

# Structural study of $A_2CuTiO_6$ ( $A = Y, Tb-Lu$ ) compounds

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

## Abstract

The  $A_2CuTiO_6$  ( $A = Y, Tb-Lu$ ) series has been reinvestigated in light of the recent discovery of cation order in structurally similar  $La_4Cu_3MoO_{12}$  and  $La_3Cu_2VO_9$ . The crystal structure has been determined by electron and powder X-ray diffraction. The phases crystallize in an hexagonal symmetry, space group  $P6_3cm$  with cell parameters  $a \approx 6.2 \text{ \AA}$ ;  $c \approx 11.5 \text{ \AA}$ . 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  $LuMnO_3$ .

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

## 1. Introduction

The ideal cubic perovskite structure of  $AMO_{3-\delta}$  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  $P6_3/mmc$  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  $Ln_{1+n}Cu_nM^{3+n}O_{3+3n}$  family ( $Ln = \text{lanthanide}$ ) where M is a  $d^0$  cation [4–6]. A powder neutron diffraction study has shown that the  $n = 1$  member  $Er_2CuTiO_6$  exhibits the same subcell as  $YAlO_3$  but presents a supercell with  $a(Er_2CuTiO_6) = a(YAlO_3) \times \sqrt{3}$ . 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  $La_3Cu_2VO_9$  [5], with 2:1 ratio of Cu:V, and  $n = 3$  member  $La_4Cu_3MoO_{12}$  [6], with a 3:1 ratio of Cu:Mo, have recently shown the ex-

istence of other supercells of the  $YAlO_3$  structure. In contrast to  $Er_2CuTiO_6$  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  $La_3Cu_2VO_9$  and  $La_4Cu_3MoO_{12}$ , we have re-investigated the  $A_2CuTiO_6$  ( $A = Y, Tb-Lu$ ) 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  $A_2CuTiO_6$  ( $A = Y, Tb-Lu$ ) were synthesized in air in two steps. Intimate mixtures of  $A_2O_3$ , CuO and  $TiO_2$  (purity > 99.9%), were weighed in stoichiometric proportions and heated in an alumina crucible at  $900^\circ\text{C}$  for 24 h. Then they were ground again, pressed into pellets and re-heated at  $1050^\circ\text{C}$  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:  $A_2Ti_2O_7$  (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  $Ho_2CuTiO_6$  were deposited on holey carbon grids. The Elec-

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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  $K\alpha$  radiation). The diffraction patterns were recorded over the angular range  $10^\circ \leq 2\theta \leq 80^\circ$  in  $0.02^\circ$  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  $a \approx 6.2 \text{ \AA}$  and  $c \approx 11.5 \text{ \AA}$ . The conditions limiting the reflection are  $h\bar{h}0l$ :  $l = 2n$  leading to the following possible space groups:  $P6_3cm$ ;  $P\bar{6}c2$  and  $P6_3/mcm$ . The  $[01\bar{1}0]$  and  $[11\bar{2}0]$  ED patterns of the air quenched  $\text{Ho}_2\text{CuTiO}_6$  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  $\text{LuMnO}_3$  structure. The PXRD study confirms the structural similarity. Other than small shifts in  $2\theta$  caused by the different sizes of the cations, all  $\text{A}_2\text{CuTiO}_6$  PXRD experimental patterns are similar to those of  $\text{LuMnO}_3$  [7],  $\text{YGaO}_3$  [9] and  $\text{YInO}_3$  [10]. A typical X-ray diffractogram ( $\text{Ho}_2\text{CuTiO}_6$ ) is shown in Fig. 2.

