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Superconducting and normal state behaviors of (Tl,Bi)$Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ ceramics

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Abstract

Effects of Bi and Ti substitutions at Tl and Sr sites, respectively, on superconducting and normal state behaviors of (Tl,Bi)$Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$–0.5) and $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ceramics have been investigated. Temperature-dependent resistance measurements on $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$) showed metallic normal state behavior with $T_{c\,onset}$ of 96 K and $T_{c\,zero}$ of 61 K. Substitution of Ti caused deterioration of superconductivity and gradual change of normal state resistance from metallic behavior ($x = 0$–0.3) to semiconductor-like behavior ($x = 0.4$–0.5). Resistance versus temperature measurements on $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.6) showed optimum superconductivity for $y = 0.3$ with $T_{c\,onset}$ of 98 K and $T_{c\,zero}$ of 68 K. The effects of Bi and Ti substitutions on superconducting and normal state behaviors of the ceramics are discussed in terms of ionic radius of elements and the concept of average Cu valence.
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1. Introduction

Tl1212 is an important member in Tl-based family of copper-oxide-based superconductors as its structure is closely related to the Y123 [1] and can be made to exhibit different electrical behaviors by partial elemental substitutions. The unsubstituted parent compound $TlSr_2CaCu_2O_7$ was reported to superconduct with critical temperature (T_c) of around 80 K [2]. However, the compound is difficult to synthesize in pure form because of high average Cu valence and overdoping of hole carrier concentration [3]. Fortunately, the 1212 phase can be stabilized by controlling the hole carrier concentration using partial substitution of various elements at mainly the Ca and Tl sites to reduce the average Cu valence [4]. In Tl1212, superconductivity can be optimized for maximum T_c by reducing the average Cu valence to between 2.20+ and 2.30+ [5].

Partial single-element substitution of RE^{3+} (RE: rare earth) for Ca^{2+} in $TlSr_2CaCu_2O_7$ produces maximum T_c of around 90 K [5]. (Tl,Bi)$Sr_2CaCu_2O_7$ was superconducting at 75–95 K [6] while (Tl,Pb)$Sr_2CaCu_2O_7$ superconducts at around 75 K [3]. Simultaneous partial double substitutions of Pb, Bi, or Cr for Tl and RE^{3+} for Ca^{2+} is known to stabilize the 1212 phase and further enhance T_c [7,8]. The valence of Cr and Pb at the Tl-site are suggested to be 3+ [7] and 4+ [3], respectively, while Bi at the Tl-site is suggested in mixed $Bi^{3+/5+}$ state [6]. Besides Tl and Ca, Sr is also a necessary element in the Tl1212 structure to provide a lattice framework conducive to superconductivity. Although, compared to Ca-site, reports on Sr-site substitution of Tl1212 is not as extensive, elemental substitutions of RE^{3+} (RE: Nd, Sm, Eu, Dy, and Pr) have shown interesting results [9–11].

In this paper we report superconducting properties of triple-substituted $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$–0.5) and $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.6). We present results from electrical resistance (dc) measurements, powder X-ray diffraction (XRD) and microstructure investigations using scanning electron microscope (SEM). The superconducting properties are discussed according to the concept of average Cu valence.

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2. Experimental procedure

2.1. Samples preparation

Samples with nominal compositions $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ (x = 0–0.5), $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ (y = 0–0.6) and $Tl_{0.9}Bi_{0.1}Sr_{1.8}Ti_{0.2}Ca_{0.9}Cu_2O_7$, were prepared from component oxides using the solid state reaction and precursor method. Appropriate amounts of high purity (≥99.99%) powders of $SrCO_3$, Ti_2O_3, CaO, Y_2O_3, and CuO were mixed and ground in an agate mortar. The precursor powders were then calcined in air at around 900 °C for 48 h with several intermittent grindings. Appropriate amounts of Tl_2O_3 and Bi_2O_3 were then added to the heated precursor and completely mixed. The powders were then pressed into pellets with diameter of 13 mm and thickness of around 2 mm under a load of 4–5 tons using a hydraulic press. The pellets were then placed in a ceramic boat and heated in a three-zone tube furnace at 1000 °C in flowing oxygen for 5 min followed by furnace cooling to room-temperature.

