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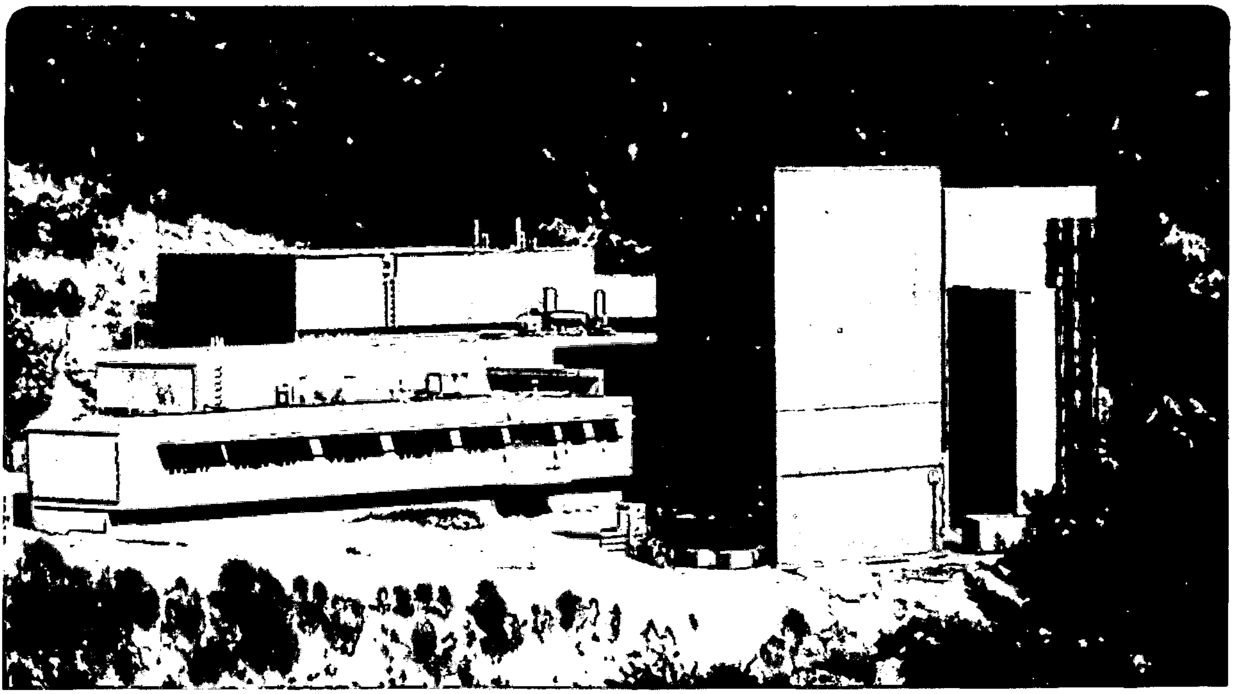
December 1990



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Superconductivity and Chemical Composition of the High-T_c Phase (T_c~111K) in the Sb-Pb-Bi-Sr-Ca-Cu-O System

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A superconducting phase with a critical temperature of 111K in the Sb-Pb-Bi-Sr-Ca-Cu-O system has been synthesized by means of a long firing period. Its crystal structure is similar to the high-T_c phase (107K) in the Pb-Bi-Sr-Ca-Cu-O system, and its average chemical composition is 4.3%, 2.6%, 19.2%, 21.4%, 15.8% and 36.9% for Sb, Pb, Bi, Sr, Ca and Cu, respectively. The summation of the Sb concentration and the Ca concentration is approximately the same for all the samples of this phase, implying that Sb substitutes for Ca, and oxygen atoms are introduced to compensate the oxygen deficiency in the central Cu-O layer sandwiched by the two Ca layers in the crystal structure of the high-T_c phase.

KEYWORDS:

superconductor,
Sb-Pb-Bi-Sr-Ca-Cu-O system,
chemical composition,
energy dispersive X-ray spectroscopy,
electrical resistivity,
magnetic susceptibility,
X-ray powder diffraction

§1. Introduction

Since the discovery of the high-T_C superconductor in the Bi-Sr-Ca-Cu-O system,1) various dopants have been tried to increase the critical temperature. The addition of Pb has been confirmed to increase the volume fraction of the high-T_C phase (T_C~107K).2-6) Recently, it has been reported that the samples with large amount of Pb have the critical temperatures above 110K.* It has also been reported that the substitution of Sb and Pb for Bi in $Bi_2Sr_2Ca_2Cu_3O_x$ increases the endpoint critical temperature ($T_{c,\,end}$) to 132K.7) In addition, it has been reported that the substitution of only Sb for Bi also increases the $T_{c,end}$ to the same temperature.8) Hongbao et al. have reported that they observed three jumps in diamagnetic signals around 90K, 115-125K and 135-140K. They observed that the 135-140K phase was so unstable that the temperature of zero resistance was decreased to 112K after thermal cycling between 77K and room temperature.

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*Jun Takada, Hitoshi Kitaguchi, Kiichi Oda, Yoshinari Miura, Hiromasa Mazaki, Hiroyuki Ito, Yasunori Ikeda and Mikio Takano: submitted to Funtai oyobi Funmatsuyakin [in Japanese].

