

Electrochemically synthesized $\text{Ag}_2\text{Cu}_2\text{O}_4$. A case of unusual charge distribution and structure.

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The direct electrochemical oxidation of an aqueous slurry of $\text{Ag}_2\text{Cu}_2\text{O}_3$ in alkaline media yields the phase $\text{Ag}_2\text{Cu}_2\text{O}_4$ [1]. A remarkable structural change, going from a 3D arrangement to a 2D one, is been achieved thus at room temperature. The phase $\text{Ag}_2\text{Cu}_2\text{O}_4$ can also be obtained by oxidation of either a mixture of AgO/CuO (1:1) or $\text{Ag}_2\text{O}/\text{CuO}$ (1:1), which again implies a big structural change carried on at ambient conditions [1] and also by direct chemical reaction from oxidizing media [2].

However, the phase is not unambiguously characterized yet. The Rietveld refinement performed using X-ray power diffraction data yields a monoclinic structure (C2/m; $a = 6.05$, $b = 2.80$, $c = 5.85$ and $\beta = 107.9$) with very good statistic factors (Table 1) [3]. This refinement only needs silver is in the oxidation state +1, forming 180° bonds with oxygen (figure 1). Notwithstanding, XPS studies of the phase show that silver is present both as Ag(I) and Ag(III) (figure 2) and that there is a high degree of oxygen disorder within the structure.

Irradiation with X-rays modifies the Ag 3d XPS spectra, implying that the structural refinement of the irradiated phase may not correspond to the original as-synthesized phase.

This work will discuss this apparent inconsistency and will present new studies that will help elucidate further structural and electronic aspects of this remarkable phase.

Acknowledgements:

Spanish Ministry of Science and Technology (PB98-0491; MAT 2002-04529-C03).

Fundación Domingo Martínez.

References:

1.- D. Muñoz-Rojas, J. Oró, J. Fraxedas, P. Gómez-Romero, N. Casañ-Pastor, *Electrochem. Comm.* **4** (2002) 684-689.

2.- J. Curda, W. Klein, M. Jansen, *J. Solid State Chem.* **162**, (2001), 220.

3.- *Crystal Eng.*, in press 2002.

Tables:

Formula weight	406.84			
Space group	C2/m (12)			
Unit cell dimensions	$a = 6.054(1) \text{ \AA}$			
	$b = 2.7997(4) \text{ \AA}$			
	$c = 5.851(1) \text{ \AA}$			
	$\beta = 107.922(4)^\circ$			
Cell volume	$94.36(3) \text{ \AA}^3$			
Z	1			
Calculated density	7.16 g/cm^3			
Data points	4251			
Effective 2 θ	5-90			
Refined Parameters	21			
R_p ; R_{wp}	4.06%, 5.43%			
χ^2	0.741			
Atom	x	y	z	Biso
Ag	0	0	0	1.15(6)
Cu	0	0.5	0.5	0.37(9)
O	0.856(1)	0	0.312(1)	0.3(2)

Table 1: Crystal and refinement data for irradiated $\text{Ag}_2\text{Cu}_2\text{O}_4$.

Figures:

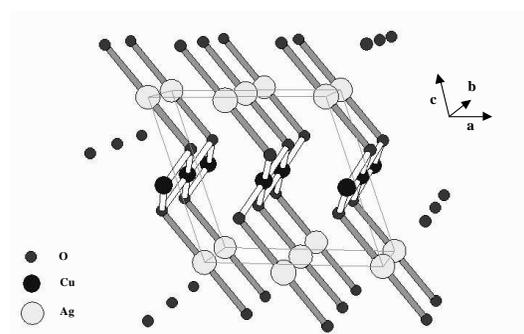


Figure 1.- Refined structure of irradiated $\text{Ag}_2\text{Cu}_2\text{O}_4$.

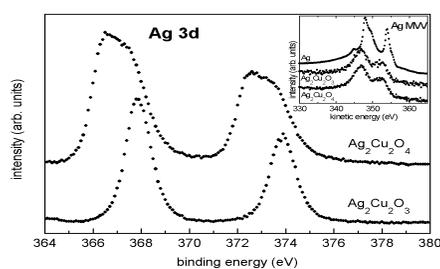


Figure 2.- Ag 3d XPS spectrum of $\text{Ag}_2\text{Cu}_2\text{O}_4$.