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New Complex Oxides in *R*–Ba–Th–Cu–O Systems (*R* = La–Gd)

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The new complex oxides $R_2Ba_{1.33}Th_{0.67}Cu_3O_{8+\delta}$ (R = La, Pr) and $La_{0.67}Ba_{1.33}R_{2-x}Th_xCu_3O_{8+\delta}$ (R = Nd–Gd, $x = 0.5, 0.67$) were synthesized. These compounds have a similar structure to the Ce-223 high-T_c oxides. The oxygen content (or δ) was varied over a wide range after annealing at high oxygen pressure (up to 90 atm). Unit cell parameters and δ values for all the new phases were determined. The resistivities of these semiconducting compounds obey the law $\rho = \rho_0 T^{-\alpha}$. A single crystal of $Nd_2Ba_{1.5}Th_{0.5}Cu_{3-x}Al_xO_{8+\delta}$ ($x = 0.3$, $\delta = 0.8$) was obtained and its structure was determined by X-ray single-crystal experiment (tetragonal system, space group *I4/mmm*, $a = 3.9057(5)$ Å, $c = 28.569(4)$ Å, $Z = 2$).

I. Introduction

The high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ (123-phase) (*1*) has an anion-deficient perovskite-like structure with the following packing of the layers along the *c*-axis: $[(CuO_2)\,(BaO)\,(CuO_{1-\delta}\square_{1+\delta})\,(BaO)\,(CuO_2)\,(Y\square)(CuO_2)]$ ($\square$—oxygen vacancy). Sawa *et al.* (*2*) obtained new high-T_c superconductors $R_2Ba_{1.33}Ce_{0.67}Cu_3O_{8+\delta}$ (223 phase, R = Nd–Gd) with structures derived from that of the 123-phase. Unlike the latter structure, in the 223 one the fluorite-type block ($R_{1.33}Ce_{0.67}O_2$) separates the (CuO_2) layers rather than the($Y\square$) layer. Th(IV) exhibits the similar crystallochemical behavior to that of Ce(IV). However, at present there is no information concerning the synthesis of Th-containing complex oxides with the 223 structure. For this reason we attempted to synthesize new phases of this type containing Th, as possible superconductors. We have already briefly reported (*3*) the synthesis of some Th-223 phases, and in this paper we describe our latest results on the preparation, structure, and resistivity properties of these new compounds.

II. Experimental

Samples were prepared from appropriate mixtures of R_2O_3 (R = La, Nd, Sm, Eu, Gd), Pr_6O_{11}, $BaCO_3$, and CuO as starting materials. ThO_2 in the active form was prepared from oxalate. The powders were ground under acetone in an agate mortar, pressed into pellets and heated at 1000°C for 15–20 hr. Then the pellets were pulverized, pressed and annealed at 1100°C for 120–150 hr. Some of the samples were heated for a further 24 hr at 1050°C under oxygen flow or at 600°C at a pressure of $P(O_2) = 90$ atm.

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TABLE I

SUMMARY OF CRYSTALLOGRAPHIC INFORMATION FOR $Nd_2Ba_{1.5}Th_{0.5}Cu_{2.7}Al_{0.3}O_{8+\delta}$

Molecular weight	931.05
Color	Black
Crystal dimensions (mm)	0.1 × 0.06 × 0.009
Crystal system	Tetragonal
Space group	$I4/mmm$ (No. 139)
Cell constants (Å)	a = 3.9057(5) c = 28.569(4) V = 435.8
Z	2
Calculated density (g/cm^3)	7.094
$\mu(MoK_\alpha)(cm^{-1})$	333.1
Diffractometer	Enraf–Nonius CAD4, Mo$K\alpha$, graphite monochromator, scintillation counter
Temperature	Ambient
Scan mode	ω
θ	2–40
Octants	$h, \pm k, \pm l$
Scan speed	Variable, depending on $\sigma(I)/I$
Structure solution program	SDP, SHELX76
Absorption correction	Analytical Crystal shape
Measured reflections	2129 ($I \geq 3\sigma(I)$)
Independent reflections	348 ($I \geq 3\sigma(I)$)
R_{int}	0.037
N_{ref}/N_{par}	12.9
R	0.039
R_w	0.041 ($w^{-1} = \sigma^2(F)$)
Weight scheme	Unit

The oxygen stoichiometry was determined by iodometric titration with an accuracy of ±3% (*4*).

