Synthesis under pressure and characterizations through optical spectroscopy of Jahn-Teller cations (LS Ni$^{3+}$, IS Co$^{3+}$) as probes diluted in a perovskite matrix

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Abstract. The objective is to explore through optical spectroscopy and magnetic measurements the coordination and electronic structures of transition-metal ions introduced as impurities with unusual valence states in the oxide perovskite LaAlO$_3$. The selected transition-metal ions Ni$^{3+}$(3d$^7$) and Co$^{3+}$(3d$^6$) are characterized by an electronic configuration likely leading to an orbital degenerate E state in O$^h$ symmetry, and thus electron-lattice coupling due to the Jahn-Teller effect may induce low symmetry distortion around the impurity oxygen octahedron. We show that a sol-gel process followed by high oxygen pressure treatments yields stabilization of trivalent state in oxide perovskite. Information about the coordination, electronic structure and aggregation around the magnetic impurity was obtained from X-ray diffraction, FTIR and optical spectroscopy. Finally, evidence on the possible existence of intermediate spin state in Co$^{3+}$ is under consideration.

1. Introduction

Here we investigate through X-ray diffraction and optical spectroscopy, the synthesis, stabilization and structural characterization (coordination and electronic structure) of 3d cations introduced as impurities in oxide perovskites ABO$_3$, which are able to exhibit a local Jahn-Teller distortion. The selected transition-metal ions (Ni$^{3+}$ d$^7$, Co$^{3+}$ d$^6$) are characterized by an electronic configuration probably leading to an orbital degenerate E state in O$^h$ symmetry (LS Ni$^{3+}$: t$_2g^6e_g^1$, IS Co$^{3+}$: d$_{xy}$d$_{yz}$d$_{zx}$d$_y^2$d$_{x^2-y^2}$d$_{z^2}$). As a result, the electron-lattice coupling may induce a low symmetry distortion of the oxygen octahedron (E$^\infty$e), which makes the complex anisotropic. The purpose of the paper is to investigate whether these transition metal can be mostly stabilised as diluted trivalent impurities in LaAlO$_3$ by high oxygen pressure treatments [1] and whether such impurities exhibit a Jahn-Teller ground state leading to local low-symmetry distortions of the octahedron [2-5]. Although the local structure of Ni$^{3+}$ ions has been largely studied by EXAFS at different dopant concentrations above 5% [6], it is not well understood yet how the low spin (LS) state of Ni$^{3+}$, which exhibits an elongated
octahedron coordination in LaAlO₃:Ni³⁺ [7], shows no distortion in LaNiO₃ and LaNi₀.₁Mn₀.₉O₃ [6]. In addition, there is no information about the 3d-electronic structure of either Ni³⁺ or Co³⁺ diluted systems in oxygen perovskites. The 3d splitting pattern of transition metal ions placed at octahedral sites provides an excellent probe to investigate low-symmetry crystal-field distortions due to the Jahn-Teller effect or to crystal anisotropy effects [2-5]. Furthermore structural information on the coordination MO₆ octahedron (M: Ni; Co) can be obtained from the energies of the optical spectra provided that structural correlations between octahedron distortion and 3d electronic energies have been established [2-4]. Jahn-Teller systems involving Cu²⁺ chlorides [4,5] and Mn³⁺ fluorides [2,3] are illustrative examples of structural precise correlations between Jahn-Teller distortion and 3d-splitting energy. In this paper we report optical spectroscopy results on diluted systems (2%) of Ni and Co – doped LaAlO₃ for which the formation of transition-metal ion aggregates can be minimised and EXAFS sensitivity may be insufficient for a suitable local structural characterization.

A major problem concerns the use of diluted probes in a perovskite matrix ABO₃. In order to avoid aggregate formation into the host lattice, it was –for the synthesis- necessary to develop specific routes able to favour dilution of the Jahn-Teller probe and homogeneous distribution. Versus the nature of the precursors, in the first step, a sol-gel process involving the citric acid and ethylene-glycol has been investigated [1]. The second step was a chemical treatment devoted to eliminate the organic residues, whereas the third step was a high oxygen pressure treatment for the Ni³⁺ and Co³⁺ valence stabilization.

