Neutron Diffraction Studies of Quadrupled Perovskites $Sm_2Ba_2Cu_2Ti_{1.5}Sn_{0.5}O_{11}$, $Sm_2Ba_2Cu_2Ti_{1.55}Sn_{0.2}Sc_{0.25}O_{11}$, and $Gd_2Ba_2Cu_2Ti_2O_{11}$ and Calcium Doping of $Gd_2Ba_2Cu_2Ti_2O_{11}$

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The structures of the recently reported quadruple perovskites $Gd_2Ba_2Cu_2Ti_2O_{11}$, $Sm_2Ba_2Cu_2Ti_{1.5}Sn_{0.5}O_{11}$, and $Sm_2Ba_2Cu_2Ti_{1.55}Sn_{0.2}Sc_{0.25}O_{11}$ have been studied by very high resolution time-of-flight powder neutron diffraction. The proposed layered B cation oxygen deficient perovskite structure has been confirmed and refinements have shown the oxygen between the (Sn/Ti) layers to be displaced by approximately 0.3 Å from the ideal (0,0,$^1/_2$) site (*P4/mmm* space group) along {100}. Doping studies on the A type perovskite site are reported and highlight the complexity of the quadruple perovskite structure and the importance of the correct choice of ion size to ensure ordering of both A and B type cations.

Introduction

Oxygen-deficient perovskites are currently of considerable interest as the structure of the high-T_c superconductor $YBa_2Cu_3O_{7-x}$[1] can be considered to have a tripled perovskite unit cell. The superconducting properties of this compound are believed to be structurally derived from the presence of copper–oxygen planes of stoichiometry CuO_2 separated by a metal or metal–oxygen layers which control the hole concentration in the CuO_2 planes. Structural requirements of these copper–oxygen layers are finely tuned by the choice of these charge reservoirs and oxygen stoichiometry. In the search for novel high-T_c superconductors, one approach is the replacement of the CuO chains present in $YBa_2Cu_3O_{7-x}$ by a new type of link between the otherwise unchanged layers of corner-sharing CuO_5 square pyramids. Cations exhibiting a strong tendency toward octahedral coordination such as group 5 and 13 elements can be successfully introduced on this interlayer site and superconductivity in some of these compounds has been reported.[2,3] A different possible substitution is the replacement of the single-layer charge reservoir by a double-layered one as shown in Figure 1. $La_2Ba_2Cu_2Sn_2O_{11}$[4] was the first reported compound of this kind which consists of double layers of square-pyramidal copper interleaved with double layers of octahedrally coordinated tin. However, a severe bond length mismatch between the copper and tin causes the SnO_6 octahedra to rotate in order to observe the formation of an ordered quadrupled oxygen deficient perovskite. This rotation results in the elongation of the copper–oxygen bonds within the structure, distances which are widely regarded as important for the occurrence of high-T_c superconductivity. More recently, $Gd_2Ba_2Cu_2Ti_2O_{11}$[5] was reported where careful choice in the nature of the lanthanide cation and the introduction of Ti instead of Sn reduced the mismatch between the two B cation layers therefore producing copper–oxygen distances within the range adopted by most high-T_c superconductors. However, this compound does not exhibit superconductivity, even when Sc(III) is introduced on the Ti(IV) site within the structure with the aim of generating holes within the CuO_2 layers.[6]

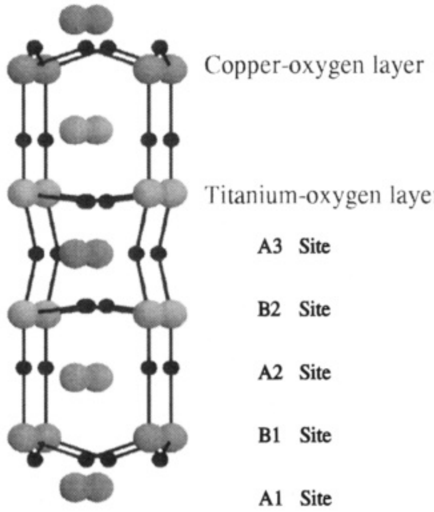

Figure 1. Structure of $Gd_2Ba_2Cu_2Ti_2O_{11}$ showing the oxygen disordering within the titanium layer and the buckering of the copper–oxygen planes and the labeling of the cation site as referred in the text.

