

Electronic state of ^{57}Fe Mössbauer probe atoms in Cu(III) oxides with perovskite and perovskite-related structures

Igor Presniakov^a, Gérard Demazeau^{b,*}, Alexei Baranov^{a,b}, Alexei Sobolev^a, Tatiyana Gubaidulina^a, Viyacheslav Rusakov^a, Alexander Vasiliev^a

^a Lomonosov Moscow State University, Moscow, 119992 Leninskie Gory, Moscow, Russia

^b ICMCB, CNRS, University BORDEAUX 1 "Sciences and Technologies", Site de l'ENSCP, 87, Avenue du Dr A. Schweitzer, 33608 PESSAC-Cedex, France

ARTICLE INFO

Article history:

Received 20 May 2008

Received in revised form 21 July 2008

Accepted 25 July 2008

Keywords:

Oxides

Cu^{3+} oxides

High pressure synthesis

Perovskite structure

K_2NiF_4 structure

Mössbauer spectroscopy

Charge transfer phenomena

ABSTRACT

Mössbauer spectroscopy studies were developed in order to obtain an evaluation of different physico-chemical factors characterizing the electronic structure of the local sites (CuO_6) into three copper(III) oxides: LaCuO_3 having a three-dimensional (3D) perovskite structure; SrLaCuO_4 and $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ with a two-dimensional (2D) K_2NiF_4 -type structure. All these matrixes have been doped with ^{57}Fe (1 at.%) Mössbauer probe atoms. Such evaluation was based on analysis of the ^{57}Fe Mössbauer parameters (isomer shift and quadrupole splitting) characterizing the formal oxidation state and the local structure of the ^{57}Fe probe atoms. The obtained results underline that four main factors play an important role in the stabilization of formally trivalent " Cu^{3+} " ions: (i) the involved preparation process (in particular the oxygen pressure level able to impede the formation of oxygen vacancies); (ii) the dimensionality (3D or 2D) of the lattice; (iii) the chemical surrounding and (iv) the local structural distortion of the transition metal site (CuO_6), both last factors governing the local crystal field energy, orbital ordering and a possible charge transfer $\text{Cu}^{3+}-\text{O}^{2-} \leftrightarrow \text{Cu}^{2+}-\text{O}^-(\text{L})$.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

In Solid State Chemistry, the high oxidation states M^{m+} of transition metals have been in the past the subject of numerous studies due to the correlations between the formal oxidation state value " m " and the strong increase of the covalency of the resulting $M^{m+}-\text{O}$ bond [1,2]. Trivalent copper oxides are obviously a very good example. Most physical properties of these compounds, including high T_C superconductivity [3,4], strongly depend on the electronic structure of the $\{\text{CuO}_x\}_{(2x-3)^-}$ sites. Few oxides containing only trivalent " Cu^{3+} " ions have been prepared. As the corresponding $\text{Cu}-\text{O}$ bonds are strongly covalent, it is necessary, in the most cases, to stabilize them by interaction with a weak bond as $\text{A}-\text{O}$ ($\text{A}=\text{alkaline metal}$). Such ionic bonds $\text{A}-\text{O}$ allows the oxygen atoms to involve mainly their 2p orbitals in the σ -bonds with the " Cu^{3+} " ions. By this method, the compounds ACuO_2 ($\text{A}=\text{Na, K, Rb, Cs}$) were first prepared by Klemm and co-workers [5,6]. Structural investigations of these oxides developed by Hestermann and Hoppe [7] and Brese et al. [8] underline that Cu(III) is stabilized in a square planar envi-

ronment (CuO_4) with shared edges thus inducing the low spin (LS) electronic configuration ($t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^0$). Then Demazeau and co-workers [9,10], using high oxygen pressures, have stabilized Cu(III) in six-coordinated sites in perovskite-type or derived structures. In particular three oxides have been prepared: LaCuO_3 having a three-dimensional (3D) perovskite structure [9]; SrLaCuO_4 and $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ characterized by a two-dimensional (2D) K_2NiF_4 -type structure [9,10]. These oxides can be distinguished by chemical bonding factors versus the nature of the competing bond existing into the lattice: ($\text{Cu}-\text{O}$) bonds within the LaCuO_3 lattice and into the perovskite planes of the SrLaCuO_4 matrix or weak ($\text{Li}-\text{O}$) bond into the $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ structure (Fig. 1). All these factors can significantly affect local parameters characterizing the (CuO_6) sites: crystal field energy (Dq/B), structural distortion (θ) and electronic anisotropy versus the possible charge transfer $\text{Cu}^{3+}-\text{O}^{2-} \leftrightarrow \text{Cu}^{2+}-\text{O}^-(\text{L})$ [11,12]. If LaCuO_3 is metallic, SrLaCuO_4 is a semiconductor and $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ is an insulator. Consequently, in such Cu(III) oxides, copper ions adopt different electronic configurations.