In order to confirm both the oxidation state and the electronic configuration, the samples were characterized by oxido-reduction titration and magnetic measurements. The Jahn-Teller distortion was investigated through the electronic structure of the transition-metal ion by optical spectroscopy. In particular, we focus on the Jahn-Teller-related splitting pattern shown by the crystal-field spectra, whose band structure contains complete information on the type and degree of the Jahn-Teller distortion as well as on its associated energy and spin state [2-5].

2. Experimental

La(Ni,Al)O₃ and La(Co,Al)O₃ powders were synthesized for different transition metal concentrations: 1, 2, 5, 15 and 100 % mol for Ni and 2, 5 and 15 % mol for Co. In the first step, a sol-gel process involving citric acid and ethylene-glycol [1] has been investigated. The second step was a chemical treatment devoted to eliminate the organic residues, whereas the third step was a treatment under high oxygen pressures. The oxygen gas till 200 MPa and 700°C during two days was applied in a reactor chamber. The high pressure equipment was reported previously [8]. The experimental setup and obtained samples are shown in figure 1.

![Figure 1. (a) LaAl₀.₉₈Ni₀.₀₂O₃ and LaAl₀.₉₈Co₀.₀₂O₃ pills (top) and gold containers used for high pressure treatments (bottom). (b) Experimental setup for synthesis under high O₂ pressure.](image)
homogeneous for the explored dilutions (figure 2). The crystal structure corresponds to the rhombohedral, nearly cubic perovskite, R3c space group [9], with hexagonal lattice parameters, \(a = 5.3654(3) \text{ Å}, c = 13.112(1) \text{ Å}\). No evidence of phase segregation or precipitate formation is shown. The infrared spectra of both Co- and Ni-doped LaAlO\(_3\) show the same bands, located around 500, 650 and 1400 cm\(^{-1}\) irrespective of the impurity. The uncertainty in positions is due to saturation effects. The first two peaks correspond to the IR-active vibrations \(E_u\) and \(E_u + A_{2u}\) (two \(T_{1u}\) in \(Pm\bar{3}m\)) perovskite modes of rhombohedric LaAlO\(_3\) [10]. The peak around 1400 cm\(^{-1}\) although exhibits some impurity-dependent band shape, likely corresponds to overtones of the fundamental vibrations: a detail study including impurity effects is currently under progress.

Figure 2. (a) XRD for LaAl\(_{0.95}\)Co\(_{0.05}\)O\(_3\) (same pattern for all samples) indexed for the pseudocubic structure of LaAlO\(_3\). (b) FTIR LaAl\(_{0.98}\)Ni\(_{0.02}\)O\(_3\) and LaAl\(_{0.98}\)Co\(_{0.02}\)O\(_3\) diluted 12.5% mol in KBr.

The optical spectra were obtained in a Cary 600i spectrophotometer operating directly in reflectance mode and in absorption mode, using sample diluted KBr pellets (12.5% mol) in the latter case.

3. Results and analysis

Figure 3. Diffuse reflectance and optical absorption (12.5% mol in KBr) spectra of (a) 2% mol Ni\(^{3+}\) in LaAlO\(_3\) and (b) 2% mol Co\(^{3+}\) in LaAlO\(_3\).

