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# Effects of Doping on the Structural Distortion of $La_{0.7}Dy_{0.3}Mn_{1-x}Zn_xO_3$

J.F. López[a,*], M. Ríos[a,b] and G.A. Mendoza[a]

[a]Magnetic Materials and Nanostructures Group, Faculty of Science, Universidad Nacional de Colombia, Carrera 45 No 26-85, Bogotá, Colombia

[b]Department of Basic Science, ECCI University, Bogotá, Colombia

Structural properties were studied in the orthorhombic perovskite $La_{0.7}Dy_{0.3}Mn_{1-x}Zn_xO_3$, synthesized in the range $0 \leq x \leq 0.4$. X-ray diffraction data, refined by the Rietveld analysis, shows for $x < 0.1$ the presence of stretched octahedra on the Mn–O plane, and, for $x > 0.1$, the existence of elongated octahedra along the $c$ axis. Increased Zn doping causes a direct structural effect: one Zn atom distorts four neighboring $MnO_6$ octahedra on the Mn–O plane. It was observed that the unit cell volume containing Dy decreases as $x$ increases, whereas the unit cell volume containing La increases as $x$ decreases.

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## I. Introduction

The $MnO_6$ octahedron, a basic unit in perovskite manganites, which is a fermion system with a degenerate partially occupied highest molecular orbitals, spontaneously deforms in such a way that the degeneracy is lifted. This phenomenon, known as the Jahn–Teller (JT) effect [1], is a structural phase transition driven by the coupling between the orbital state and the vibronic configuration of the crystal lattice. The JT coupling to the lattice manifests itself in changes of Mn–$O_i$ bond lengths $L_i$ and Mn–$O_i$–Mn angles $\theta_i$, as well as in orbital order [2, 3]. The JT split states appear as a mixing of the degenerate states, which depend parametrically on the JT distortions, i.e., distorted rotated and tilting octahedra that bind to other octahedra with a specific Mn–O–Mn bond angle. Recently, reports indicate that JT-induced orbital polarization effect can lead to orbital ordering in manganite oxides [4]. This novel problem, which relates the orbital texture to the JT effect, requires complete detailed knowledge of the distortion present on these kinds of materials. In this study, $La_{0.7}Dy_{0.3}Mn_{1-x}Zn_xO_3$ was synthesized to study the effect of doping on the structural distortion.

## 2. Experimental

The $La_{0.7}Dy_{0.3}Mn_{1-x}Zn_xO_3$ polycrystalline samples in the doping range $0 < x < 0.4$ were prepared by solid-state reaction method. In this process, stoichiometric amounts of the precursor reagent $La_2O_3$, $DyO_3$, $Mn_2O_3$ $ZnO_2$+OH were homogenized and calcined at 1000 °C for 24 h. X-ray powder diffraction patterns were taken at room temperature, using a Philips PW1710 diffractometer with copper target through $2\theta$ step size of 0.02° with a counting time of 60 s for each step. The Rietveld refinements were performed using the FullProf software [5] and using pattern files data base COD [6].

## 3. Results and discussion

The observed and calculated diffraction profile obtained from the Rietveld analysis for these samples with $x = 0.2$ is shown in Fig. 1(top). All the peaks observed were indexed in three phases: two orthorhombic phases (*Pbnm* and *Pnma*) and one trigonal phase (*R*-3*C*). The trigonal phase disappeared by calcination at 1100 °C for 24 h. Bond angles and bond lengths were calculated from the 3D diagrams (Fig. 1(left)). We calculated the samples' structural parameters considering the $LaMnO_3$ as orthorhombic. The results are listed in Table I.

TABLE I

Structural parameters of $La_{0.7}Dy_{0.3}Mn_{1-x}Zn_xO_3$. $n_1$ — fraction of orthorhombic phase *Pbnm*: $LaMn_{1-x}Zn_xO_3$, $n_2$ — fraction of orthorhombic phase *Pnma*: $DyMn_{1-x}Zn_xO_3$

| $x$ = | 0 | 0.1 | 0.2 | 0.3 | 0.4 |
|---|---|---|---|---|---|
| $\theta_1$ [°] | 157.98 | 165.21 | 156.69 | 156.72 | 152.45 |
| $\theta_2$ [°] | 157.39 | 150.73 | 147.66 | 145.57 | 146.25 |
| $L_1$ [Å] | 1.9922 | 1.9758 | 1.9870 | 1.9857 | 2.0070 |
| $L_2$ [Å] | 1.9439 | 1.9793 | 2.0114 | 2.0240 | 2.0193 |
| $n_1$ | 0.21 | 0.51 | 0.50 | 0.50 | 0.48 |
| $n_2$ | 0.25 | 0.25 | 0.23 | 0.24 | 0.22 |

Figure 2 shows $L_2 > L_1$ for $x < 0.1$, which implies stretched octahedra, while $L_1 > L_2$ for $x > 0.1$ corresponds to elongated octahedra along the $c$ axis. At $x = 0.1$, $L_1 \approx L_2$ implies that the octahedra are non-distorted.