In this study, high-resolution neutron diffraction was used as a tool to carefully study oxygen stoichiometry

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and distribution in the CuO_2 layers of a quadruple perovskite and, in addition, doping studies on the A type perovskite site are reported. Gomez-Romero et al.[7,8] have recently investigated the structure of some titanium-containing quadruple perovskites of the type originally reported by us; however, data could be obtained only on compounds containing the large lanthanides, lanthanum, and neodymium; the latter presenting an ordered arrangement of the B cations while the former showing a lack of long-range order while retaining a superstructure with a tetragonal cell. To deconvolute site occupancies, temperature factors and atomic positional disorder, diffraction data are required over a large *d*-spacing range which was not available to the aforementioned authors. We have, therefore, investigated the structures of the fully cation ordered materials, the title compounds, using isotopes and time-of-flight neutron diffraction.

Experimental Section

Samples of composition $Gd_2Ba_2Cu_2Ti_2O_{11}$, $Sm_2Ba_2Cu_2Ti_{1.5}Sn_{0.5}O_{11}$, and $Sm_2Ba_2Cu_2Ti_{1.55}Sc_{0.25}Sn_{0.2}O_{11}$ were prepared with isotopically enriched $^{160}Gd_2O_3$ (98.4%) and $^{154}Sm_2O_3$ (98.6%). To perform neutron diffraction experiments on these compounds, isotopically enriched material is necessary as naturally abundant Gd and Sm contain the strongly absorbing ^{149}Gd and ^{157}Sm isotopes. These samples were prepared by solid-state reaction of the stoichiometric amounts of $BaCO_3$, Ln_2O_3, SnO_2, TiO_2, Sc_2O_3, and CuO. The dried reagents were ground thoroughly together and fired in air at 950 °C. The partially reacted products were then quenched to room temperature and pelletized. The pellets were then fired at 1025 °C in air for 8 days with frequent intermediate regrinding and pelletizing. The samples were finally annealed under flowing oxygen at 450 °C for 1 day and then furnace cooled to room temperature.

To investigate the effect of calcium doping on the Gd/Ba site, materials of nominal composition $Gd_2Ba_2Cu_2Ti_2O_{11}$, $Gd_{1.8}Ca_{0.4}Ba_{1.8}Cu_2Ti_2O_{11}$, $Gd_{1.75}Ca_{0.4}Ba_{1.85}Cu_2Ti_2O_{11}$, $Gd_{1.7}Ca_{0.4}Ba_{1.9}Cu_2Ti_2O_{11}$, and $Gd_{1.65}Ca_{0.35}Ba_2Cu_2Ti_{1.75}Sn_{0.25}O_{11}$ were prepared with naturally abundant Gd_2O_3 in order to perform doping studies of these compounds. These samples were prepared in a manner similar to that of those described above, but the firing temperature required in order to obtain single-phase samples had to be raised to 1040 °C.

The oxygen content of these materials was measured by thermogravimetric analysis on a Stanton Redcroft TG1000 series microbalance. The materials were heated in a platinum crucible under a flowing atmosphere of 5% H_2/N_2 from room temperature to 1000 °C, held at that temperature for 40 min, and then cooled rapidly to room temperature. Experiments were duplicated in order to minimize errors. Oxygen stoichiometry was then determined from the observed weight loss of the material during the reducing process using the following equation:

$$\mathrm{Ln_2Ba_2Cu_2B'_2O_{11-\delta}} + (4-\delta)\mathrm{H_2} \rightarrow \mathrm{Ln_2O_3} + \mathrm{Ba_2B'O_4} + 2\mathrm{Cu}^0 + (4-\delta)\mathrm{H_2O}\uparrow \qquad \mathrm{B'} = \mathrm{Ti}_{2-x-y}\mathrm{Sn}_x\mathrm{Sc}_y$$

The products, except for water vapor, were identified by an X-ray diffraction trace. Oxygen content calculated for all reported materials was found to be 11 ± 0.1, value which is consistent with the presence of tetravalent tin and titanium, trivalent scandium, and mixed divalent and trivalent copper in these materials.

Powder X-ray diffraction (PXD) data were collected for each product using a monochromatic Cu Kα_1 radiation ($\lambda = 1.5406$ Å) over the 2Θ range 20–120° with step size of 0.03° over 15 h using a Siemens D5000 diffractometer on all samples, in order to check sample purity and cell parameters.