Phase composition of the samples was determined by X-ray analysis using an FR-552 camera with Cu$K_{\alpha 1}$ radiation (λ = 1.54051 Å). Germanium was added as an internal standard. A short description of the single-crystal experiment for $Nd_2Ba_{1.5}Th_{0.5}Cu_{2.7}Al_{0.3}O_{8+\delta}$ is given in Table I.

The resistivity was measured using the standard DC 4-probe method at 4.2–300 K. The uncertainty in the temperature measurement was not more than 0.2% at 70–300 K and about 3% at 4.2 K.

III. Results

The new compounds $R_2Ba_{1.33}Th_{0.67}Cu_3O_{8+\delta}$ (Th-223 phase) were obtained for R = La, Pr. The Th-223 phases also exist for the heavier lanthanides, but with different cation stoichiometries. They were found in the annealed samples with starting composition: $R_2O_3 * 1.33BaCO_3 * 0.67ThO_2 * 3CuO$ together with 123-phase, R_2CuO_4, and ThO_2. In the case of Nd we obtained the Th-223 phase with traces of these impurities using a starting composition $(1 - x/2)Nd_2O_3 * (1.33 + x)BaCO_3 * 0.67ThO_2 * 3CuO$ for $x = 0.17 - 0.33$. Only in the case of this Nd-containing Th-223 phase were we able to obtain a single crystal suitable for structure analysis (see Fig. 1).

This single crystal was obtained by melting the sample with x = 0.33 in a corundum crucible. The sample was heated at 1230°C for 2 hr, slowly cooled to 800°C over a period of 120 hr, and then furnace-cooled to room temperature. The Th-223 phase prevailed in the sample before and after melting and its crystals grew as black plates. "CAMEBAX-microBEAM" was employed for the analysis of the crystal used for structure determination, with $BaCuO_2$, Nd_2O_3, and ThO_2 as standards. Atomic percentages were determined at nine points using the K_α line of copper and the L_α lines of all other cations. The MBX COR program (ZAF-correction) was applied for the calculations. The average cation ratio was Ba : Nd : Th : C = 22(3) : 30(3) : 7(2) : 40(3), with standard deviations in parentheses. This analysis revealed the deficiency of copper in this single crystal (copper formula index 2.7 instead of 3). However the presence of Al was also detected. It is well known that aluminium can easily substitute for copper in $(CuO_{1-\delta}\square_{1+\delta})$ layer in 123-phases during