2.2. Samples characterization

The samples were examined by powder X-ray diffraction method using Bruker D8 diffractometer with Cu Kα radiation. The volume percent of the 1212 and 1201 phases in the samples were estimated by assuming that the amounts of 1212 phase and 1201 phase are proportional to the intensity of their strongest diffraction line, i.e. the (1 0 3) peak for 1212 phase and (1 0 2) peak for 1201 phase. The lattice parameter of the samples was obtained from the computer fittings of observed d values of diffractograms for individual sample. Scanning electron microscope micrographs were recorded using JEOL model JSM 6400 scanning electron microscope. Electrical resistance measurements between 16 and 300 K were carried out using the four-point probe method with silver paint contacts in a Janis model CCS 350ST cryostat in conjunction with a closed cycle refrigerator from CTI Cryogenics model 22. The temperature sensor used was a TG-120P GaAlAs diode. The onset of superconductivity, $T_{c\,onset}$ was taken as the temperature at which the tangent of the resistance versus temperature curve intersects with the tangent of the part where resistance dropped abruptly. $T_{c\,zero}$ is defined as the temperature at which the electrical resistance readings reached zero.

3. Results and discussion

Powder X-ray diffraction patterns for $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ (x = 0–0.5) revealed all samples consist of major 1212 phase with tetragonal unit cell (space group $P4/mmm$) and minor 1201 crystalline phases. X-ray diffraction pattern for $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ (x = 0 and 0.2) are shown in Fig. 1. The 1212:1201 phase ratio and calculated lattice parameters of the 1212 phase of the samples are shown in Table 1. The XRD data showed that both a- and c-lattice parameters of $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ decreased with Ti content.

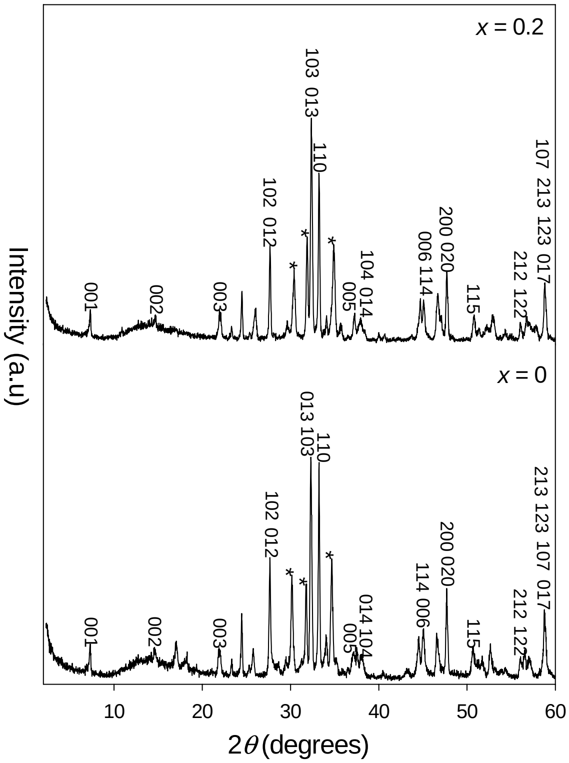


Fig. 1. Powder X-ray diffraction patterns for $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ (x = 0 and 0.2). Peaks identified as 1201 phase are marked with *.

Fig. 2 shows the electrical resistance versus temperature curve for $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ (x = 0–0.5). $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ (x = 0–0.3) showed metallic normal state behaviors and a decrease in $T_{c\,zero}$ from 61 to 57 K with Ti content. Further substitution of Ti at $x = 0.4$ caused semiconductor-like normal state behavior accompanied by a drop in the resistivity curve at around 50 K indicating a superconducting onset. However, zero resistance was not observed down to 16 K. At x = 0.5,

Table 1
$T_{c\,onset}$, $T_{c\,zero}$, resistivity (at 300 K), 1212:1201 phase ratio and 1212 lattice parameters of $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ (x = 0–0.5)

Sample	$T_{c\,onset}$	$T_{c\,zero}$	Resistivity at 300 K (ρ, Ω cm)	1212:1201 phase ratio volume (%)	1212 unit cell (Å)	
					a	c
$x = 0$	96	61	6.9	69:31	3.814	12.074
$x = 0.1$	92	60	7.5	61:39	3.813	12.072
$x = 0.2$	90	58	8.5	65:35	3.812	12.062
$x = 0.3$	91	57	1.5	74:26	3.810	12.055
$x = 0.4$	50	–	0.8	76:24	3.806	12.038
$x = 0.5$	–	–	0.6	72:28	3.806	12.027