Figures 3a and 3b show the optical spectra of the 2% diluted Ni\(^{3+}\) and Co\(^{3+}\) in LaAlO\(_3\) respectively. The comparison of the reflectance and absorption spectra allows us to confirm the presence of absorption bands, which are associated with crystal-field transitions within the NiO\(_6\) and CoO\(_6\) octahedra. It is worth noting that no trace of Ni\(^{2+}\) and Co\(^{2+}\) is detected in the optical spectra. Preliminary magnetic measurements currently in progress confirm it. Interestingly, the electronic spectra correspond neither high-spin (HS) \(^3T_2\rightarrow^3T_2\) for Ni\(^{3+}\) (d\(^3\)); nor HS \(^5T_2\rightarrow^2E\) for Co\(^{3+}\) (d\(^4\)) since the first intense transition should appear at an energy equal to the crystal field splitting, \(\Delta\), which is around 2 eV for these Ni\(^{3+}\) and Co\(^{3+}\) in oxides [11-13]. By contrast a first intense band is observed in both compounds around 1.2 and 1.5 eV respectively. The presence of this band evidences an
additional $e_g$-octahedral splitting due to the Jahn-Teller distortion [2,3]. A similar band located at 1.5 eV is observed in Mn$^{3+}$ in epidote where the Mn$^{3+}$ occupies a strongly distorted site due to the Jahn-Teller effect [13]. According to correlations established elsewhere [2], the $e_g$-octahedral splitting, $\Delta_e$, is proportional to the Jahn-Teller distortion, $\rho$, by $\Delta_e = 5.1 \rho$ (in eV and Å units, respectively). The Jahn-Teller distortion, $\rho$, is defined in terms of the tetragonal, $Q_0$, and rhombic, $Q_\epsilon$, normal coordinates as $\rho = \left[ Q_0^2 + Q_\epsilon^2 \right]^{1/2}$. Such a correlation also applies for Mn$^{3+}$ in epidote given that the coordinate measured by X-ray diffraction is $\rho = 0.28$ Å [13]. Taking the same relation for Ni$^{3+}$ we estimate $\rho = 0.2$ Å from the energy of figure 3a. It means a difference between the axial and equatorial distance of the distorted octahedra of about $\Delta R = R_{ax} - R_{eq} = 0.17$ Å. The existence of Jahn-Teller effect in Ni$^{3+}$ in LaAlO$_3$ is consistent with the LS (S = 1/2) ground state which was previously shown by EPR [7]. The band structure of figure 3a confirms the proposed Jahn-Teller established LS ground state in LaAlO$_3$.

The optical spectrum of Co$^{3+}$-doped LaAlO$_3$ is shown in figure 3b. Interestingly, the observed band structure is hard to assign to HS Co$^{3+}$ on the basis of an O$h$ crystal-field symmetry attained at the Al site. Actually, the first spin-allowed transition in high-spin Co$^{3+}$ (O$h$) corresponds to $^3T_2g \rightarrow ^5E_g$, i.e. the crystal-field splitting, and thus should appear around 2 eV [11-13]. The fact we detect an intense absorption band around 1.5 eV and above (two bands around 2.5 and 3.5 eV) is a clear indication of additional splitting in the d-orbitals of the 3$d^6$ configuration. Furthermore, it must be noted that the corresponding first allowed crystal-field transition in LS ($S = 0$), $^1A_{1g} \rightarrow ^1T_{1g}$, should also correspond to $\Delta \approx 20B \approx 2$ eV for Co$^{3+}$ (O$h$) oxides [14]. Although reflectance spectroscopy is not the best suited technique to obtain well-resolved spectra, the band structure and associated transition energies derived from figure 3b clearly suggest a low-symmetry crystal-field for Co$^{3+}$ in LaAlO$_3$. Whether this low-symmetry crystal-field is due to the Jahn-Teller effect is still under investigation. However the possible existence of Jahn-Teller effect in Co$^{3+}$ would indicate that we are dealing neither a low-spin nor a HS ground state, but an intermediate-spin (IS) state. This important result contrasts to recent findings in LaCoO$_3$ by x-ray absorption spectroscopy and magnetic circular dichroism techniques [15], and strongly suggests that the use of diluted Co$^{3+}$ systems in selected oxides may provide crystal environments which are able to stabilize the IS state.

Magnetic and EXAFS experiments in these systems are currently in progress.

Acknowledgments
This work was financed by the Spanish MEC (Project Ref. MAT2005-00099). F. Rodriguez acknowledges partial support from the I3 Research Program of the University of Cantabria. M.N. Sanz-Ortiz thanks the Spanish MEC for support her stay at the University of Bordeaux I and for a FPU grant (Ref. AP-2004-5954).

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