Structural study of A\(_2\)CuTiO\(_6\) (A = Y, Tb–Lu) compounds

Nicolas Floros, Job T. Rijssenbeek, Alex B. Martinson, Kenneth R. Poeppelmeier

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA

Received 14 August 2002; accepted 30 September 2002

Dedicated to Professor Neil Bartlett on the occasion of his 70th birthday

Abstract

The A\(_2\)CuTiO\(_6\) (A = Y, Tb–Lu) series has been reinvestigated in light of the recent discovery of cation order in structurally similar La\(_4\)Cu\(_3\)MoO\(_{12}\) and La\(_3\)Cu\(_2\)VO\(_9\). The crystal structure has been determined by electron and powder X-ray diffraction. The phases crystallize in an hexagonal symmetry, space group \(P\bar{6}_3cm\) with cell parameters \(a \approx 6.2\) Å; \(c \approx 11.5\) Å. In this series of compounds, the Cu(II) and Ti(IV) cations randomly occupy trigonal bipyramids which form layers separated by sevenfold coordinated A(III) cations. This series is isotypical with LuMnO\(_3\).

Keywords: Hexagonal structure; Transmission electron microscopy; X-ray diffraction

1. Introduction

The ideal cubic perovskite structure of AMO\(_{3−δ}\) oxides presents several distortions depending of the nature of A and M, the synthesis conditions and the oxygen ratio. The Goldschmidt tolerance factor [1,2], based on the differences of the A and M ionic radii, is frequently used to predict the type of distortion which can be expected. However, for YAlO\(_3\) an unusual non-perovskite hexagonal structure, not predicted by the Goldschmidt factor, is observed [3]. It crystallizes in the space group \(P\bar{6}_3/mmc\) and is characterized by a layered structure in which the Al(III) ions adopt fivefold trigonal bipyramidal coordination.

Several closely related phases exist for the Ln\(_{1+n}\)Cu\(_n\)-M\(_{3+n}\)O\(_{3+3n}\) family (Ln = lanthanide) where M is a \(d^0\) cation [4–6]. A powder neutron diffraction study has shown that the \(n = 1\) member Er\(_2\)CuTiO\(_6\) exhibits the same subcell as YAlO\(_3\) but presents a supercell with \(a(\text{Er}_2\text{CuTiO}_6) = a(\text{YAlO}_3) \times \sqrt{3}\). This structure is isotypical with that of LuMnO\(_3\) [7], wherein the Cu(II) and Ti(IV) cations are randomly distributed over the five coordinate sites [4]. Studies of the structurally related \(n = 2\) member La\(_3\)Cu\(_2\)VO\(_9\) [5], with 2:1 ratio of Cu:V, and \(n = 3\) member La\(_4\)Cu\(_3\)MoO\(_{12}\) [6], with a 3:1 ratio of Cu:Mo, have recently shown the existence of other supercells of the YAlO\(_3\) structure. In contrast to Er\(_2\)CuTiO\(_6\) where the Cu:Ti ratio is 1:1, cation ordering occurs within the layers leading to distinct supercells for M = V(V) and Mo(VI). In light of the cation ordering in La\(_3\)Cu\(_2\)VO\(_9\) and La\(_4\)Cu\(_3\)MoO\(_{12}\), we have re-investigated the A\(_2\)CuTiO\(_6\) (A = Y, Tb–Lu) series to establish the nature of the Cu/Ti arrangement. We report here a structural study of the complete series by powder X-ray diffraction and electron diffraction.

2. Experimental

The phases A\(_2\)CuTiO\(_6\) (A = Y, Tb–Lu) were synthesized in air in two steps. Intimate mixtures of A\(_2\)O\(_3\), CuO and TiO\(_2\) (purity > 99.9%) were weighed in stoichiometric proportions and heated in an alumina crucible at 900 °C for 24 h. Then they were ground again, pressed into pellets and re-heated at 1050°C for 150 h. Samples were slow-cooled and quenched in air without any significant change powder X-ray and electron diffraction patterns. In all cases, two secondary phases were detected: A\(_2\)Ti\(_2\)O\(_7\) (pyrochlore structure) and CuO. Although we have thus far been unable to suppress the formation of these secondary phases, we continue to investigate their origin.

For the Transmission Electronic Microscopy (TEM) studies, polycrystalline samples of air quenched and slow cooled Ho\(_2\)CuTiO\(_6\) were deposited on holey carbon grids. The Elec-
tron Diffraction studies (ED) were carried out on an 8100 Hitachi at 200 kV.

The powder X-ray diffraction (PXRD) data have been recorded with a Rigaku RINT 2000 diffractometer (Cu Kα radiation). The diffraction patterns were recorded over the angular range $10^\circ \leq 2\theta \leq 80^\circ$ in 0.02° increments and treated by profile analysis using the Rietveld technique using the FULLPROF program (Version 1.7a) [8].

