Crystal Chemistry of Ln'Ln''Ba$_2$Cu$_2$Ti$_2$O$_{11}$ (Ln = Lanthanide, Y) Materials

Kevin B. Greenwood, Gregory M. Sarjeant, and Kenneth R. Poeppelmeier*

Department of Chemistry and the Science and Technology Center for Superconductivity, Northwestern University, Evanston, Illinois, 60208

Paul A. Salvador and Thomas O. Mason

Department of Materials Science and Engineering and the Science and Technology Center for Superconductivity, Northwestern University, Evanston, Illinois, 60208

B. Dabrowski, K. Rogacki, and Z. Chen

Department of Physics and the Science and Technology Center for Superconductivity, Northern Illinois University, DeKalb, Illinois 60115

The stabilization of the quadruple perovskite structure Ln$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$ as a function of the constituent lanthanides has been investigated. Powder X-ray data show that the mixed A-site compositions Ln'Ln''Ba$_2$Cu$_2$Ti$_2$O$_{11}$ (Ln'Ln'' = LaY, LaHo, LaEr, and NdDy) concertedly order to form distinct CuO$_2$$^{2-}$ and TiO$_2$ double layers. In addition the A cations (Ln', Ln'', and Ba) order on three distinct sites, with the smaller lanthanide (Ln'') occupying the 8-coordinate site between contracted copper−oxygen planes.

Introduction

To prepare novel perovskite-like cuprates having the structural elements required for superconductivity, it is important to understand the principles that govern cation ordering. Studies of stoichiometric A'A''B'B''O$_6$ double perovskite materials have helped elucidate the factors that control cation ordering.[1−4] In the double perovskite structure, the B cations have been observed to adopt random, rock salt, and layered arrangements.[5] Differences between the B cation's charge, size, and electronic structure have been shown to govern which ordering system is favored. Many double perovskites containing copper have a random or rock salt distribution of the B cations,[5] while the layered arrangement is unique to the material La$_2$CuSnO$_6$.[6] Only the layered arrangement contains the CuO$_2$$^{2-}$ planes which are important for high-temperature superconductivity. The compositional range of layered perovskites can be extended when vacancies are introduced onto the oxygen sublattice. In stoichiometric double perovskites the B' and B'' cations exhibit the coordination numer six; however, in oxygen-deficient A'A''B'B''O$_{6-\delta}$ perovskites the average coordination number of the B cations is reduced. If the B cations have different coordination preferences, the oxygen vacancies distribute over the oxygen sites to best satisfy these preferences, and the

corner-linked polyhedra may order in a layered fashion.[7] This is illustrated in the oxygen-deficient double perovskite Ba$_2$CuHgO$_4$.[8] In this material, copper retains an octahedral environment, but the coordination about mercury is reduced to linear. Owing to mercury's preference for linear coordination, an ordered, layered distribution of both cations is adopted. In contrast, a rock salt or random distribution would not provide a structure where mercury would retain a linear coordination geometry and a coordination number of two.

In oxygen-deficient perovskites of stoichiometry A'A''B'B''O$_{5.5}$, one-twelfth of the oxygen sites are vacant and the average coordination number of the B cations is 5.5. The oxygen vacancies may arrange so that the B cations are found on both 6-coordinate (octahedral) and 5-coordinate (square pyramidal) sites. With this degree of oxygen nonstoichiometry, octahedra and square pyramids are present in a ratio of 1:1. The polyhedra are not restrained to order in a layered manner but may adopt various arrangements, two of which are described in Figure 1. In Figure 1a the polyhedra are randomly distributed, while in Figure 1b the polyhedra are separated into distinct layers as the vacancies order in planes. In both cases, two distinct B-cation environments exist. Cations which prefer square pyramidal coordination, for example the Jahn−Teller ion Cu^{2+}, will favor the 5-coordinate site, whereas large and/or highly charged cations, such as Ti^{4+} and Sn^{4+}, favor the site with greater coordination. A layered perovskite structure is obtained when the B cations and oxygen vacancies concertedly order.

La$_2$Ba$_2$Cu$_2$Sn$_2$O$_{11}$, prepared by Anderson et al.,[9] was the first A'A''B'B''O$_{5.5}$ material synthesized with the

* To whom correspondence should be addressed.
® Abstract published in *Advance ACS Abstracts*, May 15, 1995.
(1) Galasso, F.; Katz, L.; Ward, R. *J. Am. Chem. Soc.* **1959**, *81*, 820.
(2) Galasso, F.; Darby, W. *J. Phys. Chem.* **1962**, *66*, 131.
(3) Blasse, G. *J. Inorg. Nucl. Chem.* **1965**, *27*, 993.
(4) Goodenough, J. B.; Longo, J. M. *Landolt-Bornstein, Numerical Data and Functional Relationships in Science and Technology*; Hellwege, K.-H., Ed.; Springer-Verlag: Berlin, 1970; Group III/Vol. 4a.
(5) Anderson, M. T.; Greenwood, K. B.; Taylor, G. A.; Poeppelmeier, K. R. *Prog. Solid State Chem.* **1993**, *22*, 197.
(6) Anderson, M. T.; Poeppelmeier, K. R. *Chem. Mater.* **1991**, *3*, 476.

