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Ceramics International 30 (2004) 1585–1589

CERAMICS
INTERNATIONAL

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Effects of elemental substitution involving V and Cr on superconductivity of (Tl,Bi)Sr_2(Ca,Y)Cu_2O_7 ceramics

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Received 19 November 2003; received in revised form 17 December 2003; accepted 22 December 2003

Abstract

Cr and V substituted Tl1212 type phase high temperature superconductors with nominal starting compositions $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$–0.5) and $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.5) have been prepared and characterized. Powder X-ray diffraction patterns showed all samples consist of major 1212 phase and minor 1201 phase. For $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$, normal state resistance changes from metallic behavior ($x = 0$–0.3) to semi-metallic behavior ($x = 0.4$) and semiconductor-like behavior ($x = 0.5$). $T_{c\,zero}$ gradually increased from 50 K ($x = 0$) to a maximum value of 78 K at $x = 0.3$ before decreasing with further Cr substitution. The $x = 0.5$ sample was non-superconducting. For $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$, normal state resistance changes from metallic behavior ($y = 0$–0.3) to semi-metallic behavior ($y = 0.4$) and semiconductor-like behavior ($y = 0.5$). $T_{c\,zero}$ increased from 50 K ($y = 0$) to a maximum value of 76 K ($y = 0.2$) before decreasing to 62 K ($y = 0.3$). Samples with $y = 0.4$ and 0.5 were non-superconducting. The effects of Cr and V substitutions are discussed in terms of ionic radius of dopants and the concept of average Cu valence.

Keywords: C. Electrical properties; C. Superconductivity; D. Oxide superconductors

1. Introduction

High temperature superconductivity in the TlBaCaCuO system was first discovered by Sheng and Hermann in 1988 [1]. Following the discovery, many new superconducting phases have been synthesized. Tl-based 1212 type phases, i.e. $TlBa_2CaCu_2O_7$ and $TlSr_2CaCu_2O_7$ have structures similar to RE-123 (RE: rare earth) [2]. $TlSr_2CaCu_2O_7$ was reported to be superconducting at about 80 K [3] but the 1212 phase is difficult to synthesize in pure form due to high average Cu valence and overdoping of hole carriers [4]. However, it can be stabilized by various partial substitutions to reduce the formal valence of Cu to an optimum value and control charge carrier concentration.

Substitution of Pb for Tl in (Tl,Pb)$Sr_2CaCu_2O_7$ produces a superconductor with T_c of 75 K [4]. When rare earth (RE) is introduced into the TlSrCaCuO system, $TlSr_2$(Ca,RE)Cu_2O_7 forms easily and is superconducting around 90 K [5,6]. Bi-substituted 1212-phase (Tl,Bi)$Sr_2CaCu_2O_7$ was reported to superconduct at 75–95 K [7]. Double substitution of Pb or Bi for Tl and RE for Ca produced (Tl,Pb)Sr_2(Ca,RE)Cu_2O_7 and (Tl,Bi)Sr_2(Ca,RE)Cu_2O_7 with even higher T_c of above 100 K [8]. When Cr was substituted at various metal sites, the transition temperature of $TlSr_2CaCu_2O_7$ was found to increase up to 110 K [9].

Elemental substitutions at Sr-site, although not as extensively studied compared to Tl and Ca sites, are also important in stabilizing the 1212 phase. When rare earth was substituted at Sr-site in Tl($Sr_{2-x}RE_x$)$CaCu_2O_{7-\delta}$ (RE = Sm, Eu, Dy), it was found that the substitutions help to stabilize the tetragonal phase [10]. Substitution of Nd for Sr in Tl$(Sr_{1-x}Nd_x)_2CaCu_2O_7$ stabilized the 1212 phase and improves the superconducting behavior [11]. Triple substitution involving Ti at Sr-site in $Tl_{0.8}Pb_{0.2}Sr_{2-x}Ti_xCa_{0.9}Y_{0.1}Cu_2O_7$ series produces optimum superconductivity with T_c of 62 K at $x = 0.2$ [12].