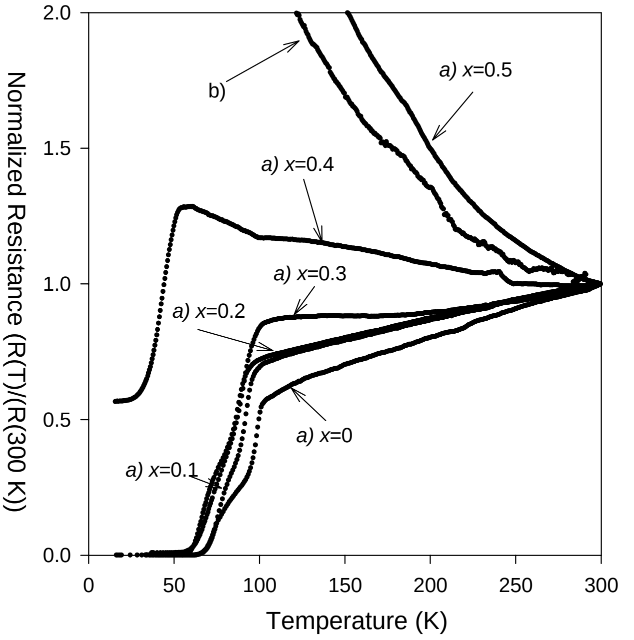


Fig. 2. Normalized resistance vs. temperature curve for (a) $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$–0.5) and (b) $Tl_{0.9}Bi_{0.1}Sr_{1.8}Ti_{0.2}CaCu_2O_7$.

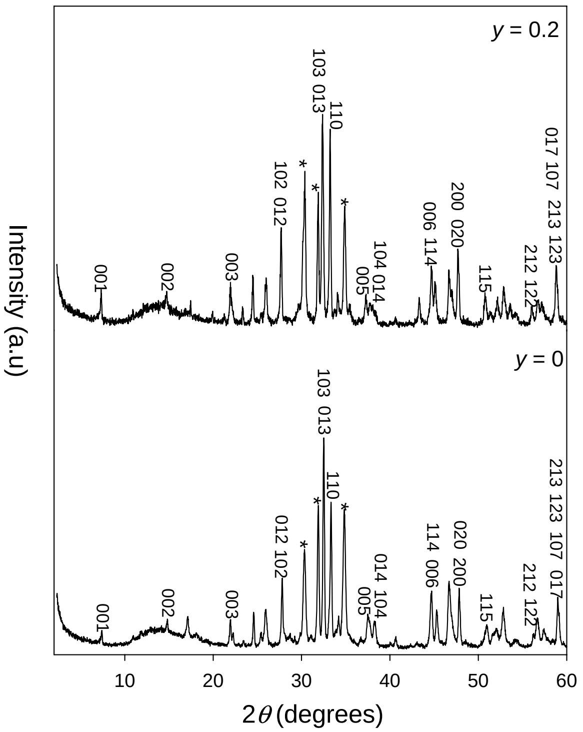


Fig. 3. X-ray diffraction patterns for $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.2) samples. Peaks identified with 1201 phase are marked with *.

$Tl_{0.9}Bi_{0.1}Sr_{1.5}Ti_{0.5}Ca_{0.9}Y_{0.1}Cu_2O_7$ showed insulating electrical behavior. The room-temperature resistivity (Table 1) was observed to initially increase from 6.9 Ω cm ($x = 0$) to 8.5 Ω cm ($x = 0.2$) but dropped to 1.5 Ω cm and below ($x = 0.3$–0.5). Changes in the hole concentration with Ti content is evidenced by the variation in room-temperature resistivity of the samples.

However, Y-free $Tl_{0.9}Bi_{0.1}Sr_{1.8}Ti_{0.2}CaCu_2O_7$ (Fig. 2(b)) was non-superconducting and showed semiconductor-like normal state behavior. Powder X-ray diffraction patterns for $Tl_{0.9}Bi_{0.1}Sr_{1.8}Ti_{0.2}CaCu_2O_7$ did not show any peak that can be indexed to the 1212 phase. This indicates that $Y_{0.1}$ substitution at the Ca-site played a major role in formation of 1212 phase.

