J Electroceram (2007) 18:289–293
DOI 10.1007/s10832-007-9166-7

Electrical properties of $BaPb_{1+x-y}Sb_yO_3$ ceramics derived from a modified sol-gel method

Yu-dong Lu · Xin Wang · Zhi-qiang Zhuang

Received: 15 January 2006 / Accepted: 25 April 2007 / Published online: 17 May 2007

Abstract $BaPbO_3$ ceramics has attracted considerable interest due to the promising electrical applications. For the best control of the microstructure and phase, Sb-doped $BaPbO_3$ ceramics were prepared by a sol-gel route. Inorganic compounds were used as starting chemicals, citric acid and Ethylene diamine tetra-acetic acid (EDTA) as complex chelate agent, and distilled water as solvent. Experimental results demonstrate that the Sb-doped $BaPbO_3$ ceramics with homogeneous composition could be prepared by the method mentioned above. Influence of Pb/Ba ratio and Sb concentration on the room-temperature resistivity and the PTCR behavior of $BaPb_{1+x-y}Sb_yO_3$ (x=0.0, 0.1, 0.2 and $0 \leq y \leq 0.2$) compositions was investigated. The PTCR behavior was related to the Pb/Ba ratio and major compensating defect in $BaPbO_3$. The lowest electrical resistivity of Sb-doped $BaPbO_3$ was calculated to be 2.69×10^{-4} Ω·cm when the Sb concentration y=12–13 mol%. The 0.5 mol% Sb-doped $BaPbO_3$ showed the best PTCR behavior, and its Curie temperature is about 850 °C.

Keywords $BaPbO_3$ · Sol-gel · Donor doping · PTCR · Room-temperature resistivity

1 Introduction

Conductive ceramics has attracted considerable interest in developing applications. In this field, $BaPbO_3$-based ceramics with high conductivity has been reported [1, 2]. Because of the low resistivity at room temperature, $BaPbO_3$-based materials have been studied as possible superconductors in numerous experimental and theoretical works during the last century [3–5]. At the same time, $BaPbO_3$ has become attractive in applications such as electrodes for lead zirconate titanate (PZT) ferroelectric thin film [6–8], corrosion resistant coating for a positive battery electrode [9] and barrier layer capacitor [10, 11] et al. Some researchers reported that $BaPbO_3$ showed positive temperature coefficient of resistivity (PTCR) characteristics [12, 13], but it can't [14, 15]. Both Pb/Ba ratio and processing may influence the PTCR properties of the samples. It is therefore of great interest to study the PTCR properties of $BaPbO_3$ ceramics. Compared with $BaTiO_3$-based PTCR ceramics, $BaPbO_3$-based PTCR ceramics have a much lower room-temperature resistivity and higher Curie temperature. If the PTCR property of $BaPbO_3$ could be improved, it would be of importance for applications such as heating devices operating at low voltage and high-current-protecting devices operating at high temperature.

In this work the influence of Ba/Pb ratio and Sb concentration doped in B-side on the properties of $BaPbO_3$ were carried out. Experiments showed that the improvement of PTCR characteristic of $BaPbO_3$ modified with Sb had been achieved. Room-temperature resistivity was about 2.69×10^{-4} Ω·cm for 12–13 mol% donor-doped $BaPbO_3$ ceramics.

2 Experimental

Sb-doped $BaPbO_3$ ceramics powder was prepared by a sol-gel route to utilize the finer control of the process on homogeneity and microstructure. Inorganic compounds $Ba(OH)_2 \cdot 8H_2O$ (98%, AR grade), $Pb(CH_3COO)_2 \cdot 3H_2O$ (99%, AR grade) and Sb_2O_3 (99%, AR grade) were used as starting

Y.-d. Lu (✉) · X. Wang · Z.-q. Zhuang
College of Material Science & Engineering,
South China University of Technology,
Guangzhou 510640, China
e-mail: yudonglu@yahoo.com.cn

materials, citric acid (99.5%, AR grade) and Ethylene diamine tetra-acetic acid (EDTA)(99.5%, AR grade) as complex chelate agent, and distilled water as solvent in this work. Powders with compositions of $BaPb_{1+x-y}Sb_yO_3$ (where x=0.0, 0.1, 0.2 and $0 \le y \le 0.2$) were prepared by the sol-gel method. The process flow chart is shown in Fig. 1. The dried gel powder was calcined in air at 850 °C for 3 h. The calcined powder was pressed into rectangular bars of 2.0×8.0×40.0 mm and sintered at 970 °C for 5 h in air.