In this paper, effects of Cr and V substitutions at Sr-site on formation and superconductivity of (Tl,Bi)Sr_2(Ca,Y)Cu_2O_7

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doi:10.1016/j.ceramint.2003.12.194

ceramics were investigated. Bi is partially substituted in the Tl1212 to enhance its transition temperature [7] while Y is partially substituted for Ca to enhance the formation of the 1212 phase [5,6]. Results of electrical resistance (dc) measurements using the four-point-probe method and powder X-ray are presented.

2. Experimental details

2.1. Samples preparation

Polycrystalline samples with nominal starting compositions $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$–0.5), $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.5) and Y-free samples of $Tl_{0.9}Bi_{0.1}Sr_{1.9}Cr_{0.1}CaCu_2O_7$ and $Tl_{0.9}Bi_{0.1}Sr_{1.9}V_{0.1}CaCu_2O_7$ were prepared using the solid-state reaction and precursor method. High purity ($\geq$99.99%) oxides of $SrCO_3$, Cr_2O_3 (or V_2O_5), Y_2O_3, CaO and CuO were mixed in appropriate amounts and ground in an agate mortar before calcination at 900 °C for over 24 h with several intermittent grindings. Appropriate amounts of Tl_2O_3 and Bi_2O_3 were then added to the heated precursors and reground. The resultant powder was then pressed into pellets of 13 mm diameter and 2 mm thickness under a pressure of 4500–5000 kg/cm^2. The pellets were heated at around 1000 °C for 5 min in flowing O_2 followed by furnace cooling.

2.2. Samples characterization

The samples were examined by powder X-ray diffraction (XRD) using Bruker model D8 Advance diffractometer with Cu Kα source. The volume fractions of 1212 and 1201 phases were estimated by assuming that the amounts of 1212 and 1201 phases are proportional to the strongest diffraction line of each phase, i.e. (1 0 3) reflection of 1212 phase and (1 0 2) reflection of 1201 phase. At least 10 diffraction peaks were indexed to the 1212 phase for each sample. Electrical resistance (dc) measurements between 16 and 300 K were measured using the four-point-probe method with silver paste contacts. A CTI Cryogenics closed cycle refrigerator model 22 and Lake Shore temperature controller model 340 were used for temperature-dependent measurements. $T_{c\,zero}$ is defined as the temperature where the resistance becomes zero and $T_{c\,onset}$ is defined as the temperature at which the tangent to the normal state curve intercepts with the tangent to the transition curve. The Van der Pauw method was used to determine room-temperature resistivity.

3. Results

3.1. Powder X-ray diffraction analyses

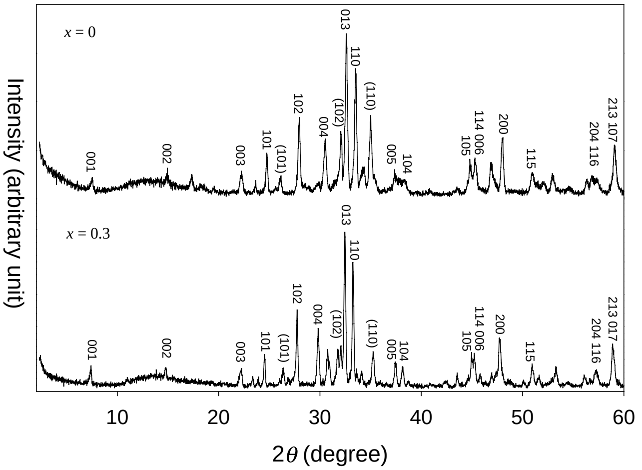

Fig. 1. Powder XRD patterns for $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$ and 0.3) showing dominant 1212 phase. Peaks due to 1201 phase are indicated in parentheses.

Powder XRD patterns of both $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ and $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ series revealed 1212 as the major phase for all samples and were indexed based on a tetragonal unit cell (space group, *P*4/*mmm*). 1201 phase constitutes the minor phase. Figs. 1 and 2 show XRD patterns of $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$ and 0.3) and $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0.1$ and 0.3), respectively. Reflection peaks due to the 1201 phase are indicated in parentheses. The powder XRD patterns for Y-free $(Tl,Bi)(Sr,Cr)_2CaCu_2O_7$ and $(Tl,Bi)(Sr,V)_2CaCu_2O_7$ (figures not shown) did not contain any observable peaks that can be related to known superconducting phases. $T_{c\,onset}$, $T_{c\,zero}$, room-temperature resistivity at 300 K, 1212:1201 phase ratio and lattice parameters of $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ and $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ are listed in Tables 1 and 2, respectively.

