductors are analysed to consist of the three phases of monoclinic CuO, tetragonal $Sr_{0.9}Bi_{1.1}O_{2.55}$, and $SrCu_2O_3$ with an undetermined structure. As shown in Fig. 4, the superconductors in the Sr–Bi–Cu–O system are located within the triangle consisting of CuO, $Sr_{0.9}Bi_{1.1}O_{2.55}$ and $SrCu_2O_3$. The problem whether the superconductivity originates from an unidentified Sr–Bi–Cu–O single phase or the three mixed phases remains unsolved, and clarification of the crystal structure is in progress using anomalous X-ray scattering with synchrotron radiation.

It has previously been reported [5] that the superconducting transition of $BaPb_{1-x}Bi_xO_3$ becomes sharper on replacement of barium by about 0.1 to 0.2 mol % K. As the T_c values of the Sr–Bi–Cu oxides are nearly the same as those of $BaPb_{1-x}Bi_xO_3$, the replacement of strontium by the alkaloid elements lithium, sodium and potassium for the Sr–Bi–Cu oxides is expected to bring about a similar enhancement of superconductivity. Fig. 5 shows the change in the normalized electrical resistance, R/R_{293}, for $K_xSr_{1-x}Bi_1Cu_2O_{4.5-0.5x}$ with the replacement by potassium. Replacement by about 0.05 to 0.1 mol % K gives rise to an increase in T_c at zero resistance from 5.0 to 5.9 K, accompanied by an increase in the positive temperature dependence of normal resistance. A further increase in the amount replaced to 0.2 mol % results in a drastic change of metallic conductive state with superconductivity to the semiconductive state.

Fig. 6 shows the change in the X-ray diffraction patterns of $K_xSr_{1-x}Bi_1Cu_2O_{4.5-0.5x}$ with potassium content. The peak position and intensity of the patterns are similar, among the samples with $x = 0$, 0.05 and 0.1, but different from that for the sample with $x = 0.2$, indicating that the replacement of strontium by more than 0.2 mol % K brings about the precipitation of the other phase.

Fig. 7 shows the normalized resistance, R/R_{293}, as a function of temperature for $Sr_{0.9}R_{0.1}Bi_1Cu_2O_{4.45}$ with different R (R = Li, Na and K) elements. It is notable that replacement of strontium by sodium gives rise to a further increase in T_c with zero resistance to 6.7 K, accompanied by a further increase in the positive slope of electrical resistance. On the other hand, the lithium-containing oxide exhibits a large negative temperature dependence of resistivity, and no trace of superconductivity is detected at temperatures above 4.2 K.

In order to investigate the reason for the difference in superconductivity between sodium or potassium and lithium elements, the structure of the oxides was

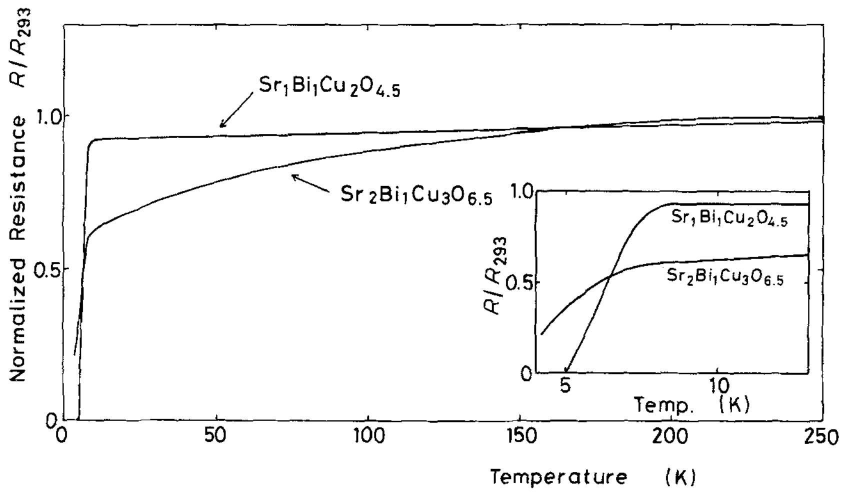

Figure 2 Normalized electrical resistance, R/R_{293}, as a function of temperature for $Sr_1Bi_1Cu_2O_{4.5}$ and $Sr_2Bi_1Cu_3O_{6.5}$.