3. Results and discussion

The reconstruction of the reciprocal space from the electron diffraction along the crystallographic axes shows a hexagonal cell with $a \approx 6.2$ Å and $c \approx 11.5$ Å. The conditions limiting the reflection are $h h 0 l: l = 2n$ leading to the following possible space groups: $P6_3cm$; $P6_3c2$ and $P6_3/mcm$. The $[01\overline{1}0]$ and $[1\overline{1}02]$ ED patterns of the air quenched Ho$_2$CuTiO$_6$ are shown Fig. 1. No super-structural reflections were observed in either the slow cooled or quenched samples.

The unit cell parameters and the possible space groups are consistent with the LuMnO$_3$ structure. The PXRD study confirms the structural similarity. Other than small shifts in $2\theta$ caused by the different sizes of the cations, all A$_2$CuTiO$_6$ PXRD experimental patterns are similar to those of LuMnO$_3$ [7], YGaO$_3$ [9] and YInO$_3$ [10]. A typical X-ray diffractogram (Ho$_2$CuTiO$_6$) is shown in Fig. 2.

To select the correct space group, the PXRD profile of each member of the A$_2$CuTiO$_6$ series was refined based on each of the three structural models suggested by the ED. Atomic positions for each space group are given in Table 1. Notice that in all three space groups there exists only a single crystallographic site for Cu/Ti, thus no cation ordering can be introduced in any of these models for A$_2$CuTiO$_6$. Electron diffraction is particularly sensitive to super-structural features, therefore the fact that no supercell reflections were observed is strong evidence that no ordering occurs. This observation emphasizes an important difference between the A$_2$CuTiO$_6$ compounds and La$_3$Cu$_2$VO$_9$ or La$_4$Cu$_3$MoO$_{12}$, where an ordering of copper and vanadium or molybdenum, respectively, was observed.

For each member of the series, Rietveld refinements have been carried out using the three different space groups. Concerning the secondary phases, only A$_2$Ti$_2$O$_7$ was taken into account in the refinements since CuO was present in such low amounts that no significant variations of the reliability factors were observed. For the refinements in the noncentrosymmetric (polar) space group $P6_3cm$, the $z$ parameter of Cu/Ti site was arbitrarily fixed to $z = 0$ in order to fix the origin along the $z$ direction. The results of this study, given in Table 2, show that whatever the A cation is, the best reliability factors are always obtained with space group $P6_3cm$. These observations clearly show that these phases adopt the structure of LuMnO$_3$ and its related series $A'MnO_3$ ($A' = Y$, Dy–Lu). The evolutions of the cell parameters and the volume are given in Table 3. As expected the cell volume decreases with the ionic radius of the A cation. A detailed structural analysis will require neutron diffraction data which are necessary to accurately determine the oxygen positions. At the present time, neutron
Table 1
A$_2$CuTiO$_6$ atomic positions in $P6_3cm$, $P6c2$ and $P6b/mcm$. The approximate values of variable parameters are given in parentheses

<table>
<thead>
<tr>
<th>Compound</th>
<th>$P6_3cm$</th>
<th>$P6c2$</th>
<th>$P6b/mcm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6c (x = 1/3; 0; 0/1)</td>
<td>6c (x = 1/3; y = 0; 1/4)</td>
<td>6c (x = 1/3; 0; 1/4)</td>
</tr>
<tr>
<td>O1</td>
<td>4b (1/3; 2/3; z = 1/4$^*$)</td>
<td>2a (0; 0; 0)</td>
<td>4d (1/3; 2/3; 0)</td>
</tr>
<tr>
<td>O2</td>
<td>4b (0; 0; z = 0$^*$)</td>
<td>2c (1/3; 2/3; 0)</td>
<td>2b (0; 0; 0)</td>
</tr>
<tr>
<td>O3</td>
<td>6c (x = 2/3; 0; z = 0.35$^*$)</td>
<td>2c (2/3; 1/3; 0)</td>
<td>2c (2/3; 1/3; 0)</td>
</tr>
<tr>
<td>O4</td>
<td>2a (1/3; 2/3; z = 1/2$^*$)</td>
<td>12l (x = 1/3; y = 0; z = 0.42$^*$)</td>
<td>12l (x = 1/3; 0; z = 0.42$^*$)</td>
</tr>
</tbody>
</table>

* Refined parameters.
† Was fixed during the refinement.