The room-temperature resistivity of the ceramics was measured with the four-point dc technique, used embedded Pt wires as voltage probes. The resistivity-temperature (R-T) curves were recorded with a heating rate of 2 °C min^{-1}. The samples were characterized by powder X-ray diffraction (XRD, Rigaku D/max-IIIA) using Cu Kα radiation.

3 Results and discussion

3.1 Influence of Pb/Ba ratio on room-temperature resistivity and PTCR behavior

Mulder et al. [16] revealed by ^{121}Sb Mössbauer measurements that Sb-doped $BaPbO_3$ existed in compositions of $BaPb_{1-y}Sb_yO_3$ with Sb in a single valance state 5+. The products in the $BaPb_{1+x-y}Sb_yO_3$ series show black in color and are stable in atmospheric condition. It was found that the room-temperature resistivity considerably decreased with the increase of lead concentration from 0 to 0.1 and the reduction was moderate beyond the lead concentration of 0.1 as y=0 (as shown in Fig. 2). Owing to the high volatile character, Pb is deficient for compositions with x=0.0 and the corresponding sample's resistivity is highest. The 10 mol% excess of Pb is always added in the starting materials. $BaPbO_3$ is non-stoichiometric with Ba deficiencies as suggested by Ikushima and Hayakawa [16], and the corresponding number of oxygen vacancies and electrons will be required to satisfy the site balance and charge neutrality conditions [17]:

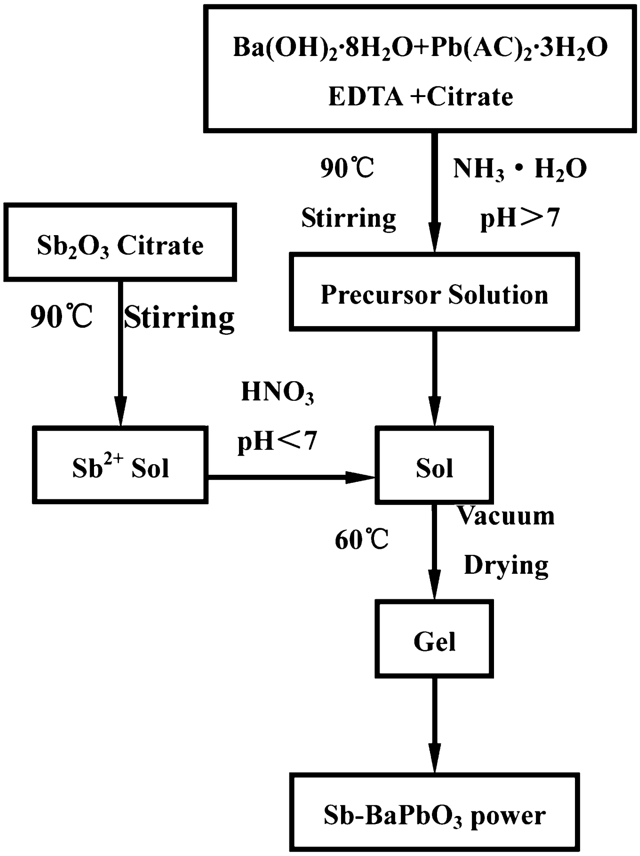

Fig. 1 Flow chart of the sol-gel route for the preparation of Sb-doped $BaPbO_3$ powder

