

A novel preparation process for LaCuO_3 involving a high pressure oxidation of precursor derived from the perovskite structure: An appropriate route for doping with ^{57}Fe Mössbauer probe

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Abstract

In order to dope LaCuO_3 by ^{57}Fe Mössbauer probe, a novel high pressure oxidation process was developed. The orthorhombic phase $\text{La}_2\text{Cu}_2\text{O}_5$: ^{57}Fe (2%) was used as a precursor due to its structure derived from the perovskite.

The role of the structure of the precursor has been underlined through a comparison of the reaction routes from both structural forms (monoclinic and orthorhombic) of $\text{La}_2\text{Cu}_2\text{O}_5$.

This example illustrates the key role by the composition and the structure of the precursor for preparing novel materials.

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1. Introduction

The stabilization of a formal oxidation state $n+$ for a transition metal M with a specific electronic configuration into the bulk of the perovskite structure AMO_3 is closely dependent on local structural and chemical factors. A preliminary study [1], based on Tanabe and Sugano diagrams [2] and the Krishnamurthy and Schaap calculations of the energy levels corresponding to the d orbitals versus the local distortion [3], has underlined that for a d^n cation ($1 < n < 9$) the stabilization of a specific electronic configuration can be related to the local structural distortion of the octahedral site [$\theta = ((M - O(oz)) / (M - O(xoy)))$] (as an elongation along oz axis, $\theta > 1$; or a compression along oz axis, $\theta < 1$), as well as to the local crystal

field energy Dq/B (correlated to the chemical bonding of such a d^n cation).

An electronic configuration corresponds to the electronic population of the different energy levels characterizing the d orbitals. The local structural distortion governs the energy splitting for the e_g (d_{z^2} and $d_{x^2-y^2}$) and for the t_{2g} (d_{yz} , d_{zx} , d_{xy}) orbitals. The local crystal field energy induces the energy splitting of orbitals with the same components (for example: d_{xy} and $d_{x^2-y^2}$).

In an oxygen lattice, the formal oxidation state $n+$ for a M^{n+} cation can also be dependent on the average energy value of the corresponding d orbitals (\bar{E}_{Md}) of M^{n+} versus that for the $2p$ orbitals of oxygen (\bar{E}_{O2p}). If (\bar{E}_{Md}) is largely smaller than (\bar{E}_{O2p}), a charge transfer phenomenon can take place leading to a reduction of the formal $n+$ oxidation state ($M^{n+} \rightarrow M^{(n-1)+}$) with the consequent formation of an electron–hole on oxygen OL [4].

In a first step, the LaCuO_3 and LaNiO_3 matrixes (3D perovskite lattice) were selected for ^{57}Fe doping. LaCuO_3

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was for the first time prepared by Demazeau et al. [5] using a stoichiometric mixture of La_2CuO_4 and CuO as precursors and a high oxygen pressure treatment (6 GPa, 950 °C, 15 min) in a belt-type apparatus, using KClO_3 as in situ oxygen source. Such a material is characterized by a rhombohedral structure and metallic character of conductivity in all temperature range due to the strong covalency of the M^{3+}O bond [6] and the small structural distortion of the lattice (Cu-O-Cu angle is being close to 180°) ($b_\delta > b_m$) [7]. A lot of authors using the same precursors or a stoichiometric mixture of La_2O_3 and CuO and different oxidizing sources (KClO_3 , KO_2 ...) have confirmed the stabilization of such a Cu^{3+} perovskite under high pressure conditions ($P > 5$ GPa) [8–10]. In parallel, the whole system of non-stoichiometric perovskites LaCuO_{3-x} was prepared under high pressures and characterized [11].

A comparative study of the rhombohedral perovskites LaCuO_3 and LaNiO_3 (both are characterized by Pauli paramagnetism) had evidenced that the differences between the magnitudes and thermal evolutions of their respective susceptibilities could be explained in terms of antiferromagnetic versus ferromagnetic superexchange enhancement and large versus small spin polarons associated with the excited states [6].

Mössbauer spectroscopy was able, through the isomer shift (δ) and the quadrupole splitting (Δ), to evaluate both the valent state and the electronic configuration adopted by a transition metal [12,13]. Hence, such a physical characterization could also be applicable to study and to compare both LaMO_3 ($M = \text{Cu}, \text{Ni}$) perovskites.