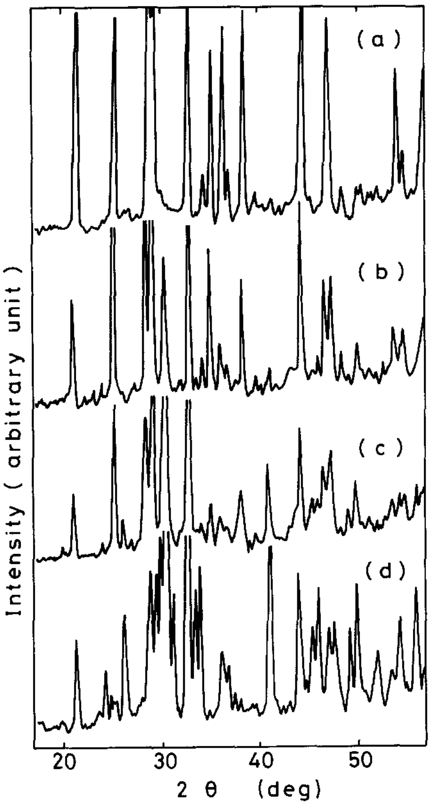

Figure 3 X-ray diffraction patterns of (a) $Sr_{0.8}Bi_{1.2}Cu_2O_{4.6}$, (b) $Sr_1Bi_1Cu_2O_{4.5}$, (c) $Sr_2Bi_1Cu_3O_{6.5}$ and (d) $Sr_{1.6}Bi_{0.4}Cu_2O_{4.2}$.

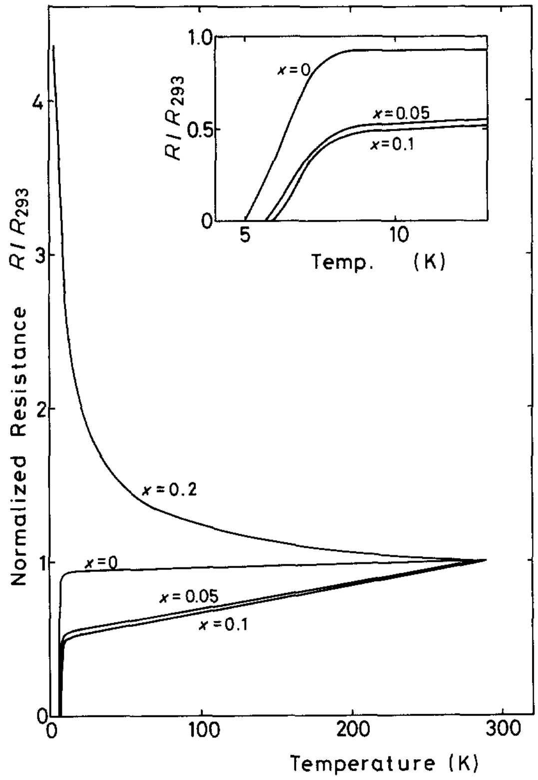

Figure 5 Change in normalized electrical resistance, R/R_{293}, of $K_xSr_{1-x}Bi_1Cu_2O_{4.5-0.5x}$ with the replacement of strontium by potassium.

examined by X-ray diffractometry. As shown in Fig. 8, the feature of the patterns for the oxides containing potassium or sodium resembles that for the Sr–Bi–Cu oxides, while the lithium-containing oxide has a significantly different diffraction pattern and its feature agrees with that for the samples containing more than 0.2 mol % K. Table I summarizes the ionic radius, the difference in ionic radius against strontium, and dissociation energy for lithium, sodium, potassium and strontium elements. The ionic radii were taken from the values of six-fold ions represented by Shannon and Prewitt [6]. The table allows us to make the following interpretation. (1) The ionic radius of sodium leading to the highest T_c value is very close to that of strontium and is the most favourable to replace the strontium site. (2) The ionic radius of lithium is too small to replace the strontium site and the resultant

