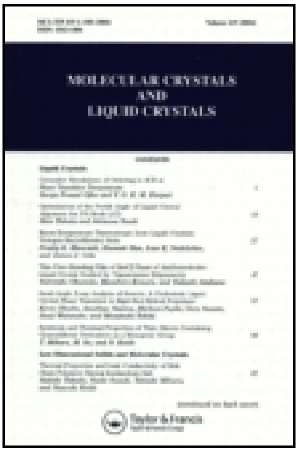
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SUPERCONDUCTIVITY IN Eu-La-Ce-Cu-O SYSTEM

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Abstract The synthesis and electric properties of a new electron-doped oxide superconductor of $(Eu,La)_{2-x}Ce_xCuO_{4-\delta}$ system with the T'-phase crystal structure are reported. The compounds were prepared by the sintering method and annealed in a stream of Ar. The $(Eu,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Eu/La=0.5) compound showed the superconductivity of T_c(onset) = 18.5K and T_c(zero) = 8.6K with a negative Hall coefficient at 300K. A preliminary study on the superconductivity in $(Gd,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Gd/La =0.5) system indicates that it has an onset at 15.7K.

INTRODUCTION

Since the recent discovery of a new type of superconductivity mediated with electron carriers in $Ln_{2-x}Ce_xCuO_{4-\delta}$ (Ln= Pr,Nd, and Sm) system by Tokura et al.,[1] extensive studies have been conducted on its structure and properties. In order to examine the nature of the electron-carrier (n-type) superconductivity, it is useful to search for new electron-doped superconductors. The electron-doped oxide superconductors have so far been extended to Pr-Th-Cu-O and Eu-Ce-Cu-O systems,[2] T_c(onset) of which were reported to be 23K and 13K, respectively. In addition, partial oxygen substitution by fluorine in T'-phase Nd_2CuO_4 induced the electron-doped superconductivity with T_c(onset) at 27K.[3] Recently, we reported the superconductivity in a new T'-structure oxide system of (Eu,La)-Ce-Cu-O.[4] In this system, the formation of solid solution composed of Eu and La is considered to play a significant role for constructing the T'-structure and developing the superconductivity. The average ionic radii of Eu^{3+} (1.07A) and La^{3+} (1.16A) mixtures are close to those of Pr^{3+} (1.13A),

Nd^{3+} (1.11A) and Sm^{3+} (1.10A). Although the formation of T'-structure with two lanthanides was already reported in $LnLaCuO_4$ (Ln=Pr ~ Gd),[5] superconductivity has not been confirmed in these systems. Judging from the similarity in valence state with the $(Nd,Ce)_2CuO_4$ system, we expected n-type character in the $(Eu,La,Ce)_2CuO_4$ system we discovered. However, no solid evidence for the n-type property has not been provided yet. In this paper, we report some electric properties of this system to elucidate its conduction mechanism.

EXPERIMENTAL

Bulk $(Eu,La)_{2-x}Ce_xCuO_{4-\delta}$ (Eu/La=0.5 ~ 2.0, x=0.05 ~ 0.25) samples were synthesized through the solid state reactions from mixtures of Eu_2O_3(99.99%), La_2O_3(99.99%), CeO_2(99.99%) and CuO(99.9%). A $(Gd,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Gd/La=0.5) sample was also prepared using Gd_2O_3(99.99%) instead of Eu_2O_3. The mixed powders were pressed into pellets and sintered at temperatures in the range of 1000°C to 1070°C for 5h in air. The pellets were subjected to reducing heat treatments at temperatures in the range of 900°C to 1070°C for 1h to 16h in a stream of Ar gas. Then, the pellets were rapidly cooled to room temperature in the same atmosphere in 30 min. The crystal structure of these samples was characterized by X-ray diffraction analysis. The resistivity was measured by a conventional four-probe method. The Hall coefficient was measured by the standard van der Pauw technique at room temperature under a magnetic field of 1 T.

RESULTS AND DISCUSSIONS

The prepared $(Eu,La)_{2-x}Ce_xCuO_{4-\delta}$ compounds (Eu/La=0.5 ~ 2.0, x = 0.05 ~ 0.25) exhibited the T'-structure from the XRD measurements. The sintering at temperatures lower than 1030°C gave impurity phases such as La_2CuO_4. Figure 1 shows the a and c lattice constants as a function of Eu/La ratio for the $(Eu,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ compounds which were sintered at 1050°C for 5h in air, annealed at 1000°C for 16h in Ar, and then cooled. The a and c lattice constants of these samples decreased linearly from 3.98A to 3.96A and from 12.3A to 12.1A, respectively with an increase in the ratio of Eu/La from 0.5 to 2, suggesting the formation of solid solution. These lattice constants are very close to the values of a = 3.95A and c = 12.1A reported for the $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ compound [1].

Figure 2 shows the resistivity vs temperature relationships for the $(Eu,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Eu/La=0.5) sample before and after the reducing treatment at 980°C in Ar. The reducing heat treatment made the specimen superconducting. The partial removal of oxygens, i.e. the increase in the oxygen vacancies should inject electron carriers as represented in the following equation;

$$(Eu,La)_{1.85}Ce_{0.15}CuO_{4-\delta} \longrightarrow (Eu,La)_{1.85}Ce_{0.15}CuO_{4-\delta-\delta'} + (\delta'/2)O_2 + \delta' e$$

Figure 3 shows the temperature dependences of resistivity for $(Eu,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Eu/La= 0.5) as well as for $(Gd,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Gd/La= 0.5) which were sintered at 1070 °C for 5h in air, annealed at 1070°C for 8h in a stream of Ar, and then cooled. T_c(onset) and T_c(zero) of the Eu-based sample were 18.5K and 8.6K, respectively. $Eu_{1.85}Ce_{0.15}CuO_{4-\delta}$ was reported by

