

Formation of a New Series of 1222 Layered Cuprates $MSr_2(LnR)_2Cu_2O_y$

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Five new layered cuprate compounds in the series $MSr_2(LnR)_2Cu_2O_y$ ($M = Ti, Nb, Ta; Ln = Pr, Nd; R = Ce, Th$) have been prepared. The structure of the compounds is directly related to that of Tl or Pb-1222, with the M occupying the Tl or Pb site. Resistivity measurements showed that all these compounds are semiconductors under the preparation conditions of the present experiments. © 1991 Academic Press, Inc.

Introduction

After the breakthrough discovery of Bednorz and Müller in the LaBaCuO system, superconductivity has been observed in about 20 different structure types encountered in cuprate compounds (1). An important feature in the structure of superconducting cuprates is that they all contain at least one layer of 4- to 6-coordinated CuO in two-dimensional (2-d) planes within the unit cells. It is thought that any compound which contains a CuO plane and an appropriate density of carriers might become a superconductor (2). Thus, finding compounds containing 2-d CuO planes is a major concern in the search for new types of superconductors.

Recently, we have described a new layered cuprate, $TaSr_2(NdCe)_2Cu_2O_y$ (Ta-1222) (3). The structure of the compound is di-

rectly related to that of $(PbCu)Sr_2(LnCe)_2Cu_2O_y$ (Pb-1222) (4), $TlBa_2Ln_2Cu_2O_y$ (Tl-1222) (5), and $(LnCe)_2(LnBa)_2Cu_3O_y$ (Cu-1222) (6), where Ta occupies the Pb, Tl, or Cu-site (Fig. 1). This structure contains two layers of CuO_5 pyramidal planes, connected by a layer of complete perovskite structure $SrTaO_3$, which differs from that of oxygen-deficient MBO_{3-x} ($M = Sr, Ba, B = Pb, Cu, Tl$) perovskite layers. In earlier publications we argued that other perovskite structure layers such as $MSnO_3$, $MTiO_3$, and $MNbO_3$ might function as connecting layers which could be incorporated between two CuO_5 planes. In Refs. (4-6) it was demonstrated that PbO, TlO, CuO can act as connecting layers in Pb-1222, Tl-1222, and Cu-1222. In the present study we examined the possible formation of the 1222 phase with connecting perovskite layers other than CuO, TlO, PbO.

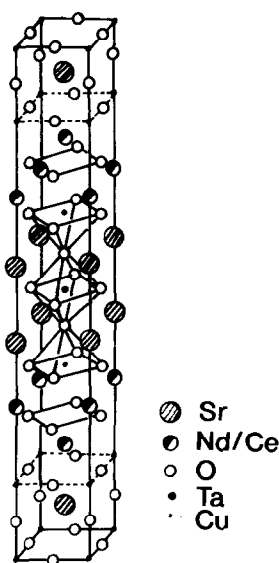


FIG. 1. The structure of the Ta-1222 compound.

Experimental

The samples with the nominal compositions $MSr_2(LnR)_2Cu_2O_y$ ($M = Ti, V, Nb, Ta, Mo, W, In, Sn, Sb$; $Ln = La, Pr, Nd, Sm, Gd, Dy$; $R = Ce, Th, Tb$) were prepared by mixing and heating stoichiometric amounts of the corresponding oxides. All samples were heated twice at 1000°C (for 24 hr) and at 1100°C (24 hr), with intermediate grinding. After slowly cooling to room temperature the samples were further annealed in flowing oxygen gas at 800°C for 12 hr in a quartz tube.

The X-ray diffraction (XRD) patterns were recorded in a Rigaku diffractometer with silicon powder as internal standard. $CuK\alpha$ radiation was used, and a graphite monochromator was set at the diffracted radiation. Selected area electron diffraction (SAED) patterns were recorded in a Hitachi Model H-800 transmission electron microscope. The resistivity measurements were performed by the standard four-probe method, with soldered indium contacts, at

an applied current of 1 mA in a helium cycling cryostat down to 13 K.