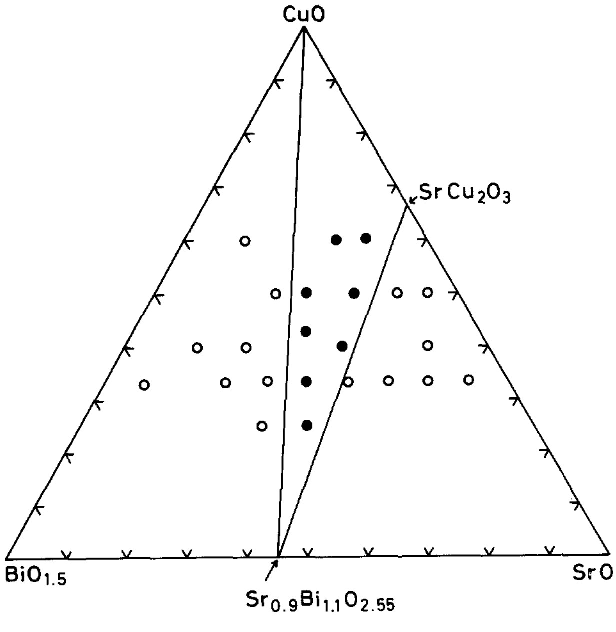

Figure 4 Correlation between the compositional range from the formation of superconducting Sr–Bi–Cu oxides and the component oxide phases of the Sr–Bi–Cu–O superconductors. (●) Superconductor, (○) semiconductor, insulator.

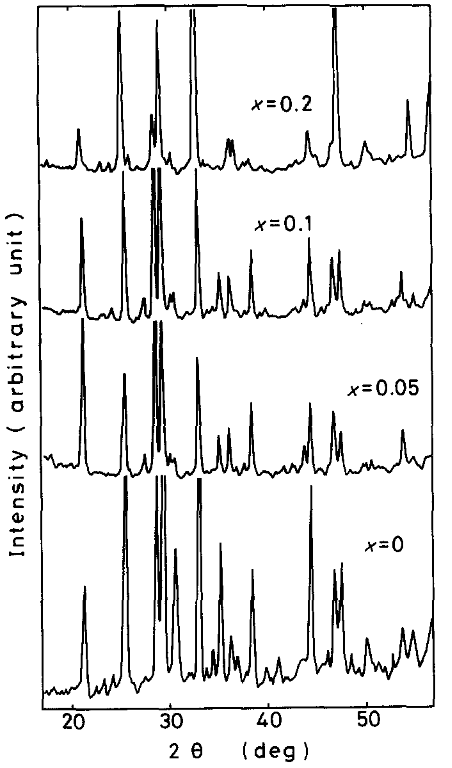

Figure 6 Change in X-ray diffraction patterns of $K_xSr_{1-x}Bi_1Cu_2O_{4.5-0.5x}$ with the replacement of strontium by potassium.

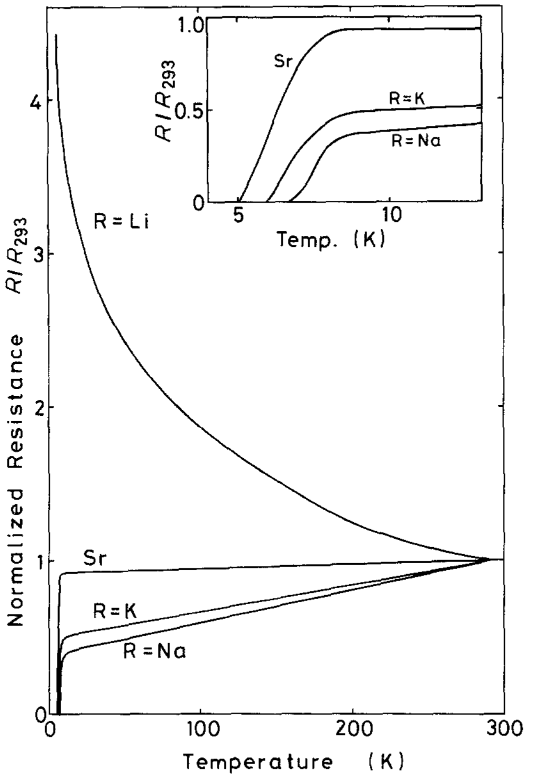

Figure 7 Normalized electrical resistance, R/R_{293}, as a function of temperature for $Sr_1Bi_1Cu_2O_{4.5}$ and $Sr_{0.9}R_{0.1}Bi_1Cu_2O_{4.45}$ (R = Li, Na or K).

structure is very unstable because of an increase in the potential energy. (3) Because the dissociation energy of lithium is larger than that of the other elements, it is thought that the bonding strength with oxygen atoms is the largest for lithium, and the formation of other types of oxide containing lithium is more favourable from the thermodynamic point of view.