Many studies have been attempted to confirm the results about the Sb substitution.9-18) No research group except the above mentioned groups, however, has succeeded in obtaining a critical temperature above 110K. The chemical compositions and the crystal structures of those phases having critical temperatures of 115-125K and 135-140K have not been reported yet. In order to clarify the chemical composition and the role of the Sb atom in the phases with T_C higher than 110K, we studied the superconductivity and the chemical composition of the high-T_C phase in the Sb-Pb-Bi-Sr-Ca-Cu-O system.

§2. Experimental

A sample with nominal composition $Sb_{0.10}Pb_{0.50}Bi_{1.40}Sr_{2.00}Ca_{2.00}Cu_{3.00}O_x$ (sample A) was prepared by a solid-state reaction in air. The starting materials were high-purity powders of Sb_2O_3, PbO, Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO. These powders were mixed, pressed into pellets, calcined at 820°C for 5 hours, fired at 865°C for 504 hours and then cooled at a rate of 50°C/h to room temperature. Another sample with nominal composition $Pb_{0.46}Bi_{1.80}Sr_{1.88}Ca_{2.06}Cu_{3.00}O_x$ (sample B) was prepared by a sol-gel process using citric salts to compare its superconducting response with sample A. The starting materials were high-purity powders of PbO, Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO, which were dissolved into nitric acid. The resulting solution was mixed with citric acid and ethylene glycol and then heated to obtain a blue gel. The gel thus obtained was calcined at 800°C for 30 minutes, ground, pressed into a pellet and fired at 850°C for 420 hours in air.

X-ray powder diffraction measurements were carried out using a Philips 1700 diffractometer with CuKα radiation. Electrical resistivity was measured by the standard dc four-terminal method. Magnetic susceptibility was measured using a S.H.E. SQUID magnetometer in a magnetic field of 20 gauss.

For energy dispersive X-ray spectroscopy (EDS), the specimen was crushed, ground, dispersed in n-propanol and spread onto a holey carbon film suspended by a beryllium mesh grid. EDS was carried out for sample A using a JEM-200CX analytical electron microscope operated at 200kV, equipped with a Kevex system 8000 spectrometer. In order to confirm that the observing parts of the specimen for EDS were superconducting crystals with no other phases, crystal forms and selected area electron diffraction patterns were observed. Figure 1 shows a typical crystal form of the superconducting crystal chosen for EDS and its selected area electron diffraction pattern. Superconducting crystals having the plate-like morphology with small thicknesses like Fig. 1(a) were chosen for EDS. The high-T_C phase with Sb has a modulated structure with b-axis wavelengths 26.9Å and 36.1Å like Fig. 1(b) as reported by the authors.** On the other hand, the high-T_C phase without Sb has a modulated structure with b-axis wavelengths 27Å and 45-54Å. The chemical composition of the each crystal was calculated by the deconvolution procedure with the intensities of the SbLα, PbLα, BiLα, SrKα, CaKα and CuKα radiations.

**Naoto Kijima, Ronald Gronsky, Hozumi Endo, Yasuo Oguri, Steffen K. McKernan and Alex Zettl: submitted to Appl. Phys. Lett.

The microstructures of the samples were observed by means of a JXA-8600 electron probe microanalyser (EPMA) operated at 15kV. For this analysis, the fired samples were wet-polished and deposited with carbon. The chemical compositions were calculated by the Z-A-

F correction method on the basis of the data which were measured by the wavelength dispersive X-ray analysis.

§3. Results and Discussion

Figure 2 shows the temperature dependence of the electrical resistivity of samples A and B. The $T_{c,end}$ of sample A is 110K, which is 5K higher than that of sample B. The $T_{c,mid}$ of sample A is 112K, which is 5K higher than that of sample B. Note that a decrease in the electrical resistivity about 132K is not observed; nevertheless, an increase of 5K in critical temperature is apparently observed for the Sb-containing sample (sample A). The difference between the two critical temperatures is not within the error of the temperature measurement.

Figure 3 shows the temperature dependence of the magnetic susceptibility of both samples. Diamagnetism is observed below 111.3K for sample A and 107.3K for sample B, showing that sample A has a 4K higher critical temperature than sample B. These results imply that Sb substitutes some of the atomic positions in the superconducting crystal and affects the superconductivity.

Hongbao et al.$^{7)}$ reported that there are two stable superconducting phases with critical temperatures of 90K and 115-125K in this system. Based upon our data, the superconductor synthesized in this research appears to be the same as one of the superconducting phases that they synthesized in the same system.

Figure 4 shows the X-ray powder diffraction patterns of sample A and sample B. The diffraction pattern of sample A is similar to that of sample B except for peaks around 30° in 2θ and other minor peaks. The low-T_c phase (T_c~80K) is not observed in either of the diffraction patterns. The data show that the high-T_c phase (T_c ~107K) is the sole precipitate in sample B without any other phases. Since the diffraction pattern of sample A consists of the same peaks as the high-T_c phase in the diffraction pattern of sample B, the crystal structure of the superconducting phase in sample A appears to be close to that of the high-T_c phase in the Pb-Bi-Sr-Ca-Cu-O system. If we assume that the superconducting crystal in sample A belongs to the orthorhombic system, the lattice parameters are a=5.411(1)Å, b=5.411(1)Å and c=37.22(6)Å, which are close to those of the high-T_c phase (107K) in the Pb-Bi-Sr-Ca-Cu-O system[19)] except for the slightly longer c-axis parameter. Even though the atomic radius of the Sb^{3+} ion is smaller than that of the other ions in the system, the cell volume of the high-T_c phase (T_c~111K) in the Sb-Pb-Bi-Sr-Ca-Cu-O system is close to that in the Pb-Bi-Sr-Ca-Cu-O system.