Neutron diffraction data were collected on the isotopically enriched samples on the high-resolution powder diffractometer (HRPD) on ISIS at the Rutherford Appleton Laboratory. Samples of 2 g mass were loaded in vanadium cans and data collected in backscattering at the 1 m position over the time-of-flight (TOF) range 30 000–120 000 μs which corresponds to a *d*-spacing range of 0.6216–2.4862 Å and approximately 400 reflections. Data were collected at room temperature for approximately 12 h in the case of the undoped samples and 18 h for $Sm_2Ba_2Cu_2Ti_{1.55}Sc_{0.25}Sn_{0.2}O_{11}$. The raw data were normalized and corrected for absorption assuming pure isotopic abundances. Visual inspection of the data from $Sm_2Ba_2Cu_2Ti_{1.55}Sc_{0.25}Sn_{0.2}O_{11}$ showed few very weak reflections that could not be indexed on a tetragonal unit cell of the quadruple perovskites and were assigned to Sc_2O_3 impurities which were isolated into excluded regions in the refinement. Two very small unindexed peaks in the 95 000 μs region can also be observed in the pattern which cannot be assigned to the quadrupled perovskite phase or the Sc_2O_3 impurities phase. The higher χ^2 obtained for this refinement compared to the other two can be rationalized by the presence of these impurities, smaller sample size reducing the background level and hence R_{exp} and poorer peak shape fit for a more disordered doped structure.

The coherent scattering lengths were taken for ^{160}Gd, ^{154}Sm, Ba, Cu, Sn, Ti, Sc, and O as 0.915, 0.93, 0.525, 0.772, 0.623, −0.58, 1.23, and 0.58 (all × 10^{-12} cm), respectively.[9] The starting model for each refinements were based on the structural details given by Gormezano and Weller[10] for $Gd_2Ba_2Cu_2Ti_2O_{11}$ and $Sm_2Ba_2Cu_2Ti_{1.5}Sn_{0.5}O_{11}$ with space group *P*4/*mmm*, lattice parameters taken from refined PXD data and the basic structure can be seen in Figure 1.

Refinements of the TOF data proceeded smoothly except for the presence of Sc_2O_3 as an impurity phase in the doped sample which was previously undetected by PXD. Forty-three parameters were refined which included a scale factor, zero-point error, 10 background variables, four pseudo-Voigt peak shape parameters, absorption correction, unit cell parameters, positional parameters, and isotropic temperature factors. Disordering of the B cations was permitted during the refinements and site occupancies of the Cu and Ti/Sn/Sc sites were refined; as previously reported, no mixing occurs between the B cations and a perfectly ordered B cations sublattice was obtained where distinct copper–oxygen and titanium/tin/scandium–oxygen layers are observed. However, negative temperature factors were initially obtained for the Ti/Sn/Sc site in $Sm_2Ba_2Cu_2Ti_{1.55}Sc_{0.25}Sn_{0.2}O_{11}$ on refinement of the site occupancy. This is probably a result of the compound stoichiometry not reflecting the starting mixture stoichiometry as shown by the presence of the Sc_2O_3 impurity. With three ions occupying one site, unconstrained refinement of the individual site occupancies is not possible; therefore, the total site occupancy was assumed to be unity and the Sn content fixed at the expected value. The final refined Ti:Sn:Sc ratio was found to be 1.65(2):0.2:0.15(2) in agreement with the scandium oxide impurity. The negative isotropic temperature factor obtained for the gadolinium sites in $Gd_2Ba_2Cu_2Ti_2O_{11}$ is expected due to the presence of a small amount of ^{157}Gd in the starting material which is very strongly absorbing.[9] Site occupancies of the two A cations present in the structure were allowed to vary but no disordering was observed. Displacement of the O2 site from the *x* axis was found to be favored and gave isotropic factors of low magnitude in comparison with that obtained for the high-symmetry position. However, in all three samples, the isotropic temperature factors of the O1 site were found to be relatively high (≈6 Å^2). Refinements of the anisotropic temperature factors for that particular site showed a high value of B_{11} while the others remained at more