Finally we shall consider the reason for the enhancement of T_c for the Sr–Bi–Cu oxides with the replacement of strontium by potassium or sodium. When a divalent strontium atom is replaced by a monovalent alkaloid atom, the balance of electrical charge in the oxide breaks down, leading to a shortage of positive electrical charge. In order to compensate for this shortage, it is presumed that the ionic state of the transition copper metal changes from Cu^{2+} to Cu^{3+} and/or O^{2-} ions are dissipated from the oxide crystal so as to form an oxygen-deficient structure. Further detailed investigation of the atomic configuration and electronic state of the Sr–R–Bi–Cu oxides will shed light on the appropriateness of the presumption. Within the present data, we may conclude that the replacement of strontium by the alkaloid elements with a different valence and a nearly equal ionic radius, is effective in enhancing the T_c value for the Sr–Bi–Cu oxides.

TABLE I Ionic radius, difference in ionic radius compared to strontium and dissociation energy for lithium, sodium, potassium and strontium [6, 7].

	Ionic radius (nm)	Difference in ionic radius (nm)	Dissociation energy (kcal mol^{-1})
Lithium	0.074	0.042	288
Sodium	0.102	0.014	240
Potassium	0.138	0.022	230
Strontium	0.116	–	256

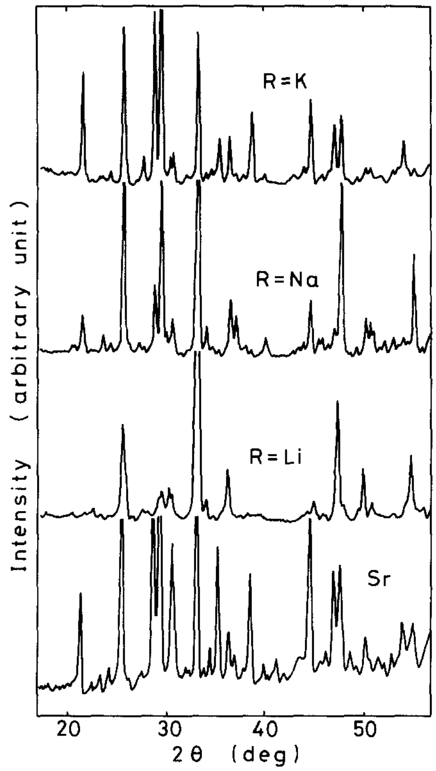

Figure 8 X-ray diffraction patterns of $Sr_1Bi_1Cu_2O_{4.5}$ and $Sr_{0.9}R_{0.1}Bi_1Cu_2O_{4.45}$ (R = Li, Na or K).

4. Conclusion

Electrical conductivity of oxides in the Sr–Bi–Cu–O system synthesized by mixing, pressing and sintering processes was examined in the temperature range 4.2 to 293 K. The oxides with compositions in the range surrounded by CuO, $Sr_{0.9}Bi_{1.1}O_{2.55}$ and $SrCu_2O_3$ were found to exhibit superconductivity at temperatures above 4.2 K. T_c values are in the range 8 to 9 K at onset and 4 to 5 K at zero resistance, and no distinct compositional dependence is observed. The replacement of strontium by alkaloid elements sodium or potassium gives rise to an increase in T_c and the highest T_c values at onset and zero resistance are 8.9 and 6.7 K, respectively, for $Sr_{0.9}Na_{0.1}Bi_1Cu_2O_{4.45}$, and 8.9 and 5.9 K, respectively, for $Sr_{0.9}K_{0.1}Bi_1Cu_2O_{4.45}$. A further increase in sodium or potassium content brings about the disappearance of superconductivity, accompanied by a significant structural change. No superconductivity at temperatures above 4.2 K was detected for $Sr_{0.9}Li_{0.1}Bi_1Cu_2O_{4.45}$. The reason for the increase in T_c on addition of sodium or potassium was discussed in terms of ionic radius and dissociation energy and interpreted on the basis of the concept that the replacement of strontium by sodium or potassium, which have ionic radii nearly equal to that of strontium and a monovalent nature, brought about the change in the valence of the copper atom from divalent to trivalent and/or the formation of an oxygen-deficient structure resulting from the dissipation of O^{2-} ions.

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