Synthesis of a new (Ta_{1-x}Sn_x)Sr₂EuCu₂O_z superconductor

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(Received 9 June 2014; revised or reviewed 20 June 2014; accepted 21 June 2014)

Abstract

We report here results of a study of superconductivity in the $(Ta_{1-x} Sn_x)Sr_2EuCu_2O_z$ system. We observe resistive superconducting transitions for the samples with x = 0.15-0.3, and the highest superconducting transition has been achieved for the sample with x = 0.2 which reveals onset T_c of 43 K and zero-resistivity of 25 K. Thermoelectric power measurements indicate that Sn doping introduces holes into the system and thereby superconductivity can be achieved in the $(Ta_{1-x}Sn_x)Sr_2EuCu_2O_z$ system.

Keywords: Ta-based 1212 cuprate; New superconductor; Sn doping; (Ta_{1-x}Sn_x)Sr₂EuCu₂O_z system

1. INTRODUCTION

 $MSr_2RCu_2O_8$ (M-1212, M = Nb or Ta) compounds (R = rare earths) [1-6] are derived from the RBa₂Cu₃O₇ (R-123 or Cu-212) phase by replacement of the CuO chain layer and Ba atoms in Cu-1212 phase by MO₂ layer and Sr atoms, respectively. Previous work on various M-1212 compounds (M = Nb, Ta, R = Nd, Sm, Eu, Gd and Tb) has shown them to be nonsuperconducting and insulators. Since all known high- T_c cuprate compounds can be varied from insulators to semiconductors, metals, or even superconductors by an appropriate carrier doping, several attempts have been made in the past to induce superconductivity in the compounds through doping of various cations such as by partial replacement of R⁺ Ca⁺² [3, 5, 6] or by partial substitution of Nb ions by Fe, Ti, Zr or Cr cations [2, 6], but no evidence of superconductivity has been observed. Very recently, however, it was found that superconductivity can be induced at T_c (onset) = 40-43 K by Sn [7] or Cd [8] doping for Nb in the NbSr $_2EuCu_2O_{8-\delta}\,system$. In the present work, we report our efforts to induce superconductivity into the (Ta_{1-x}Sn_x)Sr₂EuCu₂O_{8-δ} system and successful synthesis of new superconducting compounds with onset T_c of about 43 Κ.

2. EXPERIMENTALS

Polycrystalline samples of the nominal composition of $(Ta_{1-x}Sn_x)Sr_2EuCu_2O_z$ ($0 \le x \le 0.3$) were prepared by using a solid-state reaction from starting powders of Ta_2O_5 , SnO_2 , $SrCO_3$, Eu_2O_3 and CuO with purities above 99.9%. The powders were mixed, ground, and heated at 950 \sim 980 °C for 10 h in a 6% O_2 atmosphere. The resultant powders were then re-ground, pressed into pellets, and annealed at 1050 °C for 15 h in an oxygen atmosphere. Subsequently, the samples were again re-ground and

pressed into pellets, and sintered at $1060\,^{\circ}$ C for 15 h under flowing oxygen. The resulting samples were then slowly cooled below $200\,^{\circ}$ C in a furnace. The samples were characterized by X-ray diffraction (XRD) at room temperature by using a powder diffractometer (X'pert-pro MPD) with Ka radiation to determine their purity and lattice parameters. The temperature dependence of electrical resistivity was measured by using a conventional four-probe technique with silver paste used as contacts within a temperature range of about 10 K to room temperature. The measuring current was 10 mA. The room-temperature thermoelectric power was measured relative to copper electrodes by using a dc differential method and further calculated by correcting for the thermoelectric power of copper.

3. RESULTS AND DISCUSSION

The XRD patterns for $(Ta_{1-x}Sn_x)Sr_2EuCu_2O_z$ samples with x = 0, 0.1, 0.2, and 0.3 are shown in Fig. 1. The diffraction peaks for the x = 0 sample could be indexed on the basis of a tetragonal unit cell as denoted in Fig. 1. As the Sn-doping increased from x = 0 to x = 0.3, the impurity peaks denoted by stars are slightly increased but the tetragonality is retained in all the samples in the range of 0 \leq x \leq 0.3. The lattice parameters for the samples obtained from the least square fitting method are a = 3.868(2) Å, c =11.68(1) Å for x = 0 sample, a = 3.869(2) Å, c = 11.67(1)Å for x = 0.1 sample, a = 3.868(2) Å, c = 11.69(1) Å for x = 0.2 sample and 3.869(2) Å, c = 11.68(1) Å for x = 0.3sample. The small changes in lattice parameters with the Sn doping seem to be consistent with the slight difference in ionic size [9] of Sn^{+4} (0.69 Å for CN=6) when compared to that of Ta^{+5} (0.64 Å for CN=6). The temperature dependence of the electrical resistivity for the (Ta_{1-x}Sn_x)Sr₂EuCu₂O_z samples is shown in Fig. 2 (a) and (b). The sample with x = 0 shows a semiconducting

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behavior at low temperature. As the Sn doping content increases, the samples with $x=0.1,\,0.15,\,$ and 0.2 show a superconducting drop at about 23, 43 and 43 K, respectively.