In order to determine the mean value of the chemical composition of the high-T_c phase (T_c ~111K), several EDS measurements were carried out for many crystals in sample A. Figure 5 shows the atomic concentrations of 17 superconducting crystals within sample A. The atomic concentrations of Pb, Bi, Sr and Cu are nearly the same for all the crystals; however, the atomic concentrations of Sb and Ca in the crystals from No.1 to No.4 are slightly different than those from No.5 to No.17. The crystals from No.5 to No.17 (Sb-rich crystals) have more Sb and less Ca than the crystals from No.1 to No.4 (Sb-poor crystals). Significantly, as the Sb concentration is increased, the Ca concentration is decreased. Furthermore since the sum of the Sb concentration and the Ca concentration is the same (or very nearly so) for all the crystals, it is suggested that Sb substitutes for Ca in the crystal. The results are not coincident with those analyzed with EDS by Xu et al.[20)] They concluded that Sb cannot be doped into the high-T_c phase but goes into a new phase with the average composition $Bi_{32}Pb_3Sb_7Sr_{29}Ca_{23}Cu_7O_x$. This phase is considered identical with an amorphous-like phase with the composition $Sb_{0.5}Bi_{2.0}Sr_{1.6}Ca_{1.0}Cu_{0.4}O_x$ observed in sample A as mentioned below. Since the modulated structure of the high-T_c phase in the Sb-Pb-Bi-Sr-Ca-Cu-O system is different than that in Pb-Bi-Sr-Ca-Cu-P system, Sb may occupy some of the atomic sites in the high-T_c phase.

As for the measurements of the chemical composition by EDS, we observed the intensities of SbLα and CaKα radiations of which X-ray energies ($SbL\alpha_1$: 3.605keV and $CaK\alpha_1$: 3.691keV, respectively) are close to each other as shown in Fig. 6. Since crystal No.13 contains more Sb than crystal No.3, the width of the peak about 3.7keV of spectrum 13 in Fig. 6(b) is much broader than that of spectrum 3 in Fig. 6(a) because of the overlapping of the SbLα and CaKα radiations. The deconvolution curves for SbLα and CaKα radiations are clearly obtained for Sb-rich crystal No.13 in Fig. 6(b); however, the Sb concentration of the Sb-poor crystal is too small to determine the Sb concentration by the deconvolution method as shown in Fig. 6(a).

Table 1 shows the mean values of the chemical compositions of Sb-rich crystals and Sb-poor crystals in the Sb-Pb-Bi-Sr-Ca-Cu-O system. Those in the Pb-Bi-Sr-Ca-Cu-O system are also shown in the table to compare the difference in the chemical compositions of the high-T_c phases between the two systems. The chemical compositions of the high-T_c phase in the Pb-Bi-Sr-Ca-Cu-O system were obtained previously.[19)] The chemical composition of the Sb-poor crystal is very close to the chemical composition of the high-T_c phase in the Pb-Bi-Sr-Ca-Cu-O system determined by wavelength dispersive X-ray spectroscopy (WDS) coupled with Rietveld analysis, suggesting that the Sb-poor crystal may be identical to the high-T_c phase of the Pb-Bi-Sr-Ca-Cu-O system. On the other hand, the Sb-rich crystal (4.3 atom%) has less Ca. Takada et al.* reported that the superconducting materials with compositions $(Bi_{1-\alpha}Pb_{\alpha})_nSr_{1.0}Ca_{1.0}Cu_yO_x$, where $026 \leqq \alpha \leqq 0.36$, $n=1.1$ and 1.2, and $1.50 \leqq y \leqq 1.80$, have the critical temperatures above 110K. Since both Sb-poor phase and Sb-rich phase have much less Pb than their samples, the reason why sample A has the critical temperature of 111K is different than the large amount of Pb doped in their samples. As the high-T_c phase with less Pb in the Pb-Bi-Sr-Ca-Cu-O system has a critical temperature of 107K, the Sb-poor crystal probably does not contribute to increase the critical temperature to 111K. Rather, the Sb-rich crystal is the one with a critical temperature of 111K.

There are two Ca layers sandwiched by the Cu-O layers in the high-T_c phase (T_c~107K) of the Pb-Bi-Sr-Ca-Cu-O system. If trivalent Sb occupies a fraction of the divalent Ca sites in the high-T_c phase (T_c~111K) of the Sb-Pb-Bi-Sr-Ca-Cu-O system, more oxygen atoms will have to be introduced into the Cu-O layers to compensate for charge imbalance. With a high resolution electron microscope, Hetherington et al.[21)] observed some amount of oxygen deficiency in the central Cu-O layer of the high-T_c phase of the Pb-Bi-Sr-Ca-Cu-O system. If more oxygen atoms can be introduced as a result of the substitution of Sb for Ca, it might be possible to make up for this oxygen deficiency and to affect the electronic state of the central Cu-O layer to increase the critical temperature from 107K to 111K. Direct observations of the crystal structure by high resolution electron microscopy are necessary to confirm the compensation of the oxygen deficiency in the central Cu-O layer of the high-T_c phase in the Sb-Pb-Bi-Sr-Ca-Cu-O system.