Results and Discussions

X-ray diffraction patterns (Fig. 2) revealed that the samples of $TaSr_2(NdCe)_2Cu_2O_y$ and $NbSr_2(NdCe)_2Cu_2O_y$ were phase pure. A small amount of impurity phases was present in $TiSr_2(NdCe)_2Cu_2O_y$. However, for $M = V, Mo, W, In, Sn, Sb$, we failed to observe the formation of the 1222 phase. The XRD patterns also showed that the range of formation of the Ta-1222 phase with rare earth elements substituted for Nd is quite narrow. Only $TaSr_2(PrCe)_2Cu_2O_y$ and $TaSr_2(NdCe)_2Cu_2O_y$ have been synthesized. The reason for the much narrower

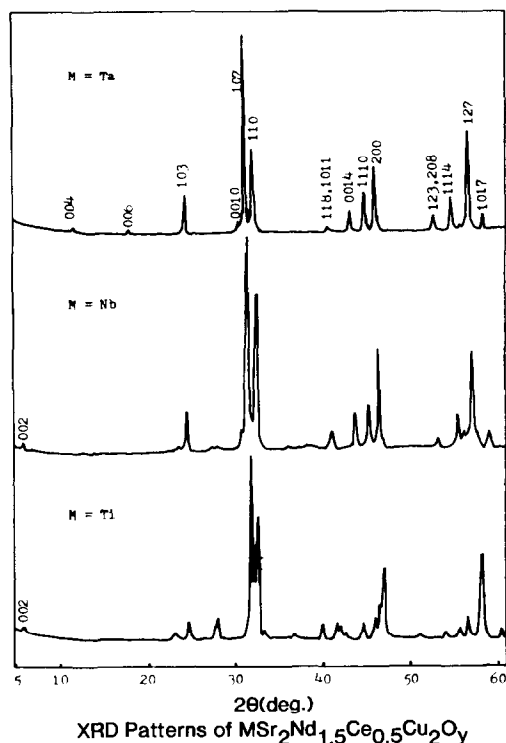


FIG. 2. The X-ray diffraction patterns of $MSr_2(NdCe)_2Cu_2O_y$ ($M = Ta, Nb, Ti$).

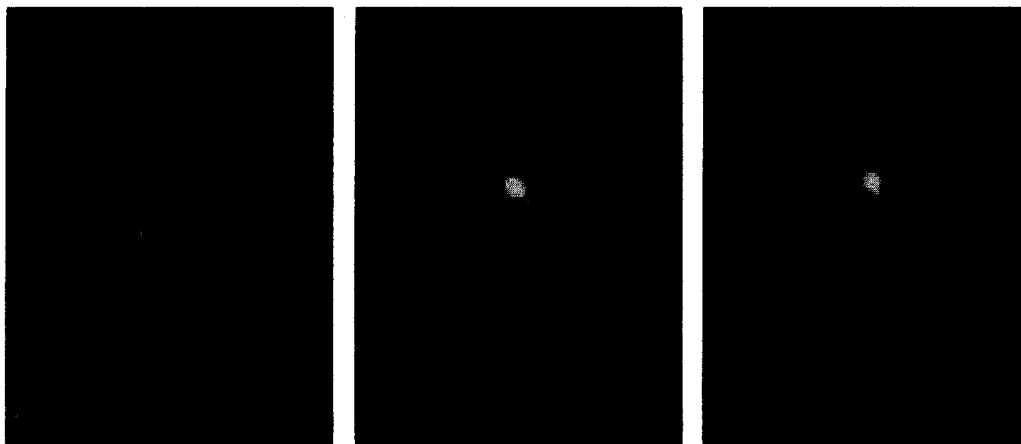


FIG. 3. The selected area electron diffraction patterns of $MSr_2(NdCe)_2Cu_2O_y$ (a, $M = Ta$; b, $M = Ti$; c, $M = Nb$).

formation range as compared to $Bi_2Sr_2(LnCe)_2O_y$ (7) (where $Ln = Pr-Tm$) and Cu-1222 (where $Ln = Nd-Dy$) is the competition in the formation of Sr_2TaLnO_y as the ionic radius of Ln^{3+} decreases from La to Dy. Since the ionic radius and valence of Th is similar to that of Ce, we have found that Th can substitute in the Ce site, forming the $TaSr_2(NdTh)_2Cu_2O_y$, as in the n -type superconductor $(NdCe)_2CuO_4$. The indexing of XRD patterns and refined atomic positions of $TaSr_2(NdCe)_2Cu_2O_y$ has been reported in a previous paper (3). The lattice parameters were $a = b = 3.881$, $c = 28.93$ Å, with a body-centered tetragonal cell. With the same space group $I4/mmm$, the cell parameters (a , c) of $TiSr_2(NdCe)_2Cu_2O_y$ and $NbSr_2(NdCe)_2Cu_2O_y$ are 3.873, 28.36 Å and 3.884, 28.83 Å, respectively. The selected area electron diffraction patterns confirmed the formation of the above compounds. The SAED patterns of the c directions of each sample are shown in Figs. 3a-3c. The parameters obtained from the SAED patterns for the Ta and Ti samples are 28.9 and 28.8 Å, which are consistent with the XRD measurements. However, the extra spots