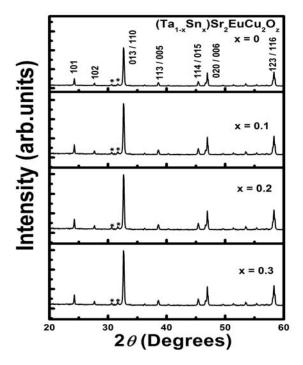


Fig. 1. Powder XRD patterns for the $(Ta_{1-x}Sn_x)Sr_2EuCu_2O_z$ (x = 0 - 0.3) samples. Peaks due to impurity phases are marked with asterisks.

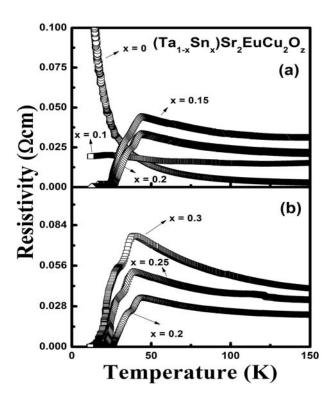


Fig. 2. Temperature dependences of the electrical resistivity of $(Ta_{1-x}Sn_x)Sr_2EuCu_2O_z$ (a)for x=0-0.2; (b) for x=0.2-0.3 samples.

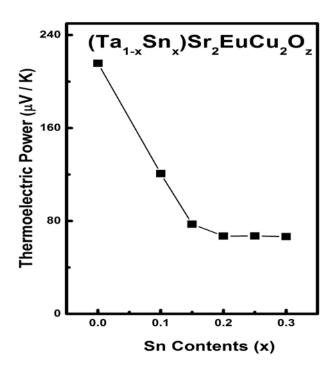


Fig. 3. Dependence of room temperature (295 K) thermoelectric power on Sn-doping content x in $(Ta_{1-x}Sn_x)Sr_2EuCu_2O_z$ samples.

Zero-resistivity temperatures for the x=0.15 and 0.2 samples are 22 and 25 K, respectively. The double transition behavior observed in the resistive transition is considered to be caused by the inhomogeneous distribution in cations and oxygen as reported typically in granular superconductors. On the other hand, when the Sn doping content increases from x=0.2 to 0.3, the normal-state resistivity of the samples increrses with increasing Sn doping content as shown in Fig1 (b) and both onset and zero-resistivity temperatures slightly decreases. The onset transition temperatures for the x=0.25 and 0.3 samples are 39 and 39 K, and the corresponding zero-resistivity temperatures are 18 and 13 K, respectively.

The results of Fig. 2 shows clearly superconductivity can be induced by the Sn doping in Ta-1212 system. For p-type cuprate superconductors, it is generally believed that one of the key parameters controlling the T_c values is the hole concentration [10]. T_c is known to vary as an inverted parabolic function of the hole concentration (p) per CuO_2 plane and maximum T_c is observed near p = 0.16. Accordingly, a superconducting cuprate may be classified as an underdoped, optimally doped and overdoped superconductor. The room-temperature thermoelectric power measurements are useful to study the carrier-doping level of a sample because room- temperature TEP for most of superconducting cuprates is known to vary in a systematic manner as a function of p. It has large positive values in the underdoped range and negative values in the overdoped range, with optimal doping being 1-2 µV/K. Fig 3 summarizes room-temperature (295 K) TEP for the $(Ta_{1-x}Sn_x)Sr_2EuCu_2O_z$ samples. The TEP values for the samples decreases initially up to x=0.2 and then nearly saturates thereafter. The respective hole concentrations estimated from these TEP data [10] are 0.017, 0.055, 0.071 and 0.071 for $x=0,\,0.15,\,0.2$ and 0.3, respectively which indicate that all studied samples are in an underdoped state. The hole concentration for the x=0 sample is much lower than the critical hole concentration of about 0.05 requiring for the appearance of superconductivity in cuprate superconductors [11]. Therefore the absence of superconductivity for the x=0 sample can be attributed to the deficiency of hole concentration.

Considering the fact that onset superconductivity of 43 K was also observed in a (Nb_{1-x}Cd_x)Sr₂EuCu₂O_z sample [8] containing hole concentration, p of 0.066, T_c dependence on hole concentration for both $(Nb_{1-x}Cd_x)Sr_2EuCu_2O_z$ and (Ta_{1-x}Sn_x)Sr₂EuCu₂O_z systems is considered to be very similar. In spite of the saturation behavior of hole concentration, the slight decrease in T_c on increasing Sn-doping content above x = 0.2 suggests that T_c can be affected not only by hole concentration but by other factors such as an increased disordering effects caused by the cation doping. Normally, chemical doping induces disorder in the doping sites owing to the random distribution of dopant atoms and the disorder can lead to hole trapping within the CuO2 planes which suppresses supperconductivity in a similar manner such as the Zn substitution for Cu [12]-[14].