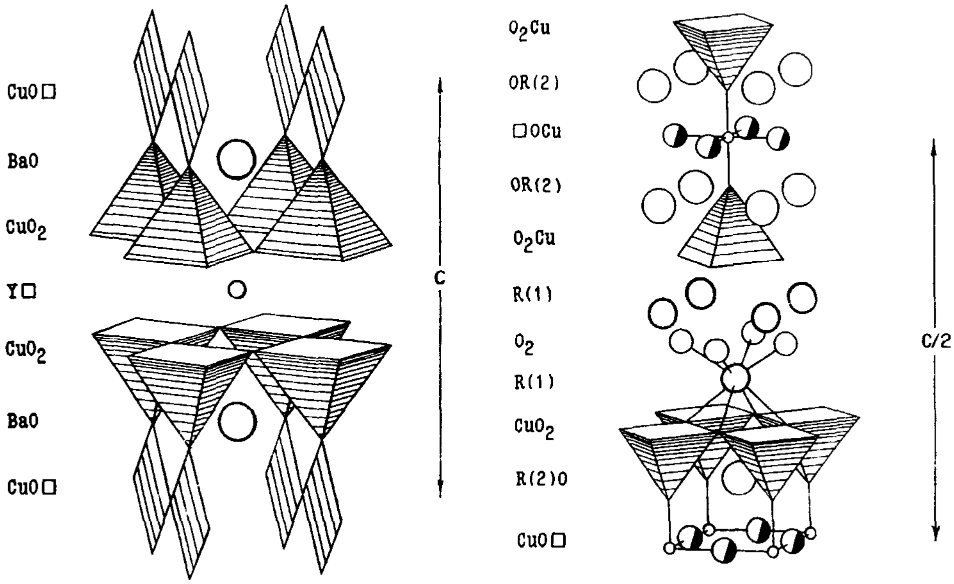

FIG. 1. The crystal structures of $Nd_2Ba_{1.5}Th_{0.5}Al_{0.3}Cu_{2.7}O_{8+\delta}$ (right) and $YBa_2Cu_3O_{7-\delta}$ (left).

crystal growth in corundum crucibles (*5*). As it was difficult to determine the exact amount of Al in this crystal, its content was taken 0.3 to achieve total formula index of (Cu + Al) equal 3. This corresponded to the formula $Nd_2Ba_{1.5}Th_{0.5}Cu_{2.7}Al_{0.3}O_{8+\delta}$, which was taken for the structure determination.

The results of the single crystal experiment are given in Tables II–IV. Lattice parameters were determined by a least-squares (LS) refinement applied to the set of 24 reflections. Cation positions (except for $R(3)$) were taken from the Patterson synthesis, those for the $R(3)$ and oxygen atoms from difference Fourier syntheses. At first the $R(3)$ position was taken as 0, 0, 0, which gave a high value for its thermal parameter (B = 3.4 (2)) during the refinement. Difference Fourier synthesis near the $R(3)$ position showed a positive peak at 0.05, 0.05, 0.0 and a negative one at the taken position. After displacement of the $R(3)$ atom from the ideal position at the origin, its thermal parameter became reasonable (B = 1.3(1)). The same procedure was used for the O(2) atom. Such displacements were found by F. Izumi *et al.* in the structure of the similar Ce-containing 223-phase determined by neutron powder diffraction (*6*). The occupation refinement of the O(1) position gave the value 0.40(8), which corresponded to the oxygen content 8.8(2). The structure was refined by full-matrix LS with isotropic thermal parameters up to $R = 0.047$, $R_w = 0.049$ for reflections with $I \geq 3\sigma(I)$. Occupation refinement of copper and aluminium in the $R(3)$ site was unsuccessful due to the strong correlation between occupation values, thermal, and positional parameters. In the final procedure, all atoms were refined anisotropically up to R = 0.039 and R_w = 0.041. The final difference Fourier synthesis showed two residual peaks of 2.3 $\bar{e}/Å^3$ at 0.5, 0.5, 0.113 (1.05 Å from the $R(2)$ site) and 1.3 $\bar{e}/Å^3$ at 0.5, 0.416, 0.0723 (0.35 Å from the $R(2)$ site).

Anisotropic refinement of the $R(3)$ atom led to the shift of this atom from 0.049, 0.049, 0.0 position to the origin with high values of thermal parameters in the *ab*-plane

TABLE II

POSITIONAL AND THERMAL PARAMETERS FOR THE ATOMS OF $Nd_2Ba_{1.5}Th_{0.5}Cu_{2.7}Al_{0.3}O_{8-\delta}$

Atom	Site	x/a	y/b	z/c	B_{eq}(Å^2)	g
$R(1)^a$	4e	$\frac{1}{2}$	$\frac{1}{2}$	0.20453(3)	0.790(7)	1
$R(2)^b$	4e	$\frac{1}{2}$	$\frac{1}{2}$	0.07653(5)	1.20(1)	1
$R(3)^c$	2a	0	0	0	4.3(1)	1
Cu(1)	4e	0	0	0.14188(8)	0.57(2)	1
O(1)	4c	0	$\frac{1}{2}$	0	2.0(7)	0.40(8)
O(2)	16m	0.069(7)	x	0.058(1)	3.3(4)	$\frac{1}{4}$
O(3)	8g	0	$\frac{1}{2}$	0.1464(3)	0.9(1)	1
O(4)	4d	0	$\frac{1}{2}$	$\frac{1}{4}$	1.1(1)	1

[a] $R(1) = Nd_{0.75}Th_{0.25}$.
[b] $R(2) = Ba_{0.75}Nd_{0.25}$.
[c] $R(3) = Cu_{0.7}Al_{0.3}$.