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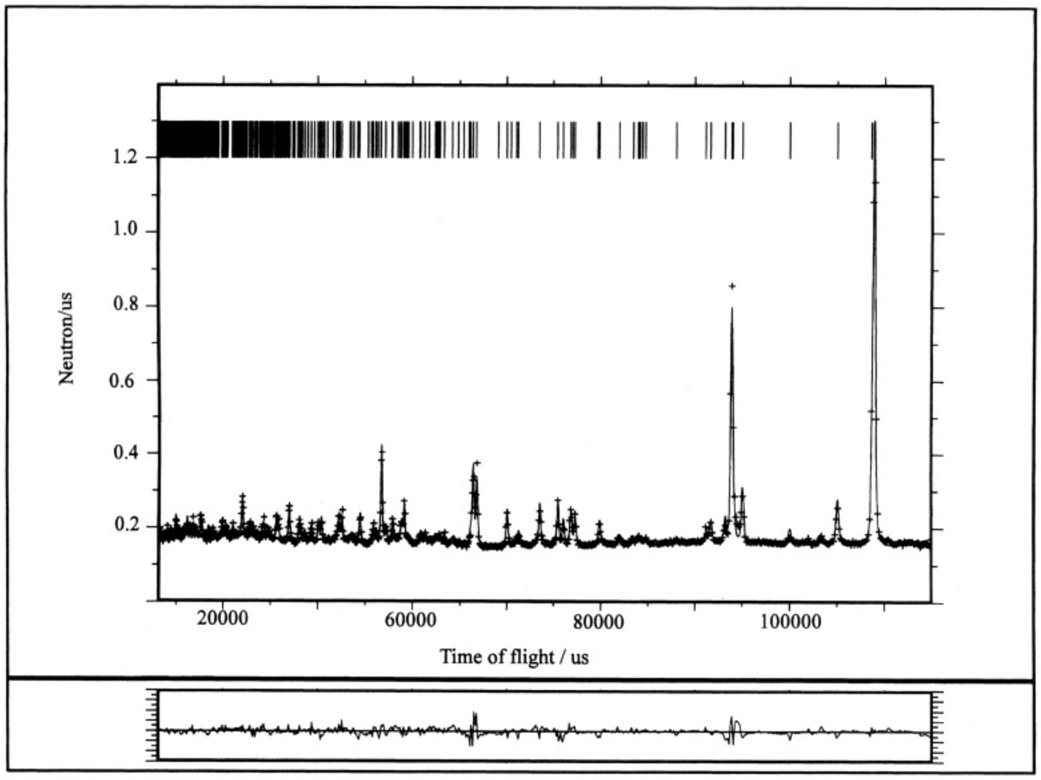

Figure 2. Observed, calculated and difference plot for $Gd_2Ba_2Cu_2Ti_2O_{11}$ in the *d*-spacing range 0.65–2.435 Å.

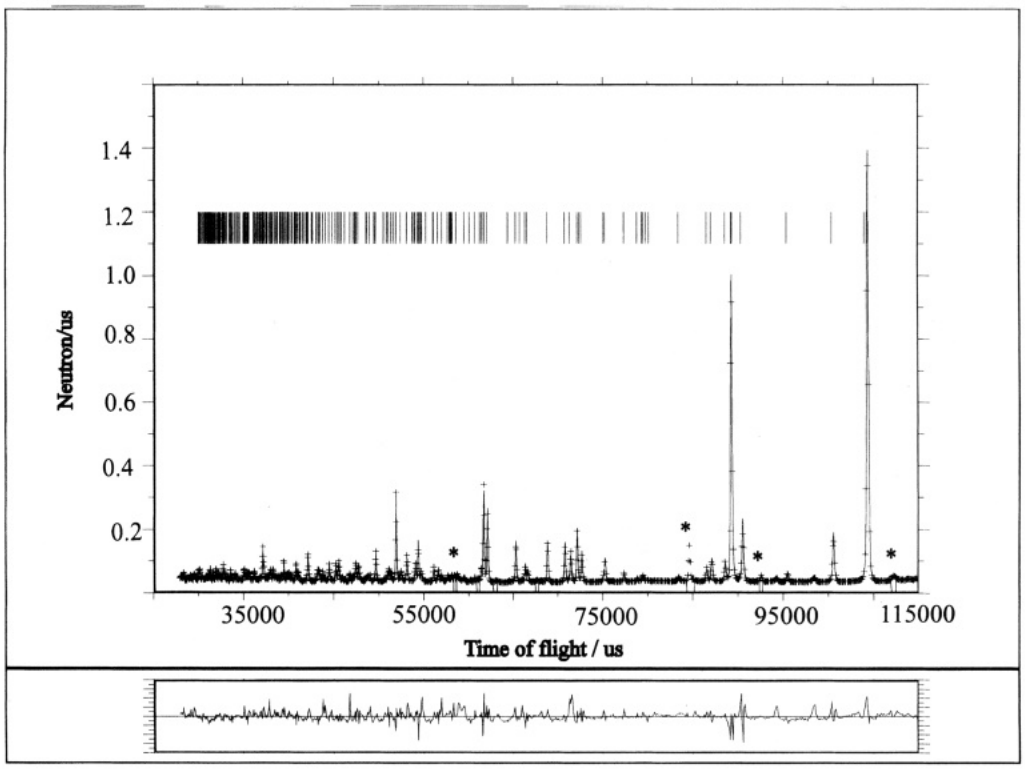

Figure 3. Observed, calculated, and difference plot for $Sm_2Ba_2Cu_2Ti_{1.65}Sc_{0.2}Sn_{0.15}O_{11}$ in the *d*-spacing range 0.68–2.435 Å, where the asterisks represents the Sc_2O_3 impurity peaks.

