J MATER SCI 41 (2006) 3799–3803

Superconducting properties of Ce-substituted $TaSr_2(Gd,Ce)_2Cu_2O_y$

R. ABD-SHUKOR*, C. A. KEK, W. K. YEOH†
School of Applied Physics, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Ehsan, Malaysia
E-mail: ras@pkrisc.cc.ukm.my

A layered cuprate $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_y$ for $x = 0.4$–0.8 has been successfully synthesized by solid state reaction. X-ray powder diffraction analysis indicates that nearly all the peaks from the samples can be indexed to a single phase of Ta-1222. The sample with nominal composition $TaSr_2Gd_{1.6}Ce_{0.4}Cu_2O_y$ showed a tetragonal structure with lattice parameters $a = 3.858$ Å, $c = 28.81$ Å with space group most likely I4/mmm. The $TaSr_2Gd_{1+x}Ce_{1-y}Cu_2O_y$ compound exhibits a narrow superconducting region near $x = 0.6$ with $T_{c-\text{onset}} = 30$ and $T_{c-\text{zero}}$=10 K as determined by d.c. electrical resistance versus temperature measurements.

1. Introduction

The discovery of n-type (electron-doped) superconductor with T_c as high as 25 K in cerium-doped $Ln_{2-x}Ce_xCuO_{4-y}$ (Ln = Pr, Nd and Sm) for $x = 0.15$ and $y = 0.02$ [1], suggests that the fluorite-type structure in the layered cuprate could play a very important role in the generation of new superconducting oxides. Based on such idea, Tokura *et al.* [2] reported a new superconducting compound in $Bi_2Sr_2(Ln,Ce)_2Cu_2O_y$ and non-superconducting compound in $Tl_2Ba_2(Ln,Ce)_2Cu_2O_y$ (Ln = Gd, Eu and Sm) [3] with a $(Ln,Ce)_2O_2$ fluorite layer. In Pb-system a series of superconducting layered compounds of $(Pb,Cu)(Sr,Eu)_2(Eu,Ce)_2Cu_2O_y$ with the so-called 1222 structure ($T_c \sim 25$ K) have been successfully synthesized by Maeda *et al.* [4]. The structure of these 1222-type cuprates is stabilized by insertion of a $(Ln,Ce)_2O_2$ fluorite layer in place of single oxygen-vacant layer between two pyramidal CuO_2 layers like the so called T^* phase $(Nd,Ce,Sr)_2CuO_4$ structure [5]. The transition temperature for all of these materials (1222-type) is below 40 K.

The layered Sr_2RuO_4 with K_2NiF_4 structure was also found to be superconducting [6]. Bauernfeind *et al.* [7] successfully synthesized the highest T_c ($T_{c-\text{onset}} \sim 45$ K and $T_{c-\text{zero}} \sim 38$ K) in $RuSr_2(Gd,Ce)_2Cu_2O_z$ system with metallic normal state under an appropriate heat treatment by applying an oxygen pressure of about 25 bar. Later, Tang *et al.* [8] showed that the $SrRuO_3$ block may be a new connector for the layered cuprates. They reported the 1222-type cuprate in $RuSr_2(Gd,Ce)_2Cu_2O_z$ with $T_{c-\text{onset}} \sim 30$ K and $T_{c-\text{zero}} \sim 14$ K. Li *et al.* [9], Cava *et al.* [10] and Wang *et al.* [11], reported superconductivity at ∼28 K in $MSr_2(Nd,Ce)_2Cu_2O_y, M = $ Nb, Ta which are isomorphous to $RuSr_2(Gd,Ce)_2Cu_2O_y$ and $TlSr_2(Nd,Ce)_2Cu_2O_y$ [12]. The typical 1222 and 1212 type structures are shown in Fig. 1.

