Spin-phonon coupling in rare-earth based manganites with double perovskite structure plays a crucial role in the magnetoelectric properties of these ferromagnetic materials. Particularly, on Y$_2$CoMnO$_6$ (YCMO), it is assumed that spin-phonon coupling is related to the induced ferroelectric polarization. This confers to YCMO a multiferroic characteristic. In this work, we probed the spin-phonon coupling in YCMO by temperature-dependent Raman spectroscopy measurements in ceramic samples obtained by the nitrate decomposition method. Raman scattering revealed some anomalies that could be attributed to a weak spin-phonon coupling, an unconventional behavior for rare-earth based manganites with double perovskite structure, in which the coupling does not fit with the quadratic magnetization.

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1. Introduction

Rare-earth based manganites with double perovskite structure RE$_2$BMnO$_6$ (RBMO), in which RE is a rare-earth and B is commonly Ni or Co, has been intensively investigated in last years, mainly due to their multiferroic and magnetoelectric properties [1–4]. In these compounds, as in other perovskites with two different transition metal (TM) cations in the B-sites, there are some factors that can greatly affect the resulting magnetic and electrical properties. Among them, the degree of B–Mn site order, which will decrease as Mn and B ions interchange the occupied sites, the different valencies of the TM cations and the oxygen stoichiometry of the samples.

The ferromagnetic properties of these rare-earth based manganites RE$_2$BMnO$_6$ can be well understood on the basis of superexchange interactions [5]. Nevertheless, their ferroelectric characteristics and the microscopic model to explain the ferroelectric observation, still need more elucidation. For example, in completely disordered La$_2$NiMnO$_6$ (LNMO) nanoparticles, Masud et al. [6] observed a relaxor ferroelectric behavior correlated to the ferromagnetism, due to the polarized nano-regions (PNRs) that originated from Ni$^{2+}$ and Mn$^{4+}$ antisite disorder. However, Bahooosh et al. [7] proposed a mechanism in which the ferroelectricity is driven by A-site displacements, as it happens in Bi-based multiferroic systems; while Kumar et al. [3] proposed a model for ferroelectricity, based on density functional theory (DFT) calculations for the Y$_2$NiMnO$_6$ (YNMO) perovskite, that is driven by the displacement of all ions. In addition, Lu$_2$CoMnO$_6$, which has a strong ferromagnetic-dielectric coupling [8,9], exhibits a magnetic-induced ferroelectric polarization due to magnetic domain boundaries between alternating Co and Mn layers along the c-axis [9].

Recently, Sharma et al. [2] observed a magnetically-induced ferroelectric transition in Y$_2$CoMnO$_6$ (YCMO), which undergoes a
ferromagnetic transition at $T_C = 80$ K and this ferromagnetic state generates ferroelectricity. In addition, new interesting properties were observed in this compound, such as disorder-induced exchange bias and multicaloric effects [10,11].

To explain the magnetically-induced ferroelectricity in YCMO Sharma et al. [2] proposed a qualitative model based on the spin-phonon coupling, effect that has been extensively investigated in rare-earth double perovskites [12–18] due to its correlation with magnetodielectric response of $\text{RE}_2\text{BMO}_6$ compounds. A powerful tool to detect such coupling, even in systems in which the coupling is weak, is Raman spectroscopy [19–21]. This technique also allows to elucidate the spin-phonon coupling origin, if it is direct or if it is due to magnetostriction [22].

In this work, we have investigated the temperature dependence of the Raman spectra of the ordered YCMO compound in order to understand how the coupling between the lattice and magnetic order happens to obtain information about the mechanism of phase transition, which according to the literature, occurs around $T_C = 80$ K [2].

2. Experimental details

$\text{Y}_2\text{CoMnO}_6$ (YCMO) sample was prepared by the nitrate decomposition method. For this purpose, $\text{Y}_2\text{O}_3$, previously treated at 1000 °C/4 h, was converted into the corresponding nitrate by dissolution in 30% nitric acid. The resulting product was then added to an aqueous solution in which stoichiometric amounts of $\text{Co(NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Aldrich, 98%) and $\text{Mn(NO}_3)_2\cdot 5\text{H}_2\text{O}$ (Aldrich, 98%) were also dissolved. The resulting solution was heated to remove the solvent and the organic matter was subsequently decomposed at 400 °C. The obtained precursor powder was ground, pelletized and then treated at 800 °C/60 h, 900 °C/24 h, 1000 °C/24 h and 1100 °C/48 h with intermediate regridings. Moreover, in the last two thermal treatments, the sample was slowly cooled to room temperature at 42°C/h.