To select the correct space group, the PXRD profile of each member of the  $\text{A}_2\text{CuTiO}_6$  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  $\text{A}_2\text{CuTiO}_6$ . 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  $\text{A}_2\text{CuTiO}_6$  compounds and  $\text{La}_3\text{Cu}_2\text{VO}_9$  or  $\text{La}_4\text{Cu}_3\text{MoO}_{12}$ , 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  $\text{A}_2\text{Ti}_2\text{O}_7$  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  $\text{LuMnO}_3$  and its related series  $\text{A}'\text{MnO}_3$  ( $\text{A}' = \text{Y}, \text{Dy-Lu}$ ). The evolutions of the

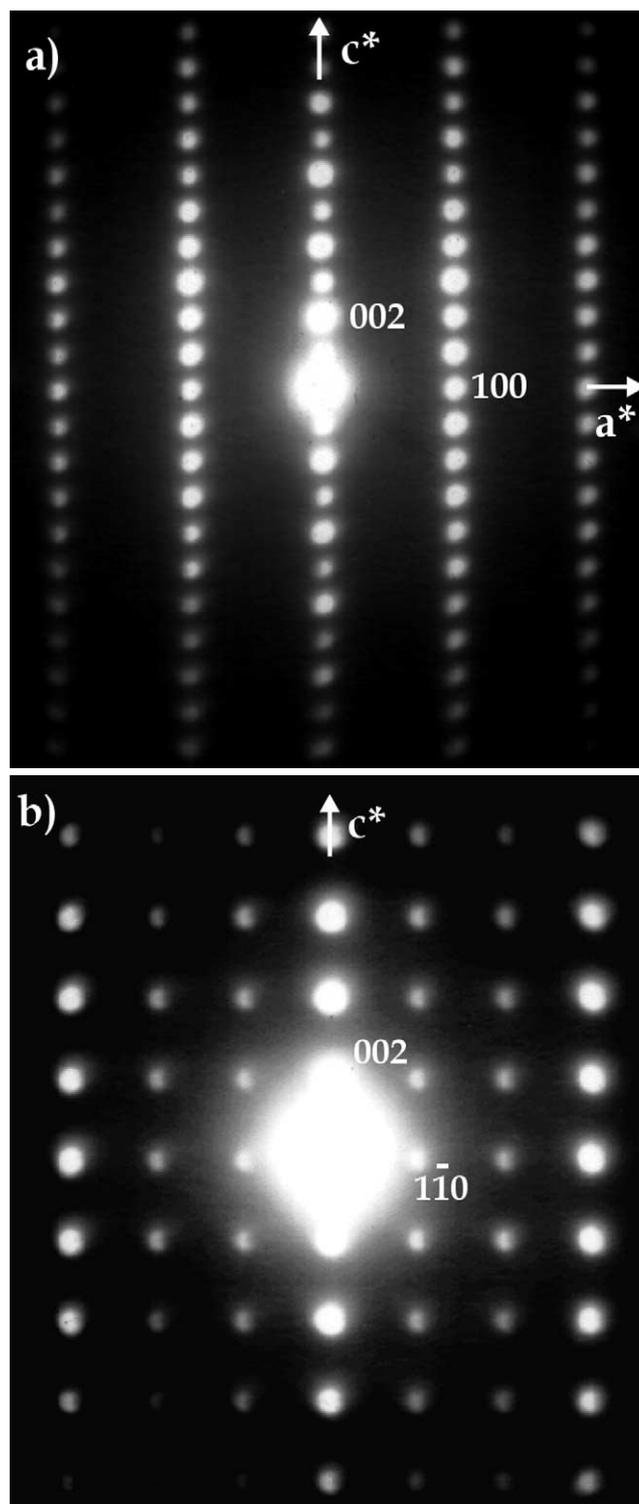


Fig. 1. ED patterns of air quenched  $\text{Ho}_2\text{CuTiO}_6$ . (a) along the  $[01\bar{1}0]$  zone axis; (b) along the  $[11\bar{2}0]$  zone axis.