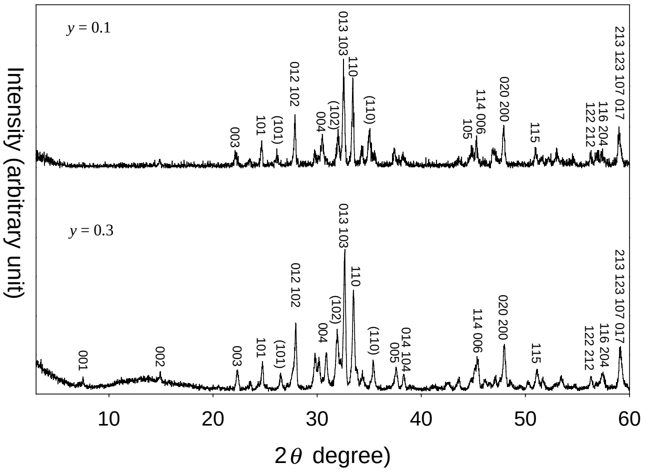

Fig. 2. Powder XRD patterns for $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0.1$ and 0.3) showing major 1212 phase. Peaks due to 1201 phase are indicated in parentheses.

Table 1
$T_{c\,\mathrm{onset}}$, $T_{c\,\mathrm{zero}}$, room-temperature resistivity at 300 K and 1212:1201 phase ratio and lattice parameters of $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$

Sample	$T_{c\,\mathrm{onset}}$ (K)	$T_{c\,\mathrm{zero}}$ (K)	Resistivity at 300 K ($\times 10^2$ mΩ cm)	1212:1201 phase ratio (vol.%)	1212 unit cell	
					a (Å)	c (Å)
$x = 0$	98	50	5.52	71:29	3.812	12.052
$x = 0.1$	83	62	0.30	73:27	3.811	12.048
$x = 0.2$	89	75	0.23	71:29	3.811	12.045
$x = 0.3$	91	78	0.17	78:22	3.810	12.033
$x = 0.4$	92	76	0.06	68:32	3.809	12.028
$x = 0.5$	–	–	0.04	57:43	3.808	12.027

Table 2
$T_{c\,\mathrm{onset}}$, $T_{c\,\mathrm{zero}}$, room-temperature resistivity at 300 K and 1212:1201 phase ratio and lattice parameters of $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$

Sample	$T_{c\,\mathrm{onset}}$ (K)	$T_{c\,\mathrm{zero}}$ (K)	Resistivity at 300 K (Ω cm)	1212:1201 phase ratio (vol.%)	1212 unit cell	
					a (Å)	c (Å)
$y = 0$	98	50	5.52	71:29	3.812	12.052
$y = 0.1$	86	68	14.99	74:26	3.796	12.017
$y = 0.2$	100	76	18.48	70:30	3.796	11.997
$y = 0.3$	80	62	9.25	69:31	3.798	11.979
$y = 0.4$	48	–	7.69	64:36	3.798	11.792
$y = 0.5$	42	–	37.23	63:37	3.802	11.943

3.2. Electrical resistance (dc) measurements

Fig. 3 shows the temperature dependence of electrical resistance of $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$–0.5). $T_{c\,\mathrm{zero}}$ was observed to increase gradually with x from 50 ($x = 0$) to 78 K ($x = 0.3$). For $x = 0.4$, $T_{c\,\mathrm{zero}}$ decreased slightly to 76 K. Metallic normal state behavior was exhibited by samples with $0 \leq x \leq 0.3$ while the sample with $x = 0.4$ showed semi-metallic normal state behavior. The $x = 0.5$ sample showed semiconductor-like normal