(Table III) that corresponded to the root-mean-square amplitude (RMSA) of anisotropic displacement of 0.28 Å. Such a result can be explained by the delocalization of the R(3) atom in the flattened sphere. Its real position inside this sphere is defined by different factors: presence of Ba or Nd in the neighboring positions and Cu or Al in that particular site, occupation of the O(1) site, etc.

The R(3)–O(2) distance 1.69 Å was obtained due to the presence of Al atoms, while in the Ce-containing 223-phase (*6*) it corresponded to the normal Cu–O bond (1.82 Å). This distance is short even for Al–O bonds. However, this distance does not correspond to real Al–O and Cu–O distances due to the delocalization of the R(3) atom as mentioned above. In each particular case the R(3) atom occupies a position suitable for its crystallochemical behaviour and interatomic distances. In contrast to the R(3) site anisotropic refinement of the O(2) atom did not shift this atom to 4-fold axis and occupation refinement revealed no deficiency of the O(2) position. We consider that the O(2) displacement from 4-fold axis is caused by the mutual occupation of R(2) site by atoms with different ionic radius. This fact can also be confirmed by the R(2)–O(2) distances, which corresponded to common Ba–O or Nd–O bonds 2.84 or 2.44 Å, respectively.

The structure of this Nd-containing Th-223 phase is similar to the Ce-223 ones (*2, 6*). Ba and Th atoms only occupy their specific position types with different coordination numbers, while Nd atoms are distributed statistically in both positions. The atoms in the perovskite R(2) site (Ba, Nd) have longer interatomic M–O distances and higher coordination numbers than the atoms in the fluorite R(1) sites (Th, Nd).

It seemed likely that it would be possible to obtain similar Th-223 structures with two types of lanthanides, where the different rare earth atoms would predominantly oc-

TABLE III

GENERAL DISPLACEMENT PARAMETER EXPRESSIONS—U's

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
R(1)	0.0106(2)	U(1,1)	0.0088(3)	0	0	0
R(2)	0.0136(3)	U(1,1)	0.0183(4)	0	0	0
R(3)	0.076(4)	U(1,1)	0.012(2)	0	0	0
Cu(1)	0.0058(4)	U(1,1)	0.0102(7)	0	0	0
O(1)	0.03(2)	0.01(1)	0.03(1)	0	0	0
O(2)	0.04(1)	U(1,1)	0.05(1)	0.02(1)	−0.033(8)	U(1,3)
O(3)	0.012(4)	0.009(3)	0.013(7)	0	0	0
O(4)	0.014(3)	U(1,1)	0.012(1)	0	0	0

Note. The form of anisotropic displacement parameter is: $\exp[-2\pi^2\{h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + hka^*b^*U(1,2) + hla^*c^*U(1,3) + klb^*c^*U(2,3)\}]$, where a^*, b^*, and c^* are reciprocal lattice constants.

TABLE IV

INTERATOMIC DISTANCES (Å) IN $Nd_2Ba_{1.5}Th_{0.5}Cu_{2.7}Al_{0.3}O_{8+\delta}$

Bond	Number	Distance
$R(1)$–O(3)	4	2.565(4)
$R(1)$–O(4)	4	2.3455(3)
$R(2)$–O(3)	4	2.791(4)
$R(2)$–O(1)	4	2.9316(6)
$R(2)$–O(2)	4	2.44(1), 2.84(1),[a] 3.19(1)[b]
$R(3)$–O(1)	4	1.952
$R(3)$–O(2)	2	1.69(2)
Cu(1)–O(3)	4	1.9570(4)
Cu(1)–O(2)	1	2.43(2)

[a] $-x,y,z$.