(7) Anderson, M. T.; Vaughey, J. T.; Poeppelmeier, K. R. *Chem. Mater.* **1993**, *5*, 151.
(8) Putilin, S. N.; Antipov, E. V.; Chmaissem, O.; Marezio, M. *Nature* **1993**, *362*, 226.
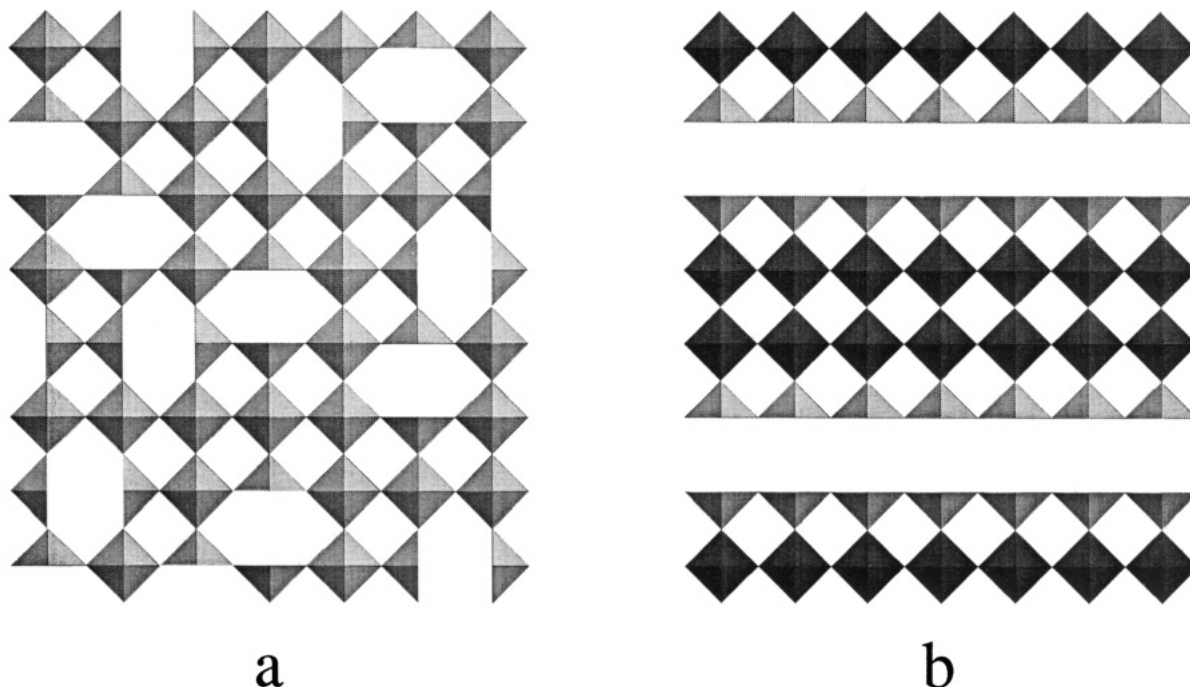
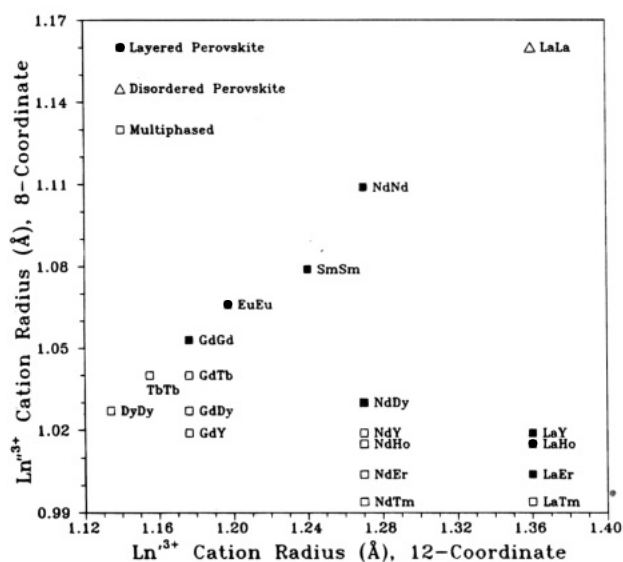**Figure 1.** Octahedra and square pyramids in a one-to-one ratio arranged (a) randomly and (b) in layers.

Figure 2. Stability window for the layered materials $Ln'Ln''Ba_2Cu_2Ti_2O_{11}$.

layered sublattice arrangement. The chemical formula of the compound is written with stoichiometric coefficients reflective of the four perovskite-like blocks contained in the unit cell. Thus, this structure type has been termed a quadruple or quaternary perovskite. The layered arrangement of $La_2Ba_2Cu_2Sn_2O_{11}$ was not stabilized when smaller lanthanides were substituted for lanthanum.[10] Gormezano et al.[11,12] discovered the layered compound $Gd_2Ba_2Cu_2Ti_2O_{11}$ in a systematic study involving cation substitutions in $La_2Ba_2Cu_2Sn_2O_{11}$. Since the discovery of $Gd_2Ba_2Cu_2Ti_2O_{11}$, other independent investigations have shown that substitution of other lanthanides for gadolinium is possible in this system.[13-17] This paper presents a comprehensive

description of which lanthanides stabilize a layered B-cation sublattice in $Ln_2Ba_2Cu_2Ti_2O_{11}$ (Ln = lanthanide) by reporting the new material $Sm_2Ba_2Cu_2Ti_2O_{11}$ and confirming the layered nature of others recently published. In addition, new layered materials with the mixed A-site stoichiometries $Ln'Ln''Ba_2Cu_2Ti_2O_{11}$ (Ln = lanthanide, Y) are reported, which lead to preferred ordering of the smaller lanthanide (Ln'') between the CuO_2^{2-} planes.