In this paper, we report superconductivity at 30 K in $TaSr_2Gd_{1.6}Ce_{0.4}Cu_2O_y$. We also investigated the Ta-1222 system by optimization of (Gd,Ce) cation ratio in the insulating layer. The results are discussed in term of average Cu valence and the ionic size effect of rare earth elements on the superconducting properties of Ta-1222.

2. Experimental details

Samples with nominal compositions $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_y$ for $x = 0.4$, 0.5, 0.6, 0.7 and 0.8 were prepared by solid state reaction methods from starting oxides of Ta_2O_5 (99.99%), $SrCO_3$ (99.9+%), Gd_2O_3 (99.999%), CeO_2 (99.999%) and CuO (99.999%). The mixed powder was thoroughly ground and calcined in air at 1000°C for 48 h with intermediate grindings. The resulting powders were reground and pressed into pellets. The pellets were then annealed at 1050°C for 24 h. Finally, the samples were slowly cooled at the rate of 1°C/min to 300°C in flowing oxygen to avoid freezing of disorder. Both

---

*Author to whom all correspondence should be addressed.

†*Permanent Address*: College of Engineering, Universiti Tenaga Nasional, 43009 Kajang Selangor, Malaysia.

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-2278-7

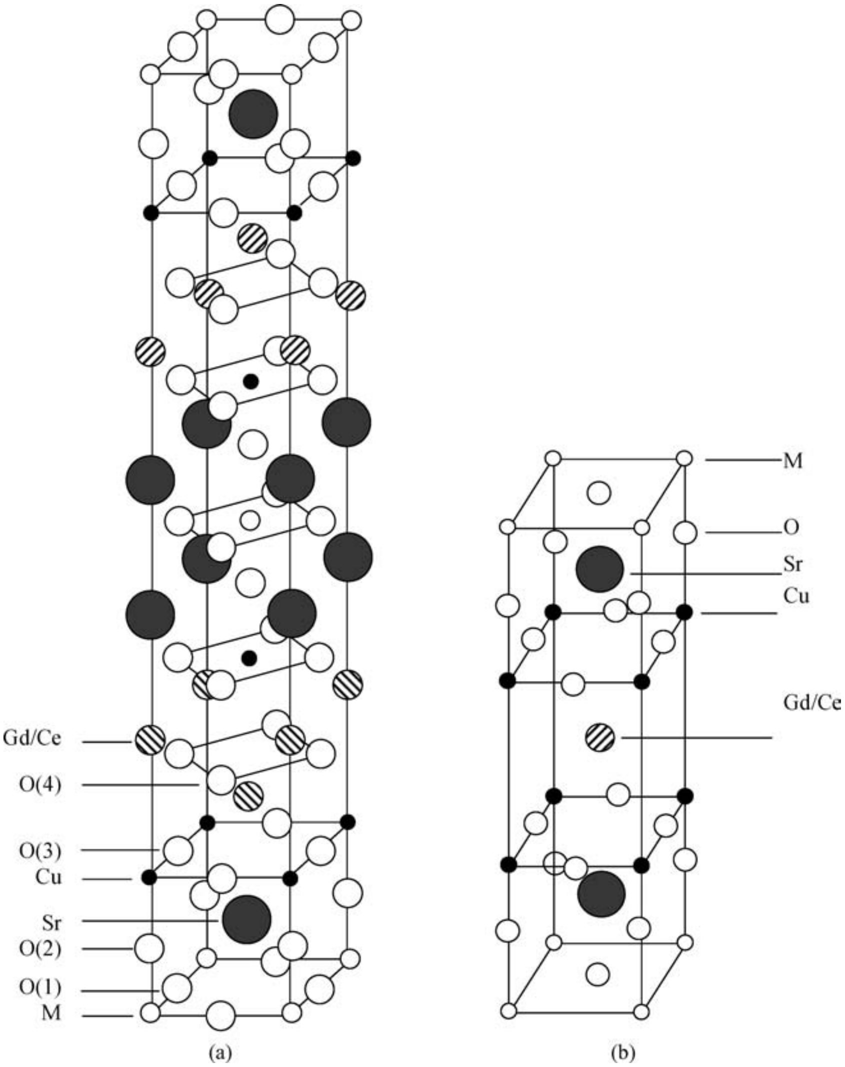


Figure 1 A typical (a) 1222 and (b) 1212 type structure. M is metal for example Ru, Nb or Ta.

pre-reaction and sintering were performed on alumina crucibles.

