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New Cubic Perovskite $Na(Cu_{2.5}Ti_{0.5})Ti_4O_{12}$ with Square Planar Coordination of Ti^{4+}

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A new perovskite, $Na[Cu_{2.5}Ti_{0.5}]Ti_4O_{12}$, has been synthesized using a conventional solid-state technique. Neutron and synchrotron X-ray powder diffraction studies in combination with density measurements and bond-valence calculations have revealed that the material crystallizes in the cubic $Im\bar{3}$ space group (a = 7.38472(2) Å, Z = 2) with the square-plane site accommodating 16.7% of Ti^{4+}. This is the highest level of non-Jahn–Teller cation substitution for Cu^{2+} reported to date for $CaCu_3Ti_4O_{12}$-type perovskites prepared at ambient pressure.

Introduction

Peculiar perovskites having the general formula $ACu_3M_4O_{12}$ (A = Na, Ca, Sr, Cd, Bi, rare-earths, Th, or vacancy; M = Ti, V, Cr, Mn, Ge, Ru, or various heterovalent combinations including Nb, Ta, Sb, Fe, Ga, etc.)[1−9] exhibit a great diversity of electrical properties, from metallic[3,4,7,9] to dielectric,[4,10−12] and interesting magnetic properties, including ferromagnetism and giant magnetoresistance.[13−16] They attracted especial attention after the dielectric constant for $CaCu_3Ti_4O_{12}$ was reported to approach 10^4 [10,11] or even 10^5.[12] This effect was attributed to grain boundaries in ceramics[17,18] or domain boundaries in single crystals.[19]

All these phases contain Cu^{2+} in a square planar oxygen environment characteristic of the Jahn−Teller d^9 ion. A typical substituent for Cu^{2+} in this site is another Jahn−Teller ion, high-spin Mn^{3+}.[15,16,20−22] Although square planar coordination is characteristic for low-spin d^8 ions too, attempts to replace Cu^{2+} with Pd^{2+} have failed;[4] only partial substitution of Cu^{3+} for Cu^{2+} was found to be possible.[4,7,9] The most exotic and very rare substitution for the $CaCu_3Ti_4O_{12}$ structure type is the incorporation of non-Jahn−Teller ions in the copper square planar site. To our knowledge, only three examples of this kind of material were reported (i.e., high-pressure phase $CaFe_3Ti_4O_{12}$,[23] $Li[Cu_{3-x}Li_x][Ti_{3-x}M_{1+x}]O_{12}$ (M = Ta^{5+}, Nb^{5+} with x up to 0.33),[24] and

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$Sr_{0.946}[Cu_{2.946}Ti_{0.054}]Ti_4O_{12}$),[25] although we noticed that the bond-valence sum for the copper site, obtained using structural data reported for the lithium compound, has a value of 2.06 which is much closer to the ideal value of 2.0 for a purely copper site than to the expected value of 1.89 and may indicate that the crystal structure has been determined incorrectly.

During our X-ray study of the $Na_2O-CuO-TiO_2$ system, we found a similar cubic phase, not reported in the literature. Initially, $NaCu_3Ti_4O_{12}$ seemed to be its most probable composition, with one-third of the copper in the 3+ oxidation state. However, all attempts to prepare this composition as a single phase failed. The samples invariably contained large amounts of free CuO. The recent work on strontium copper titanate[25] gave the idea of titanium substituting for copper, $Na[Cu_{2.5}Ti_{0.5}]Ti_4O_{12}$, which was proven experimentally.

Experimental Section

$NaCu_{2.5}Ti_{4.5}O_{12}$ (sample 2) and three additional compositions, $Na(Cu_{2.61}Ti_{0.39})Ti_4O_{11.89}$ (sample 1), $Na_{0.78}(Cu_{2.39}Ti_{0.61})Ti_4O_{12}$ (sample 3), and $Na_{1.25}Cu_{2.525}Ti_{4.775}O_{12.7}$ (sample 4), slightly enriched with copper, titanium, and sodium, respectively, were prepared using standard solid-state techniques from anhydrous Na_2CO_3, CuO, and TiO_2. Stoichiometric mixtures were first heated in air at 850 °C for 1 h, and then they were heated 3 times for 12 h at 950 °C with intermediate regrinding.