[b] $-x,-y,z$.

cupy different positions. According to their ionic radii (*7*), La atoms would have to occupy the $R(2)$-type sites, while heavier lanthanides (Nd–Gd) with smaller radii would occupy the $R(1)$ site. Based on this suggestion we synthesized the new phases $La_{0.67}Ba_{1.33}R_{2-x}Th_xCu_3O_{8+\delta}$ ($x = 0.5, 0.67$ for Nd, Sm, and $x = 0.5$ for Eu, Gd). All these compounds were obtained pure, and only in the case of Gd were small amounts of impurity phases (ThO_2 and 123) detected. The unit cell parameters and δ values for all synthesized phases are given in Table V.

All the compounds $R_2Ba_{1.33}Th_{0.67}Cu_3O_{8+\delta}$ and $La_{0.67}Ba_{1.33}R_{2-x}Th_xCu_3O_{8+\delta}$ have the semiconducting type of conductivity, and their resistivity can be described by the formula $\rho = \rho_0 T^{-\alpha}$. The values of the α coefficent are also given in Table V. A rapid growth of resistivity at decreasing temperature occurs for the Pr compound, in contrast to the other phases. This could possibly be explained by the electron transition Pr^{+3}–Pr^{+4}, which is not common for the other rare earth elements, or by the influence of the 4*f*-electron system of praseodymium on the formation of the conducting band. The use of high oxygen pressures (90 atm) led to an increase in the oxygen stoichiometry and to a concomitant decrease in the resistivity of the samples. The resistivity–temperature dependencies for some of the compounds are shown in Fig. 2. It should be mentioned that the $La_{0.67}Ba_{1.33}$

TABLE V

CELL CONSTANTS, VALUES OF OXYGEN STOICHIOMETRY, AND RESISTIVTY PROPERTIES OF THE SYNTHESIZED COMPOUNDS

Compound	$P(O_2)$ (atm)	δ	a(Å)	c(Å)	α
$La_2Ba_{1.33}Th_{0.67}Cu_3O_{8+\delta}$	0.21	1.00	3.9336(4)	28.940(5)	
	1	1.04	3.9332(3)	28.96(1)	2.6(.05)
$Pr_2Ba_{1.33}Th_{0.67}Cu_3O_{8+\delta}$	0.21	—	3.8994(1)	28.674(1)	
	1	—	3.8977(6)	28.65(1)	9.3(.3)
$La_{0.67}Ba_{1.33}Nd_{1.33}Th_{0.67}Cu_3O_{8+\delta}$	0.21	0.91	3.9071(5)	28.762(6)	
	90	1.13	3.9058(9)	28.749(9)	2.3(.05)
$La_{0.67}Ba_{1.33}Sm_{1.33}Th_{0.67}Cu_3O_{8+\delta}$	0.21	0.91	3.8935(1)	28.728(4)	
	90	1.07	3.8938(4)	28.648(5)	1.9(.05)
$La_{0.67}Ba_{1.33}Sm_{1.5}Th_{0.5}Cu_3O_{8+\delta}$	0.21	0.82	3.8904(7)	28.76(2)	
	90	1.02	3.8888(8)	28.66(1)	1.4(.05)
$La_{0.67}Ba_{1.33}Eu_{1.5}Th_{0.5}Cu_3O_{8+\delta}$	0.21	0.78	3.8866(9)	28.62(2)	
	90	0.96	3.8846(4)	28.63(1)	1.8(.05)
$La_{0.67}Ba_{1.33}Gd_{1.5}Th_{0.5}Cu_3O_{8+\delta}$[a]	0.21	—	3.8869(6)	28.575(6)	
	90	—	3.882(1)	28.46(1)	—

[a] The sample contained a small amount of ThO_2 and 123-phase.