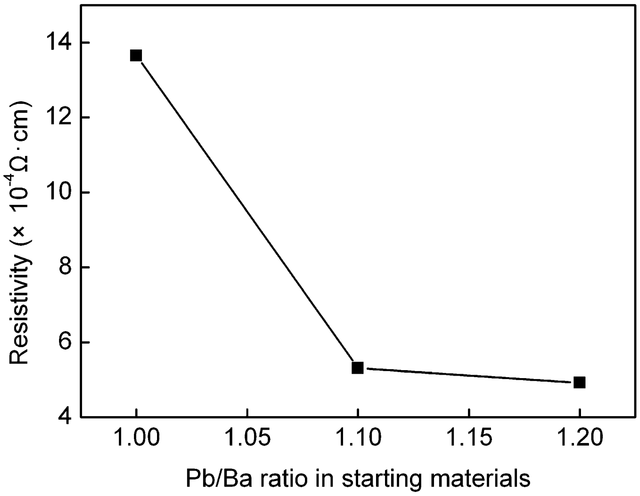

Fig. 2 Influence of Pb to Ba ratio on the room-temperature resistivity of $BaPb_{1+x}O_3$ compositions

$$PbO \xrightarrow{BPO} Pb''_{Pb} + O^{\times}_{O} + V^{\bullet\bullet}_{O} \tag{1}$$

$$Pb''_{Pb} \rightarrow Pb^{\times}_{Pb} + 2e \tag{2}$$

$$V^{\bullet\bullet}_{O} + 2e \rightarrow V^{\times}_{O} \tag{3}$$

The electron is not strongly trapped by oxygen vacancy. Therefore, some part of the excess Pb is acceptor impurity in $BaPbO_3$.

Temperature dependence of resistivity for the $BaPb_{1+x}O_3$ compositions is shown in Fig. 3. The increase of resistivity with the increase of temperature suggesting that electrical conduction is metallic. PTCR behavior was observed for composition with x=0.2, but wasn't for compositions with x=0.0 and 0.1. So the PTC properties were determined by the different Pb/Ba ratio in $BaPb_{1+x}O_3$. The observed PTCR behavior of $BaPb_{1.2}O_3$ possibly involves the Barium

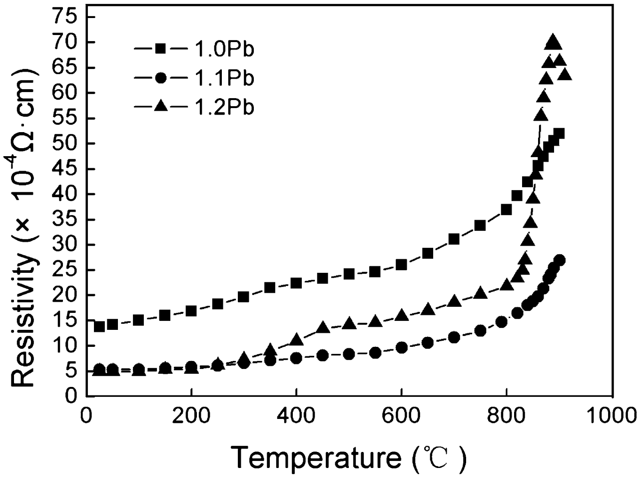

Fig. 3 Variation of the resistivity with temperature of compositions $BaPb_{1+x}O_3$

vacancies in grain boundaries. Excess of Pb causes the born of Barium vacancies (as shown in Eq. 1), leading to the build up of the potential barriers. At the Curie point, the increase in the potential barriers is likely to dominate the PTCR properties.