typical values. The O1 oxygen atom was consequently allowed to disorder around the *x* axis from site (0,0,*z*) to (*x*,0,*z*) with half-occupancy, in the same manner as the O2 position, which enabled the isotropic temperature factor to regain sensible values. Oxygen site occupancies were allowed to vary but deviated only to a small extent from one and within their estimated standard deviation; therefore, they were fixed at unity in the final cycles of refinement. Final profile fit to the TOF pattern from Gd_2-$Ba_2Cu_2Ti_2O_{11}$ and $Sm_2Ba_2Cu_2Ti_{1.55}Sc_{0.25}Sn_{0.2}O_{11}$ are shown respectively in Figures 2 and 3; Tables 1 and 2 summarize the final atomic positions and derived bond distances and angles. The final profile fit to the TOF pattern from $Sm_2Ba_2Cu_2Ti_{1.5}Sn_{0.5}O_{11}$ can be obtained as supporting information.

The PXD data of the calcium doped samples were refined using the DBWS-9006 Rietvield refinement package of Wiles

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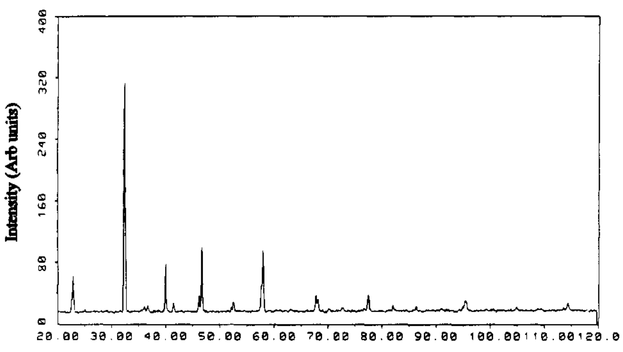

Figure 4. Powder X-ray diffraction pattern for $Gd_{1.7}Ca_{0.4}Ba_{1.9}Cu_2Ti_2O_{11}$ in the 2θ range 20−120°.

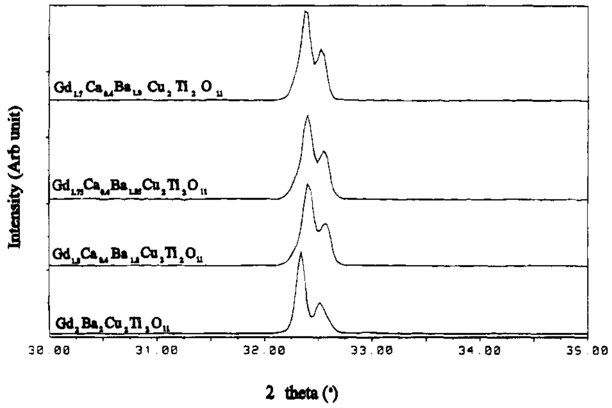

Figure 5. Shift of the most intense peak in the powder X-ray diffraction pattern of the Ca-doped samples with various A cations stoichiometry.

and Young.[11] No TOF data were collected on these materialsdue to the relatively low scattering length of Ca which would have prevented obtaining additional information on the cation ordering present in these studied phases. Twenty-nine parameters were refined which included a scale factor, zero-point error, four background variables, three pseudo-Voigt peak shape parameters, unit cell parameters, positional parameters, isotropic temperature factors, and site occupancy. The samples visually appeared to be single phase, and the calcium atoms were initially assumed to be entirely placed on the A3 site ($^1/_2$,$^1/_2$,$^1/_2$) due to ionic radii considerations, while the Cu and Ti layers were assumed to be ordered. However, all refinements showed unusually large isotropic temperature factors on the B2 (Ti) and A2 (Ba) site, while the B1 (Cu) isotropic temperature factor assumed negative values. Site occupancies of the B1 and B2 site were therefore allowed to vary and disordering was found to occur between the two, at various levels, depending on sample composition. No additional weak superstructure spots were observed in the PXD data of the doped material compared to the undoped one and the disordering of the A and B cations, causes only a change in intensity of the main peaks in the X-ray patterns. Mixing between the various A sites was also refined and it was found that the calcium preferentially occupied the A2 ($^1/_2$,$^1/_2$,z) site which forced some barium to be displaced on the A3 (Gd) site. These materials can however still be represented as $a_p \times a_p \times 4a_p$ tetragonal cell due to the *only partial* mixing of the A and B cations, i.e., the A and B cations are not located in a random manner in the structure which would result in the occupancy of a shared site to be 0.5 for each type of cations. Atomic