Phase composition of the samples was studied by X-ray powder diffraction (Rigaku diffractometer, Cu Kα radiation). The capacitance and loss tangent were measured at room temperature with a HP 4284A LCR meter using an 85% dense ceramic disk (diameter $\approx$ 8 mm, thickness $\approx$ 1 mm) with Pd-sputtered electrodes. Neutron powder diffraction data for $NaCu_{2.5}Ti_{4.5}O_{12}$ were collected at room temperature on the Special Environment Powder Diffractometer[26] at the Intense Pulsed Neutron Source, Argonne National Laboratory. Synchrotron X-ray powder diffraction data were collected on the beamline 32-ID at the Advanced Photons Source ($\lambda = 0.49581$ Å), Argonne National Laboratory. Rietveld refinement was performed using the GSAS code.[27]

Powder density for the sample 2 was measured using a Quantachrome helium multipycnometer MVP-1. Approximately 6 g of accurately weighed powder sample was placed in the sample cell of the pycnometer. After the sample cell was purged for 45 min to remove air and moisture, the reference cell of the pycnometer with a known volume was pressurized with helium to about 17 psi (~117 kPa). Then, the valve between the sample cell and the reference cell was opened and the pressure dropped because of the introduction of additional volume. The sample volume can be calculated using the ideal gas low as

$$V_P = V_C - V_R(P_1/P_2 - 1)$$

where V_C is the sample cell volume, V_R is the reference cell volume, and P_1 and P_2 are the pressure above ambient in the reference cell and the lower pressure after including the sample cell, respectively. The measurements were carried out in duplicate.

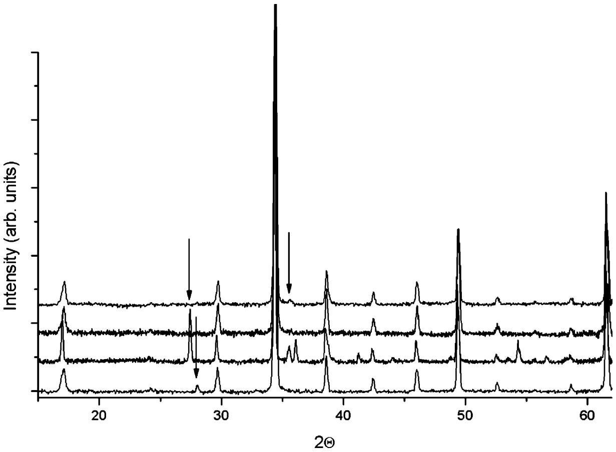

Figure 1. X-ray powder diffraction patterns for the samples 1−4 from top to bottom, respectively. Arrows indicate the impurities of CuO, TiO_2, and an unidentified phase in the samples 1, 3, and 4, respectively.

Results and Discussion

All the reflections in the diffraction data for the sample 2 were successfully indexed with a cubic cell ($a \approx 7.385$ Å), and the data for samples 1, 3, and 4 demonstrated the presence of CuO, TiO_2, and an unidentified phase, respectively (Figure 1). This indicates that, in contrast to $Li[Cu_{3-x}Li_x][Ti_{3-x}Nb_x]O_{12}$ ($0.12 \leq x \leq 0.33$),[24] sodium copper titanate does not have any extended homogeneity range.

The dielectric permittivity and losses were found to be 280 and 16%, respectively, at 100 kHz, close to the intrinsic values for other copper titanates.[4] Thus, the new sodium compound does not exhibit the giant dielectric constant reported for $CaCu_3Ti_4O_{12}$.

