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V. Mastelaro, P. Paulin Filho. XAS Study of CuAl₂O₄ Ceramic System. Journal de Physique IV Proceedings, 1997, 7 (C2), pp.C2-1241-C2-1242. 10.1051/jp4:19972213 . jpa-00255286

HAL Id: jpa-00255286

<https://hal.science/jpa-00255286>

Submitted on 4 Feb 2008

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XAS Study of CuAl_2O_4 Ceramic System

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Abstract. XAS technique was used to study changes around Cu atom in the $\text{CuAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ system, induced by composition variations. The results showed that for compositions with 30 and 43% of CuO, the Cu atoms presents the same surrounding of Cu in the CuO oxide ($N_{\text{Cu-O}}=4$, $R_{\text{Cu-O}}=1.96 \text{ \AA}$). Samples with 20% (doped or undoped) showed significant changes in the Cu nearest neighbors number ($N_{\text{Cu-O}}=3$) and in the mean bond length ($R_{\text{Cu-O}}\sim 1.93 \text{ \AA}$). The qualitative analysis of the edge region showed that for the 20% of CuO sample, some Cu atoms changes from Cu^{+2} to Cu^{+1} . This change was more pronounced for the CuO 20% undoped sample.

1. INTRODUCTION

The $\text{CuO-Al}_2\text{O}_3$ system have been investigated as a ceramic thermistor because cations can be placed in special positions in the spinel structure and defects are created. The introduction of cations with variable valence, changes the electrical conductivity of this material. For the conduction process to take place, it is necessary to exist, at the same time Cu^{+1} and Cu^{+2} ions. Their content can be changed if transitions metals oxides are added to this system or the CuO amount is changed. The aim of this study is verify the local structure variation around Cu atoms induced by compositional changes and relate this variation with the electrical properties of the system. In this study we have analyzed samples with 43 and 20% of CuO (denominated Cu43 and Cu20 respectively) and 20% of CuO doped with 5% of NiO and MnO oxides (denominated Cu20Ni and Cu20Mn respectively).

2. Experimental

$\text{Al}_2\text{O}_3\text{-CuO}$ samples were synthesized from a mixture of $\alpha\text{-Al}_2\text{O}_3$ and CuO oxide in correct proportions. A series of samples were prepared by sintering pellets using an electrical furnace at temperatures between 1200 and 1300 °C for 2 hours. X-ray diffraction experiments were performed on the pellets surface to identify the phases. The phases was analyzed using as reference the diffraction peaks of $\alpha\text{-Al}_2\text{O}_3$, CuO and CuAl_2O_4 . X-ray absorption experiments were performed using synchrotron radiation from the 1.8 GeV storage ring at LURE (DCI) situated in Orsay-France. The Cu K-edge spectra of powder samples were obtained in a transmission mode, at room temperature.

3. XANES and EXAFS Results

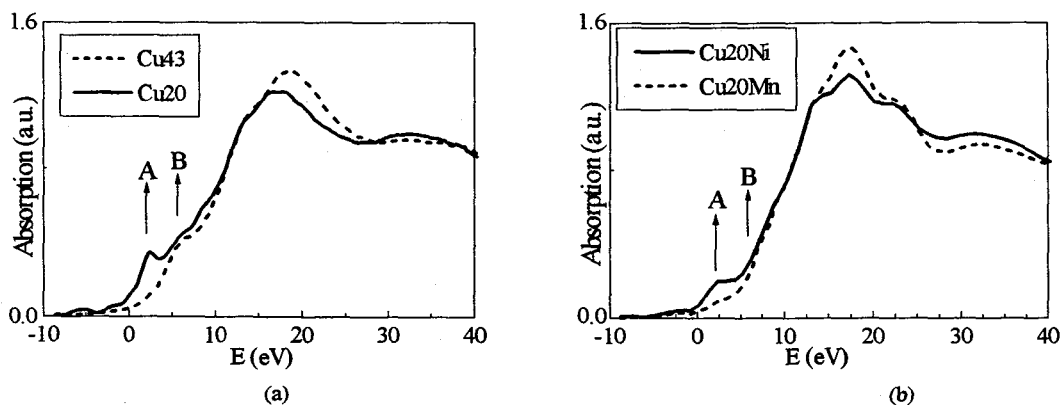


Figure 1: Cu K-edge spectra for (a) undoped and (b) doped samples.