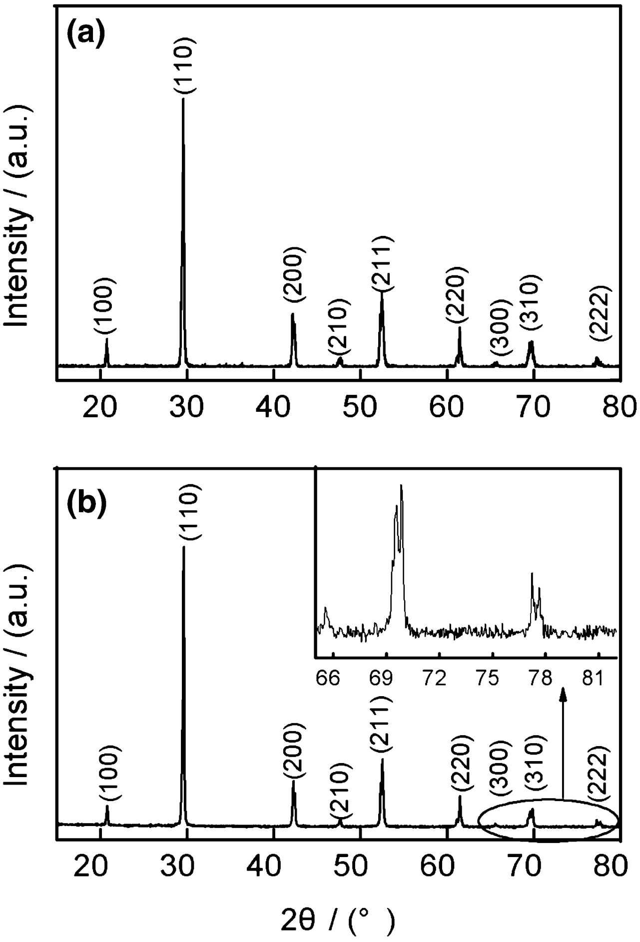

Fig. 4 XRD patterns of (**a**) undoped $BaPbO_3$, (**b**) 1 mol% Sb-doped $BaPbO_3$

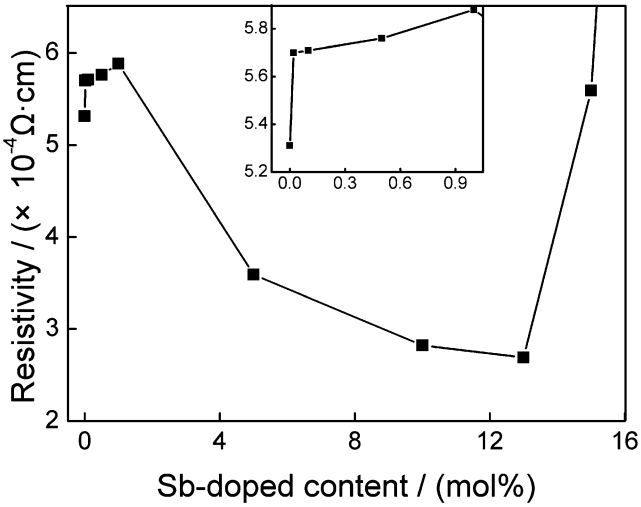

Fig. 5 Sb concentration dependence of room-temperature resistivity for the Sb-doped $BaPbO_3$

3.2 XRD analysis of Sb-doped $BaPbO_3$

The XRD studies were performed on undoped and Sb-doped $BaPbO_3$ to examine the phase formation and crystal structure. Figure 4 shows a comparison of the XRD patterns of undoped $BaPbO_3$ and 1 mol% Sb-doped $BaPbO_3$. Crystalline phase of the samples was identified by comparing the X-ray diffraction peaks of the samples with those of the standards. The XRD patterns revealed that the samples are polycrystalline perovskite structure with no evidence of any secondary phases. But these peaks were found to be splitting at 2θ=69.7 and 77.4° in Sb-doped $BaPbO_3$. This transition might be explained that the phase changes from cubic phase to orthorhombic or pseudocubic one. It should not seem strange that the cubic, orthorhombic and pseudocubic phases of $BaPbO_3$ were all reported by earlier workers [18, 19].

3.3 Influence of Sb-doped concentration on room-temperature resistivity

As shown in Eqs. 1–3, carriers are electrons, which are not strongly trapped by oxygen vacancies for the undoped $BaPbO_3$. V_{Ba}'' and e are two probable alternative compensating defects for incorporating a donor oxide into $BaPbO_3$. Figure 5 shows the variation of resistivity with doped concentration for Sb-doped $BaPbO_3$. The room-temperature resistivity increases with Sb concentration increased from 0.0 to 0.01. the lightly Sb-doped sample has the similar microstructure to undoped sample (as shown in Fig. 6). Thus the change of room-temperature resistivity as functions of donor concentration is mainly because of the switch of the major defects. Doping of Sb in B side causes the born of $Sb_{Pb}^{\bullet}$ and V_{Ba}'':