Table 1. Refined Atomic Positions

atom	site	occupancy	x	z	ITF
		$Gd_2Ba_2Cu_2Ti_2O_{11}$			
Gd1	1c	1.00	0.50	0.5	−0.25(8)
Ba2/Gd2	2h	0.91/0.09(4)	0.50	0.2350(3)	−0.67(12)
Gd3/Ba3	1d	0.82/0.18(4)	0.50	0.0	0.39(14)
Ti	2g	1.00	0.00	0.3705(6)	0.31(15)
Cu	2g	1.00	0.00	0.1059(3)	0.54(9)
O1	4m	0.25	0.102(2)	0.50	0.06(3)
O2	8t	0.50	0.073(1)	0.3882(3)	1.52(12)
O3	2g	1.0	0.00	0.2557(4)	0.40(10)
O4	4i	1.0	0.00	0.0941(2)	0.57(7)
		$Sm_2Ba_2Cu_2Ti_{1.5}Sn_{0.5}O_{11}$			
Sm1	1c	1.00	0.50	0.5	0.05(5)
Ba	2h	1.00	0.50	0.2320(1)	0.46(5)
Sm2	1d	1.00	0.50	0.00	0.91(6)
Ti/Sn	2g	0.8/0.2(2)	0.00	0.3684(6)	0.69(30)
Cu	2g	1.00	0.00	0.1053(1)	1.21(6)
O1	4m	0.25(1)	0.079(2)	0.50	1.93(27)
O2	8t	0.92(1)	0.0762(1)	0.3848(1)	2.01(12)
O3	2g	0.87(1)	0.00	0.2556(1)	0.95(10)
O4	4i	0.98(1)	0.00	0.0940(1)	1.12(6)
		$Sm_2Ba_2Cu_2Ti_{1.55}Sn_{0.2}Sc_{0.25}O_{11}$			
Sm1	1c	1.00	0.50	0.5	0.11(4)
Ba	2h	1.00	0.50	0.2317(2)	0.13(5)
Sm2	1d	1.00	0.50	0.00	0.49(5)
Ti/Sn/Sc	2g	0.825/0.1/0.075(2)	0.00	0.3713(6)	0.33(18)
Cu	2g	2.00	0.00	0.1051(1)	0.82(5)
O1	4m	0.22(1)	0.065(3)	0.50	2.33(29)
O2	8t	0.92(1)	0.0686(8)	0.3852(1)	2.06(11)
O3	2g	0.91(1)	0.00	0.2555(1)	0.94(9)
O4	4i	0.96(1)	0.00	0.0940(1)	0.66(6)

[a] *P4/mmm*; a = 3.8892(1) Å, c = 15.7443(1) Å; R_{wp} = 5.15; R_{exp} = 2.55; χ^2 = 4.06.[10] [b] *P4/mmm*; a = 3.9064(1) Å, c = 15.8323(1) Å; R_{wp} = 9.72; R_{exp} = 5.04; χ^2 = 3.72. [c] *P4/mmm*; a = 3.9054(1) Å, c = 15.8039(1) Å; R_{wp} = 9.86; R_{exp} = 2.52; χ^2 = 15.21.

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

	$Sm_2Ba_2Cu_2Ti_{1.5}Sn_{0.5}O_{11}$	$Sm_2Ba_2Cu_2Ti_{1.55}Sn_{0.2}Sc_{0.25}O_{11}$	$Gd_2Ba_2Cu_2Ti_2O_{11}$
Ln1−O4	2.456(1)	2.454(2)	2.445(1)
Ba1−O2	2.931(4)	2.954(8)	2.927(7)
	3.304(5)	3.355(8)	3.286(5)
Ba1−O3	2.787(1)	2.787(1)	2.769(1)
Ba1−O4	2.931(2)	2.924(1)	2.950(2)
Ln2−O1	2.553(3)	2.530(3)	2.485(2)
	2.988(2)	3.014(3)	3.044(3)
Ln2−O2	2.897(7)	2.868(4)	2.842(1)
	2.463(9)	2.476(2)	2.418(5)
Cu−O3	2.380(1)	2.377(1)	2.358(1)
Cu−O4	1.961(1)	1.961(1)	1.953(1)
Sn/Ti−O1	2.106(3)	2.063(2)	2.077(5)
Sn/Ti−O2	1.993(7)	1.983(4)	1.985(6)
Sn/Ti−O3	1.786(5)	1.830(7)	1.807(1)

