

The Design and Synthesis of a New Layered Cuprate: $\text{Ti}_2(\text{Ba}_2\text{Gd})\text{Gd}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{13}$

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We have succeeded in preparing a new layered cuprate compound with the composition $\text{Ti}_2(\text{Ba}_2\text{Gd})(\text{Gd}, \text{Ce})_2\text{Cu}_2\text{O}_y$. From X-ray diffraction patterns, its space group $I_{41/mmm}$ and cell parameters $a = 3.883 \text{ \AA}$, $c = 36.972 \text{ \AA}$ ($x = 1.0$) have been determined. The structure of the compound can be viewed as an alternating stack of a double Ln_2O_2 fluorite layer and a quadruple layer containing a double MTiO_3 perovskite layer joining two CuO_5 pyramidal layers. Although it contains complete CuO_5 planes as in high- T_c cuprates, resistance measurements showed that the samples were semiconductive. © 1995 Academic Press, Inc.

INTRODUCTION

After the pioneering discovery of superconductivity in the LaBaCuO system (1), many layered cuprate compounds have been found to be new high- T_c superconductors. In order to explore a new cuprate superconductor, two important factors must be kept in mind. First, the compound must contain at least one CuO_n plane in the unit cell. Second, it must also contain some additional layers for tuning the carrier density in the CuO_n plane and for stabilizing the structure.

Based on knowledge of crystal chemistry, we have proposed that structural units other than CuO_n planes in layered cuprates can be classified as *connecting* and *separating* layers (2). The connecting layer normally joins the CuO_n ($n = 5, 6$) planes by sharing their common apical oxygen atoms, whereas the separating layer separates the CuO_n ($n = 4, 5$) planes at the side without apical oxygen atoms. By combining different types of connecting and separating layers, one may forecast some new layered cuprates which might be high- T_c superconductors when successfully prepared. Following this approach, we have designed and prepared several new cuprates (3-8) (e.g., $\text{MSr}_2(\text{Ln}, \text{Ce})_2\text{Cu}_2\text{O}_y$ (M -1222, $M = \text{Ta}, \text{Nb}, \text{Ti}, \text{Ga}$), $(\text{Y}, \text{Ce})_n\text{SrCuFeO}_y$ ($n = 2, 3$), and $\text{LnBaCuO}_2\text{BO}_3$); among them, Ta-1222, Nb-1222, and Ga-1222 have been discovered to be new superconductors (9, 5).

Recently, Anderson *et al.* (10) and Gormezano and Weller (11) have reported two new layered cuprates with the chemical formulas $\text{Ba}_2\text{La}_2\text{Cu}_2\text{Sn}_2\text{O}_{11}$ and $\text{Gd}_2\text{Ba}_2\text{Ti}_2\text{Cu}_2\text{O}_{11}$. The important structural feature of both new compounds (Fig. 1a) is that they are constructed by alternate stacking of a CuO_5 - Ln - CuO_5 triple layer (which can also be found in the 123 structure) and a new connecting layer $\text{M}_2\text{Ba}_2\text{LnO}_y$ ($M = \text{Ti}, \text{Sn}$). Considering the structural similarity to other layered cuprates (2), the compounds can be classified as Sn-2312 and Ti-2312, and the connecting layer $\text{M}_2\text{Ba}_2\text{LnO}_y$ can be assigned to 2300. Based on this classification, one could expect that other members of the 23 mn family containing the connecting layer 2300 combined with different separating layers might also exist. When $\text{M}_2\text{Ba}_2\text{LnO}_y$ is combined with the double fluorite layer Ln_2O_2 , we should get a new structure type 2322 (Fig. 1b) with the possible composition $\text{M}_2(\text{Ba}_2\text{Ln})(\text{Ln}, \text{Ce})_2\text{Cu}_2\text{O}_y$. In the present paper, the preparation and properties of the new 2322 compound $\text{Ti}_2(\text{Ba}_2\text{Gd})(\text{Gd}, \text{Ce})_2\text{Cu}_2\text{O}_{13}$ will be reported.

