



ELSEVIER

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Doping effect on the structural properties of $\text{Cu}_{1-x}(\text{Ni}, \text{Zn}, \text{Al and Fe})_x\text{O}$ samples ($0 < x < 0.10$): An experimental and computational study



J.B. Amaral^a, R.M. Araujo^b, P.P. Pedra^c, C.T. Meneses^d, J.G.S. Duque^d, M.V. dos S. Rezende^{d,*}

^a Faculdade Estácio de Sergipe, 49020-530 Aracaju, SE, Brazil

^b Coordenação de Química, IPISE/PIC, Faculdade Pio Décimo, 49095-000 Aracaju, SE, Brazil

^c CETEC, Universidade Federal do Recôncavo da Bahia, 44380-000 Cruz das Almas, BA, Brazil

^d Departamento de Física, Universidade Federal de Sergipe, Campus Prof. Alberto Carvalho, 49500-000 Itabaiana, SE, Brazil

ARTICLE INFO

Article history:

Received 13 December 2015

Received in revised form

26 May 2016

Accepted 27 May 2016

Available online 31 May 2016

Keywords:

Copper oxide

Defects

X-ray diffraction, dopants

ABSTRACT

In this work, the effect of insertion of transition metal, TM (=Ni, Zn, Al and Fe), ions in $\text{Cu}_{1-x}\text{TM}_x\text{O}$ samples ($0 < x < 0.10$) prepared via co-precipitation method is studied through experimental and computational methods. The analyses of X-ray diffraction (XRD) patterns using Rietveld refinement show that i) at $x=0$, all samples present a monoclinic crystal system with space group $C2/c$ and ii) for increasing the TM-doping, Ni and Zn-doped samples show a small amount of spurious phases for concentrations above $x=0.05$. Based on these results, a defect disorder study for using atomistic computational simulations which is based on the lattice energy minimization technique is employed to predict the location of the dopant ions in the structure. In agreement with XRD data, our computational results indicate that the trivalent (Al and Fe ions) are more favorable to be incorporated into CuO matrix than the divalent (Ni and Zn ions).

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Over the last few decades the copper oxide (CuO) has been one of the materials used to understand the origin of the superconductivity in the High- T_c cuprates [1,2]. Besides, the strong magneto-phonon interaction and the quasi-one-dimensional nature of T -dependence of magnetic susceptibility have also been the subject of many reports found in the literature [3–7]. Recent studies showed that the simultaneous observation of the magnetic and electronic transport (semiconductor) properties in CuO samples doped with magnetic ions have attracted attention of the scientific community due to their high potential of application as spintronic devices [8,9]. Meneses et al. [10] show that the disorder in the spatial distribution of magnetic ions and the change in the cell parameters can play an important role in the magnetic properties of the TM-doped CuO samples. In this scenario, it is very important to comprise the changes in the electronic and lattice structures induced by the incorporation of dopants in the CuO host. In this sense, this paper presents a systematic experimental and computational study carried out in $\text{Cu}_{1-x}\text{TM}_x\text{O}$ (TM=Ni, Zn, Al and Fe) systems at microscopic levels. Samples have been prepared via the co-precipitation method. The X-Ray diffraction

measurements were used to analyze the crystalline phases of the obtained samples. Besides, an atomistic computational simulations based on the lattice energy minimization technique were employed to study the incorporation of divalent and trivalent dopant ions inside the CuO host. The use of this method allows us to estimate with details the lattice relaxation around defect species. Finally, it is worth to note that we have obtained a good accordance between experimental and theoretical results.

2. Methodology

2.1. Experimental details

Polycrystalline $\text{Cu}_{1-x}\text{TM}_x\text{O}$ samples (TM= Fe^{3+} , Ni^{2+} , Zn^{2+} and Al^{3+}) were prepared by annealing a precursor powder obtained by the co-precipitation method [10]. The starting solutions were prepared by dissolving stoichiometric amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 20 ml of distilled water (at room temperature) while a NaOH precipitating agent was dropwise followed by a mechanical stirring during 30 min. The precipitate were collected by centrifuging and washed several times to remove completely the Na ions. After that, it was then dried at 60 °C and the resulting powder was calcined in oxygen atmosphere at 800 °C for 5 h.