X-ray diffraction measurements showed the presence of α - Al_2O_3 and CuAl_2O_4 as major phases and CuO phase, in small quantity (few percents). Thus, the Cu atoms was considered to belong to the CuAl_2O_4 spinel structure.

Figure 1(a) and 1(b) show the XANES spectra of the samples. According to the literature [1] the A transition situated at approximately 3.0 eV after the edge is associated to the Cu^{+1} atom whereas the transition called B, at approximately 6.0 eV after the edge, is associated to the Cu^{+2} atoms. As can be observed in figure 1, the Cu^{+1} content increase as the CuO content decrease. When the 20% of CuO sample is doped with Ni and Mn, the Cu^{+1} content also decreases; the A resonance practically disappears for the MnO doped sample and a new resonance appears (named C). The literature [2] showed that the XANES spectra of MnO doped sample agrees with that of La_2CuO_4 compound, that exhibit a copper coordination in a elongated oxygen octahedron.

The Fourier transform around copper atoms for some samples are given in figure 2. The amplitude of the first peak (first Cu-O shell) decreases when CuO content decreases. Significant changes are also observed at the second and third peaks. After doping, we observed a small decrease in the amplitude. In the doped samples we observe that the peak situated at approximately 6 Å practically disappears.

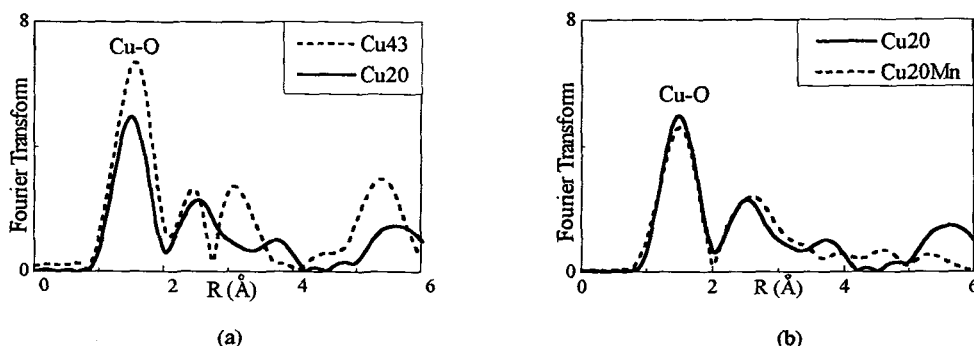


Figure 2- Fourier transform at the Cu K-edge for (a) undoped and (b) doped samples.

First shell fitting is shown in Table I. In the first case, for undoped samples, we observed a decrease in the Cu-O neighbors number and Cu-O mean bond length when the CuO content increases. In the doped samples we observed only a small increase in the Debye-Waller factor. This means that the introduction of Ni or Mn only introduces a small structural disorder at the copper first shell coordination.

Sample	$N_{\text{Cu-O}}$	$R_{\text{Cu-O}} (\text{\AA})$	$\Delta\sigma_{\text{Cu-O}} (\text{\AA}^2)$
CuO	4.0	1.96	-----
Cu43	4.0	1.97	0.03
Cu20	3.0	1.92	0.03
Cu20Ni	3.0	1.91	0.04
Cu20Mn	3.0	1.93	0.04

Table I- Cu K-edge First shell EXAFS results.

4. Conclusions

The XANES results obtained indicated the presence of Cu^{+1} atoms (A resonance) for Cu20 compositions. When the Cu20 was doped with MnO oxide, the A resonance disappeared, a new C resonance appeared. Significant changes were also observed in the Cu-O first neighbors and mean bond length for the doped samples. The semiconductor behavior observed in the Cu20 samples can be explained by the hopping process phenomena which occurs only in the presence of Cu^{+1} and Cu^{+2} atoms.

Acknowledgments

We gratefully acknowledge the support of FAPESP and CNPq and the team who run the DCI (LURE) machine.

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