The crystalline structure of the sample was characterized by X-ray powder diffraction (XRPD) using a Siemens D-5000 diffractometer with Cu (Kα) $\lambda = 1.5418$ Å radiation. XRPD data were collected with a step of 0.015° between 20° and 80° during 12 h and then were inspected using Match software [23] to identify the crystallographic phases present.

In addition, synchrotron X-ray powder diffraction (SXRPD) studies were carried out at 300 K on the BM25A beamline ($\lambda = 0.8261$ Å) at the ESRF (Grenoble, France). For this purpose, the samples were loaded in a borosilicate capillary ($\phi = 0.3$ mm) and rotated during data collection. The Rietveld analysis were performed with Fullprof program [24], where the atomic positions, lattice and thermal parameters were refined until convergence. The peak shape was described as a pseudo-Voigt function and the background was refined with a 6-coefficients polynomial function. Furthermore, using Bond Valence Sum (BVS) the Mn and Co cations charges were estimated from the obtained bond distances [25,26].

Iodometric titrations were carried out to analyze the oxygen content of the material. For this purpose, the sample was dissolved in acidified KI solutions and the $I_2$ generated was titrated against a thiosulphate solution. The whole process was carried out under an argon atmosphere.

Magnetic properties were studied in a Quantum Design MPMS SQUID magnetometer. The magnetic susceptibility was measured in the temperature range from 5 K up to 300 K, applying a magnetic field of 1000 Oe. The measurements were performed in cooling conditions without field, ZFC (Zero Field Cooled) and with field, FC (Field Cooled), collecting the data at intervals of 5 K. Hysteresis loops in ZFC conditions were obtained at 5 K varying the field up to $\pm 50$ kOe.

Raman spectroscopy measurements were performed in a Horiba spectrometer model iHR550. A 630 nm HeNe laser radiation was taken to the sample through an Olympus microscope model BX30 equipped with a long-working distance objective ($20\times$, 20.5 mm) lens. The scattered light was collected in a Horiba peltier-cooled CCD detector model Synapce. The slits were set to achieve a precision of 1 cm$^{-1}$ in the peak position. Temperature-dependent measurements were performed with the sample inside a He closed-cycle CRYO cryostat, using a temperature controller LakeShore model 330. The Raman spectra were fitted with lorentzians using the software FitYk (Version 0.9.8).

3. Results and discussions

According to X-ray diffraction measurements this sample is single phase and can be indexed in the monoclinic space group $P2_1/n$. On the other hand, the results of the iodometric titrations indicate that the sample has a very small oxygen deficiency (3) of 0.02. The room-temperature SXRPD pattern and its refinement are shown in Fig. 1. Following the structure determined for $\text{La}_2\text{MnCoO}_6$ [27,28], and a model proposed for $\text{Y}_2\text{MnCoO}_6$ [29], the constraint of complete transition-metal cationic ordering was imposed to this refinement (Wyckoff positions 2$c$ and 2$b$ sites for the Mn and Co cations, respectively). That is, a full Mn–Co B-site order, obtaining a very good agreement. The obtained structure is shown as an inset in Fig. 1. According to this Rietveld refinement, at room temperature YCMO shows lattice parameters $a = \sqrt{2}/2$, $b = \sqrt{2}/2$, $c = 2a_p$, as indicated in Table 1 (the subscripts “p” refers to the pseudocubic lattice), and $\text{Mn}–\text{O}$ and $\text{Co}–\text{O}$ averaged bond distances of 2.11 Å and 1.87 Å, respectively (more details are shown in Table 2). The average superexchange $\text{Mn}–\text{O}–\text{Co}$ angle is around 145°, which is a relatively low angle. This small value is due to the high monoclinic distortion compared to the cubic aristotype structure for double perovskite. When the double perovskites are cubic, they have a Co–O–Mn angle equal to 180°, which gives the maximum super-exchange interaction between Co$^{2+}$ (occupied t$_2g$ and half-filled e$_g$ orbitals) and Mn$^{4+}$ (occupied t$_2g$ and empty e$_g$ orbitals) mediated by oxygens from the Co$^{2+}$–O–Mn$^{4+}$ bonds [5]. However, due to the small iodric radii of Y, the (B,Mn)O$_6$ octahedra tilts to accommodate. 

![Fig. 1. Synchrotron X-ray powder diffraction data for $\text{Y}_2\text{CoMnO}_6$. The red spheres indicate the SXRPD measured data, the black line the SXRPD refined data, the blue line the difference between the measured and the refined data, and the green tickmarks the positions of the allowed Bragg reflections. The inset shows the unit cell of the here prepared B-site ordered double perovskite $\text{Y}_2\text{CoMnO}_6$, which crystallizes in a monoclinic $P2_1/n$ structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
Structural parameters we have calculated the BVS for YCMO, and the octahedral tilt notation, this monoclinic structure comes from the cubic one by the Wyckoff sites, which are special positions with atomic coordinates (0,0,0) and (0,1/2,0), respectively.