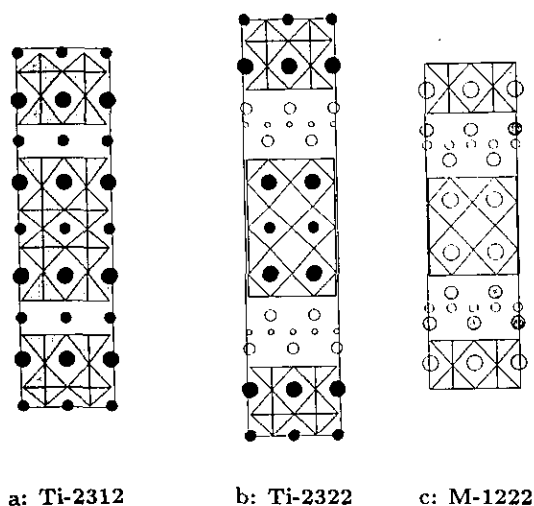


FIG. 1. Ideal structure models of (a) $\text{Ti}_2\text{Ba}_2\text{Gd}_2\text{Cu}_2\text{O}_{11}$, (b) $\text{Ti}_2\text{Ba}_2\text{Gd}(\text{Gd}, \text{Ce})_2\text{Cu}_2\text{O}_{13}$, and (c) $\text{MSr}_2(\text{Nd}, \text{Ce})_2\text{Cu}_2\text{O}_9$ ($M = \text{Ta}, \text{Nb}, \text{Ti}$).

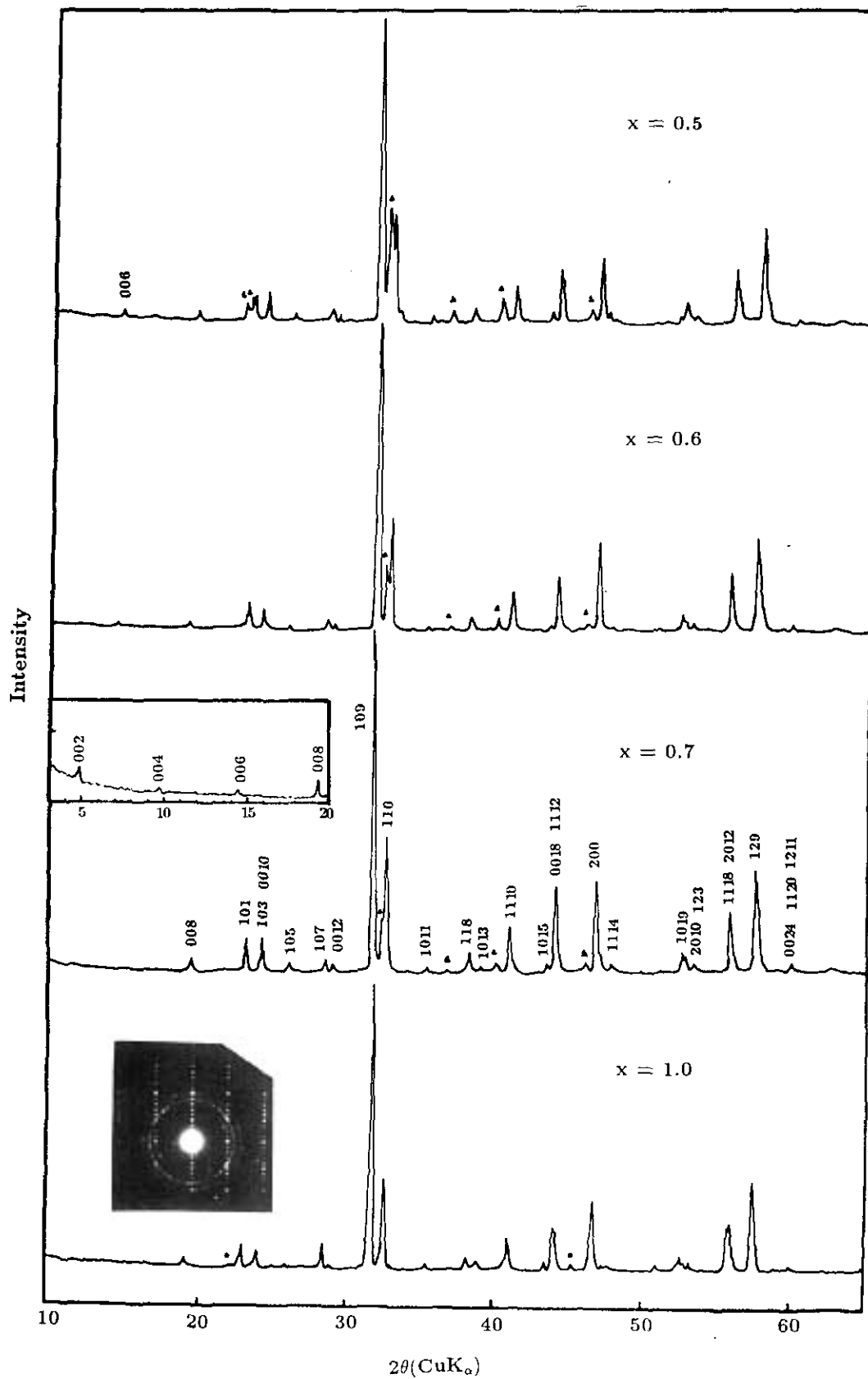


FIG. 2. X-ray diffraction patterns of $\text{Ti}_2\text{Ba}_2\text{Gd}_{3-x}\text{Ce}_x\text{Cu}_2\text{O}_y$. The two insets are the low-angle XRD pattern for $x = 0.75$ (upper) and the electron diffraction pattern of the 110 zone for $x = 1.0$ (lower). The triangles and dots represent the impurity phases Ti-2312 and BaTiO_3 , respectively.