Very high resolution and peak/background ratio synchrotron data unambiguously confirmed the cubic symmetry and single-phase nature of the $NaCu_{2.5}Ti_{4.5}O_{12}$ sample. The data were successfully refined using the $CaCu_3Ti_4O_{12}$ structure as a starting model and the Rietveld plot is shown in Figure 2. Careful examination of the diffraction data revealed very weak peaks of TiO_2 (Figure 2, inset), which were not observed in either the laboratory X-ray or neutron powder diffraction data. However, the value of rutile weight fraction was found to be 0.12(1) wt %, which can be neglected without correction of the nominal composition. No superlattice reflections were observed indicating statistical distribution of Cu and Ti atoms over square planar site.

Because the neutron scattering lengths of Cu and Ti are opposite in sign (7.72 and −3.37 fm, respectively), neutron diffraction is extremely sensitive to Ti/Cu substitution. Rietveld refinement of neutron diffraction data with a square planar site occupied only by Cu atoms converged to an abnormally high thermal parameter ($U_{iso}(Cu) = 0.0118$ Å^2) more than twice that of titanium in an octahedral site ($U_{iso}(Ti) = 0.0053$ Å^2), which clearly indicated presence of titanium in this site. After Ti atoms were allowed to occupy the copper site, the quality of the refinement significantly

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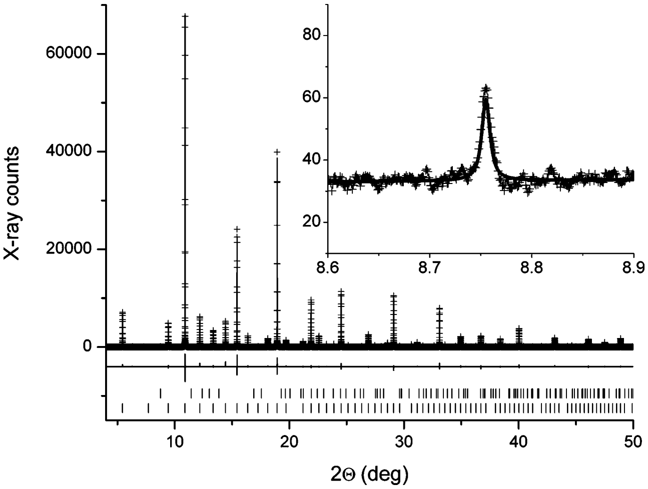

Figure 2. Rietveld refinement plot showing the observed (+) and calculated (solid line) X-ray diffraction data and their difference for $NaCu_{2.5}Ti_{4.5}O_{12}$. The tick marks indicate cubic perovskite phase (top) and rutile TiO_2 (bottom). Inset shows the strongest rutile peak; its intensity is ~0.04% of that of the strongest perovskite peak. $R_p = 7.05\%$, $R_{wp} = 9.58\%$, $\chi^2 = 2.459$.

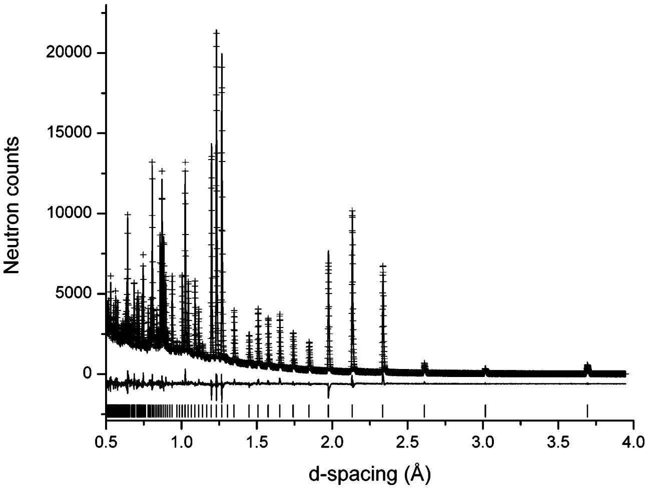

Figure 3. Rietveld refinement plot showing the observed (+) and calculated (solid line) neutron diffraction data and their difference for $NaCu_{2.5}Ti_{4.5}O_{12}$. $R_p = 4.08\%$, $R_{wp} = 5.73\%$, $\chi^2 = 2.87$.