* Corresponding author.

E-mail address: mvsrezende@gmail.com (M.V. dos S. Rezende).

The crystalline structures of samples were investigated by the X-ray powder diffraction (XRPD) measurements using an Empyrean diffractometer (PANalytical) with Cu-K α radiation ($\lambda=1.5406$ Å) for Cu $_{1-x}$ Fe $_x$ O and Cu $_{1-x}$ Ni $_x$ O samples and a Rigaku diffractometer with Co-K α radiation ($\lambda=1.789$ Å) for Al and Zn-doped CuO samples. All data were collected in the continuous mode with 2θ range from 30° to 95° , step size of 0.02° and a scanning speed of $0.5^\circ/\text{min}$. The obtained XRD patterns were compared with that found in the Joint Committee Powder Diffraction Standards (JCPDS) database and analyzed using the Rietveld refinement [11] approach as implemented in the DBWSTools2.3 free software [12,13]. The pseudo-Voigt function was selected to provide the best fits of the observed peak profiles.

2.2. Computational details

In order to describe the defect disorder produced by the TM-doping in our CuO samples, we have employed static simulation techniques based on energy minimization procedures. It worth to comment that the long-range (Coulombic) and short-range pair potentials were used to treat the interaction among all the ions of the solid. For this last interaction, the Harmonic and Buckingham functions were employed. The Buckingham potential can be described by following equation

$$V(r_{ij}) = A_{ij} \exp\left(\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

Where, the first term describes the Pauli short-range repulsion and the second term the Van der Waals attraction. The ionic polarizability was taken into account for the O $^{2-}$ ions through the shell model [14]. On the other hand, the interionic interactions between Cu $^{2+}$ -O $^{2-}$ and O $^{2-}$ -O $^{2-}$ were extracted initially from Ref. [15] and then refitted in order to reproduce the structural properties of Cu $_{1-x}$ TM $_x$ O (TM=Fe $^{3+}$, Ni $^{2+}$, Zn $^{2+}$ and Al $^{3+}$) samples studied in this work. The point defects were calculated using the Mott-Littleton method [16] which consider that the region close to the defects is partitioned into two spherical regions – one next to the defect and other to larger distances. In the first case, the ions are relaxed individually under the defect perturbation while in the second case, the distance extends theoretically to infinity and the ionic relaxation is treated by using the approximate Mott-Littleton quasi-continuum procedures. In order to study the effect of dopant concentration in the CuO matrix, the partial occupancy mean-field was used. Calculations were performed to investigate the substitution of Cu $^{2+}$ and the term of charge compensation was included when needed. Another important feature is that in the mean-field approximations the substituted ions are randomly distributed in the CuO host for all concentrations, that is, there is no interaction between the substituted ions. In this way, the general utility lattice program (GULP) [17] was used to predict the structural properties discussed in this work. The details of the methodology used in the simulations have been described elsewhere [18–20].

It is important to state that atomistic simulations generally must start with a set of interatomic potentials which can describe accurately the studied material. In this sense, the potential parameters for CuO oxide obtained by empirical fitting method were used (see Table 1). The difference between the calculated and experimental lattice parameters was less than 2%, indicating that our potential reproduces well the CuO structure.

3. Results

The experimental and calculated XRD patterns for Ni, Zn-doped

Table 1
Potential parameters, shell model constants and ionic charges used in present work.

