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A Series of Metallic Oxides of the Formula $La_3LnBaCu_5O_{13+\delta}$ (Ln = Rare Earth or Y)*

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Oxides of the formula $La_3LnBaCu_5O_{13+\delta}$ (Ln = Nd, Sm, Gd, Dy, or Y) exhibiting metallic resistivity have been prepared and characterized. In the case of yttrium, a composition close to $La_2Y_2BaCu_5O_{13+\delta}$, which is also metallic, could be prepared.

$La_4BaCu_5O_{13+\delta}$ is an interesting oxygen-deficient perovskite possessing a tetragonal structure (*1*). It is built up of CuO_6 octahedra and CuO_5 square pyramids with the oxygen vacancies along (001) of the cubic perovskite cell. The resultant framework forms tunnels within which La and Ba ions are located. $La_4BaCu_5O_{13+\delta}$ shows metallic behavior (*2*). Changes in oxygen stoichiometry brought about by annealing the oxide under different atmospheres give rise to a metal–insulator transition (*3*). More interestingly, a metal–insulator transition is also caused by varying the La : Ba ratio (*3*). Accordingly, with increase in the Ba content, the resistivity of $La_{4-x}Ba_{1+x}Cu_5O_{13+\delta}$ increases, but the structure remains tetragonal over the whole range of La : Ba ratios, with x varying from zero to 1. We sought to explore whether we can prepare metallic, oxygen-deficient perovskites of the type $La_{4-x}Ln_xBaCu_5O_{13+\delta}$ by substituting La in $La_4BaCu_5O_{13+\delta}$ with other rare earths or by Y. We report the results of such a study in this communication.

Oxides of the type $La_{4-x}Ln_xBaCu_5O_{13+\delta}$ (Ln = rare earth or Y) were prepared by the ceramic method. Stoichiometric quantities of Ln_2O_3, $BaCO_3$, and CuO were mixed thoroughly and heated at 1170 K for 16 hr. The product was ground, pelletized and reheated at 1270 K for 24 hr in air. Repeated grinding and pelletizing were carried out to ensure the formation of monophasic products. X-ray diffraction patterns were recorded with a JEOL JDX-8P diffractometer with Cu$K\alpha$ radiation. Four-probe electrical resistivity measurements were made on sintered pellets with a home-built apparatus over the 20–300 K range. Thermogravimetric analysis was carried out with a Sartorius balance.

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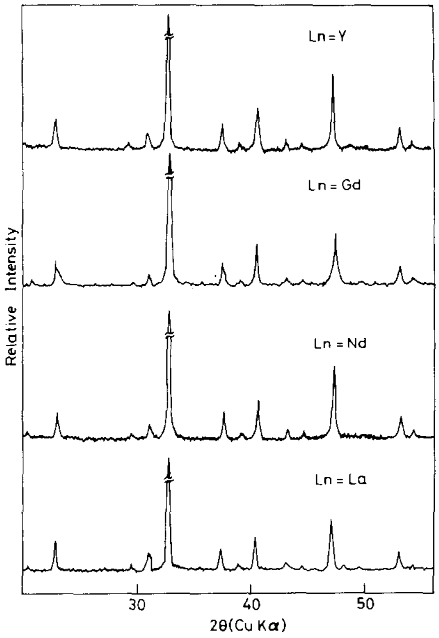

FIG. 1. X-ray diffraction patterns of a few members of the $La_3LnBaCu_5O_{13+\delta}$ series.

Studies with a variety of $La_{4-x}Ln_xBaCu_5O_{13+\delta}$ compositions showed that the maximum value of x tolerated was unity. All the oxides of the formula $La_3LnBaCu_5O_{13+\delta}$ were monophasic, yielding well-defined X-ray diffraction patterns (Fig. 1). The structure of these oxides was tetragonal independent of *Ln*. In Table I, we list the unit cell parameters of $La_3LnBaCu_5O_{13+\delta}$ prepared by us. The unit cell volume increases slightly as the radius of *Ln* ion decreases. $La_4BaCu_5O_{13+\delta}$ has an oxygen-excess with $\delta \approx 0.2$; δ was close to 0.2 in $La_3LnBaCu_5O_{13+\delta}$ as well.

TABLE I

PROPERTIES OF $La_3LnBaCu_5O_{13+\delta}$

Ln	*a* (Å)	*c* (Å)	ρ (300 K) (mohm · cm)
La	8.645	3.867	2.6
Nd	8.640	3.884	2.8
Sm	8.634	3.900	3.0
Gd	8.630	3.905	3.4
Dy	8.626	3.909	4.8
Y	8.620	3.916	6.4

Electrical resistivity data of the various $La_3LnBaCu_5O_{13+\delta}$ members are shown in Fig. 2. We see that all of them exhibit metallic resistivity behavior. In Table I are listed the resistivities at 300 K of all the compositions. The value of the resistivity at 300 K is generally in the range 2.6–6.4 × 10^{-3} ohm · cm. This value corresponds closely to Mott's value of minimum metallic conductivity (*4*, *5*). The value of the resistivity at any given temperature increases progressively with the decrease in size of the *Ln* ion or the increase in the unit cell volume.

We could not prepare oxides of the composition $La_2Ln_2BaCu_5O_{13+\delta}$ except when *Ln* was Y. Samples of $La_2Y_2BaCu_5O_{13+\delta}$ prepared by us did not actually possess this stoichiometry. They were slightly yttrium-deficient and the stoichiometry was closer to $La_{2.2}Y_{1.8}BaCu_5O_{13+\delta}$. The structure of this oxide was tetragonal with a =

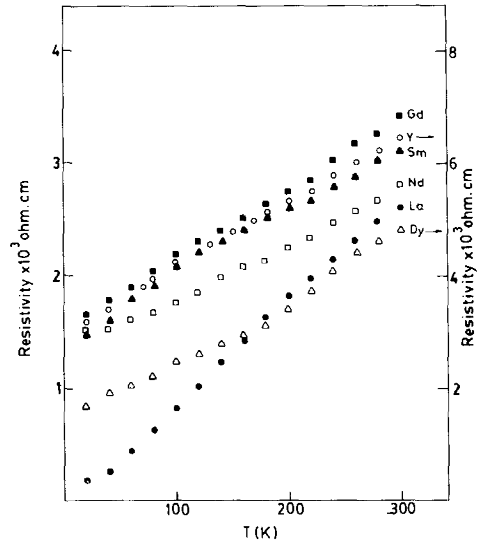

FIG. 2. Electrical resistivity behavior of $La_3LnBaCu_5O_{13+\delta}$.

8.615 Å and $c = 3.920$ Å. The oxide exhibited metallic behavior with a 300 K resistivity of 23 mohm · cm, which is higher than that of $La_3YBaCu_5O_{13+\delta}$.

We have seen that the metallicity of $La_3LnBaCu_5O_{13+\delta}$ is essentially independent of *Ln*. The unit cell dimensions vary systematically with *Ln*, the variation, though small, being well outside the experimental uncertainty (±0.005 Å). These observations can be understood in terms of the structure of $La_4BaCu_5O_{13+\delta}$. This oxygen-deficient perovskite has a Cu_5O_{13} framework with hexagonal tunnels where $La^{3+}(Ln^{3+})$ ions are located in an ordered manner; the Ba^{2+} ions are located in perovskite cages. By virtue of the location of the *Ln* ions in the hexagonal tunnels, the observed properties of the $La_3LnBaCu_5O_{13+\delta}$ are indeed as one would expect.

Acknowledgments

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