The reason why there are both Sb-rich and Sb-poor phases in the same specimen may be due to the inhomogeneous mixing of the raw powders. More homogeneous mixing like that resulting from the sol-gel process is preferable. The chemical composition of the Sb-rich crystal in the table corresponds to $Sb_{0.39}Pb_{0.23}Bi_{1.72}Sr_{1.92}Ca_{1.42}Cu_{3.31}O_x$, which has more Sb, Bi, Cu and less Pb, Sr, Ca than the starting nominal composition of $Sb_{0.10}Pb_{0.50}Bi_{1.40}Sr_{2.00}Ca_{2.00}Cu_{3.00}O_x$. Large amount of impurities with chemical compositions of $Sr_{0.2}Ca_{1.9}Cu_{1.0}O_x$, $Sr_{1.0}Ca_{0.8}Cu_{3.0}O_x$ and $Sb_{0.5}Bi_{2.0}Sr_{1.6}Ca_{1.0}Cu_{0.4}O_x$, were observed with small amount of the superconducting phase in sample A by EPMA. Therefore, the difference between the composition of Sb-rich crystals and the nominal composition may be due to the segregation of these impurities. As for Pb, it is suspected that Pb has evaporated from the specimen during the long firing period.

In conclusion, a superconducting phase with a critical temperature of 111K in the Sb-Pb-Bi-Sr-Ca-Cu-O system has been synthesized using a long firing period. Its orthorhombic lattice parameters are a=5.411(1)Å, b=5.411(1)Å and c=37.22(6)Å, in close agreement with those of the high-T_c phase (107K) in the Pb-Bi-Sr-

Ca-Cu-O system. The average chemical composition of the phase with the 111K critical temperature is 4.3%, 2.6%, 19.2%, 21.4%, 15.8% and 36.9% for Sb, Pb, Bi, Sr, Ca and Cu, respectively. It is implied that Sb substitutes for Ca in the lattice, requiring that excess oxygen be introduced to compensate for the oxygen deficiency in the central Cu-O layer of the structure. It may be this Sb substitution for Ca that increases the critical temperature from 107K to 111K.

Acknowledgments

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Figure Captions

Fig. 1. A typical crystal form (a) of the superconducting crystal chosen for EDS and its selected area electron diffraction pattern with the incident beam along the [001] zone axis (b). Superconducting crystals having the plate-like morphology with small thicknesses were chosen for EDS. The high-T_C phase with Sb has a modulated structure with b-axis wavelengths 26.9Å and 36.1Å. The corresponding satellite spots are observed in the selected area electron diffraction pattern.

Fig. 2. Temperature dependence of the electrical resistivity of the superconductors in the Sb-Pb-Bi-Sr-Ca-Cu-O system (sample A) and the Pb-Bi-Sr-Ca-Cu-O system (sample B). The $T_{c,end}$ of sample A and that of sample B are 110K and 105K, respectively.

Fig. 3. Temperature dependence of the magnetic susceptibility of the superconductors in the Sb-Pb-Bi-Sr-Ca-Cu-O system (sample A) and the Pb-Bi-Sr-Ca-Cu-O system (sample B). The T_C of sample A is 111.3K and that of sample B is 107.3K.

Fig. 4. X-ray powder diffraction patterns of the superconductors in the Sb-Pb-Bi-Sr-Ca-Cu-O system and the Pb-Bi-Sr-Ca-Cu-O system. Diffraction peaks from impurities are marked (O).

