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Phase Study of the (La, *Ln*, Ce)$_2$CuO$_4$ (*Ln* = Tb, Dy, and Ho) System

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We studied the formation of the (La, *Ln*)$_2$CuO$_4$ T'-structure with a small amount of Ce-doping. The results show that La*Ln*CuO$_4$ has a T'-structure for *Ln* = Tb. The addition of Ce is necessary to form the T'-structure for *Ln* = Dy and Ho. We also report the T^*-structure La$_{1.1}$Dy$_{0.9}$CuO$_4$. © 1989 Academic Press, Inc.

The lanthanide cuprate oxide of general formula *Ln*$_2$CuO$_4$ has been reported (*1–5*) to form two types of structures: For *Ln* = La, it forms a K$_2$NiF$_4$ structure; for *Ln* = Pr, Nd, Sm, Eu, and Gd, it forms a Nd$_2$CuO$_4$ structure (referred to as the T'-structure hereafter). The ternary oxides *LnLn'*CuO$_4$ also form a T'-structure (*6*) when (i) *Ln* = La; *Ln'* = Pr, Nd, Sm, Eu, Gd, but not Tb and Dy, and (ii) when *Ln* = Pr, Nd, Sm, Eu; *Ln'* = Nd, Sm, Eu, Gd, Tb, and Dy. Among all these oxides, only La$_2$CuO$_4$ shows a metallic behavior, whereas all others are semiconductors (*7*). The recent discovery of superconductivity in Nd$_{2-x}$Ce$_x$CuO$_4$ has attracted great attention because of the electron-character of the charge carriers in these compounds as evident from the Hall and Seebeck measurements (*8*). In a study of superconductivity in the La*Ln*$_{1-x}$Ce$_x$CuO$_4$ system (*9*) (*Ln* = rare-earth element), LaTb$_{0.85}$Ce$_{0.15}$CuO$_4$ and LaDy$_{0.85}$Ce$_{0.15}$CuO$_4$ were reported to form the T'-structure. The formation of the T'-structure in these two cases had not been reported previously and was further studied in this work.

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Most samples were prepared as follows: An appropriate amount of rare-earth oxides and CuO were mixed and fired at 950°C for 8–16 hr. The powders thus obtained were pelletized into 5-mm-diameter * 1.5-mm-thick disks and fired at 1050°C (referred to as second-firing temperature) for another 8–16 hr, then air quenched. Some samples had a different second-firing temperature, which will be specified in a later publication.

In contrast to Nedil'ko's results (*6*), the samples with nominal compositions LaTbCuO$_4$ and LaTb$_{0.85}$Ce$_{0.15}$CuO$_4$ show a pure T'-structure as indicated by the X-ray diffraction pattern. The synthesis route of Nedil'ko was different from ours, which might account for the difference in results. After annealing in flowing Ar at 900°C for 16 hr,

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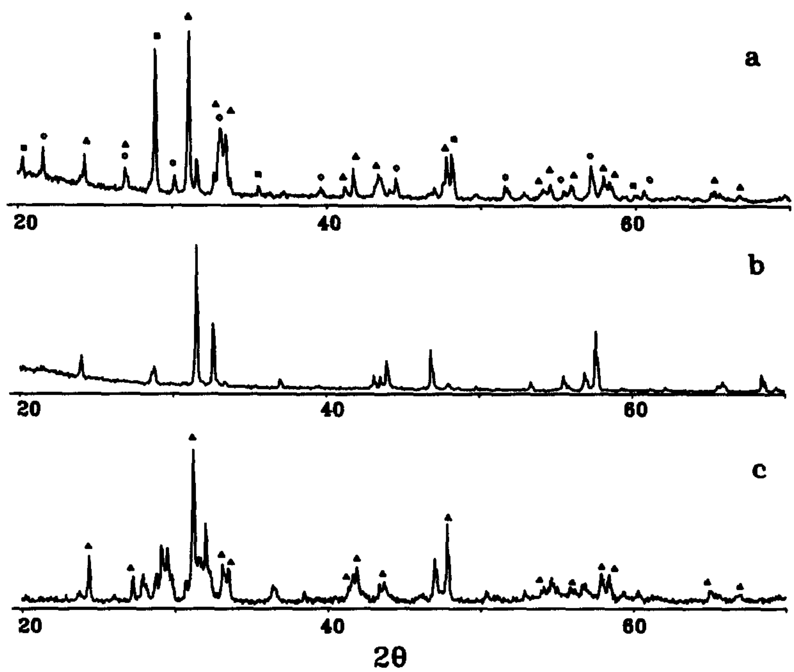

FIG. 1. The X-ray diffraction patterns of $La_{1.1}Dy_{0.9}CuO_4$ samples with second-firing temperatures (a) 950°C (▲, La_2CuO_4; ○, $Dy_2Cu_2O_5$; and ■, Dy_2O_3), (b) 1050°C, and (c) 1200°C.

both samples show semiconducting behavior from room temperature down to liquid helium temperature.