The powder X-ray diffraction method using a Siemens D 5000 diffractometer with Cu K_α source has been used to identify the resultant phase. The d.c. electrical resistance-temperature measurement of samples was carried out by the four point probe technique with silver paste contacts in a CTI Closed Cycle Refrigerator down to 9 K.

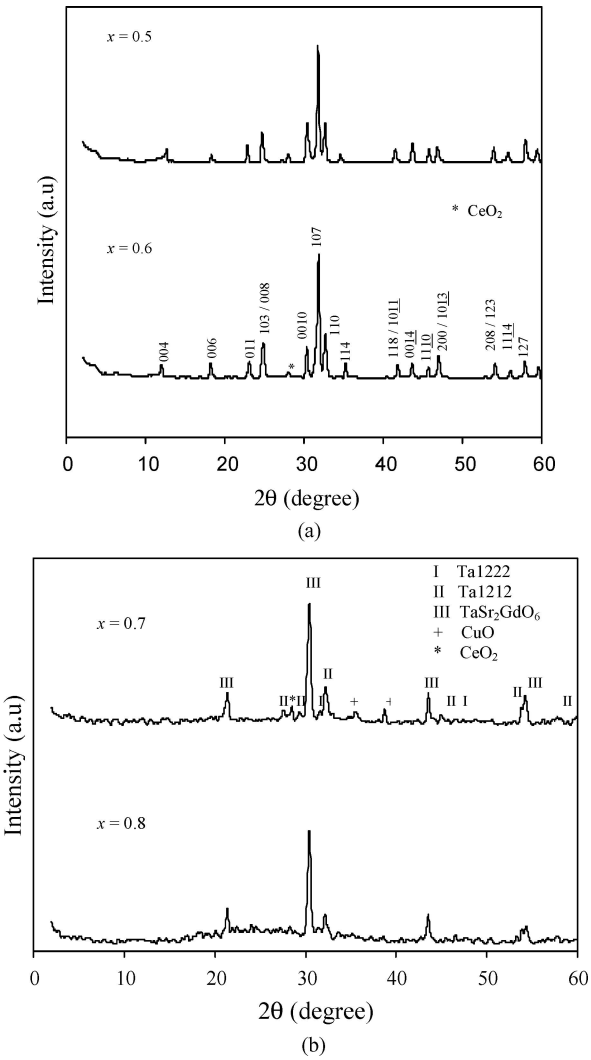
3. Results and discussion

The powder X-ray diffraction patterns of $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_y$ with $x = 0.5$ and $x = 0.6$ as shown in Fig. 2a indicate that all the peaks can be indexed on the basis of a tetragonal unit cell with space group most likely I4/mmm. A nearly Ta-1222 single phase is observed. This result also reflects that the phase stability limit of $TaSr_2(R,Ce)_2Cu_2O_y$ series can be extended to a smaller rare earth ions like Gd. On the other hand, we found that the range of formation of $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_y$ is as narrow as the other Ta-1222 phase with rare earth substituted for Pr or Nd [13]. For example, for the XRD patterns of sample with $x = 0.7$ and 0.8 are multiphase (Fig. 2b). The Ta-1222 phase can only be indexed as a minority phase and the main phase likely to appear as a cubic perovskite $TaSr_2(Gd,Ce)O_6$ and unreacted CuO [14]. The $TaSr_2(Gd,Ce)Cu_2O_8$ phase and unreacted CeO_2 are also observed. The results imply that the formation of the Ta-1222 phase not only needs a suitable ionic radius of lanthanide elements for (R,Ce) cation, R = Pr, Nd and Gd in the fluorite-type layered materials. The conditions of oxygen pressure, temperature, reaction time, range of compositions and cooling rate will also play an important role to stabilize the 1222-phase. Therefore, further study on the formation of Ta-1222 phase is needed.