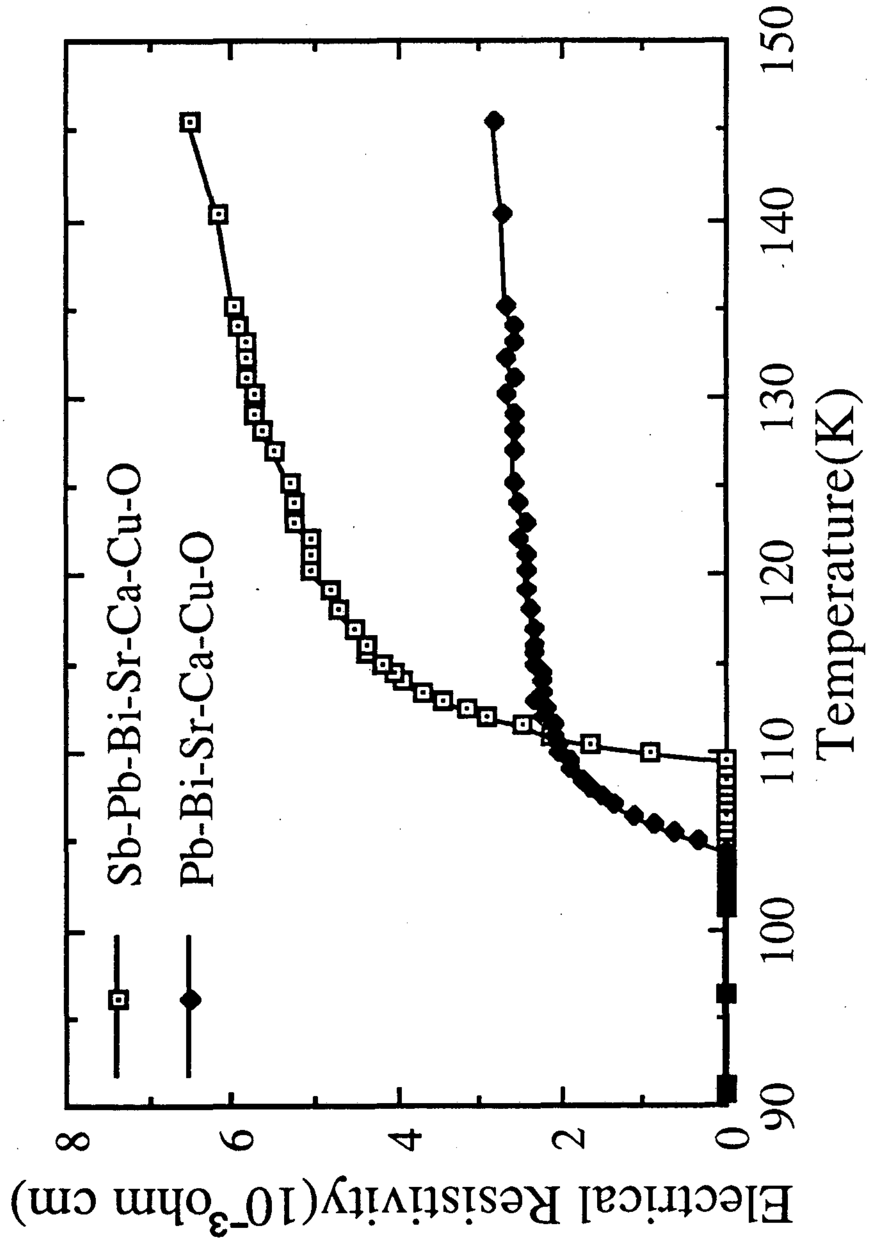
Fig. 5. Atomic concentrations of the superconducting phase in the Sb-Pb-Bi-Sr-Ca-Cu-O system determined by energy dispersive X-ray spectroscopy. Error bars attached to the marks have almost the same height as the marks themselves. Note that the summation of the Sb

concentration and the Ca concentration is nearly the same for all the crystals.

Fig. 6. Energy dispersive X-ray spectra and the deconvolution curves for Sb (□), Ca (Δ) and the sum of Sb and Ca (O) for crystals No. 3 (a) and No. 13 (b). Since crystal No.13 contains more Sb than crystal No.3, the width of the peak about 3.7keV of spectrum 13 is much broader than that of spectrum 3 because of the overlapping of the SbLα and CaKα radiations.