4. CONCLUSIONS

The effect of Sn substitution for Ta on the structure and superconducting properties of TaSr₂EuCuO_z were investigated. Although phase purity was slightly degraded, tetragonality was retained in a range of $0 \le x \le 0.3$. We find that the Sn doping introduces holes into the system and thereby superconductivity can be achieved in $(Ta_{1-x}Sn_x)Sr_2EuCu_2O_z$ (x=0.15-0.3) where the hole concentration is higher than the critical value requiring for the appearance of superconductivity in cuprates. The highest superconducting transition has been achieved for the sample with x=0.2 which reveals onset $\mathit{T_c}$ of 43 K and zero-resistivity of 25 K.

ACKNOWLEDGMENT

This work was supported by Korea Research Foundation Grant (KRF-2012R1A1A2042519). We express our thanks to the central laboratory of Kangwon National University for help with the XRD measurements.

REFERENCES

- C. Greaves and P. R. Slater, "The synthesis of new phases related to YBCO by complete replacement of the chain copper sites," *IEEE Trans. Mag.*, vol. 27, pp. 1174-1177, 1991.
- [2] T. G. N. Babu and C. Greaves, "The electrical effects of Fermi energy changes in EuSr₂Cu₂NbO₈ and related phases," Physica C, vol. 185 – 189, pp. 585-586, 1991.
- [3] H. W. Zanderbergen, R. J. Cava, J. J. Krajewski and W. F. Peck, JR., "High resolution electron microscopy study of Sr₂NdNbCu₂O₈," J. Solid State Chem., vol. 101, pp. 322-330, 1992.
- [4] B. Hellebrand, X. Z. Wang and P. L. Steger, "Preparation and characterization of new 1-2-1-2 compounds MA₂RECu₂O_{8-δ} and Nb_{1-x}Ru_xSr₂RECu₂O_{8-δ}(M = Nb or Ta, A = Ba or Sr, and RE = Pr or Sm)," J. Solid State Chem., vol. 110, pp. 32-35, 1994.
- [5] M. Vybornov, W. Perthold, T. Holubar and G. Hilscher, P. Rogl, P. Fisher and P. Divis, "Synthesis and characterization of compounds Sr₂RMCu₂O_{8-δ} (R = Pr, Nd, Sm, Eu, Gd; M = Nb, Ta)," *Phys. Rev. B*, vol. 52, pp. 1389-1404, 1995.
- [6] E. M. Kopnin, M. V. Lobanov, A. M. Abakumov, S. V. Lubarskii, O. I. Lebedev, E. V. Antipov and J. J. Capponi, "Synthesis and properties of NbM₂RCu₂O₈ phases (M = Ba, Sr; R = Pr, Nd, Sm, Eu and Gd)," *J. Alloys Compd.*, vol. 241, pp. 63-68, 1996.
- [7] K. Kim, M. Kato, T. Noji and Y. Koike, "New superconductor EuSr₂Cu₂(Nb, Sn)O₈₋₆ with the RE-123 type structure," *Physica C*, vol. 492, pp. 165-167, 2013.
- [8] H. K. Lee, G.W. Kim and M. S. Lee, "Synthesis of new superconducting Nb-based 1212 cuprates, (Nb_{1-x}Cd_x) Sr₂EuCu₂O_{8-δ}," *J. Supercond. Nov. Magn.*, vol. 27, pp. 1207-1209, 2014.
- [9] R. D. Shannon, "Revised Effective Radii and Systematic studies of Interatomic distances in Halides and Chalcogenides," *Acta. Cryst. A*, vol. 32, pp. 751-767, 1976.
- [10] J. L. Tallon, C. Bernhard, H. Shaked, R. L. Hitterman and J. D. Jorgensen, "Generic superconducting phase behavior in high T_c cuprates: T_c variation with hole concentration in YBa₂Cu₃O₇₋₈," Phys. Rev. B, vol. 51, pp. 12911-12914 1995.
- [11] H, K. Lee, "Effect of Co doping on the superconducting properties of overdoped (Lu_{0.8}Ca_{0.2})Ba₂Cu₃O_z," Advances Sci. Tech., vol. 47, pp. 108-112, 2006.
- [12] J.P. Attfield, A.L.Kharnanov and J.A. MaAllister, "Cation effects in doped La₂CuO₄ superconductors," *Nature*, vol. 394, pp. 157-159, 1998 and *Phys. Rev. B*, vol. 51, pp. 12911-12914, 1995.
- [13] H. K. Lee and B. S. Seong, "Effect of Fe doping on the structure and superconducting properties of (Ga,Co)Sr₂(Tm,Ca)Cu₂O_z," *J. Korean Phys. Soc.*, vol. 53, pp. 3650-3654, 2008.
- [14] H. K. Lee, "Effect of Co substitution on the structure and superconducting properties of GaSr₂(Tm,Ca)Cu₂O_z," *J. Supercond. Nov. Magn.*, vol. 24, pp. 1381-1384, 2011.