Experimental Section

Synthesis. Materials with the stoichiometries $Ln_2Ba_2Cu_2Ti_2O_{11}$ and $Ln'Ln''Ba_2Cu_2Ti_2O_{11}$ (Ln = lanthanide, Y) were prepared using La_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Y_2O_3, $BaCO_3$, CuO, and TiO_2, all of purity 99.99% or greater. Figure 2 reports the combinations of Ln' and Ln'' that were chosen for the $Ln'Ln''Ba_2Cu_2Ti_2O_{11}$ study. The La_2O_3 was preheated in air before use to remove traces of water. The $BaCO_3$ was annealed for more than 8 h under a blanket of flowing CO_2 at 900 °C to remove hydroxide and nitrate impurities. The reagents for each reaction were ground together using an agate mortar and pestle and then pressed into two pellets. One pellet was stacked on top of the other with the lower sacrificial pellet resting on an alumina surface. This technique prohibits alumina from reacting with the sample to be studied. The materials were calcined at 1025 °C for 5–25 days with at least one intermediate regrinding and were then furnace cooled. Samples of stoichiometry $Ln'Ln''Ba_2Cu_2Ti_2O_{11}$ (Ln'Ln'' = LaTm, NdY, NdHo, NdEr, NdTm, GdTb, GdDy, and GdY), which were multiphased after the above treatment, were subsequently treated at 1100 °C under 600 bar of oxygen in an effort to stabilize single-phase layered materials.

(9) Anderson, M. T.; Poeppelmeier, K. R.; Zhang, J.-P.; Fan, H.-J.; Marks, L. D. *Chem. Mater.* **1992**, *4*, 1305.
(10) Private communication with Mark T. Anderson.
(11) Gormezano, A.; Weller, M. T. *J. Mater. Chem.* **1993**, *3*, 771.

(12) Gormezano, A.; Weller, M. T. *J. Mater. Chem.* **1993**, *3*, 979.
(13) Greenwood, K. B.; Anderson, M. T.; Poeppelmeier, K. R.; Novikov, D. L.; Freeman, A. J.; Dabrowski, B.; Gramsch, S. A.; Burdett, J. K. *Physica C* **1994**, *235–240*, 349.
(14) Salvador, P. A.; Shen, L.; Mason, T. O.; Greenwood, K. B.; Poeppelmeier, K. R. Submitted to *J. Solid State Chem.*
(15) Palacin, M. R.; Fuertes, A.; Casañ-Pastor, N.; Gómez-Romero, P. *Adv. Mater.* **1994**, *6*, 54.
(16) Gómez-Romero, P.; Palacín, M. R.; Rodríguez-Carvajal, J. *Chem. Mater.* **1994**, *6*, 2118.
(17) Palacín, M. R.; Krumeich, F.; Caldés, M. T.; Gómez-Romero, P. *J. Solid State Chem.*, in press.

Table 1. Refined Atomic Coordinates for $Ln'Ln''Ba_2Cu_2Ti_2O_{11}$

atom	site	x	y	$LaYBa_2Cu_2Ti_2O_{11}$		$NdDyBa_2Cu_2Ti_2O_{11}$		$Nd_2Ba_2Cu_2Ti_2O_{11}$[a]		$Sm_2Ba_2Cu_2Ti_2O_{11}$		$Eu_2Ba_2Cu_2Ti_2O_{11}$[b]	
				z	occup	z	occup	z	occup	z	occup	z	occup
Ln'	1d	1/2	1/2	1/2	0.93 La/0.07 Y	1/2	1.00 Nd/0.00 Dy	1/2	1	1/2	1	1/2	1
Ln''	1c	1/2	1/2	0	0.93 Y/0.07 La	0	1.00 Dy/0.00 Nd	0	1	0	1	0	1
Ba	2h	1/2	1/2	0.2320(2)	1	0.2336(2)	1	0.2339(2)	1	0.2339(2)	1	0.2340(2)	1
Cu	2g	0	0	0.1046(4)	1	0.1055(5)	1	0.1086(4)	1	0.1071(5)	1	0.1071(5)	1
Ti	2g	0	0	0.3692(7)	1	0.3722(8)	1	0.3744(7)	1	0.3743(9)	1	0.3728(9)	1
O(1)	1b	0	0	1/2	1	1/2	1	1/2	1	1/2	1	1/2	1
O(2)	4i	0	1/2	0.3808(14)	1	0.3897(15)	1	0.3917(13)	1	0.3923(15)	1	0.3927(15)	1
O(3)	2g	0	0	0.2530(19)	1	0.2581(22)	1	0.2593(21)	1	0.2643(22)	1	0.2672(21)	1
O(4)	4i	0	1/2	0.0877(10)	1	0.0893(12)	1	0.0892(11)	1	0.0891(13)	1	0.0894(13)	1