Table 1. Chemical compositions of the superconducting phases in the Sb-Pb-Bi-Sr-Ca-Cu-O system analyzed by Energy Dispersive X-ray Spectroscopy and in the Pb-Bi-Sr-Ca-Cu-O system analyzed by Wavelength Dispersive X-ray Spectroscopy (WDS) and Rietveld analysis of X-ray powder diffraction data.

	Sb-Pb-Bi-Sr-Ca-Cu-O		Pb-Bi-Sr-Ca-Cu-O	
	Sb-rich phase (atom%)	Sb-poor phase (atom%)	WDS (atom%)	Rietveld analysis (atom%)
Sb	4.3(0.7)	[0.5]	----	----
Pb	2.6(0.3)	2.7(0.4)	3.7(0.2)	4.2(0.2)
Bi	19.2(1.2)	19.1(0.5)	19.9(0.2)	20.3(0.4)
Sr	21.4(1.2)	21.3(0.4)	20.4(0.9)	20.7(0.3)
Ca	15.8(0.9)	20.4(1.2)	20.9(0.3)	21.4(0.3)
Cu	36.9(2.7)	36.1(0.5)	35.1(0.3)	33.3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Pb-Bi-Sr-Ca-Cu-O
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120
130
140
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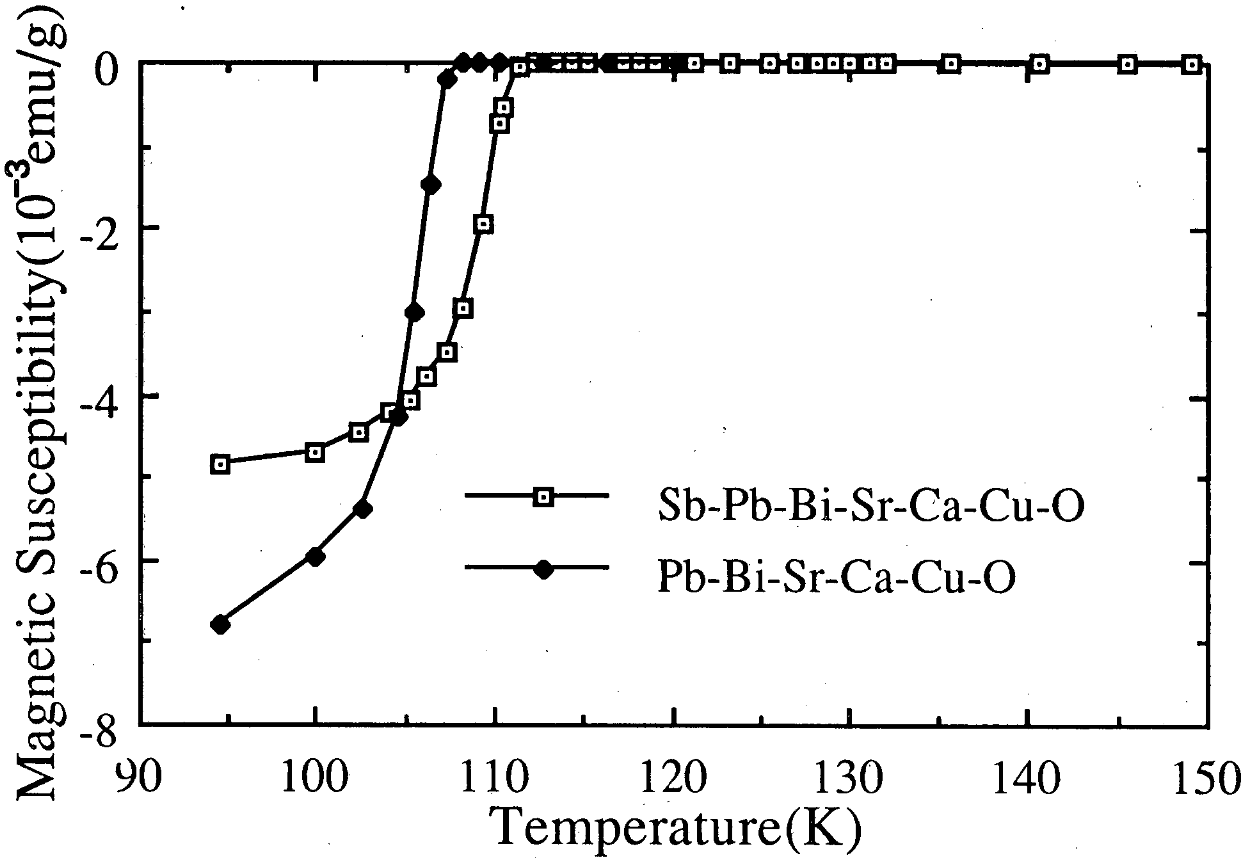
Fig. 2