The lattice parameters of some 1222-type cuprate superconductors are listed in Table I. We can see that the c-axis of Ta-1222 and Nb-1222 are significantly greater than that of Ru1222. This is because the ionic radius of Ta^{5+} (0.68 Å) and Nb^{5+} (0.68 Å) are larger than the ionic radius of Ru^{5+} (0.565 Å). Although the ionic radius of Gd^{3+} (0.938 Å) is smaller than Nd^{3+} (0.995 Å) and Pr^{3+}

TABLE I Lattice parameters of $MSr_2(R,Ce)_2Cu_2O_y$. (M = Ru, Ta, Nb, and R = Gd or Nd)

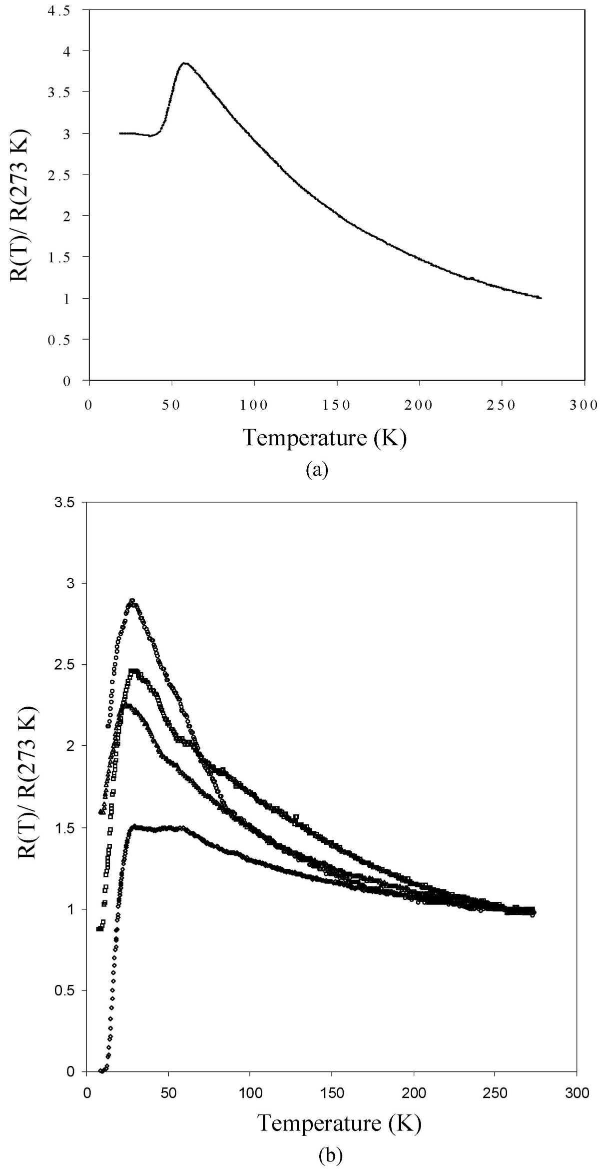
Compound	a (Å)	c (Å)	V (Å^3)	$T_{c-\text{onset}}$ (K)	$T_{c-\text{zero}}$ (K)	Ref
$RuSr_2(Gd,Ce)_2Cu_2O_y$	3.847	28.64	423.9	40	30	[7, 8]
$TaSr_2(Gd,Ce)_2Cu_2O_y$	3.858	28.81	428.8	30	10	This work
$TaSr_2(Nd,Ce)_2Cu_2O_y$	3.881	28.93	435.8	28	13	[9, 10, 13]
$NbSr_2(Gd,Ce)_2Cu_2O_y$	3.867	28.74	429.8	27	13	[11]
$NbSr_2(Nd,Ce)_2Cu_2O_y$	3.884	28.83	434.9	28	13	[10]



(a)

(b)

Figure 2 (a) Powder X-ray diffraction pattern of samples with nominal starting composition $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_{10}$ for x=0.5 and 0.6. (b) Powder X-ray diffraction pattern of samples with nominal starting composition $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_{10}$ for $x = 0.7$ and 0.8.