	$Sm_2Ba_2Cu_2Ti_{1.5}Sn_{0.5}O_{11}$	$Sm_2Ba_2Cu_2Ti_{1.55}Sn_{0.2}Sc_{0.25}O_{11}$	$Gd_2Ba_2Cu_2Ti_2O_{11}$
Cu−O4−Cu	169.7(2)	169.4(1)	169.4(1)
Ti−O2−Ti	157.1(5)	159.9(3)	156.8(3)
O4−Cu−O4	86.7(3)	86.2(2)	85.7(3)
O2−Ti−O2	89.2(4)	88.9(6)	88.2(5)

Table 3. Cell Parameters of the Ca-Doped Quadruple Perovskites

	a (Å)	c (Å)	R_{wp}	R_{exp}	χ^2
$Gd_2Ba_2Ti_2Cu_2O_{11}$	3.8873(1)	15.7335(2)	5.15	2.55	4.06
$Gd_{1.8}Ca_{0.4}Ba_{1.8}Cu_2Ti_2O_{11}$	3.8877(1)	15.6942(2)	7.46	5.70	1.71
$Gd_{1.85}Ca_{0.4}Ba_{1.85}Cu_2Ti_2O_{11}$	3.8844(1)	15.6899(4)	7.60	5.81	1.71
$Gd_{1.7}Ca_{0.4}Ba_{1.9}Cu_2Ti_2O_{11}$	3.8877(1)	15.6942(3)	7.47	5.69	1.72
$Gd_{1.65}Ca_{0.35}Ba_2Cu_2Ti_{1.75}Sn_{0.25}O_{11}$	3.8949(1)	15.7557(4)	8.51	6.48	1.72

coordinates and thermal parameters are very similar to the undoped material but the disordering present among the B cations made these materials unlikely candidates for superconductivity. The cell parameters and site occupancies are summarized in Tables 3 and 4. Refined atomic positions and temperature factors are available as supporting information.

Results and Discussion

The structural refinements of the neutron TOF data are in good agreement with those determined previously from X-ray data. Owing to the large difference between the coherent scattering lengths of Cu and Ti, the ordering of the B and B′ cations within the structure could be determined unambiguously. The structure consists of double layers of square pyramidal copper separated by a lanthanide cation, with a copper−copper interplanar distance of 2.97 Å and a puckering of the Cu−O plane of 174.2°. These double layers are split by double layers of octahedrally coordinated tin/titanium cations, where an off-axis displacement of the O1 oxygen position around the lanthanide site was found. The magnitude of this disordering around the x axis in the Ti/Sn layer remains approximately constant when the lanthanide cation is changed from samarium to gadolinium, which seems to indicate that this displacement is independent of the nature of the lanthanide cation present between these Sn/Ti layers and, therefore, probably associated with the mismatch in size of the B and B′ cations. However, this disordering has little effect on the copper−oxygen planes within the structure and therefore should not interfere with the electronic character of these layers. The lack of superconductivity found in these compounds when apparently doped with Sc(III) can be explained by the presence of Sc_2O_3 as an impurity. This impurity, which previously was undetected by XRD, results in a lower calculated copper valence than the desired value of +2.175. As a result, scandium site occupancy was refined and a value of 0.15(2) was obtained which would indicate a copper valence of 2.075. Indeed, the refined copper−oxygen bond lengths were found to be very similar in $Sm_2Ba_2Cu_2Ti_{1.5}Sn_{0.5}O_{11}$ and $Sm_2Ba_2Cu_2Ti_{1.55}Sn_{0.2}Sc_{0.15}O_{11}$, which indicates that the copper−oxygen sheets are hardly oxidized by the introduction of scandium in the structure. However, changes in the lattice parameters and some structural parameters demonstrate that a low level of scandium can be doped into the quadruple perovskite structure. It seems that the upper level of scandium dopant in this structure may be too low to induce superconductivity.