EXPERIMENTAL

Samples with nominal compositions $Ti_2Ba_2Gd_{3-x}Ce_xCu_2O_y$ ($x = 0.5, 0.6, 0.67, 0.7, 0.75, 1.0$) were prepared by solid-state reaction from the starting compounds TiO_2 (99.99%), $BaCO_3$ (99%), Gd_2O_3 (99.95%), CeO_2 (99.9%), and CuO (99%). Well-ground mixtures of the starting materials were first heated at 1050°C for 48 hr with intermittent grinding. After cooling to room temperature, the samples were reground, pelletized, and calcined at 1100°C for another 48 hr and allowed to cool in the furnace. The as-prepared samples were then divided for X-ray diffraction measurements, resistance measurements, and further treatment.

The X-ray diffraction (XRD) measurements were made with a Rigaku $D_{max}\text{-}\gamma_A$ diffractometer equipped with a rotating anode source. Powder diffraction patterns of the samples were collected using $CuK\alpha$ radiation with step width 0.02° (2θ) and a counting time of 1 sec. A curved graphite monochromator was set in the diffraction path, and silicon powder was added as internal standard. The resistances of the samples were measured using the standard four-probe method down to 15 K in a commercial He circling refrigerator. The contacts were made by soldering fine Cu wires on indium pressed onto the sample surface. The temperatures were measured with a calibrated Rh-Fe resistance thermometer placed close to the sample.

RESULTS AND DISCUSSION

As mentioned above, the structural relation between the title compound and Ti-2312 is that the Ln^{3+} layer in Ti-2312 is replaced by the Ln_2O_2 fluorite layer. Such a replacement not only increases the thickness of the separating layer (from 3.2 to 6 Å), but also introduces a glide plane n within the unit cell. Thus the ideal structure of the new Ti-2322 compound must be body centered with space group $I_{4/mmm}$, and the cell parameter c could be derived as

$$c_{2322} \approx 2c_{2312} + 2(6 - 3.2) \approx 37 \text{ \AA}.$$

In addition, the 2322 structure is also related to 1222 by adding one more perovskite unit in the connecting layer. Thus c could also be derived as

$$c_{2322} = c_{1222} + 2a_p \approx 28.9 + 2 \times 4 \approx 36.9 \text{ \AA}.$$

The XRD patterns of the samples (Fig. 2) revealed that a new phase with the predicted cell parameters for Ti-2322 was actually formed in the entire range investigated. For $x = 0.67, 0.75$, and 1.0, the samples are almost single phases of Ti-2322. The cell parameters obtained from

TABLE 1
X-ray Diffraction Pattern of
 $Ti_2Ba_2Gd_{2.25}Ce_{0.75}Cu_2O_y$

$h k l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}
0 0 2	18.43	18.44	3
0 0 4	9.16	9.22	1
0 0 6	6.14	6.15	1
0 0 8	4.610	4.612	4
1 0 1	3.856	3.855	9
1 0 3	3.692	3.697	10
0 0 10		3.690	
1 0 5	3.426	3.432	2
1 0 7	3.127	3.123	2
0 0 12	3.074	3.075	2
1 0 9	2.816	2.817	100
1 1 0	2.741	2.741	26
1 1 2	—	2.711	1
0 0 14	2.636	2.636	1
1 0 11	2.537	2.536	2
1 1 8	2.355	2.356	4
0 0 16	2.306	2.306	2
1 1 10	2.200	2.200	10
1 0 15	2.078	2.077	3
0 0 18	2.050	2.050	20
2 0 0	1.938	1.938	19
1 1 14	1.899	1.900	2
2 0 4		1.897	
2 0 8	1.785	1.787	1
1 0 19	1.737	1.736	3
1 2 1	—	1.731	2
1 2 3	1.715	1.716	2
2 0 10		1.716	
1 1 18	1.641	1.642	15
2 0 12		1.640	
1 0 21	1.597	1.600	21
1 2 9		1.597	

Note. Indexed with the space group $I_{4/mmm}$ and cell parameters $a = 3.874 \text{ \AA}$, $c = 36.887 \text{ \AA}$.

least-squares fitting of the XRD peaks (see Table 1 for $x = 0.75$) are

$$a = 3.867 \text{ \AA}, c = 36.862 \text{ \AA} \quad \text{for } x = 0.67;$$

$$a = 3.874 \text{ \AA}, c = 36.887 \text{ \AA} \quad \text{for } x = 0.75; \quad \text{and}$$

$$a = 3.881 \text{ \AA}, c = 36.972 \text{ \AA} \quad \text{for } x = 1.0.$$

The systematic absences of the diffraction indices also agreed with the choice of the space group $I_{4/mmm}$. Concerning lower Ce content, a substantial amount (about 30% for $x = 0.5$) of Ti-2312 coexisted with the major Ti-2322 phase. The Ti-2312 phase gradually diminished for increasing Ce content x and disappeared at about $x = 0.6\text{--}0.7$.

