



Genesis of Superconductivity in the Layered Cuprates: $(ACuO_{2.5})_2(ATiO_3)_m$; $2 \leq m \leq 4$ †

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The internal chemistry of the quadruple perovskite $Ln'Ln''Ba_2Cu_2Ti_2O_{11}$ ($Ln'Ln'' = NdDy$), such as solid solution behavior, stable defect species, and oxidation behavior, has been investigated by structural and physical property measurements and related to the inner architecture of these interesting layered compounds.

1. INTRODUCTION

Our interests have been in the electronic and structural features which stabilize two dimensional (layered) perovskite-like systems. X-ray and neutron diffraction, electron microscopy, and in-situ, simultaneous high-temperature electrical conductivity and thermopower measurements have been carried out on some pure perovskite oxides (e.g. $A_{2+2m}Cu_2Ti_mO_{3m+5}$; $2 \leq m \leq 4$) containing double $CuO_{4/2}$ sheets and two, three, and four octahedral blocking layers [1]. High-temperature electrical conductivity and thermopower measurements have been conducted as a function of oxygen partial pressure, temperature, and chemical substitution to elucidate the unique internal chemistry, defect structures, and conduction parameters associated with these materials. This report will focus solely on the $m = 2$ mixed A-site stoichiometry $Ln'Ln''Ba_2Cu_2Ti_2O_{11}$ ($Ln' = Nd$, $Ln'' = Dy$), which contains the smaller lanthanide (Dy) ordered between the facing sheets of Cu-O square pyramids.

2. EXPERIMENTAL SECTION

All samples were synthesized by the usual solid state reactions of oxides. Powder XRD, TGA, magnetic susceptibility, HR-TEM and in-situ electrical conductivity/thermopower measurements were carried out as described before [2].

3. RESULTS AND DISCUSSION

The absence of superconductivity in the quadruple perovskites has been partly attributed to the long Cu-O in-plane bond lengths ($\approx 1.95\text{\AA}$ for $Tb_2Ba_2Cu_2Ti_2O_{11}$ and $Gd_2Ba_2Cu_2Ti_2O_{11}$, $\approx 2.00\text{\AA}$ in $La_2Ba_2Cu_2Sn_2O_{11}$) which are 0.01\AA to 0.06\AA larger than known hole-type superconductors. In-situ high-temperature electrical conductivity and thermopower measurements of several of these materials ($La_2Ba_2Cu_2Sn_2O_{11}$, $La_2Ba_2Cu_2Ti_2O_{11}$ and $Eu_2Ba_2Cu_2Ti_2O_{11}$) demonstrated the similarity of their transport properties to those of the superconducting layered cuprates, and showed that low carrier concentrations were predominantly responsible for the absence of superconductivity [3]. Control of the inner architecture will be required if optimal doping concentrations are to be realized. In addition, the chemical factors which restrict oxidation in these

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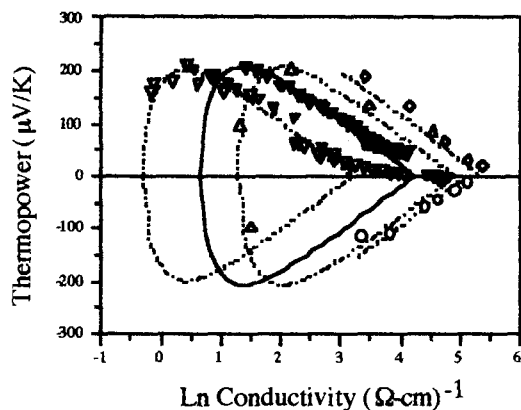


Figure 1. Comparative Jonker plot of the $\text{NdDyBa}_{1.5}\text{Sr}_{0.5}\text{Cu}_{2.2}\text{Ti}_{1.8}\text{O}_{11\pm\delta}$ samples (\blacktriangledown) and several known superconducting layered cuprates: ∇ - $\text{Bi}_{2.1}\text{Sr}_{1.9}\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$, Δ - $\text{YBa}_2\text{Cu}_3\text{O}_y$, \circ - $\text{Nd}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_4$, and \diamond - $\text{La}_{2-x}\text{Ba}_x\text{Cu}_2\text{O}_{4\pm\delta}$

materials are important to understand in order to realize superconductivity in this structure and other related layered cuprates.