Calcium doping for gadolinium of these compounds was investigated in order to try to raise the copper oxidation state above +2. The synthesis of a compound of stoichiometry $Gd_{1.6}Ca_{0.4}Ba_2Cu_2Ti_2O_{11}$ was attempted, but a mixture of $Gd_2Ba_2Cu_2Ti_2O_{11}$ and CaO was obtained. Hence replacement of both gadolinium and barium was envisaged and compounds of the aforementioned stoichiometry were prepared. However, higher sintering temperatures were needed during the synthesis in order to obtain single-phase compounds.

The structure refinements show disordering of the A as well as B cations which could be explained in terms of this difference in synthesis conditions between the doped and undoped samples. However, the magnitude of the disordering highlights the fine balance required for the formation of these phases with a *fully* ordered arrangement of B cations. This type of disordering for also observed in the calcium doping of $Nd_2Ba_2Cu_2Ti_2O_{11}$,[12] where introduction of calcium on the neodymium and barium site resulted in the loss of discrete copper and titanium layers otherwise present in the structure. The necessary conditions for a "rock salt" ordered arrangement of B cations in double perovskites structure are normally taken to be a difference of 2 in charge of the B cations and the presence of B cations that have different coordination geometries,[13] conditions which can also be assumed to be of great significance for the formation of an ordered oxygen-deficient perovskites structure. Although all these conditions are satisfied in the doped compounds, no ordering occurs. One additional factor that contributes toward the formation of layered oxygen-deficient perovskites has, therefore, to be taken into account, namely, the ordering of the A cations within the structure. One noticeable trend in the A cation distribution within the structure is the strong preference of Ca for the A2 site, a site located between the copper−oxygen square pyramids and tin/titanium−oxygen octahedra. This is surprising in terms of ionic size as Ca(II) ionic radius is closer to that of Gd(III) than Ba(II) ($r(Ca^{2+})$ = 1.32 Å; $r(Gd^{3+})$ = 1.25 Å; $r(Ba^{2+})$ = 1.61 Å)[14] as well as in terms of coordination geometry, i.e., a low coordination number is often favored by Ca^{2+} over Ln^{3+} (ionic radii which were unavailable for a particular coordination number in the cited reference were linearly extrapolated from the available ones). One possible explanation would lie in the disordering of the oxygen positions resulting from the rotations of the BO_6 octahedra which may, in certain structural domains, produce A2 sites of dimensions suitable for calcium. This new A cation arrangement within the structure interferes with the careful geometric constraints needed for the ordering of the B cations and hence result in the formation of disordered quadruple perovskites.

Conclusion

Quadrupled cuprate perovskites may be synthesized containing alternate double layers of copper and tin/

Table 4. Cation Distribution in Ca-Doped Quadruple Perovskites

	A1	A2	A3	B1	B2
$Gd_{1.8}Ca_{0.4}Ba_{1.8}Cu_2Ti_2O_{11}$	1.00 Gd	1.6 Ba/0.4 Ca	0.8 Gd/0.2 Ba	0.5 Cu/0.5 Ti	0.5 Ti/0.5 Cu
$Gd_{1.75}Ca_{0.4}Ba_{1.85}Ti_2Cu_2O_{11}$	1.00 Gd	1.6 Ba/0.4 Ca	0.75 Gd/0.25Ba	0.7 Cu/0.3 Ti	0.7 Ti/0.3 Cu
$Gd_{1.7}Ca_{0.4}Ba_{1.9}Ti_2Cu_2O_{11}$	1.00Gd	1.6 Ba/0.4 Ca	0.7 Gd/0.3Ba	0.8 Cu/0.2Ti	0.8 Ti/0.2 Cu
$Gd_{1.65}Ca_{0.35}Ba_2Ti_{1.75}Sn_{0.25}Cu_2O_{11}$	0.85Gd/0.15Ca	1.8 Ba/0.2 Ca	0.8 Gd/0.2 Ba	0.7 Cu/0.3 Ti	0.6 Ti/0.3Cu/0.25Sn

titanium. Disordering of the oxygen atoms within the double layers was found to be present only in the titanium layers and is attributed to the mismatch present between the copper–oxygen and tin/titanium–oxygen layers. Neutron diffraction experiments highlighted the presence of Sc_2O_3 impurities in the doped sample which implied that the copper valency was not raised sufficiently above 2 and therefore rationalized the lack of superconductivity observed in these materials. Doping studies of these compounds on the A site revealed the complex structural interactions involved in the formation of these compounds, producing disordered phases.

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Supporting Information Available: The final profile fit to the TOF pattern from $Sm_2Ba_2Cu_2Ti_{1.5}Sm_{0.5}O_{11}$ and refined atomic positions and temperature factors for the calcium doped compounds (3 pages). Ordering information is given on any current masthead page.

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