material	space group	a (Å)	c (Å)	$\beta_{overall}$ (Å²)	R_p[c]	R_{wp}[c]
$LaYBa_2Cu_2Ti_2O_{11}$	$P4/mmm$	3.8969(3)	15.716(2)	0.251	4.84	6.71
$NdDyBa_2Cu_2Ti_2O_{11}$	$P4/mmm$	3.8892(2)	15.720(2)	0.424	3.21	4.34
$Nd_2Ba_2Cu_2Ti_2O_{11}$[a]	$P4/mmm$	3.9071(2)	15.759(1)	0.157	4.92	6.42
$Sm_2Ba_2Cu_2Ti_2O_{11}$	$P4/mmm$	3.8950(3)	15.749(2)	0.605	3.84	5.00
$Eu_2Ba_2Cu_2Ti_2O_{11}$[b]	$P4/mmm$	3.8905(3)	15.744(2)	0.203	3.01	4.02

[a] See also ref 16. [b] See also refs 13 and 15. [c] $R_p = 100(\sum|Y_{obs} - Y_{calc}|/\sum Y_{obs})$; $R_{wp} = 100\sqrt{(\sum W(Y_{obs} - Y_{calc})^2/\sum WY_{obs}^2)}$ where $W = 1/Y_{obs}$. Y_{obs} and Y_{calc} are the observed and calculated profile intensities at a given 2θ angle.

X-ray Diffraction. A Rigaku diffractometer with nickel-filtered Cu Kα radiation was used to collect data on the polycrystalline samples. Silicon was employed as an internal standard. Data were collected from 10 to 90° 2θ by counting for 20 s every 0.05°. Lattice constants and structural parameters were refined using Reitveld analysis.[18]

Results

The materials of composition $Ln_2Ba_2Cu_2Ti_2O_{11}$ and $Ln'Ln''Ba_2Cu_2Ti_2O_{11}$ (Ln = lanthanide, Y) were observed to adopt either a layered quaternary perovskite structure, a disordered perovskite structure, or were multiphased. Figure 2 displays the observed products and maps the regions where the layered perovskites, as a function of the size of the Ln' and Ln'' cations, are formed. The data in this figure for $Gd_2Ba_2Cu_2Ti_2O_{11}$ and $La_2Ba_2Cu_2Ti_2O_{11}$ ($LaBaCuTiO_{5.5}$) were taken from refs 11 and 14, respectively.

$Ln_2Ba_2Cu_2Ti_2O_{11}$ (Ln = Nd, Sm, Eu, Tb, Dy). Compounds with Ln = Nd, Sm, and Eu may be indexed on primitive tetragonal $1a_p \times 1a_p \times 4a_p$ cells, where a_p is the lattice parameter of a typical cubic perovskite, i.e., ~4 Å. Their average structures have been refined from powder X-ray diffraction data in $P4/mmm$ symmetry, using the structure of $Gd_2Ba_2Cu_2Ti_2O_{11}$ as a starting model.[11] The Ba and one of the Ln cations were allowed to mix over the 12 coordinate $1d$ and $2h$ sites located between the double layers of Ti octahedra and between Cu–O and Ti–O layers, respectively, while the other Ln was constrained to the smaller 8-coordinate $1c$ site between the Cu–O sheets. For Ln = Eu, europium exclusively occupied the $1d$ site between the Ti octahedra. Although a degree of site mixing was observed when Ln = Nd or Sm, the extent of this mixing could not be conclusively determined owing to the similar scattering capabilities of these lanthanides and barium. In the final refinements these cations were constrained to similar sites as those found for Ln = Eu. This is chemically reasonable because the largest cation (Ba^{2+}) occupies the largest 12-coordinate A site, and the smallest A cation (Ln^{3+}) occupies both the 8-coordinate and smaller 12-coordinate sites. Furthermore, Nd and

Ba site mixing was not observed in a recent neutron diffraction study of $Nd_2Ba_2Cu_2Ti_2O_{11}$.[16]

For Ln = Sm and Eu, the positions of O(2) and O(4) were allowed to disorder off the a axis from $4i$ onto $8t$ sites, but a better fit was achieved with these atoms located on the $4i$ sites. If the A cations were sufficiently small, the Cu–O and Ti–O polyhedra could rotate along c to lessen half of the A–O bond lengths in order to best coordinate the A cations. This rotation has been seen for O(2) in the $Gd_2Ba_2Cu_2Ti_2O_{11}$ and $La_2Ba_2Cu_2Sn_2O_{11}$ systems[9,11] but was not observed in recently published studies of $Eu_2Ba_2Cu_2Ti_2O_{11}$ and $Nd_2Ba_2Cu_2Ti_2O_{11}$.[13,14] Gd^{3+} is sufficiently small to allow rotation of the Ti–O octahedra while the larger Eu^{3+}, Sm^{3+}, and Nd^{3+} cations are not. Lattice parameters and crystallographic data for these compounds are summarized in Table 1, while bond lengths and angles are given in Table 2.