Recently, we reported [4] several new materials belonging to the quadruple perovskite family with the stoichiometries $\text{Ln}'\text{Ln}''\text{Ba}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$ ($\text{Ln}'\text{Ln}'' = \text{LaY}, \text{LaEr}, \text{LaHo}, \text{and NdDy}$). Substitutions of both strontium for barium and copper for titanium were successful in the $\text{NdDyBa}_{2-x}\text{Sr}_x\text{Cu}_{2-y}\text{Ti}_{2+y}\text{O}_{11\pm\delta}$ system. The $\text{NdDyBa}_{1.5}\text{Sr}_{0.5}\text{Cu}_{2.2}\text{Ti}_{1.8}\text{O}_{11\pm\delta}$ sample has the smallest lattice constants of the phase-pure compositions, with $a = 3.8834(3)\text{\AA}$ and $c = 15.643(2)\text{\AA}$. Compared to those of the parent compound, $\text{NdDyBa}_2\text{Cu}_2\text{Ti}_2\text{O}_{11\pm\delta}$ ($a = 3.8892(2)\text{\AA}$ and $c = 15.720(2)\text{\AA}$) the cell contraction is most evident along the c -axis, while a minor decrease in the a -axis is observed. The oxygen content of the as-synthesized material was 10.78 ± 0.1 .

The doped NdDy system ($\text{NdDyBa}_{1.5}\text{Sr}_{0.5}\text{Cu}_{2.2}\text{Ti}_{1.8}\text{O}_{11\pm\delta}$) exhibits extrinsic, p-type behavior, where the carrier concentrations are functions of both the temperature and oxygen partial pressure. Thermopowers as low as $60\mu\text{V/K}$ (at the lowest temperature and highest oxygen partial pressure, see Figure 1) demonstrate that the oxidation of the $\text{CuO}_{4/2}$ sheets can be achieved in the quadruple

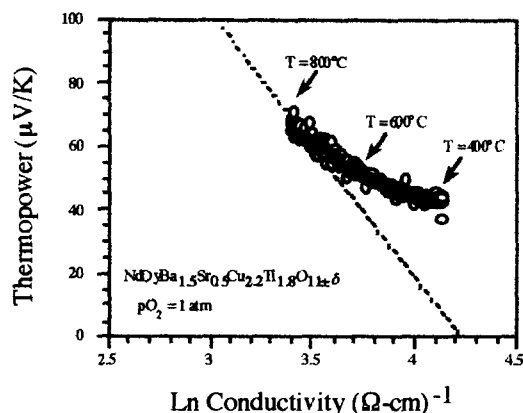


Figure 2. A Jonker plot of the electrical properties of this system as it was slow cooled ($\approx 20^\circ\text{C/hr}$) in pure oxygen. Approximate temperatures are indicated in the illustration.

perovskite materials. While the oxygen content analysis indicated that limited oxidation occurred under the synthesis conditions ($T \approx 1050^\circ\text{C}$, $P_{\text{O}_2} \approx 0.21\text{atm}$), the electrical property measurements demonstrate that carrier concentrations can be increased by appropriate annealing (see Figure 2). The thermopower values of the doped NdDy system correspond to an underdoped state on the cusp of the region where superconducting materials are observed (thermopower values below $\approx 40\mu\text{V/K}$). The absolute conductivity values are greater in the doped NdDy system than in any of the quadruple perovskites, and are similar to those observed for YBCO.

4. REFERENCES

1. Kenji D. Ottschi et al., *J. Am. Chem. Soc.*, **118** (1996) 8951 - 8952; W. J. Zhu et al., *Mat. Res. Bull.*, **30** (1995) 243 - 246.
2. P. A. Salvador et al., to be published in *J. Am. Chem. Soc.* and references therein.
3. P. A. Salvador et al., *J. Solid State Chem.* **119** (1995), 80 - 89.
3. K. B. Greenwood et al., *Chem. Mater.* **7** (1995) 1355 - 1360.