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[*] corresponding author; e-mail:

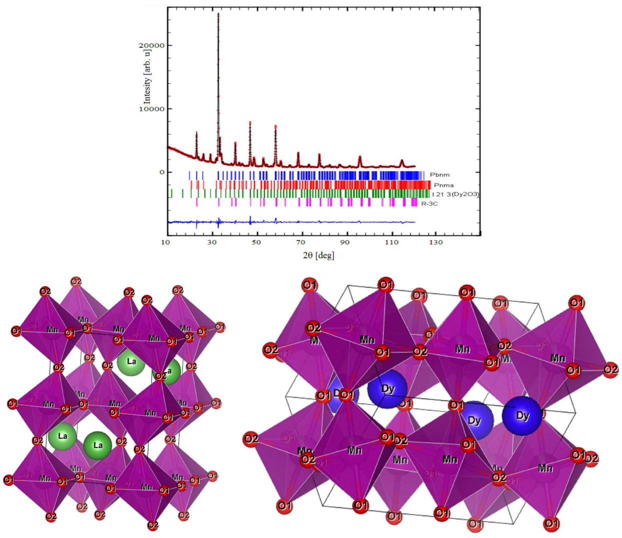

Fig. 1. (top) XRD Rietveld refinement results for $La_{0.7}Dy_{0.3}Mn_{0.8}Zn_{0.2}O_3$ sample. (left) $LaMn_{1-x}Zn_xO_3$ orthorhombic structures and (right) $DyMn_{1-x}Zn_xO_3$ orthorhombic structures.

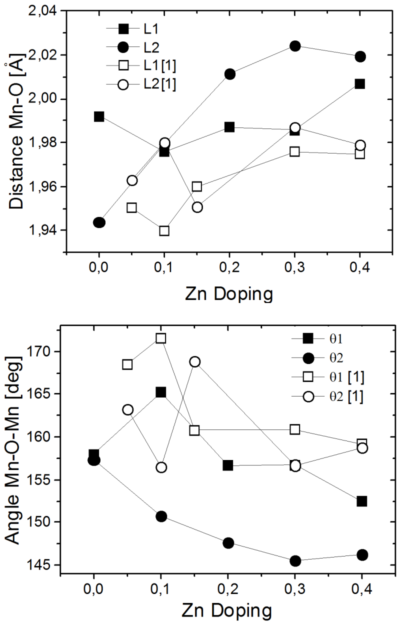

Fig. 2. Structure parameters of $La_{0.7}Dy_{0.3}Mn_{1-x}Zn_xO_3$ (top) $L_1$ (filled squares), $L_2$ (filled circles) compared to bond distances reported (open symbols) [9]. (bottom) Tilting $\theta_1$ (■) and tilting $\theta_2$ (●) compared to angles reported for $La_{0.7}Mn_{1-x}Zn_xO_3$ (open symbols) [9].

TABLE II

Volume of the unit cell.

| $XMn_{1-x}Zn_xO_3$ | $V$ [Å$^3$], $XMn_{1-x}Zn_xO_3$ | | |
|---|---|---|---|
| concentration | La [9] | La (*Pbnm*) | Dy (*Pnma*) |
| $x = 0.1$ | 233.8 | 235.4 | 226.1 |
| $x = 0.2$ | 235.2 | 235.9 | 224.2 |
| $x = 0.4$ | 236.6 | 236.21 | 223.1 |

Note, from Table II, that the unit cell volume of the $LaMn_{1-x}Zn_xO_3$ (*Pbnm*) phase increases as $x$ increases, agreeing with reports by other authors [7, 8, 10]. This change in the cell volume is expected because the Zn radius is greater than the Mn radius.

On the contrary, the unit cell volume in the $DyMn_{1-x}Zn_xO_3$ (*Pnma*) orthorhombic phase decreases even though $x$ increases. Given that the atomic radius of Dy is smaller than that of La, we suggest that the Dy allows the enlarged octahedra (by the Zn inclusion) to tilt into the cell, reducing the net volume of the cell.

## 4. Conclusions

$La_{0.7}Dy_{0.3}Mn_{1-x}Zn_xO_3$ was synthesized in the range $0 < x < 0.4$. Change in bond length and bond angles, depending on $x$, can be attributed to a distortion of four neighboring octahedra on the Mn–O plane by one $Zn^{2+}$.

The relationship between $L_2$ and $L_1$ shows two regions: the first for $x < 0.1$, where stretched octahedra are present; the second for $x > 0.1$, where elongated octahedra along the $c$ axis are present. For $x = 0.1$, the octahedra are non-distorted.

The presence of Dy allows increasing the octahedra tilting, reducing the cell volume.

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