Short-range interactions				
Buckingham	A (eV)	ρ (Å)	C (eV Å)	Cutoffs (Å)
Cu _{Core} -O _{Shell}	1650.0	0.3280	0.00	12.00
O _{Shell} -O _{Shell}	22764.0	0.1490	27.88	12.00
Harmonic	k (eV Å²)	r₀ (Å)		
Cu _{Core} -O _{Core}	25.0	1.65		
Shell model parameters				
Ion	Y (e)		K (eV Å⁻²)	
O $^{2-}$	-2.2		48.0	

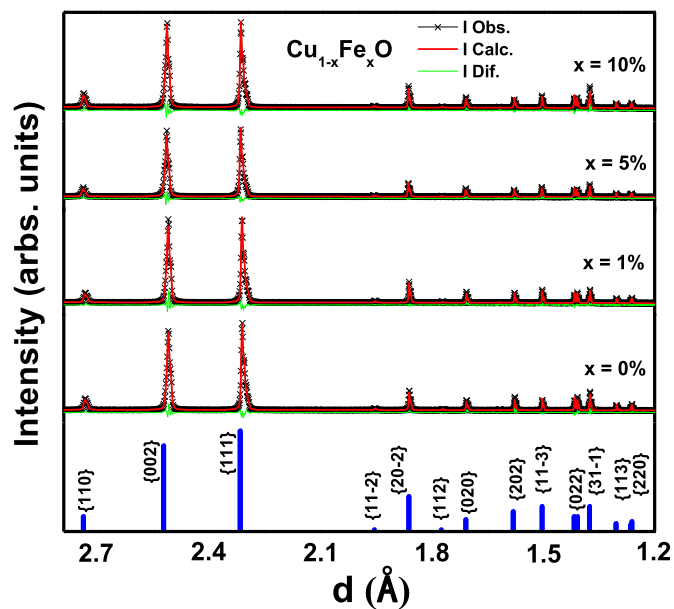


Fig. 1. XRD patterns for Cu $_{1-x}$ Ni $_x$ O samples ($x=0$; 0.01; 0.05 and 0.10). The red and green solid lines mean the calculated pattern and the difference between experimental and simulated patterns, respectively. The blue vertical bars are an indexation obtained from the JCPDS database (48–1548). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

CuO samples with concentration 1%, 5% and 10% are showed in Figs. 1 and 2, respectively. The XRD analysis show that only the sample obtained with the lowest TM-doping ($x=0.01$) present single phase with structure isomorphous to the monoclinic CuO structure (space group: $C2/c$). However, we observed the appearing of spurious phases of hexagonal ZnO (space group: $P63mc$) and cubic NiO (space group: $Fm3m$) for the samples with higher concentration of Ni or Zn ($x=0.05$ and 0.10).

Figs. 3 and 4 show the XRD patterns for Cu $_{1-x}$ Fe $_x$ O and Cu $_{1-x}$ Al $_x$ O samples ($x=0, 0.01, 0.05$ and 0.10), respectively. One can note that, independently of doping concentration, all samples present a single phase with monoclinic CuO type structure (space group: $C2/c$). Liu et al. [21] show that CuO nanopowders doped with Fe synthesized by the co-precipitation method also present similar behavior [21]. On the other hand, a spurious phase of iron oxide (Fe $_2$ O $_3$) have been observed for Cu $_{1-x}$ Fe $_x$ O samples ($0 < x < 0.30$) grown by the combustion synthesis method [22]. In this case, the Fe $_2$ O $_3$ phase was observed to concentrations higher than $x=0.25$. In the same sense, by using the microwave combustion method, Mohamed et al. [23] synthesized Fe-doped CuO nanostructures with $x=0, 0.05, 0.1, 0.15,$ and 0.20. They show that Fe ions were successfully introduced into the lattice substituting the Cu ions without affecting the crystal structure of the CuO host [9]. According the above mentioned experimental results, the

Download English Version:

<https://daneshyari.com/en/article/1331282>

Download Persian Version:

<https://daneshyari.com/article/1331282>

[Daneshyari.com](https://daneshyari.com)