(a)

(b)

Figure 3 (a) Electrical resistance *vs* temperature of $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_{10}$ for $x = 0.8$. (b) Electrical resistance *vs* temperature of $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_{10}$ for $x = 0.4$ (○), x=0.5 (□), $x = 0.6$ (◇) and $x = 0.7$ (Δ).

(1.013 Å), the unit cell volume corresponding to Ta and Nb system are almost the same. The ideal structure model of $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_y$ is proposed in [9–11]. The decrease of a-axis and c-axis in $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_y$ indicates that the Gd ions are readily incorporated into the structure.

Fig. 3a and b display the normalized resistance-temperature curve of $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_y$ for $x = 0.8$ and $x = 0.4$–0.7, respectively. The $x = 0.4$, 0.5 and 0.7 samples show electrical resistance anomaly around 30 K while the x=0.8 sample exhibits electrical resistance anomaly at 58 K.

In order to study the effect of annealing prolongation to the occurrence of superconductivity, the samples with $x = 0.5$ and $x = 0.6$ were reground and repelletized and

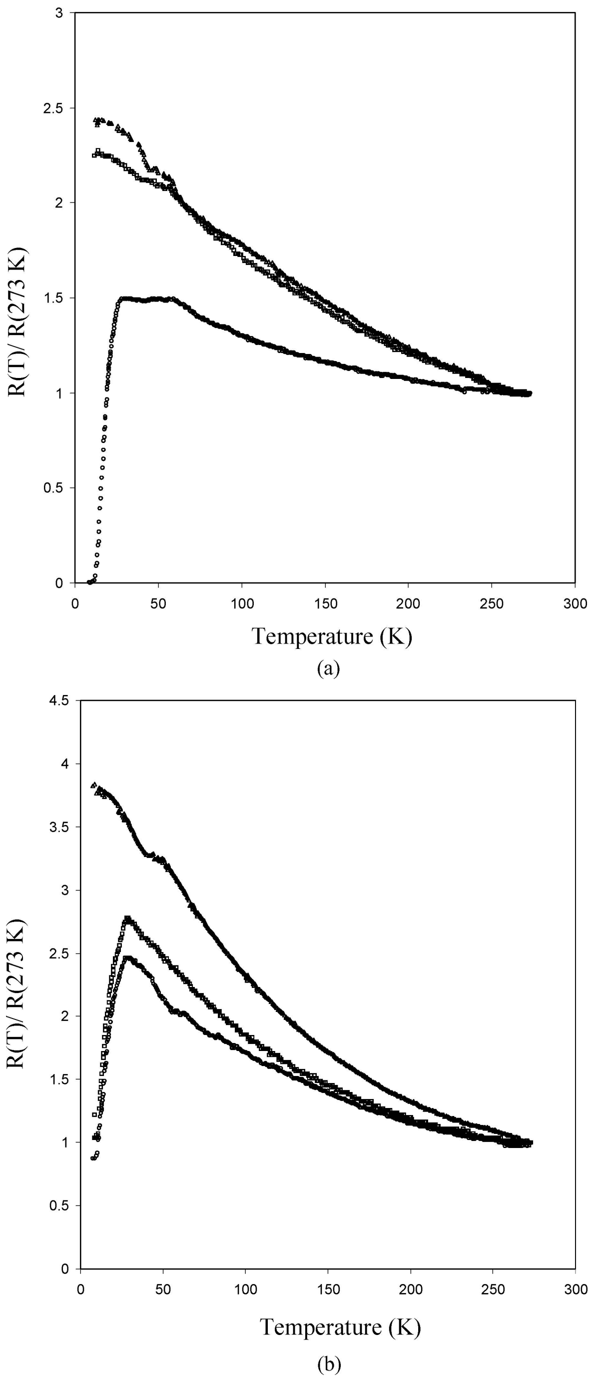


Figure 4 (a) Electrical resistance *vs* temperature of $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_{10}$ for x=0.6 annealing for different duration: (○) 24 h, (□) 48 h and (Δ) 72 h. (b) Electrical resistance *vs* temperature of $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_{10}$ for $x = 0.5$ annealing for different duration: (○) 24 h, (□) 48 h and (Δ) 72 h.

were then annealed at 1050°C for another 24 h. The resistance as a function of temperature for the samples with $x = 0.5$ and $x = 0.6$ after annealing for different duration are shown in Fig. 4a and b. The results show that annealing prolongation not only suppress the quality of samples but also destroy the superconductivity. The disappearance of superconductivity might be due to cation disordering effect. This finding also suggests that the bulk superconductivity of $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_y$ can only be obtained under a narrow range of doping condition.