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

$A_2CuTiO_6$  atomic positions in  $P6_3cm$ ,  $P\bar{6}c2$  and  $P6_3/mcm$ . The approximate values of variable parameters are given in parentheses

	$P6_3cm$	$P\bar{6}c2$	$P6_3/mcm$
Cu/Ti	6c ( $x \approx 1/3^*$ ; $0; 0^f$ )	6k ( $x \approx 1/3^*$ ; $y \approx 0^*$ ; $1/4$ )	6g ( $x \approx 1/3^*$ ; $0; 1/4$ )
A	4b ( $1/3; 2/3; z \approx 1/4^*$ ) 2a ( $0; 0; z \approx 1/4^*$ )	2a ( $0; 0; 0$ ) 2c ( $1/3; 2/3; 0$ ) 2e ( $2/3; 1/3; 0$ )	4d ( $1/3; 2/3; 0$ ) 2b ( $0; 0; 0$ )
O1	6c ( $x \approx 1/3^*$ ; $0; z \approx 0.16^*$ )	12l ( $x \approx 1/3^*$ ; $y \approx 0^*$ ; $z \approx 0.42^*$ )	12k ( $x \approx 1/3^*$ ; $0; z \approx 0.42^*$ )
O2	6c ( $x \approx 2/3^*$ ; $0; z \approx 0.35^*$ )		
O3	4b ( $0; 0; z \approx 0^*$ )	2b ( $0; 0; 1/4$ )	4c ( $1/3; 2/3; 1/4$ )
O4	2a ( $1/3; 2/3; z \approx 1/2^*$ )	2d ( $1/3; 2/3; 1/4$ ) 2f ( $2/3; 1/3; 1/4$ )	2a ( $0; 0; 1/4$ )

\* Refined parameters.

<sup>f</sup> Was fixed during the refinement.

Table 2

$R_{Bragg}$  and  $\chi^2$  values obtained for the different compositions of  $A_2CuTiO_6$  in  $P6_3cm$ ,  $P\bar{6}c2$  and  $P6_3/mcm$

Compound	$P6_3cm$		$P\bar{6}c2$		$P6_3/mcm$	
	$R_{Bragg}$ (%)	$\chi^2$	$R_{Bragg}$ (%)	$\chi^2$	$R_{Bragg}$ (%)	$\chi^2$
$Y_2CuTiO_6$	9.5	3.9	11.1	6.4	11.2	6.7
$Tb_2CuTiO_6$	9.8	2.3	12.5	2.6	12.3	2.5
$Dy_2CuTiO_6$	8.9	1.8	10.0	1.9	10.1	1.9
$Ho_2CuTiO_6$	4.2	2.6	11.1	6.9	20.2	10.6
$Er_2CuTiO_6$	6.2	2.2	9.1	3.7	9.0	3.5
$Tm_2CuTiO_6$	5.7	2.1	12.3	3.5	11.9	4.4
$Yb_2CuTiO_6$	7.2	1.6	21.3	2.9	11.9	2.1
$Lu_2CuTiO_6$	6.4	2.1	19.2	4.7	11.8	3.6

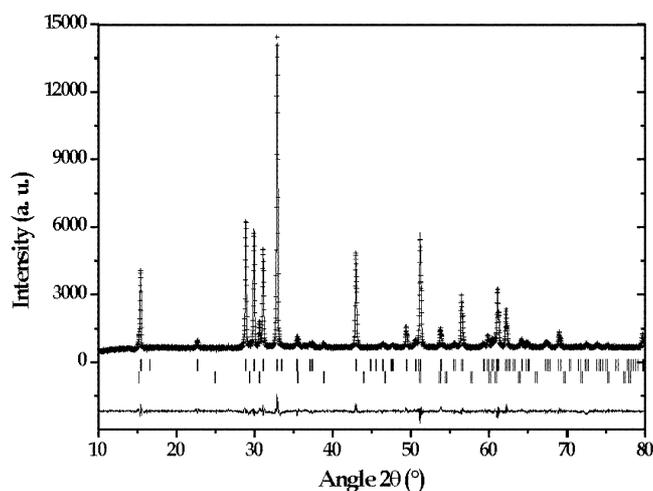


Fig. 2. Experimental (cross), calculated and difference (solid lines) powder X-ray diffraction patterns of  $Ho_2CuTiO_6$ . The positions of the Bragg reflections (top  $Ho_2CuTiO_6$ , bottom  $Ho_2Ti_2O_7$ ) are shown by small vertical lines.

diffraction data are only available for one member of the series,  $Er_2CuTiO_6$  (see below).