The structure model of the present compound could be

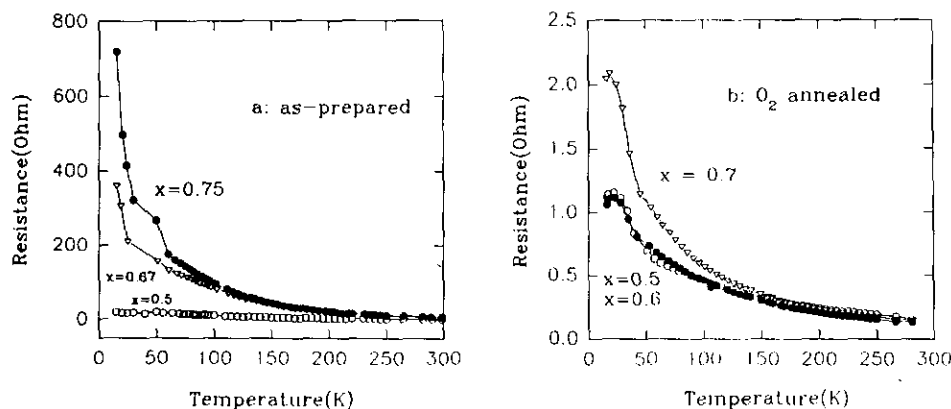


FIG. 3. Temperature-dependent resistances of the $\text{Ti}_2\text{Ba}_2\text{Gd}_{3-x}\text{Ce}_x\text{Cu}_2\text{O}_y$ samples: (a) as prepared and (b) annealed under flowing O_2 at 1100°C .

constructed from those of Ti-2312 and T' phases (12). It can be viewed as composed of two main blocks. One block contains the two CuO_5 pyramidal layers connected by a double perovskite $M_2\text{Ti}_2\text{O}_6$ layer through the apical O atoms. Such a quadruple layer block is further separated by the double $(\text{Ln}, \text{Ce})_2\text{O}_2$ fluorite layer among the bases of the CuO_5 pyramidal layers. The complete CuO_5 planes in the structure may provide conducting paths for the carriers, and thus such a compound may be a promising candidate in which to induce superconductivity. Furthermore, the flexibility of varying the Ln/Ce ratio in the fluorite layer in the present compound may be superior to that in Ti-2312 since variation of the Ln/Ce ratio may eject holes into the CuO_5 planes.

Figure 3a shows the temperature-dependent resistances of the as-prepared samples. All of them are semiconducting with room temperature resistances ranging from 1 to 10Ω . When annealed in flowing O_2 (1000 or 1100°C , 60 hr), the samples showed both lower resistances (reduced to 0.1 – 0.8Ω at room temperature) and weaker temperature dependences (Fig. 3b). However, we have not observed zero resistance or metallic conductance in all the samples investigated, even under further annealings. The semiconducting behavior of the samples indicates that the carrier concentration in the CuO_5 plane is not high enough to sustain superconductivity. If the carriers are p -type, as inferred from the in-plane Cu – O bond length, we suspect that the oxygen deficiency may likely be present in the fluorite layer. Such behavior has also been observed in the Ta-1222 system (4), which was subsequently made superconducting by Cava *et al.* (9). If this is also the case for Ti-2322, we expect that under a proper heat treatment procedure and/or by high-oxygen-pressure annealing, the 2322 compounds might be new-structure-type superconductors.

It may also be worth noting that a preliminary study showed that when one substitutes Nd for Gd, the compound $\text{Ti}_2(\text{Ba}_2\text{Nd})(\text{Nd}, \text{Ce})_2\text{Cu}_2\text{O}_y$ can also be prepared. If the stability of the 2322 phase is only governed by ion size, the formation of 2322 compounds can be extended at least from Gd to Nd. Thus it is possible to prepare many new $M_2(\text{Ba}_2\text{Ln}^1)(\text{Ln}^2, \text{Ce})\text{Cu}_2\text{O}_y$ compounds by substituting other rare-earth elements for Gd or by combining different Ln^1 and Ln^2 ions. Further study on this subject is in progress.

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