To investigate the optimum Bi content, samples with nominal composition $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.6) were synthesized. Powder X-ray diffraction patterns for $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.6) showed all samples consist of 1212 major phase with tetragonal unit cell (space group *P*4/*mmm*) and 1201 minor phase. The volume fraction of 1212 phase was found to generally increase with Bi content. Fig. 3 shows X-ray diffraction patterns for $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0.1$ and 0.2). The calculated lattice parameters of the 1212 phase for the samples showed an increase of *a*-lattice with Bi content for $y = 0$–0.3 before decreasing for $y = 0.4$–0.6. Table 2 lists the results of $T_{c\,\mathrm{onset}}$, $T_{c\,\mathrm{zero}}$, resistivity (at 300 K), 1212:1201 phase ratio and 1212 lattice parameters for $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.6).

Fig. 4 shows the electrical resistance versus temperature curves for $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.6). $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$) was non-superconducting and showed semiconductor-like normal state behavior. $Tl_{0.9}Bi_{0.1}Sr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ superconducts with $T_{c\,\mathrm{onset}}$ of 90 K and $T_{c\,\mathrm{zero}}$ of 60 K. $T_{c\,\mathrm{zero}}$ increased from 60 to 68 K ($y = 0.1$–0.3) before decreasing to 65 K ($y = 0.4$). Metallic normal state behaviors were observed for $y = 0.1$–0.4. At $y = 0.5$ the sample showed semiconductor-like normal state behavior with $T_{c\,\mathrm{onset}}$ at around 80 K. A tail in the resistivity versus temperature curve was also observed below 50 K. The sample with $x = 0.6$ was insulating.

The results showed that for $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ series, the best superconducting behavior was achieved at Bi content of 0.3. Compared to previous reports [9] where maximum $T_{c\,\mathrm{onset}}$ was observed when 40–50% of Tl was substituted by either Bi or Pb, our results showed

Table 2
$T_{c\,\mathrm{onset}}$, $T_{c\,\mathrm{zero}}$, resistivity (at 300 K), 1212:1201 phase ratio and 1212 lattice parameters of $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$, ($y = 0$–$0.6$)

Sample	$T_{c\,\mathrm{onset}}$	$T_{c\,\mathrm{zero}}$	Resistivity at 300 K (ρ, Ω cm)	1212:1201 phase ratio volume (%)	1212 unit cell	
					a (Å)	*c* (Å)
$y = 0$	–	–	–	60:40	3.802	12.015
$y = 0.1$	90	60	7.5	66:34	3.808	12.072
$y = 0.2$	93	62	2.4	61:39	3.814	12.056
$y = 0.3$	93	68	3.0	64:36	3.815	12.051
$y = 0.4$	92	65	1.5	69:31	3.810	12.045
$y = 0.5$	80	–	0.8	78:28	3.811	12.029
$y = 0.6$	–	–	0.6	77:23	3.804	12.027