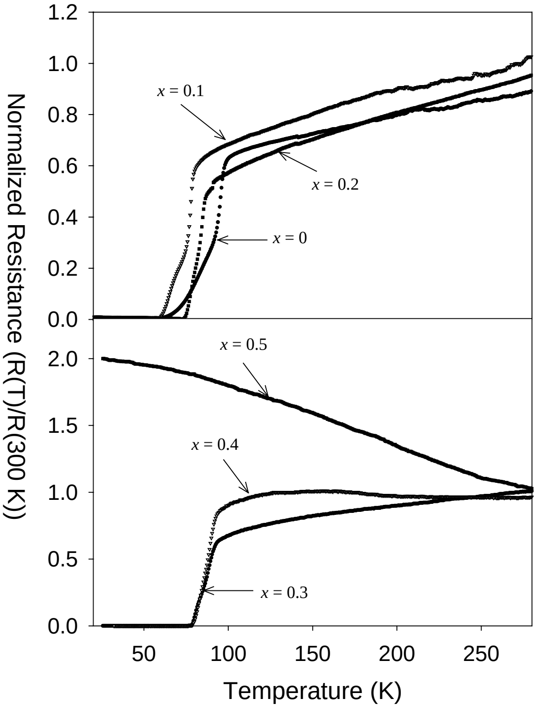

Fig. 3. Normalized resistance vs. temperature curves for $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$–0.5).

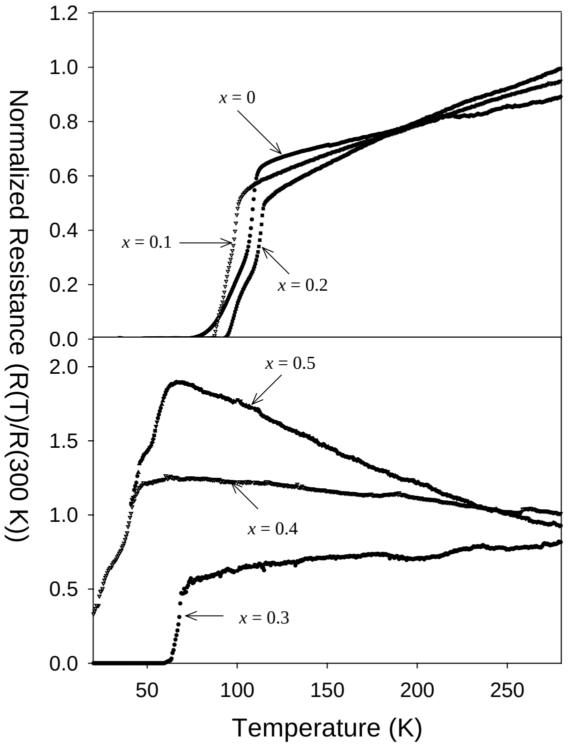

Fig. 4. Normalized resistance vs. temperature curves for $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$–0.5).

state behavior and was not superconducting down to 16 K. Room-temperature resistivity (Table 1) was observed to decrease sharply for $x = 0$–0.1 before gradually decreasing with x.

Temperature dependence of electrical resistance of $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.5) samples are shown in Fig. 4. $T_{c\,zero}$ increased from 50 ($y = 0$) to 76 K ($y = 0.2$) with y before decreasing to 62 K for $y = 0.3$. Normal state resistance changes from metallic behavior ($0 \leq y \leq 0.3$) to semi-metallic behavior ($y = 0.4$) and semiconductor-like behavior ($y = 0.5$). Samples with $y = 0.4$ and 0.5 were not superconducting but showed $T_{c\,onset}$ of 48 and 42 K, respectively. Room-temperature resistivity (Table 2) increased with V content for $y = 0$–0.2 before decreasing with further V substitution. Both resistance curves (not shown) for the Y-free samples showed insulating behavior.

4. Discussion

4.1. Effects of substitutions on structure and phase formation

Cr substitution in place of Sr caused a reduction in c-lattice parameter of $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ with x (Table 1). This is probably due to ionic size effect as smaller Cr ion (ionic radius: Cr^{2+} (0.94 Å), Cr^{3+} (0.76 Å), Cr^{4+} (0.69 Å), Cr^{5+} (0.63 Å), Cr^{6+} (0.58 Å)) is substituted for much larger Sr^{2+} ion (1.18 Å). The decrease in c-lattice agrees well with previous reports [2,9,12]. However, the reason for the decrease in a-lattice of $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ (Table 1) with x is not clear. It is also possible that Cr in $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ may go into other suitable atomic sites such as Cu as Cu and Cr have almost similar ionic radii [9]. Substitution of Y in place of Ca is important to stabilize the 1212 structure. This can be seen as Y-free $Tl_{0.9}Bi_{0.1}Sr_{1.9}Cr_{0.1}CaCu_2O_7$ and $Tl_{0.9}Bi_{0.1}Sr_{1.9}V_{0.1}CaCu_2O_7$ were not superconducting and XRD showed absence of 1212 phase. This is in agreement with previous reports that suggest the importance of rare earth (RE) substitution in stabilizing the 1212 phase [5,6].

