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Structural transformation, spectroscopic characterization and magnetic properties of $La_{1-x}Gd_xCoO_3$

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ABSTRACT

$La_{1-x}Gd_xCoO_3$ for $x < 0.2$ crystallize in the rhombohedral structure, and it is orthorhombic for $x \geq 0.2$. The lattice volume systematically decreases as x increases. The analysis of the Co $2p_{3/2}$ xps spectra indicates that the Co ions are at both +3 and +8/3 valence states, and the calculated oxygen content is about 2.93 per formula unit. The bending vibration of the Co–O bond linearly shifts from 429 cm^{-1} to 482 cm^{-1} with the increasing x, and it is coincident with the increasing Co–O–Co angle. The shoulder peak at approximately 575 cm^{-1} becomes obviously wide with the increasing doping Gd^{3+} content owing to the magnetic interactions of the Gd^{3+} ions with the surrounding CoO6 octahedra. The energy band gap slightly increases from about 2.40 eV to about 2.75 eV as the structure transforms from the rhombohedral to the orthorhombic structure. The magnetic properties are ferrimagnetic with $x = 0.05$, 0.3 and 0.7. However, the calculated Curie-Weiss temperature and constant of $La_{0.3}Gd_{0.7}CoO_3$ are not reasonable, it is probably due to a nonlocalized electronic state.

1. Introduction

In the past, $LnCoO_3$ (where Ln = La, lanthanides, or yttrium) has attracted an intensive interest because of its mercurial behaviors in response to the various distortions. As a classical perovskite (ABO_3), $LnCoO_3$ is composed of BO6 octahedral units with A^{3+} ions at the corners [1–4]. $LaCoO_3$ is a nonmagnetic insulator at the ground state, and a paramagnetic insulating state develops above about 50 K, and at around 500 K an insulator to metal transition is observed [5–7]. In general, either the La^{3+} ion or the Co^{3+} ion can be substituted by a variety of transition and non-transition metal ions. The relative ionic radii of the La, the Co and the substituted ions give rise to 'distorted' perovskite structures [8]. Patil et al. revealed a structure transition in $Ba_xLa_{1-x}CoO_3$ from the distorted rhombohedral to the cubic perovskite at $x = 0.4$ [9]. And Ryu et al. assigns the structure of $Gd_{1-x}Sr_xCoO_3$ with $x = 0.00$, 0.25, and 1.00 to the orthorhombic system, $x = 0.5$ to the cubic system, and $x = 0.75$ to the tetragonal system [10]. In this paper, we investigated the effect of the substitution of Gd^{3+} for La^{3+} on the crystal structure, the energy band gap variation and the magnetic properties of the $La_{1-x}Gd_xCoO_3$ compounds with the refined Powder x-ray diffraction (xrd) patterns, the Fourier transform infrared spectroscopies (FT-IR), UV–vis spectra and magnetic property measurements.

2. Experimental section

The $La_{1-x}Gd_xCoO_3$ ($x = 0.05$, 0.1, 0.2, 0.3, 0.5, 0.7) compounds are synthesized with solid state reaction. The starting materials La_2O_3, Gd_2O_3 and CoO with proper weights were ground in an agate mortar, and heated at 850 °C in the air for 12 h. Then the obtained powder was reground and fired at 1150 °C for 24 h and repeated this process for 3 times. The xrd measurements were carried out on Rigaku D/max2500 powder X-ray diffraction with Cu K_α radiation. The diffraction data were collected for the structure analysis, with the scan range 2θ from 5° to 80°, a scanning step of $2\theta = 0.01°$ and a sampling time 1 s. The x-ray photoelectric spectroscopy (xps) was carried out on Thermo escalab 250Xi with Al K_a photons (μ_B) and a hemispherical energy analyzer. The binding energy was calibrated using the C 1s level (248.6 eV) of the Carbon contamination. Fourier transform infrared spectroscopies (FT-IR) were obtained with the

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wave numbers ranging from 4000 cm^{-1} to 400 cm^{-1} via a NICOLET AVATAR 330 spectro-photo meter manufactured by Thermo Electron Corporation. The resolution was set at 2 cm^{-1} during the measurement. The ultraviolet–visible spectroscopies were obtained using a Perkin Elmer Lambda750 UV–visible spectrophotometer at room temperature with the wavelength from 200 nm to 800 nm with the sampling pitch 2 nm. The magnetic properties were measured with a commercial Quantum Design SQUID magnetometer in the temperature range of 5–400 K.

3. Results and discussion

With x = 0.05 and 0.1, the xrd patterns are refined as the rhombohedral structure with the space group *R*-3*c*. As x ≥ 0.2, the compounds crystallize in the orthorhombic structure with the space group *Pnma*. Fig. 1 shows the refined xrd patterns of $La_{0.9}Gd_{0.1}CoO_3$ and $La_{0.3}Gd_{0.7}CoO_3$, as representatives. It echoes with the earlier reports that the space group of $LaCoO_3$ is *R*-3*c* (JCPDF number: 50713) and that of $GdCoO_3$ is *Pnma* (JCPDF number: 154055) [11,12]. The doping Gd^{3+} fairly effectively lowers the crystal symmetry, as the space group transforms to *Pnma* with the Gd^{3+} content as low as 0.2. Table 1 lists the space groups, the lattice parameters, the refined atomic parameters, and the angle of Co–O–Co bond. Considering that the relationship between the lattice parameters (a_r and c_r) of the rhombohedral structure and those (a_o b_o, and c_o) of the orthorhombic structure is expressed as μ_B, μ_B, σ. Both of a_r (or a_o) and the volume monotonously decrease with the increasing doping Gd^{3+} content x. The lattice contraction is consistent with the smaller ionic radius of Gd^{3+} than that of La^{3+}.