Magnetic Susceptibility(10^{-3}emu/g)
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-2
-4
-6
-8
90
100
110
120
130
140
150
Temperature(K)
Sb-Pb-Bi-Sr-Ca-Cu-O
Pb-Bi-Sr-Ca-Cu-O

Fig. 3

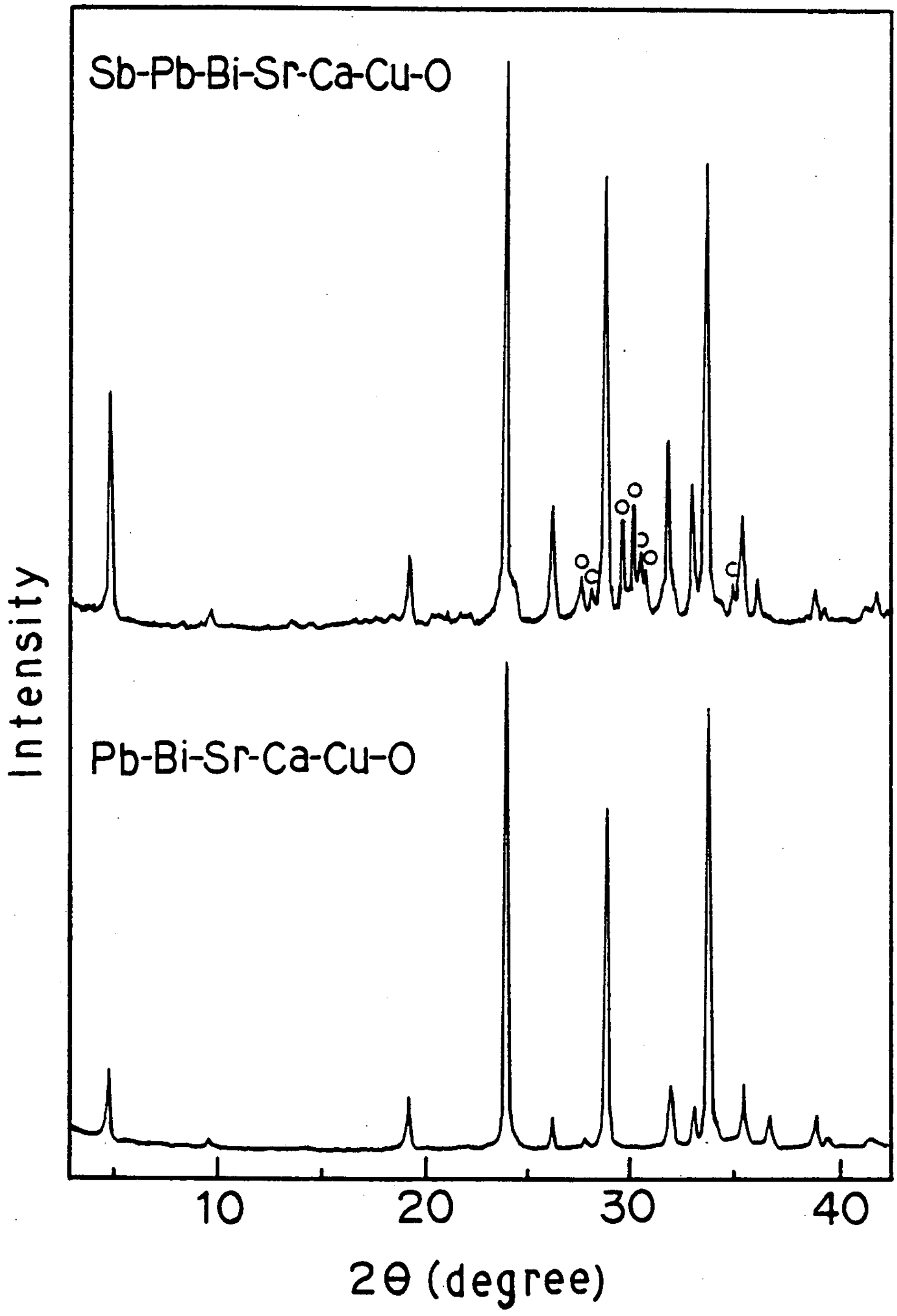
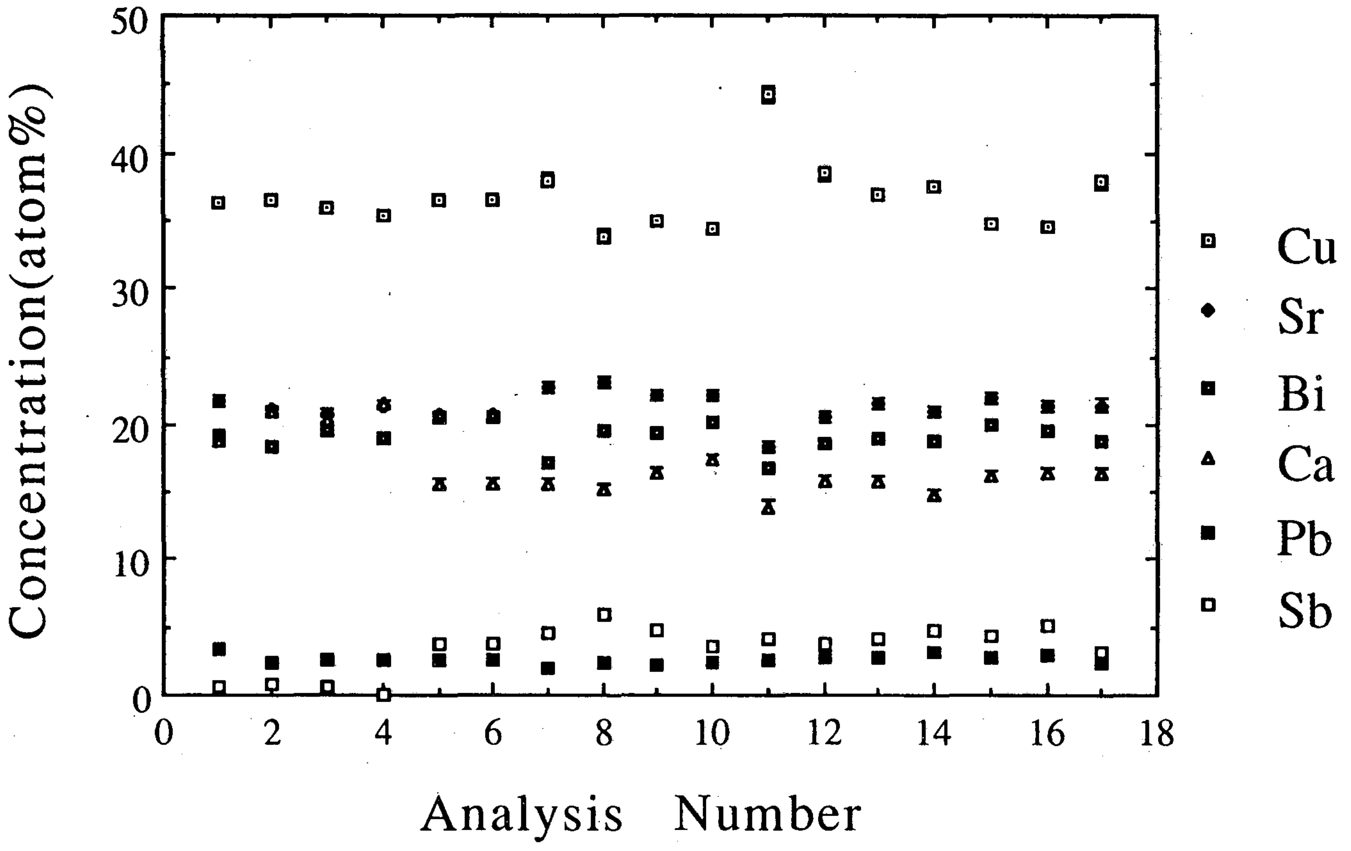