In this paper we report results of comparative investigation of LaCuO_3 , SrLaCuO_4 and $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ matrix doped with ^{57}Fe (1 at.%) Mössbauer probe atoms. The objective of this work was to characterize, using Mössbauer spectroscopy, the electronic state and local surrounding of ^{57}Fe probe atoms through

* Corresponding author. Tel.: +33 5 40 00 83 58; fax: +33 5 40 00 27 10.
E-mail address: demazeau@icmcb-bordeaux.cnrs.fr (G. Demazeau).

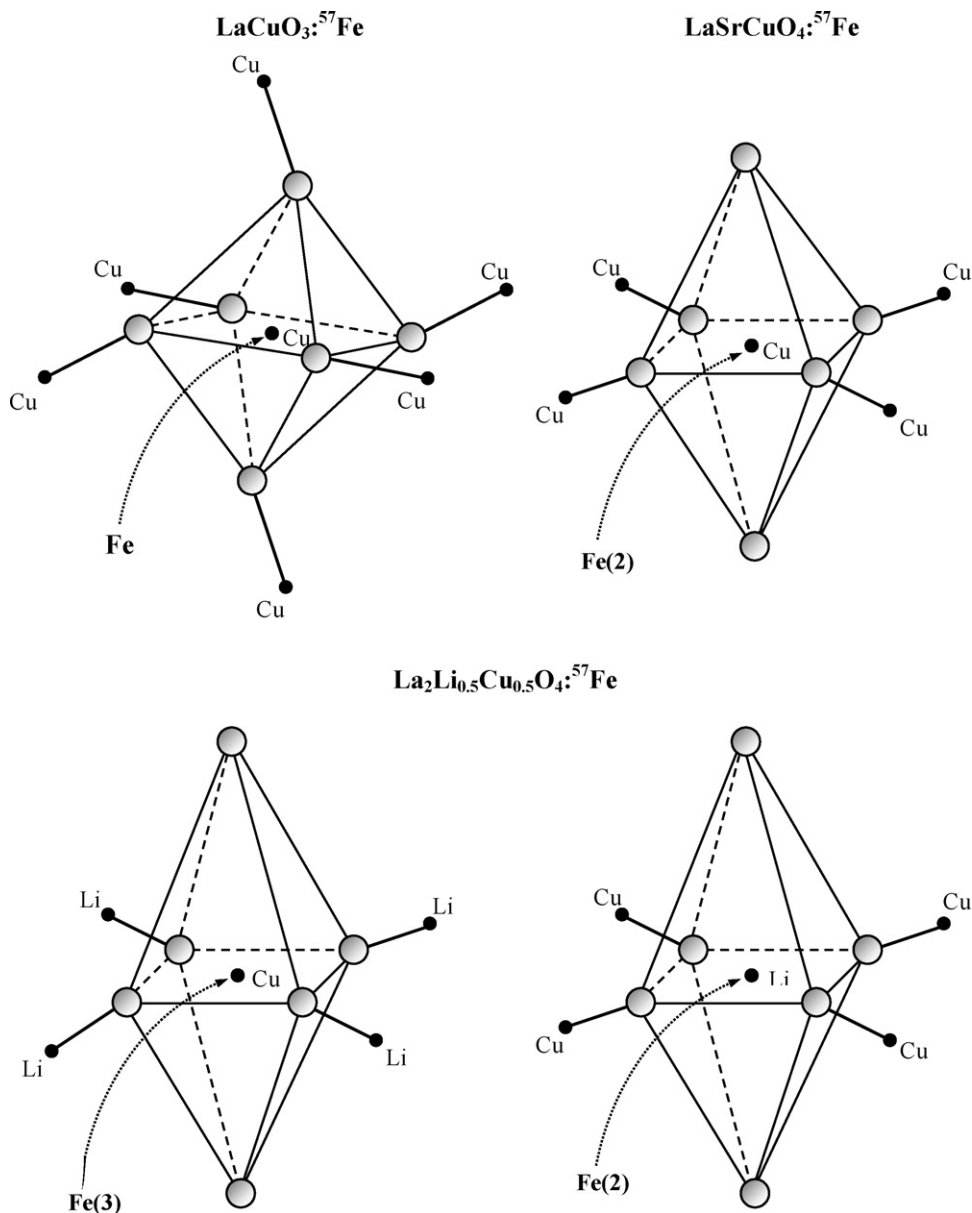


Fig. 1. Schematic representation of the local structure in the iron-doped: (a) 3D $\text{LaCu}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_3$; 2D K_2NiF_4 -type, (b) $\text{LaSrCu}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_4$ and (c) $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ lattices.

its observed isomer shift and quadrupole splitting values. This method was recently developed for the physical characterization of manganite $\text{CaMn}_7\text{O}_{12}$ containing in octahedral sub-lattices mixed valence $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions [13,14]. It has been shown that ^{57}Fe probe atoms reflect structural and chemical factors characterizing not only its local environment but also the electronic phenomena in the bulk. Moreover, the behaviour of iron atoms – as local probe in perovskite-type or derived matrixes – appears to be an interesting approach for studying the mechanisms of substitution on the different six-coordinated sites and the corresponding induced electronic phenomena characterizing the bulk.

2. Experimental

In all cases, instead of undoped CuO oxide, a $\text{Cu}_{0.99}^{57}\text{Fe}_{0.01}\text{O}$ precursor was used for introducing the ^{57}Fe Mössbauer probe atoms into the corresponding lattices. This precursor was prepared through the thermal decomposition of the iron-doped hydroxide $\text{Cu}(\text{OH})_2:^{57}\text{Fe}$.