The possible valences of metallic ions in $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_y$ are Ta^{5+}, Sr^{2+}, Gd^{3+}, Ce^{3+}/Ce^{4+} and Cu^{2+}/Cu^{3+}. Assuming that only Cu is multivalent and that Ce is in a single valence state, Ce^{4+} [15], the average Cu valence in the Ta-1222 phase with an ideal stoichiometry is $2.0 + x/2$. An average Cu valence of 2.0 + represents an underdoped hole state. Our results show that the average Cu valence for the best superconductive property ($x = 0.6$, $T_{c-\max} = 30$ K) is 2.30+. Therefore, we suggest that this sample is nearly optimally doped with Cu valence for 1222-phase superconductors should be in between 2.20+– 2.30+. On this basis, we strongly believe that partial substitution of Ce^{4+} for Gd^{3+} introduces holes into the CuO_2 planes of $TaSr_2Gd_{1+x}Ce_{1-x}Cu_2O_y$. Thus, the narrowness of concentration range for the occurrence of superconductivity in the present case may be related to the persistence of Cu–Cu antiferromagnetic (AFM) correlations with increasing Ce doping. A systematic comparative compositional study of both Ce and other ions with 4+ valence for example Th-doped in Ta-1222 systems is needed to confirm if the Ce dopant ions exhibit single tetravalent behavior. In general, thorium is assumed to be purely tetravalent, and indeed, Th^{4+} is the most electropositive among the elemental tetravalent ion [16]. If the valence of Ce ions were in the mixed 3+ and 4+ state, thus donating less than one additional electron per ion, the Ce-doped series would require a greater dopant concentration than that for Th^{4+} to achieve the same concentration as in the well known electron-doped compound $Ln_{2-x}M_xCuO_{4-\delta}$ where Ln = Pr, Nd, Sm, Eu and M = Ce, Th. Recently, these assertions become possible when Li Rukang *et. al.* [13] have shown that Th^{4+} can be substituted in Ce site to form $TaSr_2(Nd,Th)_2Cu_2O_z$.

It is well known that Gd^{3+} ion is one of the strongest magnetic elements in the lanthanide series with the effective magneton number near 7.94 μ_B at room temperature [17]. However, the magnetic ordering in Gd sublattice does not affect superconductivity in the 1222 material. It shows that the exchange interactions between the spin of the Gd^{3+} ion and that of the conducting electron (hole) in the CuO_2 plane are very weak, and do not induce magnetic pair breaking [11]. This is similar to the case of $GdBa_2Cu_3O_{7-\delta}$ and Ta-1222 system giving yet another opportunity to study the interaction between superconductivity and magnetism as in $RuSr_2(Gd,Ce)_2Cu_2O_z$.