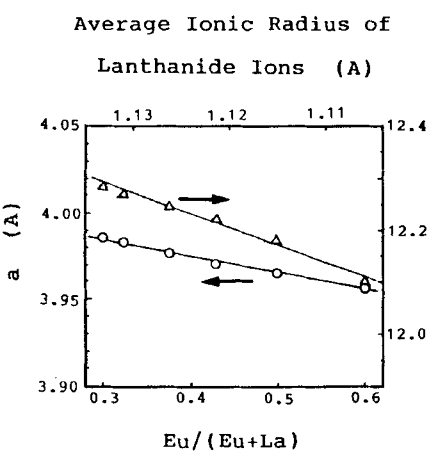

FIGURE 1 The a and c lattice constants for the $(Eu,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ as a function of Eu/La ratio.

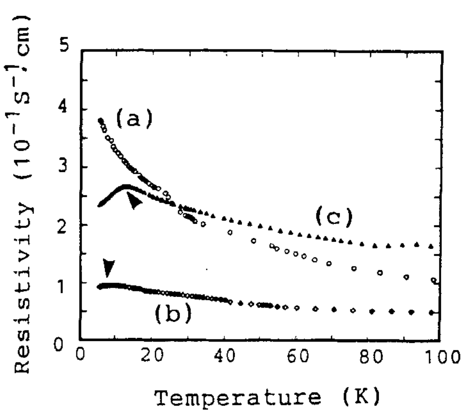

FIGURE 2 Temperature dependences of resistivity for the $(Eu,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Eu/La=0.5) sample before (a) and after the reducing treatment at 980°C in Ar ; (b) for 1h , (c) for 3h .

Markert et al. to show T_c(onset) and T_c(zero) at 12.5K and 6.5K, respectively [2]. Hall measurement was conducted on the Eu-based sample to give a negative Hall coefficient at 300K. The negative sign indicates that the charge carrier is electron in the normal state of this Eu-La-Ce-Cu-O system. As an alternative origin of superconductivity in the Eu-La-Ce-Cu-O system, we must think about the possibility of carrier (hole) generation by the transition in valence state of Eu: $Eu^{3+} \rightarrow Eu^{2+} + h$. This possibility could be excluded not only by the observed negative Hall coefficient but also by the measurement of the Mossbauer effect. ^{151}Eu-Mössbauer effect was measured for the present compounds at room temperature by using $^{151}Sm_2O_3$ as the γ-ray source. There was no peak at the isomer shift of -12 ~ -11 mm/s which corresponded to Eu^{2+} ion, while the peak solely observed appeared at the isomer shift of 0.7 ~ 0.8mm/s which was attributed to Eu^{3+} ions.[6] As seen in Fig.3, the resistivity change indicating T_c(onset) was observed at 15.7K for the $(Gd,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Gd/La= 0.5). The Gd-Ce-Cu-O compounds

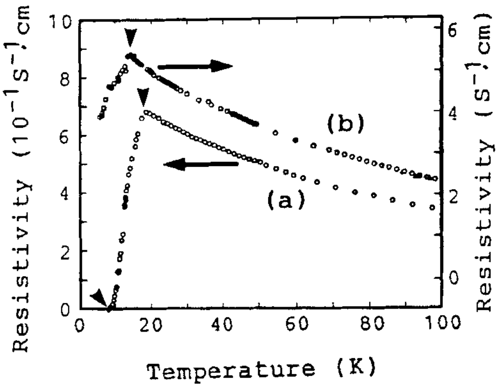

FIGURE 3 Temperature dependence of resistivity for $(Eu,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Eu/La=0.5) (a) and $(Gd,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Gd/La= 0.5) (b).

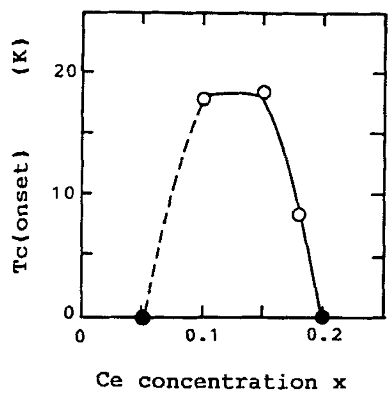

FIGURE 4 Relationship between T_c(onset) and Ce concentration x for the $(Eu,La)_{2-x}Ce_xCuO_{4-\delta}$ (Eu/La= 0.5).

treated likewise have shown no sign of superconductivity yet.

Figure 4 shows the relationship between T_c(onset) and Ce concentration x for the $(Eu,La)_{2-x}Ce_xCuO_{4-\delta}$ (Eu/La=0.5). The samples were sintered at 1070°C for 5h in air, annealed at 1070°C for 8h in a stream of Ar and then cooled. The T_c(onset)was observed for the samples with x ranging from 0.1 to 0.20. This Ce doping range for superconductivity is similar to x= 0.14 to 0.18 reported for the $Nd_{2-x}Ce_xCuO_{4-\delta}$ compounds.[7]

CONCLUSION

A new electron-doped oxide superconductor of $(Eu,La)_{2-x}Ce_xCuO_{4-\delta}$ system with the T'-structure was synthesized. The $(Eu,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Eu/La=0.5) showed the superconductivity of T_c(onset) = 18.5K and T_c(zero) = 8.6K and a negative Hall coefficient at 300K. The $(Gd,La)_{1.85}Ce_{0.15}CuO_{4-\delta}$ compound (Gd/La=0.5) also showed an T_c(onset) at 15.7K.

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