The structure can be described as a stacking, along the  $c$  axis, of hexagonal layers of A and layers of corner sharing  $(Cu/Ti)O_5$  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

Table 3

$A_2CuTiO_6$  cell parameters and volume

Compound	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
$Tb_2CuTiO_6$	6.252(1)	11.422(1)	386.6
$Dy_2CuTiO_6$	6.214(1)	11.483(1)	384.0
$Ho_2CuTiO_6$	6.180(1)	11.499(1)	380.3
$Y_2CuTiO_6$	6.172(1)	11.482(1)	378.8
$Er_2CuTiO_6$	6.144(1)	11.506(2)	376.1
$Tm_2CuTiO_6$	6.113(1)	11.504(1)	372.5
$Yb_2CuTiO_6$	6.095(2)	11.515(3)	370.5
$Lu_2CuTiO_6$	6.057(1)	11.516(2)	365.9

diffraction study [4] of  $Er_2CuTiO_6$ , 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  $(Ln,Y)_2CuTiO_6$  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  $(Ln,Y)_2CuTiO_6$  series: the orthorhombic perovskite structure is observed for lanthanides larger than Tb and the

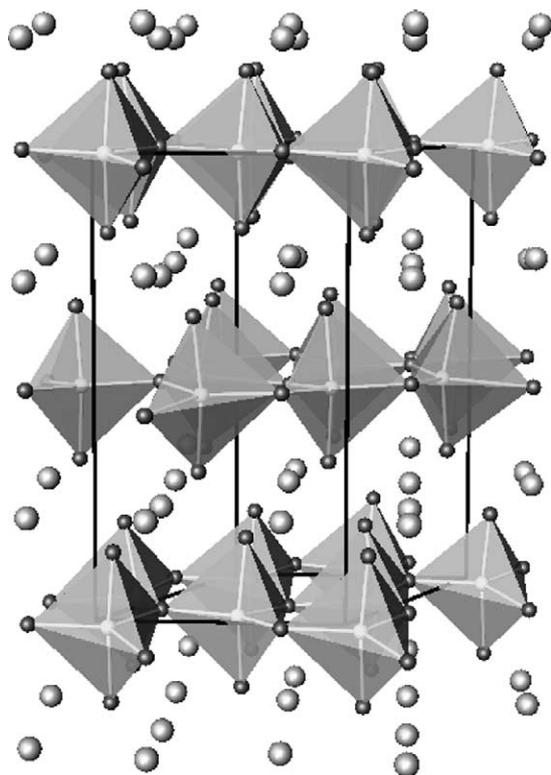


Fig. 3. Perspective drawing of the structure of A<sub>2</sub>CuTiO<sub>6</sub>.

hexagonal structure from Tb to Lu including Y [4]. Moreover, any attempt to substitute part of the manganese by another transition element in YM<sub>x</sub>Mn<sub>1-x</sub>O<sub>3</sub> (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<sub>2</sub>CuTiO<sub>6</sub> (A = Y, Tb–Lu) series. These compounds crystallize in space group  $P6_3cm$  and are isostructural with LuMnO<sub>3</sub>. In contrast to both La<sub>4</sub>Cu<sub>3</sub>MoO<sub>12</sub> and La<sub>3</sub>Cu<sub>2</sub>VO<sub>9</sub>, no ordering of the Cu and Ti cations has been observed, which is in agreement with the previous neutron diffraction study of Er<sub>2</sub>CuTiO<sub>6</sub>. Owing to the non-centrosymmetry of the  $P6_3cm$  space group, A'MnO<sub>3</sub> compounds exhibit ferro-

electric properties [17–19] and further efforts to synthesize A<sub>2</sub>CuTiO<sub>6</sub> single crystals and thin films, to measure the expected ferroelectric properties, are in progress.

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