The decrease in c-lattice with y in $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ (Table 2) may be due to the ionic size effect as Sr^{2+} (1.18 Å) is much larger than V ion (ionic radius: V^{3+} (0.78 Å), V^{4+} (0.72 Å) and V^{5+} (0.68 Å)). The increase in a-lattice parameters with y in $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ (Table 2) is probably due to a decrease in the average copper oxidation state due to substitution of higher valent V ion for Sr^{2+}, leading to expansion of Cu–O bonding lengths within the copper oxygen sheets.

Based on observed $T_{c\,onset}$ values and results of XRD for $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ ($x = 0$–0.5) and $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0$–0.3), it is clear that the 1212 phase is responsible for the observed superconductivity. The 1201 phase cannot be responsible for the observed superconductivity of the samples as its $T_{c\,onset}$ was reported to be below 50 K [13].

4.2. Effect of substitutions on average Cu valence

Although determination of valence of ions in Tl1212 involving triple substitution is complicated, meaningful understanding of the material can be derived if an ideal stoichiometry is assumed. The possible valences of metallic ions in $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ are Tl^{1+}/Tl^{3+}, Bi^{3+}/Bi^{5+}, Sr^{2+}, $Cr^{2+}/Cr^{3+}/Cr^{4+}/Cr^{5+}/Cr^{6+}$, Ca^{2+}, Y^{3+} and Cu^{2+}/Cu^{3+}. Assuming that Tl and Cr are in single valence states of Tl^{3+} [14] and Cr^{3+} [9], the average Cu valence in the 1212 phase can be calculated if the valence of Bi is known. Based on the critical temperature data for $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ (Table 1) the sample with ($x = 0.3$) is suggested to have the best superconducting behavior. If the average Cu valence for the sample is taken to be +2.25 the average valence of Bi is calculated to be +4. This result is consistent with previous report of Bi substitution which suggests mixed $Bi^{3+/5+}$ at Tl site [7].

Similarly, for $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ series, the possible valences of metallic ions are Tl^{1+}/Tl^{3+}, Bi^{3+}/Bi^{5+}, Sr^{2+}, $V^{3+}/V^{4+}/V^{5+}$, Ca^{2+}, Y^{3+} and Cu^{2+}/Cu^{3+}. In addition to the assumptions above and the fact that the valence of vanadium in Tl1212 is suggested as +3 [15], the average Cu valence in the 1212 phase with an ideal stoichiometry is $2.4 - y/2$. Based on our T_c results (Table 2), the best superconducting behavior is suggested to be at $y = 0.2$. Our calculation revealed that the optimum average Cu valence for maximum T_c in $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ ($y = 0.2$) is +2.30 and this value is in agreement with previous suggestion for optimum Cu valence in Tl1212 [13]. If the valence of V is taken to be +4 or +5, the average Cu valence will be much lower and represents an underdoped state. This contradicts our results which showed optimum superconductivity at $y = 0.2$.

5. Conclusion

In conclusion, effects of Cr and V substitutions at Sr site on superconductivity of $(Tl,Bi)Sr_2(Ca,Y)Cu_2O_7$ have been investigated. The best superconducting behavior for $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa_{0.9}Y_{0.1}Cu_2O_7$ and $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$ are suggested to be at $x = 0.3$ and $y = 0.2$, respectively. Based on the concept of average Cu valence for Tl1212 superconductors and assuming an optimum Cu valence between +2.25 and +2.30, both Cr and V in $Tl_{0.9}Bi_{0.1}Sr_{2-x}Cr_xCa0._9Y_{0.1}Cu_2O_7$ and $Tl_{0.9}Bi_{0.1}Sr_{2-y}V_yCa_{0.9}Y_{0.1}Cu_2O_7$, respectively, are suggested to be in the +3 valence states. Bi in both compounds is suggested to be in mixed $Bi^{3+/5+}$ state.