Fig. 4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Analysis Number
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Bi
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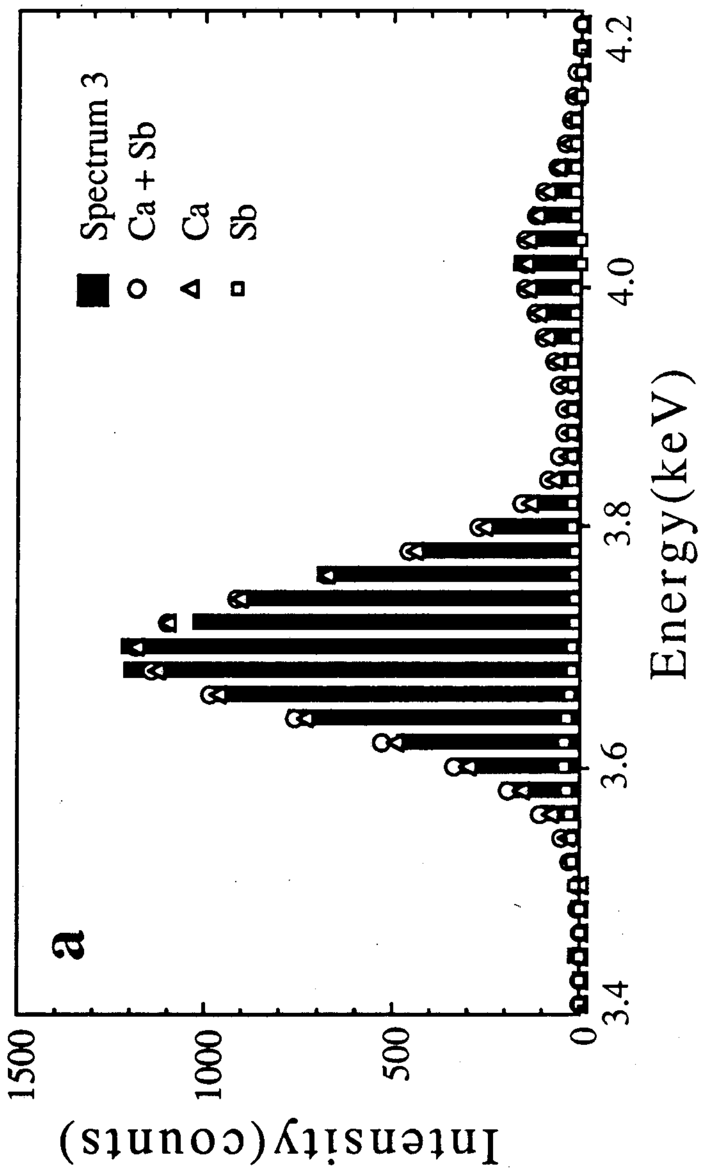
Sb

Fig. 5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□ Sb
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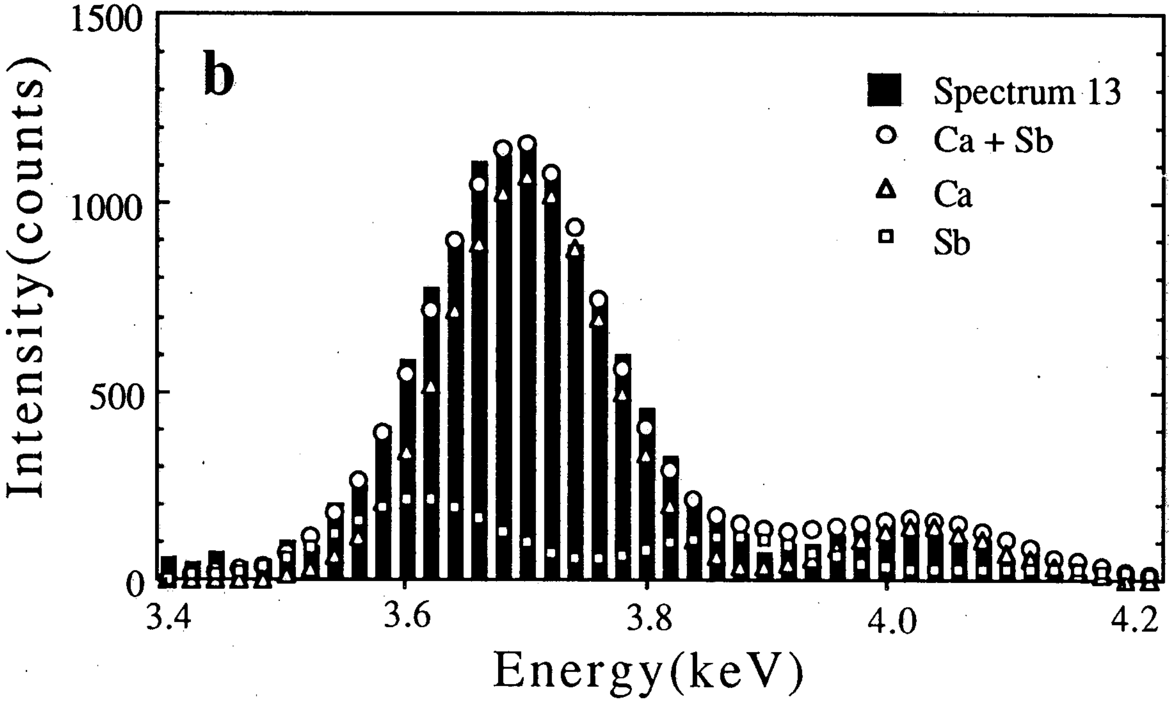
Fig. 6a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Spectrum 13
Ca + Sb
Ca
Sb
Intensity(counts)
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500
0
3.4
3.6
3.8
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4.2
Energy(keV)

Fig. 6b

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