The same preparation technique was used to form $LaDyCuO_4$. However, a mixed-phase sample was obtained. The major feature in the X-ray pattern remains quite simple and matches well with the T^*-structure reported by Takayamma-Muromachi *et al.* (*10*). (The T^*-structure consists of alternative stackings of K_2NiF_4-type slabs and T'-type slabs.) By adjusting the La:Dy ratio, the purest T^*-phase was found in the $La_{1.1}Dy_{0.9}CuO_4$ sample. The X-ray diffraction patterns of $La_{1.1}Dy_{0.9}CuO_4$ samples fired at different second-firing temperatures are shown in Fig. 1. This shows that this T^*-phase forms only over a limited temperature range. With a small amount of Ce substitution for Dy, the phase immediately changes from the T^*- to the T'-structure. Figure 2 shows the X-ray diffraction patterns of the T^*-structure $La_{1.1}Dy_{0.9}CuO_4$ and the T'-structure $LaDy_{0.85}Ce_{0.15}CuO_4$. After annealing in flowing Ar at 900°C for 16 hr, $LaDy_{0.85}Ce_{0.15}CuO_4$ exhibits semiconducting behavior from room temperature down to liquid helium temperature.

By optical microscopy, the product of nominal composition $LaHoCuO_4$ appears to be a cluster of black and green particles. La_2CuO_4, $Ho_2Cu_2O_5$, and Ho_2O_3 were identified in the X-ray diffraction pattern. With a small amount of Ce substitution for Ho, the T'-phase forms. The X-ray diffraction pattern of $LaHo_{0.85}Ce_{0.15}CuO_4$ shows that the major phase consists of the T'-structure.

In summary, we found that the T'-phase exists in (La, *Ln*)$_2CuO_4$ with *Ln* extended beyond Gd to Ho with the presence of a small amount of Ce-substitution. $LaTb_{0.85}Ce_{0.15}CuO_4$ and $LaDy_{0.85}Ce_{0.15}CuO_4$ exhibit semiconducting behavior from room tem-

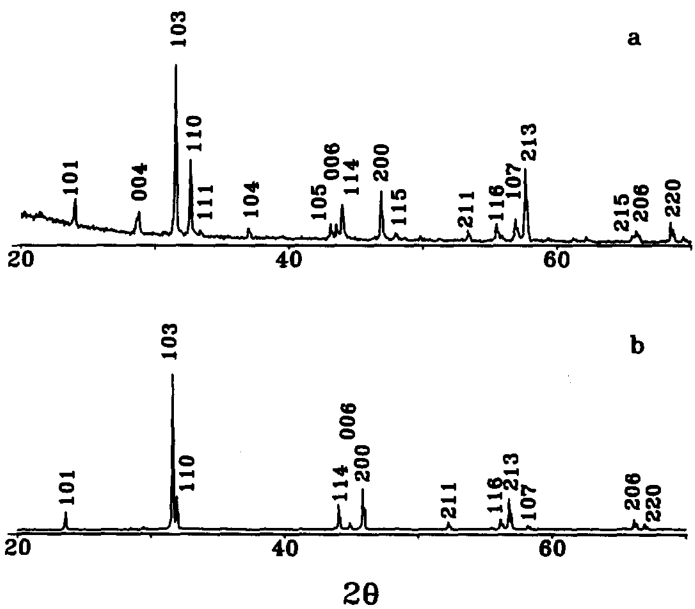

FIG. 2. The X-ray diffraction patterns of (a) T^*-structure $La_{1.1}Dy_{0.9}CuO_4$ and (b) T'-structure $LaDy_{0.85}Ce_{0.15}CuO_4$.

perature down to liquid helium temperature. The possible connection between the formation of the T'-structure by addition of Ce and superconductivity induced by Ce-doping in the T'-structure are being investigated. By varying the La to Dy ratio, a pure T^*-structure compound $La_{1.1}Dy_{0.9}CuO_4$ was also obtained.

Acknowledgments

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