4. Conclusions

In conclusion, we have successfully synthesized superconducting $TaSr_2(Gd,Ce)_2Cu_2O_y$ with onset superconducting transition at 30 K and zero resistance temperature at 10 K prepared without oxygen pressure. We believe that the optimum superconducting properties of $TaSr_2(Gd,Ce)_2Cu_2O_y$ has not been determined yet. The formation of $TaSr_2(R,Ce)_2Cu_2O_y$ series can be extended from a bigger ion like Pr to a smaller rare earth ions like Gd. The magnetism of Gd^{3+} does not suppress the superconductivity has led us to conclude that the Gd 4f state are well shielded.

Acknowledgements

This research has been supported by the Ministry of Science, Technology and Innovation, Malaysia through IRPA Grant no. 09-02-02-0072-EA199.

References

1. Y. TOKURA, H. TAKAGI and S. UCHIDA, *Nature* **337** (1989) 345.
2. T. ARIMA, Y. TOKURA, H. TAKAGI, S. UCHIDA, R. BAYERS and J. B. TORRANCE, *Physica C* **168** (1990) 79.
3. Y. TOKURA, T. ARIMA, H. TAKAGI, S. UCHIDA, T. ISHIGAKI, K. ASANO, R. BEYERS, A. I. NAZZAL, P. LACORRE and J. B. TORRANCE, *Nature* **342** (1989) 890.
4. T. MAEDA, K. SAKUYAMA, S. KORIYAMA, A. ICHINOSE, H. YAMAUCHI and S. TANAKA, *Physica C* **169** (1990) 133.
5. H. SAWA, S. SUZUKI, M. WATANABE, J. AKIMITSU, H. MATSUBARA, H. WATABE, S. UCHIDA, K. KOKUSHO, H. ASANO, F. IZUMI and E. TAKAYAMA-MUROMACHI, *Nature* **337** (1989) 347.
6. Y. MAENO, H. HASHIMOTO, K. YOSHIDA, S. NISHIZAKI, T. FUJITA, J. G. BEDNORZ and F. LICHTENBERG, *ibid.* **372** (1994) 532.
7. L. BAUERNFEIND, W. WIDDER and H. F. BRAUN, *Physica C* **254** (1995) 151.
8. K. B. TANG, Y. T. QIAN, Y. D. ZHAO, L. YANG, Z. Y. CHEN and Y. H. ZHANG, *ibid.* **259** (1996) 168.
9. R. K. LI, Y. J. ZHU, Y. T. QIAN and Z. Y. CHEN, *ibid.* **176** (1991) 19.
10. R. J. CAVA, J. J. KRAJEWSKI, H. TAKAGI, H. W. ZANDBERGEN, R. B. VAN DOVER, W. F. PECK JR. and B. HESSEN, *ibid.* **191** (1992) 237.
11. S. W. WANG, Y. T. QIAN, R. K. LI and Z. Y. CHEN, *ibid.* **210** (1993) 463.
12. Z. Y. CHEN, Z. Z. SHENG, Y. Q. TANG and D. O. PEDERSON, *ibid.* **212** (1993) 206.
13. R. K. LI, Y. J. ZHU, C. XU, Z. Y. CHEN, Y. T. QIAN and C. G. FAN, *J. Solid State Chem.* **94** (1991) 206.
14. M. VYBORNOV, W. PERTHOLD, H. MICHOR, T. HOLUBAR, G. HILSCHER, P. ROGL, P. FISCHER and M. DIVIS, *Phys. Rev.* **B52** (1995) 1389.
15. T. SUZUKI and M. NAGOSHI, *ibid.* **42** (1990) 4263.
16. N. Y. AYOUB, J. T. MARKERT, E. A. EARLY, C. L. SEAMAN, L. M. PUALIUS and M. B. MAPLE, *Physica C* **165** (1990) 469.
17. H. JHANS, S. K. MALIK and R. VIJAYARAGHAVAN, *ibid.* **215** (1993) 181.

Received 9 December 2004
and accepted 16 May 2005