$$Sb_2O_5 \xrightarrow{BPO} 2Sb_{Pb}^{\bullet} + V_{Ba}'' + 5O_O \qquad (4)$$

The antimony ions occupy Pb sites, and because Sb^{5+} has a higher valance than Pb^{4+}, it behaves as a donor. The donor charge is compensated by V_{Ba}''. There is an intrinsic equilibrium:

$$\text{nil} \rightarrow V_{Ba}'' + V_O^{\bullet\bullet} \qquad (5)$$

The concentration of oxygen vacancies decreases with the addition of barium vacancies, then the carrier concentration decreased resulting in the increase of resistivity. As the Sb concentration sequentially increased, however, the resistivity decreases. V_{Ba}'' is the compensating defect in lightly Sb-doped $BaPbO_3$. As the donor concentration increases, electrons become the major compensating defect:

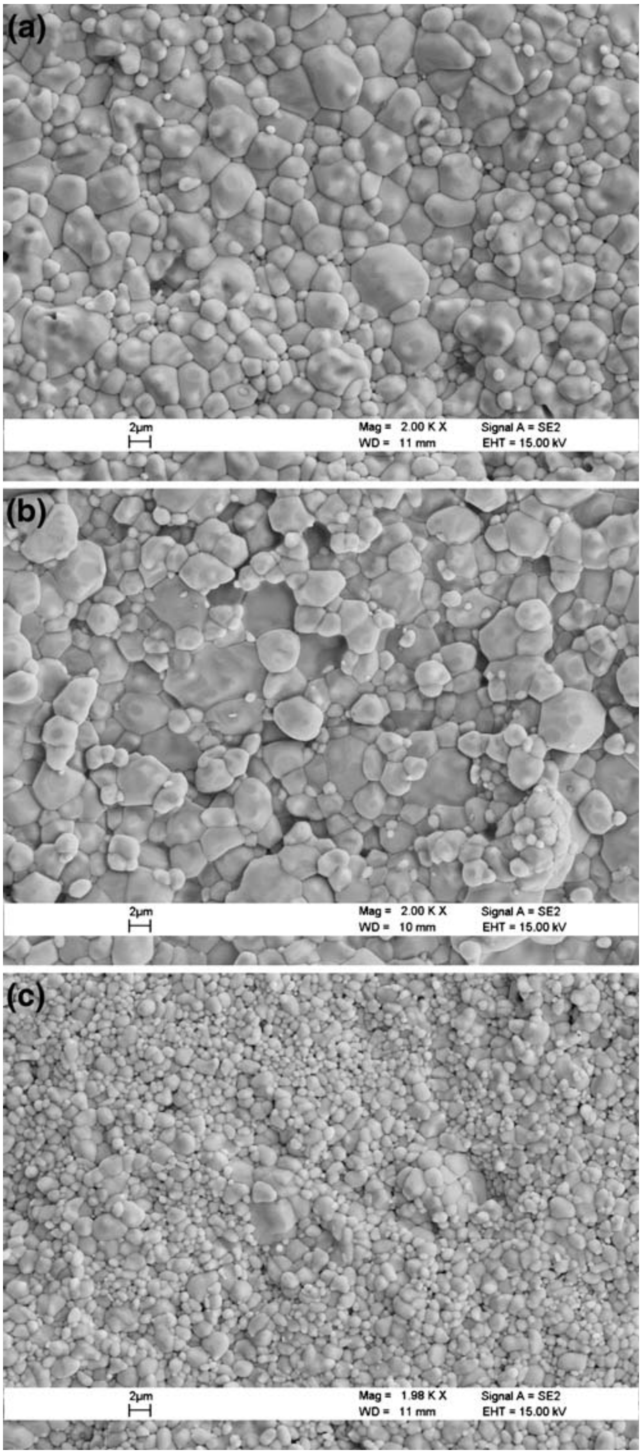

Fig. 6 SEM images of sintered $BaPbO_3$. (**a**) undoped; (**b**) 0.15mol% Sb-doped; (**c**) 13 mol% Sb-doped

$$Sb_2O_5 \xrightarrow{BPO} 2Sb_{Pb}^{\bullet} + 4O_O + \frac{1}{2}O_2 + 2e \qquad (6)$$