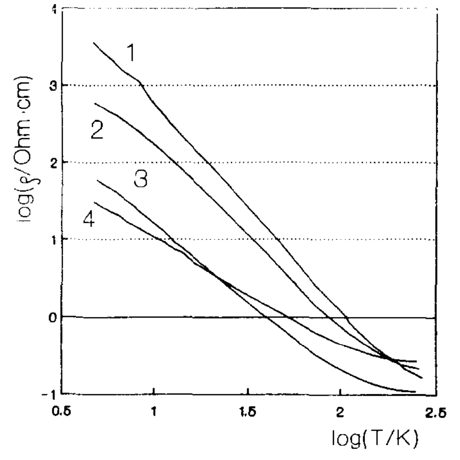

FIG. 2. Resistivity–temperature dependencies for (a) $La_2Ba_{1.33}Th_{0.67}Cu_3O_{9.04}$, (2) $La_{0.67}Ba_{1.33}Nd_{1.33}Th_{0.67}Cu_3O_{9.13}$, (3) $La_{0.67}Ba_{1.33}Sm_{1.33}Th_{0.67}Cu_3O_{9.07}$, (4) $La_{0.67}Ba_{1.33}Sm_{1.5}\ Th_{0.5}Cu_3O_{9.02}$.

$R_{1.5}Th_{0.5}Cu_3O_{8+\delta}$ (R = Sm, Eu) compounds have a resistivity which is two orders of magnitude lower than all the other phases.

IV. Discussion

The synthesized compounds $R_2Ba_{1.33}Th_{0.67}Cu_3O_{8+\delta}$ (R = La,Pr) and $La_{0.67}Ba_{1.33}R_{2-x}Th_xCu_3O_{8+\delta}$ (R = Nd–Gd) are the first examples of thorium-containing complex copper oxides of the 223 structural type. These compounds have structures similar to the Ce-containing 223-phases (*2*). However, some of the Th-containing phases have a different composition to that of the Ce-containing phases. $R_2Ba_{1.33}M_{0.67}Cu_3O_{8+\delta}$ can be obtained with R = Nd–Eu for M = Ce (*2*) but only with R = La,Pr for M = Th. This fact could possibly be explained by the larger radius of thorium as compared with cerium. The parameters of the fluorite-like block occupied by these cations become larger in the case of Th, as well as the size of the space for the cation in the perovskite-like block—$R(2)$ site. As a result, compounds of such stoichiometry cannot be obtained with the smaller lanthanides, which should partially occupy this $R(2)$ site. Th-223 phases with R = Nd–Eu were obtained pure, with partial substitution of La, which predominantly occupies the $R(2)$ site, for these elements.

It should be noted, that the cation position in the perovskite-like block ($R(2)$ site) is not usual for Ce and Th cations, although their ionic radii are suitable for such a structure. This fact can be demonstrated by the unsuccessful attempts to synthesize the solid solution $Y_{1-x}Th_xBa_2Cu_3O_{7-\delta}$ (*8*). Possibly it is necessary for these cations to form the stronger covalent bonds with oxygen atoms, in contrast to Y^{3+}. Oxygen atoms O(4) in the fluorite-like block of the 223-type structure are bonded only with cations in this part of the structure, and the distances $R(1)$–O(4) are much shorter than $R(1)$–O(3) (Table IV). The formation of such covalent bonds between oxygen and four-valent cation (Th or Ce) possibly results in the stability of 223 structures containing these elements.

Th-containing superconducting compounds wth p-type of conductivity have not so far been obtained. The synthesized Th-223 phases have semiconducting properties, although the copper valency can be strongly varied (up to +2.31). The electron localization in this case can be explained by the Cu–O equatorial distances, which are relatively longer than those usually found in high-T_c copper oxides. At the same time these distances become smaller for the heavier lanthanides in the case of $La_{0.67}$-$Ba_{1.33}R_{2-x}Th_xCu_3O_{8+\delta}$ and "metallization" of these samples occurs, which can be illustrated by the decrease of α (Table V). The statistical occupation of the $R(1)$ and $R(2)$ sites by the different cations can also lead to strong local distortions of these Cu(1)–O(3) bonds in the (CuO_2) layer, which are mainly responsible for superconductivity, and to the electron localization. All of the above mentioned facts will be taken into account in our further investigations of these Th-223 phases.

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