Table 1. Crystallographic Data for $Na(Cu_{2.5}Ti_{0.5})Ti_4O_{12}$

chemical formula	$Na(Cu_{2.5}Ti_{0.5})Ti_4O_{12}$
fw	589.39
space group	$Im\bar{3}$ (No. 204)
a (Å)	7.38472(2)
V (Å^3)	402.719(1)
Z	2
D_{obsd} (g cm^{-3})	4.89(3)
D_{calcd} (g cm^{-3})	4.86
radiation	neutron, time-of-flight
R_p	4.08%
R_{wp}	5.73%
χ^2	2.87

Table 2. Positional and Displacement Parameters for $Na(Cu_{2.5}Ti_{0.5})Ti_4O_{12}$[a]

	Na	Cu/Ti	Ti	O
Wyckoff site	2a	6b	8c	24g
x	0	0	0.250	0
y	0	0.5	0.25	0.30890(8)
z	0	0.5	0.25	0.18179(8)
U_{eq} (Å^2)	0.0146(7)	0.0041(1)	0.0096(1)	0.0086(1)

[a] Numbers in parentheses are the standard deviations of the last significant digit. Na: $U_{11} = U_{22} = U_{33} = 0.0146(7)$, $U_{12} = U_{13} = U_{23} = 0$. Cu/Ti: $U_{11} = 0.0032(6)$, $U_{22} = 0.0053(5)$, $U_{33} = 0.0037(4)$, $U_{12} = U_{13} = U_{23} = 0$. Ti: $U_{11} = U_{22} = U_{33} = 0.0097(2)$, $U_{12} = U_{13} = U_{23} = -0.0021(3)$. O: $U_{11} = 0.0110(3)$, $U_{22} = 0.0103(3)$, $U_{33} = 0.0046(2)$, $U_{12} = 0.0034(2)$, $U_{13} = U_{23} = 0$.

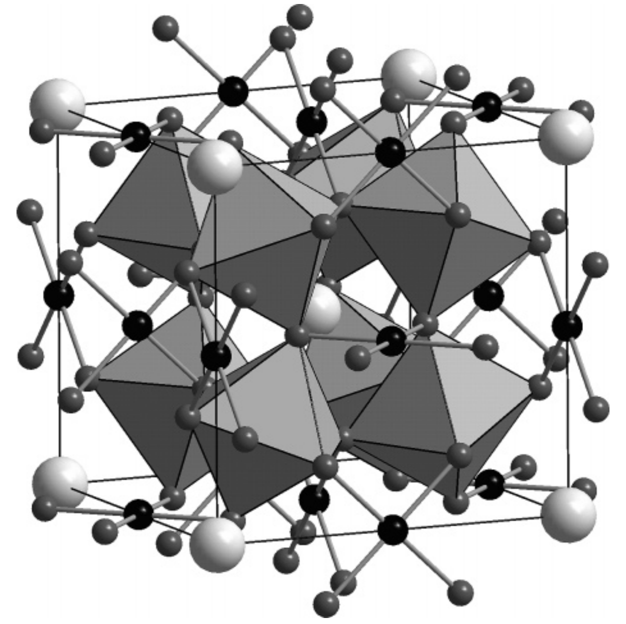

Figure 4. Crystal structure of $NaCu_{2.5}Ti_{4.5}O_{12}$ with TiO_6 octahedra, $(Cu_{5/6}Ti_{1/6})O_4$ squares, and Na ions as light spheres.

improved (R_p, R_{wp}, and χ^2 dropped from 4.52%, 6.87%, and 4.125 to 4.08%, 5.73%, and 2.87, respectively), and the thermal parameter of Cu/Ti decreased to a physically meaningful value. Because neutron scattering is more sensitive to the structural parameters of interest, we report the results of the Rietveld analysis of the neutron powder diffraction data, rather than those for the X-ray diffraction data. The final Rietveld plot is presented in Figure 3; crystallographic details are listed in Tables 1 and 2, and the structure is shown in Figure 4.