Acknowledgements

This research has been supported by the Malaysian Ministry of Science, Technology and the Environment under IRPA grant no. 09-02-01-007-EA007.

References

[1] Z.Z. Sheng, A.M. Hermann, Bulk superconductivity at 120 K in the Tl–Ca/Ba–Cu–O system, Nature 332 (1988) 138–139.

[2] S. Nakajima, M. Kikuchi, Y. Syono, N. Kobayashi, Y. Muto, Superconductivity of high-T_c $TlBa_2Ca_{1-x}RE_xCu_2O_7$ (RE = Nd, Gd or Y) system, Physica C 168 (1990) 57–62.

[3] Z.Z. Sheng, A.M. Hermann, D.C. Vier, S. Schultz, S.B. Oseroff, D.J. George, R.M. Hazen, Superconductivity in the Tl–Sr–Ca–Cu–O system, Phys. Rev. B 38 (1988) 7074–7076.

[4] M.A. Subramanian, C.C. Torardi, J. Gopalakrishnan, P.L. Gai, J.C. Calabrese, T.R. Askew, R.B. Flippen, A.M. Sleight, Bulk superconductivity up to 122 K in the Tl–Pb–Sr–Ca–Cu–O system, Science 242 (1988) 249–250.

[5] Z.Z. Sheng, L. Sheng, X. Fei, A.M. Hermann, Superconductivity above 77 K in the R–Tl–Sr–Ca–Cu–O system, Phys. Rev. B 39 (1989) 2918–2920.

[6] J.K. Liang, Y.L. Zhang, G.H. Rao, X.R. Cheng, S.S. Xie, Z.X. Zhao, The crystal structure and superconductivity of new superconductor phase $TlSr_2Ca_{0.5}Sm_{0.5}Cu_2O_{6.75}$, Solid State Commun. 70 (1989) 661–665.

[7] S. Li, M. Greenblatt, Preparation and superconducting properties (Tl, Bi)$Sr_2CaCu_2O_y$, Physica C 157 (1989) 365–369.

[8] Y.T. Huang, R.S. Liu, W.N. Wang, P.T. Wu, A new series of $(Tl_{1-y}Bi_y)$ $(Ca_{1-x}Y_x)Sr_2Cu_2O_z$ superconductors with '1122' structure, Physica C 162–164 (1989) 39–40.

[9] Z.Z. Sheng, D.X. Gu, Y. Xin, D.O. Pederson, L.W. Finger, C.G. Hadidiacos, R.M. Hazen, A new 1212-type phase: Cr-substituted $TlSr_2CaCu_2O_7$ with T_c up to about 110 K, Mod. Phys. Lett. B 5 (1991) 635–642.

[10] W.H. Lee, B.C. Huang, Changes in doping state of $Tl(Sr_{2-x}R_x)CaCu_2O_{7-\delta}$ (R = Sm, Eu, Dy) system, Physica C 289 (1997) 114–122.

[11] R. Abd-Shukor, A. Das Arulsamy, Superconductivity and transport critical current density of Nd substituted Tl-1212 phase $Tl(Sr_{1-x}Nd_x)_2CaCu_2O_7$, J. Phys. D: Appl Phys. 33 (2000) 1–4.

[12] A.K. Yahya, F.M. Salleh, N. Ibrahim, R. Abd-Shukor, Effects of Ti substitutions on superconductivity of TlSr-1212 ceramics, Physica C 388–389 (2003) 371–372.

[13] Z.Z. Sheng, Y.F. Li, D.O. Pederson, Derivatives of $TlSr_2CaCu_2O_7$ from elemental substitutions of Pb for Tl, Solid State Commun. 80 (1991) 913–915.

[14] S. Nakajima, M. Kikuchi, Y. Syono, T. Oku, D. Shindo, K. Hiraga, N. Kobayashi, H. Iwasaki, Y. Muto, Synthesis of bulk high T_c superconductors of $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ ($n = 2$–5), Physica C 158 (1989) 471–476.

[15] R.S. Liu, W. Zhou, R. Janes, P.P. Edwards, An investigation of the new high-T_c Tl–V–Sr–Ca–Cu–O and Tl–V–Sr–Ca–Y–Cu–O superconductors, Supercond. Sci. Technol. 4 (1991) S310–312.