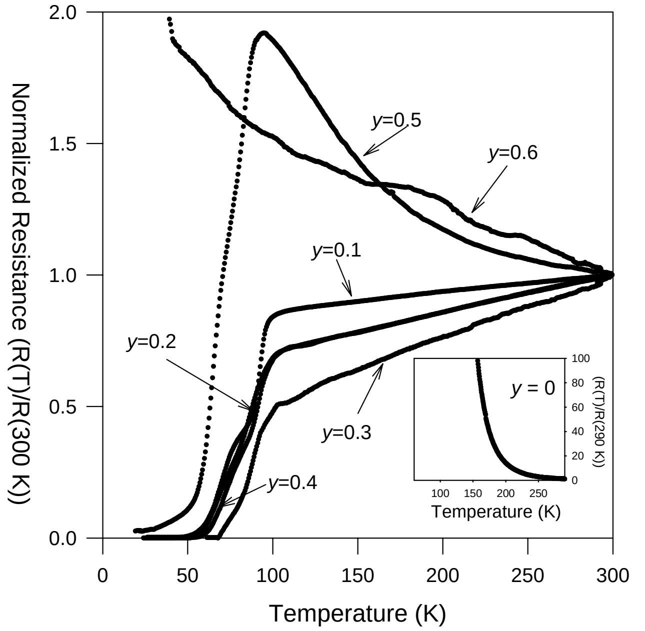
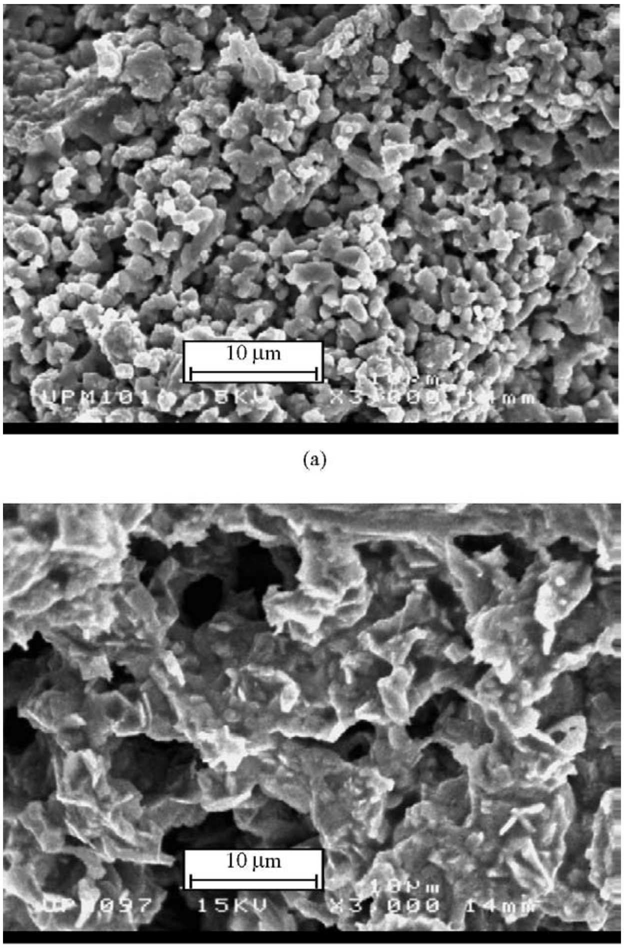


Fig. 4. Normalized resistance vs. temperature curves for $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.6).



(a)

(b)

Fig. 5. Scanning electron micrographs of $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ for (a) $y = 0.1$ and (b) $y = 0.3$.

that optimum superconductivity was achieved at slightly lower Bi concentration.

SEM micrographs of fractured section of $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.3) samples showed increasing average grain size with Bi content. Fig. 5 shows SEM micrographs for $y = 0$ and 0.3. The increase in grain size with Bi substitution may be due to partial melting of starting materials during final sintering at 1000 °C. The fact that Bi_2O_3 has a melting point of 860 °C and the increase in grain size was observed with increasing Bi content strongly suggest partial melting of Bi_2O_3. In addition, the increase in grain size probably caused the drop in room-temperature resistivity with Bi content (Table 2) due to improved connectivity between grains. In contrast, $Tl_{0.9}Bi_{0.1}Sr_{1-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ did not show any systematic change in grain morphology with increasing Ti. Fig. 6 shows SEM micrograph for $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0.1$).

Elemental substitutions may result in stoichiometric or off-stoichiometric compounds. For $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$, considering ionic sizes of Ca and Ti, the smaller Ti ion (Ti^{3+}-ionic radius: 0.67 Å, Ti^{4+}-ionic radius: 0.61 Å) may substitute easily for the larger Sr^{2+} (ionic radius: 1.18 Å) spacer ion. The decrease in c-lattice observed for $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$–0.5) (Table 1) suggests Ti substitution for Sr^{2+}. However, considering the ionic radius of Ti which is close to that of Cu^{2+} (0.73 Å), it is also possible that some Ti^{3+}/Ti^{4+} may substitute for Cu^{2+} causing a decrease in a-lattice. Since our results showed simultaneous reduction in a- and c-lattice parameters with Ti content, it is possible that some Ti may substitute into Cu sites. For $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.3), the increase of a-lattice (Table 2) indicates hole doping and can be explained in terms of the concept of the average Cu valence. When $Bi^{3+/5+}$ is substituted for Tl^{3+}, in order to satisfy charge neutrality requirement, smaller