The reaction of stoichiometry $Tb_2Ba_2Cu_2Ti_2O_{11}$ produced a phase with a diffraction pattern similar to those given by the layered structures described above. However, $Tb_2Cu_2O_5$, $BaTiO_3$, and other impurities remained incorporated in the reaction product though it was repeatedly ground and fired at 1025 °C for 25 days. At 1100 °C, a more complete reaction has been observed.[17] The reaction involving Ln = Dy produced only $Dy_2Cu_2O_5$ and $BaTiO_3$.

$Ln'Ln''Ba_2Cu_2Ti_2O_{11}$ (Ln = Lanthanide, Y). The materials with Ln'Ln'' = LaY, LaHo, LaEr, and NdDy formed single-phase layered quaternary perovskites, while those with Ln'Ln'' = LaTm, NdY, NdHo, NdEr, NdTm, GdTb, GdDy, and GdY were multiphased. Powder X-ray diffraction did not reveal any difference in the multiphased nature of the air treated and the high oxygen pressure treated samples. A cubic perovskite phase similar to $LaBaCuTiO_{5.5}$ was identified by powder diffraction among the products of the multiphasic "$LaTmBa_2Cu_2Ti_2O_{11}$" reaction. $LaBaCuTiO_{5.5}$ has a complex perovskite-like structure that has been elucidated by neutron diffraction and transmission electron microscopy.[16] It does not contain distinct layers of Cu–O and Ti–O as the quaternary perovskites do, but does have a degree of cation order giving a superstructure tetragonal cell with a c/a ratio of 4.015. By powder X-ray diffraction techniques, the superstructure reflec-

(18) Wiles, D. B.; Sakthivel, A.; Young, R. A. *Rietveld Analysis Program, Version DBWS-9006*; School of Physics, Georgia Institute of Technology, 1990.

Table 2. Derived Bond Lengths (Å) and Angles (deg)

Ln'Ln"Ba$_2$Cu$_2$Ti$_2$O$_{11}$	Cu–O(3) ×1	Cu–O(4) ×4	Ti–O(1) ×1	Ti–O(2) ×4	Ti–O(3) ×1	Ln"–O(4) ×8	Ln'–O(1) ×4	Ln'–O(2) ×8
LaYBa$_2$Cu$_2$Ti$_2$O$_{11}$	2.33	1.97	2.06	1.96	1.82	2.39	2.75	2.70
NdDyBa$_2$Cu$_2$Ti$_2$O$_{11}$	2.40	1.96	2.01	1.96	1.79	2.40	2.75	2.61
Nd$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$^{a}	2.37	1.98	1.98	1.97	1.81	2.41	2.77	2.59
Sm$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$	2.48	1.97	1.98	1.97	1.73	2.40	2.75	2.58
Eu$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$^{b}	2.52	1.96	2.00	1.97	1.66	2.40	2.75	2.58

compound	Ba–O(2) ×4	Ba–O(3) ×4	Ba–O(4) ×4	Cu–O(4)–Cu	Ti–O(2)–Ti	O(4)–Cu–O(4)	O(2)–Ti–O(2)
LaYBa$_2$Cu$_2$Ti$_2$O$_{11}$	3.04	2.77	2.99	164	169	89.0	89.5
NdDyBa$_2$Cu$_2$Ti$_2$O$_{11}$	3.13	2.78	2.99	165	164	89.0	88.9
Nd$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$^{a}	3.16	2.79	3.00	162	164	88.6	88.9
Sm$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$	3.16	2.79	3.00	163	163	88.8	88.8
Eu$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$^{b}	3.17	2.80	2.99	164	162	88.8	88.6

^{a} See also ref 16. ^{b} See also refs 13 and 15.

tions are not observed and LaBaCuTiO$_{5.5}$ is best modeled as a cubic perovskite with the La and Ba, Cu and Ti, and oxygen and vacancies randomly distributed over the respective A-cation, B-cation, and oxygen sites.[14] The lattice parameter of the cubic phase observed in the "LaTmBa$_2$Cu$_2$Ti$_2$O$_{11}$" reaction was 3.915(2) Å, which is shorter than the 3.9399(3) Å reported for LaBaCuTiO$_{5.5}$, indicating that Tm may be partially substituting for La in LaBaCuTiO$_{5.5}$. Similarly, a layered Nd$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$-like phase was observed in the multiphased "NdLn"Ba$_2$Cu$_2$Ti$_2$O$_{11}$" reactions. In the multiphasic "NdYBa$_2$Cu$_2$Ti$_2$O$_{11}$" reaction the quaternary perovskite phase had lattice parameters of $a = 3.9004(12)$ Å, $c = 15.726(9)$ Å (compared with $a = 3.9071(2)$ Å and $c = 15.759(1)$ Å for Nd$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$), suggesting that Y may partially replace Nd in Nd$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$. The other products of the "NdYBa$_2$Cu$_2$Ti$_2$O$_{11}$" reaction were BaTiO$_3$, Y$_2$O$_3$, and Y$_2$Cu$_2$O$_5$.