are observed in the c -direction SAED pattern of the Nb sample, which corresponds to a c -axis parameter of 54.8 Å if we choose the body-centered lattice, consistent with the ordered arrangement of atoms in the c direction.

The resistivity measurements (Fig. 4) show that Ta- and Nb-1222 samples are narrow gap semiconductors. The Ti-1222 sample is a large gap semiconductor, with a room temperature resistivity as high as 1000 ohm-cm, thousands of times greater than that of its Ta and Nb counterparts. A strange phenomenon was observed in $TaSr_2Nd_{1.5}Th_{0.5}Cu_2O_y$; the resistivity versus temperature showed a peak in the range of 40 to 60 K, which may be caused by a structural or magnetic phase transition, or perhaps by a trace of superconductivity in a minority component in the sample. A similar phenomenon has also been observed in $TaSr_2Nd_{1.25}Ce_{0.75}Cu_2O_y$ (8). The above results clearly show that the Ta, Nb, Ti perovskite layers can act as connecting layers for the CuO_5 pyramid layers, similar to that of Tl, Pb, Cu in their superconducting analogs. However, no clear evidence of bulk super-

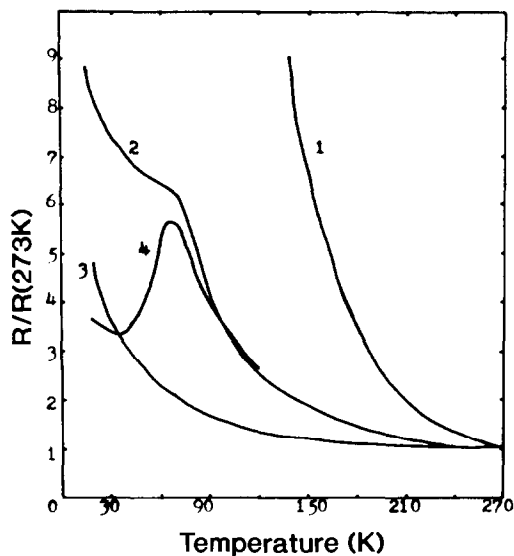


FIG. 4. The temperature-dependent resistivity of $MSr_2(NdCe)_2Cu_2O_y$ (1, $M = Ti$; 2, $M = Nb$; 3, $M = Ta$) and $TaSr_2(NdTh)_2Cu_2O_y$ (4) samples.

conductivity has been observed for samples of the Ta, Ti, Nb compounds down to 13 K, although some of them showed quite low resistivities (Ta, Nb), and an abrupt decrease (change) of resistivity in the temperature range about 40 to 60 K. The absence of superconductivity may be due to an improper density of carriers. It is possible that upon varying the composition and heat treatments such compounds might become superconductors.

A conclusion which may be drawn from calculations of the peak intensity is that Ta and Cu are well ordered in the Ta compounds. However, because of the small difference between the scattering factors of Ti and Cu, we cannot determine whether the

Ti, Cu positions are ordered or randomly occupied. Also, a very complicated rearrangement of Nb with Cu or other elements may exist in the Nb-1222 compound, as the electron diffraction pattern (Fig. 3c) has shown.

Conclusion

Five new layered cuprate compounds, $MSr_2(NdCe)_2Cu_2O_y$ ($M = Ti, Nb, Ta$), $TaSr_2(PrCe)_2Cu_2O_y$, and $TaSr_2(NdTh)_2Cu_2O_y$, in the $MSr_2(LnR)_2Cu_2O_y$ series have been successfully prepared. All the compounds are isostructural with their superconducting polymorphs Pb-1222 and Cu-223. However, no clear evidence of bulk superconductivity has been observed for the samples under present preparation conditions down to 13 K.

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