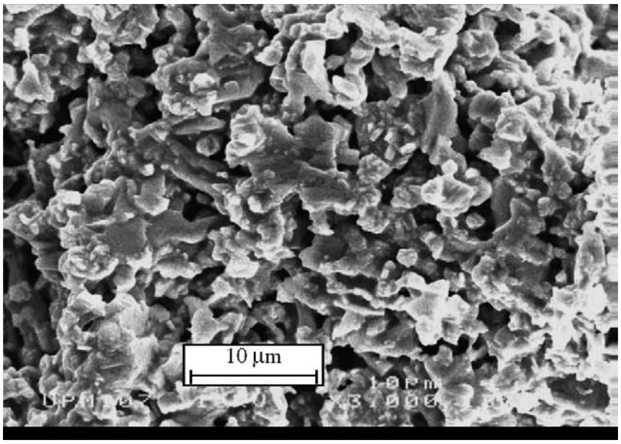


Fig. 6. Scanning electron micrographs of $Tl_{1.9}Bi_{0.1}Sr_{2-x}Ti_{1-x}Ca_{0.9}Y_{0.1}Cu_2O_7$ for $x = 0.1$.

Cu^{3+} is converted to larger Cu^{2+}. Since *a*-lattice depends mainly on CuO plane, the conversion from Cu^{3+} to Cu^{2+} caused expansion of the CuO framework and increased the *a*-lattice.

Considering the values of $T_{c\,onset}$, and $T_{c\,zero}$ and the normal state behavior for $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ (y = 0–0.6) series, the sample with $y = 0.3$ is suggested to have the best superconducting behavior. The onsets of superconductivity between 90 and 93 K observed for $y = 0.1$–0.4 are most probably due to the 1212 phase and not the 1201 phase as the highest $T_{c\,onset}$ reported for 1201 phase was only around 50 K [12]. It is difficult to determine accurately the valence of the ions in $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ due to multivalency of Tl, Bi, Ti, and Cu. However, several assumptions may be made in order to verify the optimum Cu valence. If full stoichiometry is assumed and the fact that the valence of Tl [13] and Ti [14] are both suggested to be 3+ in Tl1212 compounds, the average Cu valence can be computed. So, assuming that valences of metallic ions in $Tl_{0.7}Bi_{0.3}Sr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ are Tl^{3+}, Sr^{2+}, Ti^{3+}, Ca^{2+}, Y^{3+}, and Cu^{2+}/Cu^{3+}, simple calculation based on charge neutrality requirement shows that to achieve average Cu valence of 2.25+, Bi must be in mixed $Bi^{3+/5+}$ state. This is in agreement with previous suggestion of mixed Bi valence at the Tl-site in Tl1212 [6]. This means that for $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$, if Bi is in mixed valence state of $Bi^{3+/5+}$, maximum T_c is achieved at $y = 0.3$ with optimum average Cu valence between 2.20+ and 2.30+.

4. Conclusions

In conclusions, the effects of elemental substitutions on samples with nominal compositions $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ (x = 0–0.5), $Tl_{1-x}Bi_xSr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ (x = 0–0.6) and $Tl_{0.9}Bi_{0.1}Sr_{1.8}Ti_{0.2}CaCu_2O_7$ were investigated. Substitution of Y^{3+} at Ca-site in $Tl_{0.9}Bi_{0.1}Sr_{1.8}Ti_{0.2}Ca_{0.9}Y_{0.1}Cu_2O_7$ was found crucial for formation of Tl1212 phase. Ti substitution in $Tl_{0.9}Bi_{0.1}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ series caused gradual deterioration of superconductivity accompanied by change of normal state resistance from metallic behavior to semiconductor-like behavior with increasing Ti. Bi-substitution in $Tl_{1-y}Bi_ySr_{1.9}Ti_{0.1}Ca_{0.9}Y_{0.1}Cu_2O_7$ series showed optimum superconductivity for Bi content of 0.3. Simple valence calculation indicates optimum average Cu valence between 2.20+ and 2.30+ is possible if Bi is assumed to be mixed $Bi^{3+/5+}$ valence and the remaining elements were monovalent.

Acknowledgements

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