The layered structures of LaYBa$_2$Cu$_2$Ti$_2$O$_{11}$ and NdDyBa$_2$Cu$_2$Ti$_2$O$_{11}$ were modeled by constraining the Ba to the large 12-coordinate 2h site while the other A cations were allowed to mix over the 1c (8-coordinate) and 1d (12-coordinate) sites. For LaYBa$_2$Cu$_2$Ti$_2$O$_{11}$, Y was found to almost exclusively occupy the smaller 8-coordinate site between the Cu–O planes. Whereas the X-ray scattering capabilities of La and Y are distinct enough to ascertain their distribution over the 1c and 1d sites, those of Nd and Dy do not allow conclusive determination of their distributions. Allowing Nd and Dy to randomly mix over these sites did not improve the fit, as compared to that obtained when Dy was artificially constrained to the 1c site between the Cu–O planes. Therefore, in the final refinement Dy was constrained to the 1c site as this allows the smallest cation to occupy the 8-coordinate site. Further arguments for this distribution will be discussed below. Lattice parameters and crystallographic data for LaYBa$_2$Cu$_2$Ti$_2$O$_{11}$ and NdDyBa$_2$Cu$_2$Ti$_2$O$_{11}$ are compared with other Ln$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$ materials in Tables 1 and 2. The diffraction data of LaHoBa$_2$Cu$_2$Ti$_2$O$_{11}$ and LaErBa$_2$Cu$_2$Ti$_2$O$_{11}$ were refined using the structural model of LaYBa$_2$Cu$_2$Ti$_2$O$_{11}$, and the lattice parameters were determined to be $a = 3.8975(3)$ Å, $c = 15.713(2)$ Å, and $a = 3.8959(3)$ Å, $c = 15.714(2)$ Å, respectively.

Discussion

There are three distinct A-cation environments in the layered quaternary perovskite structure. These sites are illustrated for the material LaYBa$_2$Cu$_2$Ti$_2$O$_{11}$ in

Figure 3. The distance separating the planes of oxygen anions along c can be related to the size of the A-cation sites located between these planes. Elucidated from the refinement of the average structure of LaYBa$_2$Cu$_2$Ti$_2$O$_{11}$ from powder X-ray diffraction data, the interplanar spacing between O(4) planes is 2.76 Å, between O(2) planes is 3.74 Å, and between O(2) and O(4) planes is 4.61 Å. The three A-site cations Y^{3+}, La^{3+}, and Ba^{2+} (ionic radii[19] of 1.019, 1.36, and 1.61 Å, respectively) order over these sites according to their size. The plane of ordered oxygen vacancies located between the CuO$_2$$^{2-}$ layers result in the contraction between O(4) planes, while the long Cu–O(3) bond of Jahn–Teller distorted Cu^{2+} provides the large separation between O(2) and O(4) planes. In LaYBa$_2$Cu$_2$Ti$_2$O$_{11}$, Y^{3+} almost exclusively occupies the 8-coordinate site between O(4) sheets, resulting in the structural motif BaO|CuO$_2$|Y|CuO$_2$|BaO. This pattern is found in many high-temperature superconductors including YBa$_2$Cu$_3$O$_7$.

The stability of layered Ln'Ln"Ba$_2$Cu$_2$M$_2$O$_{11}$ (M = Ti, Sn) phases is dependent on the sizes and preferred coordination numbers of the constituent Ln' and Ln" cations. The copper–tin–oxygen framework of La$_2$Ba$_2$Cu$_2$Sn$_2$O$_{11}$ is large enough to support lanthanum on both the 8-coordinate site between the Cu–O sheets and the 12-coordinate site between the Sn–O octahedra. The copper–titanium–oxygen frameworks of the Ln$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$ materials are necessarily smaller because of the substantial size difference between Ti^{4+} and Sn^{4+} (ionic radii of 0.605 vs 0.69 Å, respectively[19]). The large size of lanthanum does not allow a layered quaternary perovskite of composition La$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$ to form. When half of the La^{3+} cations are replaced by smaller Y^{3+}, as in LaYBa$_2$Cu$_2$Ti$_2$O$_{11}$, lanthanum preferentially occupies the larger 12-coordinate site while the smaller yttrium occupies the 8-coordinate site between the Cu–O sheets and thus stabilizes the layered structure. The fact that lanthanum preferentially occupies the higher coordinate site suggests that occupation of the 8-coordinate site by lanthanum is the structural feature that destabilizes a layered La$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$ perovskite. Thus, the preference for an 8-coordinate environment by smaller cations (Y^{3+}, Ho^{3+}, and Er^{3+}) acts to stabilize the layered quaternary perovskite structure in this system. The quaternary perovskite structure is also unstable for "Dy$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$" because half of the small dysprosium cations would occupy 12-coordinate sites. Instead a mixture of the binary oxides Dy$_2$Cu$_2$O$_5$