Therefore, the resistivity decreases when electrons concentration increases. The lowest electrical resistivity of Sb-doped $BaPbO_3$ was calculated to be 2.69×10^{-4} Ω·cm when the Sb concentration y=12–13 mol%. The resistivity significantly increases again when the donor concentration is larger than 13 mol%. It was possibly accounted for the reducing of the grain size (Fig. 6) and the Sb impurities beyond the limit of solid solubility segregating in grain boundary.

3.4 PTCR properties in the Sb-doped $BaPbO_3$

There is no PTCR property for composition $BaPb_{1.1}O_3$ as mentioned above. Figure 7 shows the temperature dependence of the resistivity for the $BaPbO_3$ ceramics doped with Sb of 0, 0.02, 0.1, 0.5, 1.0, 5.0, 10, 13.0, and 15.0%. In lightly

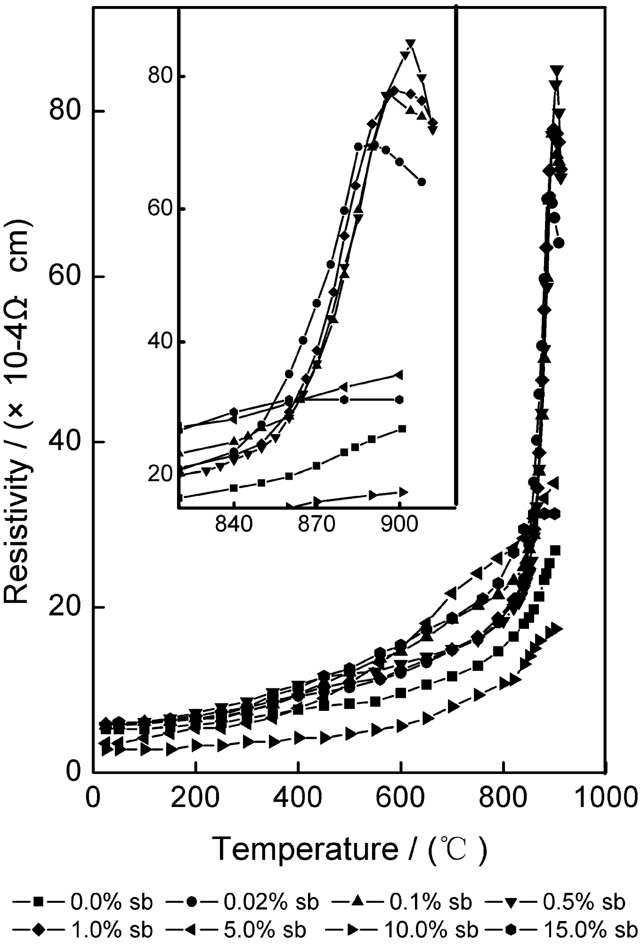

Fig. 7 Measured values of resistivity vs. temperature in Sb-doped $BaPbO_3$

Sb-doped $BaPbO_3$ ($0 \leq y \leq 1.0$ mol %), the PTCR behavior was also accounted for the impurity incorporation equation (Eq. 2). It is demonstrated that barium vacancies cause to the build up of potential barriers, leading to the PTCR behavior [20]. In the oxidized condition (such as in air), the equilibrium defect chemistry of lightly donor-doped $BaPbO_3$ is dominated by donor impurities and their compensating cation vacancies [21]. There is extensive evidence that cation diffusion is very slow in the perovskite structure. Thus the Ba vacancies are mainly accumulated at grain boundary. Many Barium vacancies led to a wide range of grain boundary structures and high potential barriers, and ultimately produced the PTCR behavior. No PTCR behavior was found in highly donor-doped $BaPbO_3$. The changes of PTCR behavior also indicated a change of compensating defect from $V_{Ba}^{''}$ to electron with the increase of the donor concentration. The 0.5 mol% Sb-doped $BaPbO_3$ showed the best PTCR behavior, and its Curie temperature is about 850 °C.