Table 2
$R_{Bragg}$ and $\chi^2$ values obtained for the different compositions of A$_2$CuTiO$_6$ in $P6_3cm$, $P6c2$ and $P6b/mcm$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$P6_3cm$</th>
<th>$P6c2$</th>
<th>$P6b/mcm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$CuTiO$_6$</td>
<td>9.5</td>
<td>3.9</td>
<td>11.1</td>
</tr>
<tr>
<td>Tb$_2$CuTiO$_6$</td>
<td>9.8</td>
<td>2.3</td>
<td>12.5</td>
</tr>
<tr>
<td>Dy$_2$CuTiO$_6$</td>
<td>8.9</td>
<td>1.8</td>
<td>10.0</td>
</tr>
<tr>
<td>Ho$_2$CuTiO$_6$</td>
<td>4.2</td>
<td>2.6</td>
<td>11.1</td>
</tr>
<tr>
<td>Er$_2$CuTiO$_6$</td>
<td>6.2</td>
<td>2.2</td>
<td>9.1</td>
</tr>
<tr>
<td>Tm$_2$CuTiO$_6$</td>
<td>5.7</td>
<td>2.1</td>
<td>12.3</td>
</tr>
<tr>
<td>Yb$_2$CuTiO$_6$</td>
<td>7.2</td>
<td>1.6</td>
<td>21.3</td>
</tr>
<tr>
<td>Lu$_2$CuTiO$_6$</td>
<td>6.4</td>
<td>2.1</td>
<td>19.2</td>
</tr>
</tbody>
</table>

Fig. 2. Experimental (cross), calculated and difference (solid lines) powder X-ray diffraction patterns of Ho$_2$CuTiO$_6$. The positions of the Bragg reflections (top Ho$_2$CuTiO$_6$, bottom Ho$_2$Ti$_2$O$_7$) are shown by small vertical lines.

diffraction data are only available for one member of the series, Er$_2$CuTiO$_6$ (see below).

The structure can be described as a stacking, along the c axis, of hexagonal layers of A and layers of corner sharing (Cu/Ti)O$_3$ trigonal bipyramids (Fig. 3). Each equatorial oxygen (O3 and O4) is shared by three bipyramids and the apical oxygens (O1 and O2) lead to two non-equivalent, long and short, Cu/Ti–O$_{ap}$ distances. According to the neutron diffraction study [4] of Er$_2$CuTiO$_6$, the difference between the two Cu/Ti–O$_{ap}$ distances is large (0.115 Å) compared to that observed in YMnO$_3$ (0.001 Å) [11], ErMnO$_3$ (0.032 Å) [12], YbMnO$_3$ (0.001 Å) [13], LuMnO$_3$ (0.023 Å) [14], YGaO$_3$ (0.002 Å) [9] and YInO$_3$ (0.01 Å) [10].

Although the (Ln,Y)$_2$CuTiO$_6$ and (Ln,Y)MnO$_3$ series are very similar, some significant differences should be noted. Both series exhibit an orthorhombic (GdFeO$_3$-type distorted perovskite structure) to hexagonal structural transition as a function of the lanthanide size. In the case of the A’MnO$_3$ series, the orthorhombic phase is stabilized from La to Tb, the hexagonal one for Tm, Yb and Lu whereas both symmetries are observed for Y, Dy, Ho and Er [7]. On the other hand, a sharp separation between the two symmetries occurs in (Ln,Y)$_2$CuTiO$_6$ series: the orthorhombic perovskite structure is observed for lanthanides larger than Tb and the
hexagonal structure from Tb to Lu including Y [4]. Moreover, any attempt to substitute part of the manganese by an other transition element in YM$_x$Mn$_{1-x}$O$_3$ (M = Fe, Cr, Al, Co, Ni, Cu) series [15,16] inevitably changes the structure to perovskite for small amounts of M with a maximum of $x = 0.15$ in the cases of Al and Fe. These observations highlight the fact that the hexagonal phase is more easily stabilized when the trigonal bipyramidal site is occupied by a 50:50 Cu($d^9$)/Ti($d^0$) mixture compared to manganese ($d^4$) alone.

4. Conclusion

We have reported a structural study of the A$_2$CuTiO$_6$ (A = Y, Tb–Lu) series. These compounds crystallize in space group $P6_3cm$ and are isostructural with LuMnO$_3$. In contrast to both La$_4$Cu$_3$MoO$_{12}$ and La$_3$Cu$_2$VO$_6$, no ordering of the Cu and Ti cations has been observed, which is in agreement with the previous neutron diffraction study of Er$_2$CuTiO$_6$. Owing to the non-centrosymmetry of the $P6_3cm$ space group, A’MnO$_3$ compounds exhibit ferro-electric properties [17–19] and further efforts to synthesize A$_2$CuTiO$_6$ single crystals and thin films, to measure the expected ferroelectric properties, are in progress.

Acknowledgements

This work was supported by National Science Foundation (NSF), Solid State Chemistry (Award No. DMR-9727516) for NF and JTR and by a NSF graduate fellowship for JTR. The use of the Central Facilities at the Materials Research Center of Northwestern University was supported by the MRSEC program of the NSF (Grant DMR-0076097). ABM participated in the Research Experience for Undergraduates program of the NU-MRSEC (NSF DMR-0076097).

References