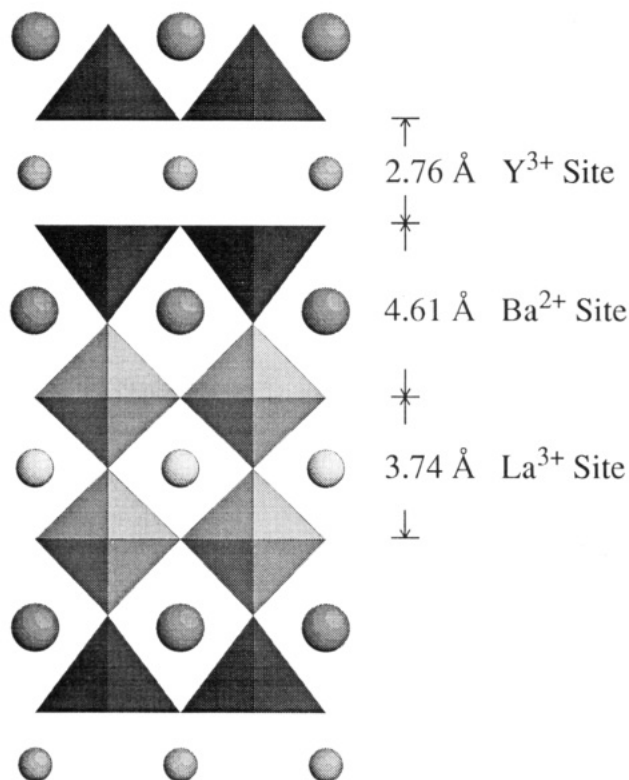(19) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

Figure 3. Spacing between oxygen planes and the A-cation sites in LaYBa₂Cu₂Ti₂O₁₁. Cu, square pyramids; Ti, octahedra; O, verticies.

Figure 4. Selected lattice parameters for tetragonal Ln'Ln''Ba₂-Cu₂Ti₂O₁₁ layered materials.

and BaTiO₃ forms. The coordination preference of Dy³⁺ is better met by the octahedral environment in Dy₂-Cu₂O₅,[20] as opposed to the 12-coordinate site in the quaternary perovskite. The layered structure is only accessible when a larger cation, which prefers a higher coordination number, partially substitutes for Dy³⁺ as in NdDyBa₂Cu₂Ti₂O₁₁.

The compositional range of the layered Ln'Ln''Ba₂-Cu₂Ti₂O₁₁ structure is mapped out in Figure 2. The ionic radius data were taken from Shannon,[19] or in the case of the 12-coordinate radii of the smaller lanthanides and Y³⁺, extrapolated from the values of La³⁺ and Nd³⁺. For a particular choice of the Ln' cation, there is a lower limit on the size of the Ln'' cation which will stabilize the layered structure. For instance, when Ln' = Nd³⁺, Ln'' = Dy³⁺ is the smallest lanthanide that can support the layered structure, while smaller cations result in multiphasic materials. However, a layered quaternary perovskite (of approximate stoichiometry Ln₂'Ba₂Cu₂-Ti₂O₁₁) is always present among the components of the multiphasic systems. The inherent stability of Ln₂'Ba₂-Cu₂Ti₂O₁₁ is in competition with that of the mixed Ln'Ln''Ba₂Cu₂Ti₂O₁₁ materials.

The lattice parameters of the layered quaternary perovskites as a function of the average ionic radii of the Ln' and Ln'' cations are plotted in Figure 4. The lattice constants relate linearly to the Ln cation size in the single lanthanide Ln₂Ba₂Cu₂Ti₂O₁₁ materials, but a deviation from this linear dependence is observed for the mixed lanthanide materials. Quaternary perovskites containing two different lanthanides are not expected to obey this linear relationship when the
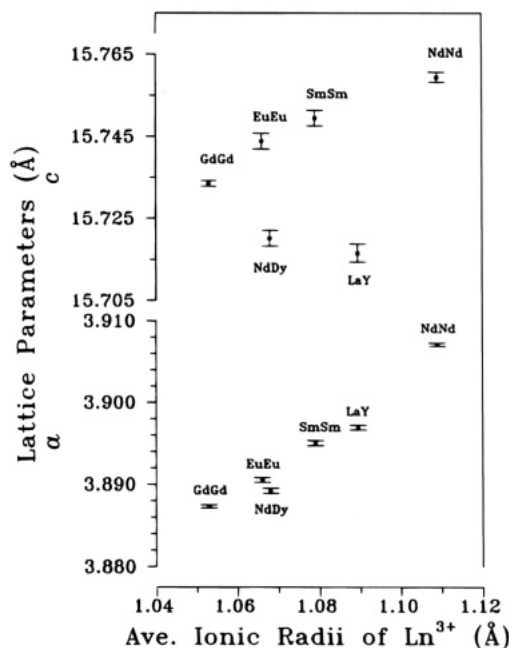
different Ln cations (Ln', Ln'') are site specific across the $1c$ (Ln'') and $1d$ (Ln') sites. This is evidenced in the contraction of the c axis for LaYBa₂Cu₂Ti₂O₁₁, owing to the ordering of Y on the $1c$ site and La on the $1d$ site. The pronounced contraction of the c axis, from that expected by a random distribution of the two lanthanides in NdDyBa₂Cu₂Ti₂O₁₁, is in agreement with an ordered model, placing the small Dy on the 8-coordinate $1c$ site. The contraction of the a lattice parameter is less sensitive to this ordering and deviates only slightly from the linear relationship.