In the case of LaCuO_3 (^{57}Fe : 1 at.%), the preparation process developed for the undoped material [with La_2CuO_4 and CuO as reagents and KClO_3 as an in situ oxygen source, using a belt type equipment (6 GPa, 900 °C, 15 min)] was inoperative to get a pure perovskite phase. Consequently a new process was developed with monoclinic $\text{La}_2\text{Cu}_2\text{O}_5:^{57}\text{Fe}$ (2 at.%) as precursor, KClO_3 as in situ oxygen source but using more severe pressure conditions (11 GPa, 900 °C, 15 min) [15]. Such a strong difference in the preparation process was attributed to the metallic behaviour of LaCuO_3 , the corresponding band structure being perturbed by the ^{57}Fe probe substituting Cu^{3+} cations.

In the case of SrLaCuO_4 simple doped with ^{57}Fe (1 at.%), the preparation process developed for preparing the undoped simple [10] (SrO , La_2O_3 and $\text{Cu}_{0.99}^{57}\text{Fe}_{0.01}\text{O}$ as reagents; 300 MPa of oxygen gas pressure and 820 °C) was appropriated for obtaining a pure phase with the K_2NiF_4 -type structure.

The ^{57}Fe (1 at.%) doped $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}^{3+}\text{O}_4$ matrix was also synthesized using the previous process developed for preparing the undoped material [9] (200 MPa of oxygen gas pressure, 870 °C, 48 h using La_2O_3 , Li_2O and $\text{CuO}:^{57}\text{Fe}$ as reagents) [16]. XRD data were collected at 298 K using a STOE diffractometer ($\text{K}\alpha\text{Cu}$ $\lambda = 1.5451 \text{ \AA}$).

The ^{57}Fe Mössbauer spectra were recorded at 300 K using a conventional constant-acceleration spectrometer. The radiation source $^{57}\text{Co}(\text{Rh})$ was kept at room temperature. All isomer shifts refer to the $\alpha\text{-Fe}$ absorber at 300 K.

Download English Version:

<https://daneshyari.com/en/article/1526536>

Download Persian Version:

<https://daneshyari.com/article/1526536>

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