In the case of LaNiO_3 doped with ^{57}Fe (2%) the conventional preparation process was operating through the solid state reaction $\text{La}_2\text{O}_3 + 2 \text{NiO} \cdot ^{57}\text{Fe}$ under gaseous O_2 pressure 100 MPa at 900 °C. For the LaCuO_3 matrix, the previous preparation method [6] ($\text{La}_2\text{CuO}_4 + \text{CuO} \cdot ^{57}\text{Fe}$ with KClO_3 as oxygen source) did not lead to a pure rhombohedral phase; consequently, it was necessary to find a novel preparation process for $\text{LaCu}_{0.98}\text{Fe}_{0.02}\text{O}_3$.

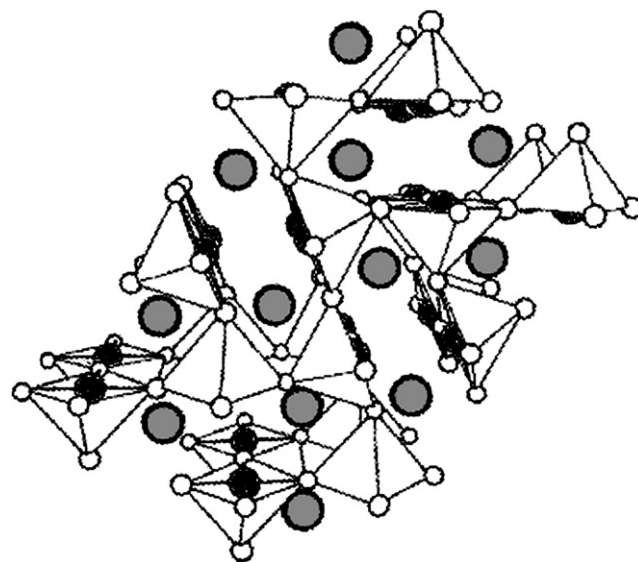


Fig. 1. Schematic view of the orthorhombic $\text{La}_2\text{Cu}_2\text{O}_5$ structure (approximately 15° off c axis). Two perovskite slabs are shown: La atoms being represented by large grey-shaded circles, Cu by black-shaded circles and O by small open circles.

2. Preparation of the sample $\text{LaCuO}_3 \cdot ^{57}\text{Fe}$ (2%)

A novel preparation method was developed, taking into account that in the previous high pressure processes a mixture of precursors ($\text{La}_2\text{CuO}_4 + \text{CuO}$ doped with ^{57}Fe) and an in situ oxidizing medium (KClO_3) have been used. The preparation of the ^{57}Fe doped LaCuO_3 required two steps: (i) the reaction between the precursors and (ii) the oxidation of copper cations ($\text{Cu}^{2+} \rightarrow \text{Cu}^{3+}$). In order to reduce the number of steps, a new precursor $\text{La}_2\text{Cu}_2\text{O}_5 \cdot ^{57}\text{Fe}$ was selected. $\text{La}_2\text{Cu}_2\text{O}_5$ can be considered as the end member of the oxygen-defect perovskite series LaCuO_{3-x} [14]. The orthorhombic form of $\text{La}_2\text{Cu}_2\text{O}_5$ can be prepared through two different routes: a high pressure synthesis from the starting La_2O_3 and CuO oxides [15] or the reduction of the tetragonal form of the $\text{LaCuO}_{3-\delta}$ perovskite [10,14].

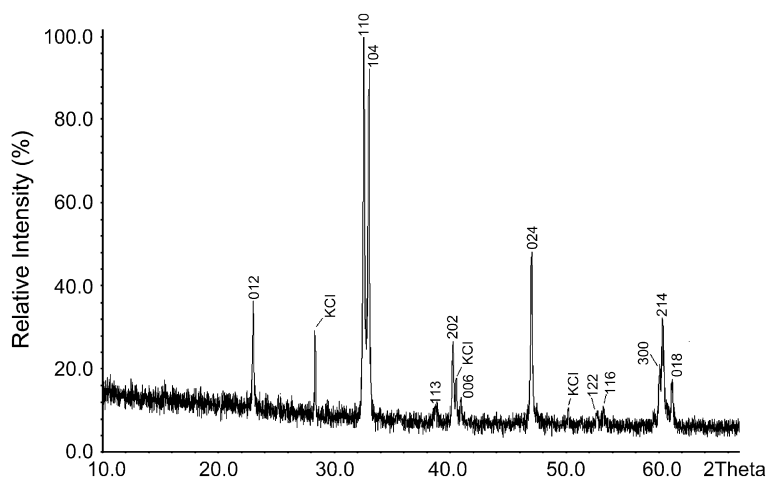


Fig. 2. X-ray diffraction pattern of LaCuO_3 doped with ^{57}Fe (2%).

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