4 Conclusions

Sb-doped $BaPbO_3$ ceramics were prepared by a modified sol-gel route with citric acid and EDTA as complex chelate agent and distilled water as solvent. Excess of Pb causes the born of barium vacancies, and the observed PTCR behavior of $BaPb_{1.2}O_3$ involves the Barium vacancies in grain boundaries. $V_{Ba}^{''}$ is the compensating defect in lightly Sb-doped $BaPbO_3$, while electrons become the major compensating defect as the donor concentration increases. The room-temperature resistivity of 2.69×10^{-4} Ω·cm for composition of 12 to 13 mol% Sb-doped in B-side were achieved. The 0.5 mol% Sb-doped $BaPbO_3$ showed the best PTCR behavior and its Curie temperature is about 850 °C.

Acknowledgement The present work was supported by Guangdong Natural Science Foundation of China under grant no. 033177 and Natural Science Foundation of South China University of Technology under grant no. 040140. The authors are also thankful to Professor D.M. Smyth for providing his literature on defect chemistry.

References

1. R.D. Shannon, P.E. Bierstedt, J. Am. Ceram. Soc. **53**, 635 (1970)
2. T. Kodenkandath, Mater. Chem. Phys. **62**, 23 (2000)
3. A.W. Sleight, J.L. Gillson, P.E. Bierstedt, Solid State Commun, **17**, 27 (1975)
4. R.J. Cava, B. Batlogg, J.J. Krajewski, R. Farrow, L.W. Rupp Jr., A.E. White, K. Short, W.F. Peck Jr., T. Kometani, Nature **332**, 814 (1988)
5. R.J. Cava, B. Batlogg, G.P. Espinosa, A.P. Ramirez, J.J. Krajewski, W.F. Peck Jr., L.W. Rupp Jr., A.S. Cooper, Nature **339**, 291 (1989)
6. C.S. Liang, J.M. Wu, M.C. Chang, Appl. Phys. Lett. **81**, 3624 (2002)
7. Y.R. Luo, J.M. Wu, Jpn. J. Appl. Phys. **42**, 242(2003)
8. Y.R. Luo, J.M. Wu, Appl. Phys. Lett. **11**, 3669 (2001)
9. W.H. Kao, S.L. Haberrichter, K.R. Bullock, J. Electrochem. Soc. **139**, L105 (1992)
10. B.V. Hiremath, R.E. Newnham, L.E. Cross, J. Am. Ceram. Soc. **75**, 2953 (1992)
11. F.P. Skeele, R.E. Newnham, L.E. Cross, J. Am. Ceram. Soc. **71**, c263 (1988)
12. H. Nagamoto, H. Kagotani, T. Okubo, J. Am. Ceram. Soc. **76**, 2053 (1993)
13. Z.C. Li, H. Zhang, B. Bergman, J. Mater. Sci., Mater. Electron. **15**, 183 (2004)
14. Y. Kodama, N. Murayaman, Y. Torii, J. Mater. Sci. Lett. **17**, 1999 (1998)
15. Y.D. Lu, X. Wang, Z.Q. Zhuang, Chin. J. Rare Metals **29**, 643 (2005)
16. F.M. Mulder, R.C. Thiel, Physica C: Superconductivity **201**, 80 (1992)
17. H. Ikushima, S. Hayakawa, Solid State Electron. **9**, 921 (1966)
18. C.L. Sun, H.W. Wang, M.C. Chang, M.S. Lin, S.Y. Chen, Mater. Chem. Phys. **78**, 507 (2003)
19. S.M. Moussa, B.J. Kennedy, T. Vogt, Solid State Commun. **119**, 549 (2001)
20. J. Daniels, R. Wernicke, Philips Res. Rep. **31**, 544 (1976)
21. Y.D. Lu, X. Wang, Z.Q. Zhuang, J. Chin. Ceram. Soc. 35, 308 (2007)