

HIGH PRESSURE SYNTHESIS AND STRUCTURAL STUDY OF  $R_2CuO_4$  COMPOUNDS WITH  
 $R=Y, Tb, Dy, Ho, Er, Tm$

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The title compounds were synthesized by high pressure/high temperature reactions. TEM revealed the existence of three types of superstructures of the  $T'$ -structure, which were also observed by powder and single crystal x-ray diffraction. The result of an average structure refinement with the  $T'$  unit cell and space group is presented for  $Tm_2CuO_4$ .

## 1. SYNTHESIS AND CHARACTERIZATION

Powder samples of  $R_2CuO_4$  ( $R=Y, Tb, Dy, Ho, Er, Tm$ ) were obtained by high pressure and high temperature reactions using a belt-type apparatus. Starting materials were either stoichiometric mixtures of copper and rare earth oxides, or precursors obtained by spray pyrolysis of nitrate solutions.  $Y_2CuO_4$  was observed for pressures and temperatures above 5 GPa and 900°C, while for  $Tb, Dy, Ho$  and  $Er$  the minimum values were  $\approx 8$  GPa and 1000 °C.  $Tm_2CuO_4$  was obtained at 9 GPa and 1200 °C. Single crystals of  $Y_2CuO_4$  and  $Tm_2CuO_4$  were also synthesized by a similar procedure.

The temperature stability of these compounds was checked by thermogravimetric experiments up to 800 °C in a He flow. For all compounds, the sample weight remains approximatively constant up to  $\approx 300$  °C where an abrupt weight loss is observed. Guinier films taken with samples annealed above this temperature showed that the  $R_2CuO_4$  phase had decomposed.

## 2. ELECTRON MICROSCOPY

Samples of  $Y_2CuO_4$  and  $Tm_2CuO_4$  were

studied by electron microscopy/diffraction. In every case, the strongest reflections observed corresponded to the  $Nd_2CuO_4$ -type cell; however, three different supercells were found to exist for both compounds: (A) a superstructure corresponding to a  $(2a_p\sqrt{2} \times a_p\sqrt{2} \times c)$  cell; (B) a superstructure corresponding to an A-centered  $(2a_p\sqrt{2} \times 2a_p\sqrt{2} \times 2c)$  cell; (C) a superstructure corresponding to a  $(a_p\sqrt{2} \times a_p\sqrt{2} \times c)$  cell.

The (A) superstructure was the most commonly present while the (B) one could be observed clearly in the  $Tm_2CuO_4$  samples and was only barely visible in the  $Y_2CuO_4$  samples. The third superstructure (C) is very weak and diffuse in both compounds and seems to exist only in very small grains.

Besides the difference in vector length among these superstructures, their cause may also be different. The intensities of the (A) superstructure reflections are nearly as strong as those of the subcell reflections. The (A) as well as the (B) superstructures are probably due to a displacive cation modulation. The intensity of the (C) superstructure reflections is much weaker than that of the subcell reflections and it could be

related to oxygen/vacancy ordering or to oxygen displacements.

### 3. X-RAY DIFFRACTION

As a first approximation, the Guinier films can all be indexed with the  $Nd_2CuO_4$ -type unit cell and the  $I4/mmm$  space group. Figure 1 represents the variation of the  $c/a$  ratio vs. the ionic radii of the rare-earth cations. These results are in qualitative agreement with those reported in <sup>1</sup>. Three different intervals can be distinguished in the plot, which indicates that the small rare-earth compounds should have a structure different from that corresponding to large rare-earths. A closer analysis of the Guinier films revealed the presence of many superstructure reflections. A satisfactory indexing of the  $Tm_2CuO_4$  film could be obtained with all reflections indexed on the unit cell of the A superstructure. Therefore, for this sample, this superstructure seems to be predominant. The cell parameters ( $a_s=10.8388(9)\text{\AA}$ ,  $b_s=5.4341(4)\text{\AA}$  and  $c_s=11.5984(7)\text{\AA}$ ) correspond clearly to an orthorhombic symmetry.

The single crystals x-ray diffraction study was carried out on a single crystal of the  $Tm_2CuO_4$  compound with  $Ag\ K\alpha$  radiation. Scans of reflections indexable on the A, B and C

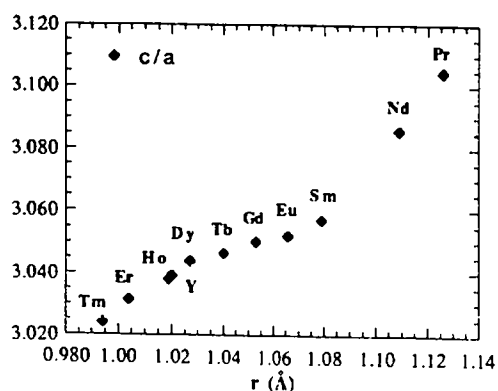


FIGURE I

Variation of  $c/a$  ratio vs. ionic radii of R cations

TABLE I  
Positions, thermal factors ( $\text{\AA}^2$ ) and interatomic distances ( $\text{\AA}$ ) for  $Tm_2CuO_4$  as determined by average structure refinement.

	x	y	z	U11	U22	U33
Y	0	0	.34579(9)	.0255(7)	.0255	.0364(5)
Cu	0	0	0	.014(2)	.014	.006(1)
O1	.091(7)	1/2	0	.01(2)	.01(1)	.11(1)
O2	0	1/2	1/4	.022(9)	.022	.078(8)
Cu-O1 (x4)	1.950(5)		Tm-O1 (x2)	2.89(2)		
Tm-O2 (x4)	2.216(1)		Tm-O1 (x2)	2.38(2)		

superstructure unit cells showed that the unit cell of the B superstructure had to be taken into account in order to index all reflections. Since A-centering extinction condition was verified, all reflections indexable on this cell and obeying the A-centering condition were collected up to  $\theta=20^\circ$ . Comparison of the superstructure reflection intensities indicated that the A superstructure was again predominant. Attempts to refine the structure with this unit cell and various orthorhombic space groups failed to give reasonable results.

The results of a least square refinement of the average structure with the unit cell and  $I4/mmm$  space group of the T' phase are presented in Table I. Due to very large and anisotropic thermal factors, the O1 atom had to be displaced from its special position. Details about the refinement will be given elsewhere<sup>2</sup>.

This average structure is very similar to that reported by Galez et al.<sup>3</sup> for  $Gd_2CuO_4$ . A displacement of the O1 atom along the  $a$  axis was also found by these authors. However, the displacement found for  $Tm_2CuO_4$  ( $x=0.91$ ) is approximately twice as large as that for  $Gd_2CuO_4$  ( $x=0.046$ ).

### REFERENCES

- 1 H.Okada et al. , Physica C166 (1990) 111.
- 2 P. Bordet et al., to be published.
- 3 P. Galez et al., J. Phys. France 51 (1990) 579