Further compression of the lattice constants is minor when smaller lanthanides replace Y in the LaLn''Ba₂-Cu₂Ti₂O₁₁ system. The a lattice constants of LaYBa₂-Cu₂Ti₂O₁₁, LaHoBa₂Cu₂Ti₂O₁₁, and LaErBa₂Cu₂Ti₂O₁₁ are similar despite the range of sizes of the Ln'' cation (Y³⁺, 1.019 Å; Ho³⁺, 1.015 Å; Er³⁺, 1.004 Å, 8-coordinate ionic radii). The Cu–O(4) and Ti–O(2) bonds are not easily further compressed with the large cations La³⁺ and Ba²⁺ on the $1d$ and $2h$ A sites. Because La³⁺ lies in the O(1) plane, the distance separating La³⁺ from O(4) is equal to $\sqrt{2}/2$ times the lattice parameter a. For LaYBa₂Cu₂Ti₂O₁₁ this value is equal to 2.75 Å. A summation of the ionic radii of La³⁺ (1.36 Å) and O²⁻ (1.40 Å) gives 2.76 Å, showing that the La³⁺ cation can be thought of as contacting the O(4) anions. Thus the size of La³⁺ restricts further compression of the lattice in the ab plane. However, substitution of a smaller lanthanide on the 12-coordinate A-site can lead to contracted lattice parameters as observed in NdDyBa₂-Cu₂Ti₂O₁₁.

Contracted lattice parameters in the ab plane are advantageous to superconductivity as they indicate better overlap of the copper $d_{x^2-y^2}$ and oxygen $2p$ orbitals. The Cu–O(4) bond lengths for Ln'Ln''Ba₂Cu₂-Ti₂O₁₁ materials are plotted as a function of the average size of Ln' and Ln'' in Figure 5. Gd₂Ba₂Cu₂Ti₂O₁₁[11] and Tb₂Ba₂Cu₂Ti₂O₁₁[17] exhibit the shortest Cu–O(4) bond lengths of ~1.95 Å, which are approaching the upper limit of known hole-doped superconductors (~1.94

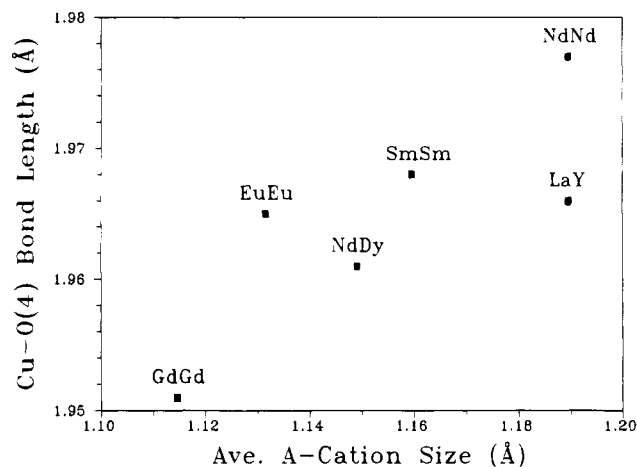(20) Freund, H.-R.; Muller-Buschbaum, Hk. *Z. Naturforsch.* **1977**, *32b*, 609.

Figure 5. Cu—O(4) bond lengths in Ln'Ln''Ba$_2$Cu$_2$Ti$_2$O$_{11}$ materials.

Å).[21] However, superconductivity has not been observed in Ca-doped Gd$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$ systems.[22] Efforts to further contract the a lattice parameter (which is related to the length of the in-plane Cu—O bond) in Gd$_2$Ba$_2$-Cu$_2$Ti$_2$O$_{11}$ by replacing half of the gadolinium with smaller lanthanides resulted in multiphased compounds. The mixed lanthanide materials reported here display Cu—O(4) bond lengths which are reduced with respect to their analagous single lanthanide compounds. For instance, this bond length is contracted in NdDyBa$_2$-Cu$_2$Ti$_2$O$_{11}$ (1.96 Å) as compared with Nd$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$ (1.98 Å). Efforts to understand the role of chemical substitutions in these mixed lanthanide compounds are currently being pursued.

Conclusions

The compositional range of layered quaternary perovskite structures has been extended through the discovery of novel Ln'Ln''Ba$_2$Cu$_2$Ti$_2$O$_{11}$ (Ln = lanthanide, Y) materials. This was achieved by recognizing the three distinct A-cation site environments in the quaternary perovskite structure and using A cations which have the proper size and coordination preferences needed to stabilize the layered structure. The mixed A-site compositions Ln'Ln''Ba$_2$Cu$_2$Ti$_2$O$_{11}$ (Ln'Ln'' = LaY, LaHo, LaEr, NdDy) exhibit reduced cell constants and volumes compared to expected values. It is clear that the preference of the smaller lanthanide (Ln'') for the 1d site reduces the separation between the copper—oxygen planes. These layered materials are composed of closely spaced, facing sheets of Cu—O square pyramids separated by double layers of Ti—O octahedra and are promising candidates for high-T_c materials. Further investigations are currently underway to determine the role various dopants and high oxygen pressure have on the superconducting behavior of mixed A-site compositions Ln'Ln''Ba$_2$Cu$_2$Ti$_2$O$_{11}$.

(21) Hazen, R. M. In *Physical Properties of High Temperature Superconductors II*; Ginsberg, D. M., Ed.; World Scientific: Singapore, 1990; Chapter 3.

(22) Fukuoka, A.; Adachi, S.; Sugano, T.; Wu, X-J.; Yamauchi, H. *Physica C* **1994**, *231*, 372.