The lattice distortions are important factors in the perovskite oxide, and are described as the global distortion in terms of the tolerance factor t and the local distortion σ telling the different ionic radii at A-site. The tolerance factor is *hν* and the local distortion is $\sigma^2 = (1-x)r_{La}^2 + xr_M^2 - \langle r_A \rangle^2$, with $r_A = (1-x)r_{La^{3+}} + xr_{Gd^{3+}}$, where the ionic radii of the Co, the O, the La^{3+} and Gd^{3+} ions are $r_{Co} = 0.61\AA$ $r_O = 1.35\AA$, $r_{La^{3+}} = 1.36\AA$ with the coordination number as 6. Table 1 lists the tolerance factor t and the local distortion σ^2. The calculated lattice distortions, both the global and the local, increases with the substitution of Gd^{3+} for La^{3+}, i.e., the tolerance factor deviates from 1 and the local distortion deviates from 0, as illustrated in Table 1. For $La_{0.8}Gd_{0.2}CoO_3$, t = 0.9594 and $\sigma^2 = 0.01024$, the distortion becomes large enough to induce the crystal transformation from the rhombohedral (the space group *R*-3*c*) with a high symmetry to the orthorhombic (*Pnma*) structure with a low symmetry.

The xps spectra can give the information of the valence state. Fig. 2 shows the Co $2p_{3/2}$ core level peaks of the xps spectra of $La_{0.95}Gd_{0.05}CoO_3$ with the highest intensity. Before evaluating the xps data, the background is linearly corrected. The interpretation of the Co $2p_{3/2}$ peak is based on two contributions, Co^{3+} and $Co^{8/3+}$. One peak is located at 780.03 eV, which resembles the binding energy in Co_2O_3 [15]. The other one at 781.63 eV is related to the binding energy in Co_3O_4 [15]. The integral peak areas were employed to calculate the concentration ratios of Co^{+3} and $Co^{+8/3}$ with the formula $t_{2g}^4 e_g^1$, where $S = 3/2$ and $t_{2g}^3 e_g^2$ are the concentrations of atoms of types A and B, and $S = 5/2$ and *hν* denote peak

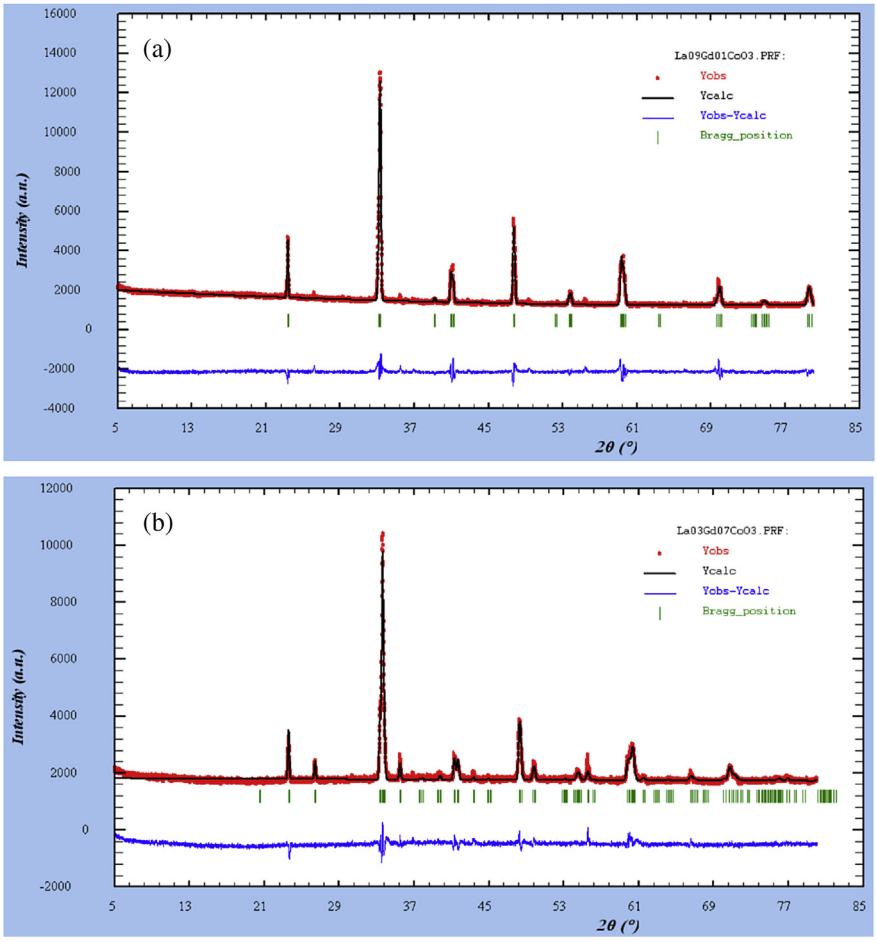

Fig. 1. The xrd diffraction patterns of $La_{1-x}Gd_xCoO_3$ (x = 0.1 and 0.7).