Strictly speaking, mixture of 2.5 Cu and 0.5 Ti is indistinguishable, by neutron scattering, from 2.28 Cu. However, the scenario with formation of vacancies at the copper site and the oxidation of copper to +3 state, first, is inconsistent with the phase purity of the sample and, second, was easily ruled out by density measurements. The experimental density value was found to be 4.89(3) g/cm^3, which is very close to the theoretical value of 4.86 g/cm^3 for $NaCu_{2.5}Ti_{4.5}O_{12}$, while for the $NaCu_{2.33}^{+3}Ti_4O_{12}$ composition, the theoretical density is 4.57 g/cm^3.

The results were also verified by calculating the bond valence sums (BVS).[28] The values of R_0 were taken from refs 28 and 29. For the mixed Cu/Ti site, the bond valence was calculated as $V(\mathrm{M-O}) = 5/6V(\mathrm{Cu-O}) + 1/6V(\mathrm{Ti-O})$. The values calculated from the refinement results are in excellent agreement with the formal oxidation states (Table 3). We notice that for the square-planar site the interaction

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Table 3. Selected Interatomic Distances, Bond Angles, and Bond Valence Sums (BVS) for $NaCu_{2.5}Ti_{4.5}O_{12}$

Na−O (×12, Å)	2.6468(7)
Cu−O (×4, Å)	1.9477(5), 2.7411(3)
Ti−O (×6, Å)	1.96248(16)
Ti−O−Ti (deg)	140.35(3)
BVS(Na)	1.08
BVS(Cu/Ti)	2.32
BVS(Ti)	4.03
BVS(O)	2.01

with four next-nearest-neighbor oxygen ions contributing ∼0.24 valence units is too significant not to be included in BVS calculations.

The bond valence approach also rules out the possibility of substitution of Cu^{2+} into an octahedral B site. The calculated global instability index[30] (Figure 5) shows that this scenario, according to the hypothetical formula $Na[Cu_{2.5-x}Ti_{0.5+x}][Ti_{4-x}Cu_x]O_{12}$, would significantly destabilize the crystal structure. Rietveld refinement of the model with copper atoms in the octahedral site yielded zero occupancy in agreement with Figure 5.

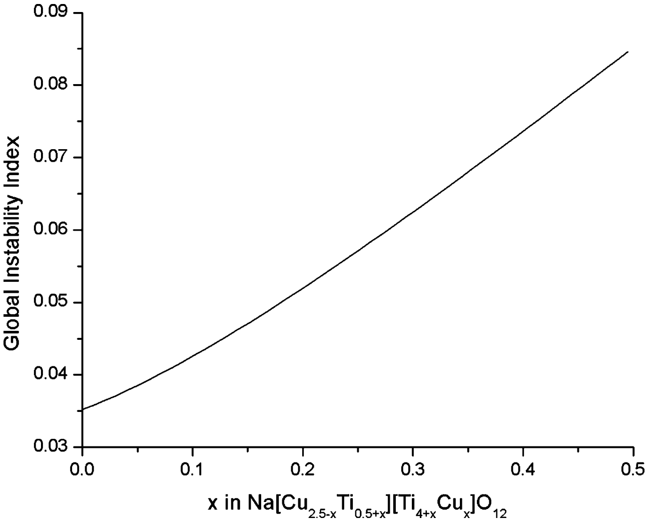

Figure 5. Global instability index as a function of hypothetical copper substitution into octahedral site.

Conclusions

The crystal structure of the new cubic perovskite $Na[Cu_{2.5}Ti_{0.5}]Ti_4O_{12}$ has been characterized using X-ray and neutron powder diffraction. One out of six square planar sites is statistically occupied by Ti^{4+} atoms. The high level of substitution of transition metal in a d^0 electronic configuration for Cu^{2+} in square-planar coordination typical for Jahn−Teller ions suggests that many more copper-substituted $CaCu_3Ti_4O_{12}$-type perovskites with potentially interesting properties may be prepared.

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Supporting Information Available: Crystallographic data files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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