Table 1
- Structural parameters of the polycrystalline Y₂CoMnO₆ sample obtained for the Rietveld refinement of the SXRPD pattern. Mn and Co ions are in the 2c and 2b Wyckoff sites, which are special positions with atomic coordinates (0,0,0) and (0,1/2,0), respectively.

<table>
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<tr>
<th>Parameters</th>
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<tr>
<td>Space Group</td>
<td>P2₁/n</td>
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<tr>
<td>Number of molecules per unit cell, Z</td>
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</tr>
<tr>
<td>a (Å)</td>
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</tr>
<tr>
<td>b (Å)</td>
<td>5.5859(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.4694(2)</td>
</tr>
<tr>
<td>β (deg)</td>
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<tr>
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</tr>
<tr>
<td>Density, (gm/cm³)</td>
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</tr>
<tr>
<td>Independent atomic coordinates</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>x = 0.5185(3), y = 0.5725(2), z = 0.2500(5)</td>
</tr>
<tr>
<td>O₁</td>
<td>x = 0.3942(12), y = 0.9657(12), z = 0.2362(20)</td>
</tr>
<tr>
<td>O₂</td>
<td>x = 0.2060(20), y = 0.1810(20), z = -0.0506(16)</td>
</tr>
<tr>
<td>O₃</td>
<td>x = 0.3290(20), y = 0.7140(20), z = -0.0575(16)</td>
</tr>
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<td>Refinement data</td>
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</tr>
<tr>
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</tr>
<tr>
<td>χ²</td>
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</table>

The ions originating the monoclinic structure. According to Glazer’s notation, this monoclinic structure comes from the cubic one by the octahedral tilt a = c’ [30]. From the structural data, the octahedral tilts in YCMO are 21.22° and 23.52°. In addition, based on the structural data we have calculated the BVS for YCMO, and the obtained results confirm the presence of Co²⁺ and Mn⁴⁺ ions in our polycrystalline ceramic, as shown in Table 2.

Fig. 2 shows the temperature dependence of magnetic susceptibility curve obtained for YCMO. As it can be seen from Fig. 2, the reciprocal magnetic susceptibility follows the Curie-Weiss law χ⁻¹ = (T - θ)/C at high temperatures, whose linear fit shows a Weiss constant (θ) = 80 K, which is a value similar to those obtained by other authors [2,31].

Unfortunately, as the magnetization of this compound did not reach saturation under the maximum field applied, 50 kOe, we could not calculate the magnetic moment per unit formula. The same situation was observed in the case of the closely related Lu₂MnCoO₆ compound, for which a field of 60 T was required to achieve full magnetization [9].

However, the magnetization curve did not exhibit more than one magnetic transition, which is also indicative of a well ordered sample. In addition, considering its oxygen stoichiometry, the results of the structural studies and the BVS calculations are considered, we can assume that the here prepared material is a high quality sample containing the ordered (or almost fully ordered) double perovskite Y₂Co²⁺Mn⁴⁺O₆ compound.

Fig. 3(a) shows the Raman spectrum recorded for this YCMO sample at T = 10 K. At this temperature, the crystalline structure of YCMO holds the same monoclinic structure belonging to space group P2₁/n observed at room temperature, since no structural phase transitions have been reported for YCMO at low temperatures. Considering the group theory analysis based on site occupation in this structure, 24 Raman-active modes are predicted, whose distribution into the irreducible representation of the 2/m factor group is 12Aₑ + 12Bₐ. As Fig. 3(a) shows, we can observe 10 of these 24 Raman-active modes, but only 5 of these modes are intense enough to be observed in all the temperature range studied. This is a relatively large number of resolved modes at room temperature in based rare-earth manganites with double perovskite structure [32,33]. This can be understood based on the Y³⁺ ionic radius. In general, large ionic rare-earth radii, such as La³⁺, lead to relative minor distortions and small octahedral tilts. Consequently, the emerged modes from the low symmetry show weak intensity at low wavenumbers if we compare them with those of the original cubic Fm3m arysterite lattice [33]. Upon reduction of the ionic radii in the A site, those modes become more intense as observed in the YCMO Raman spectrum, and also in isostuctural Y₂NiMnO₆ [16]. Also, more distorted lattices, as it happens when containing RE ions with small ionic radii, tend to split more the degenerate modes due to the distortion.

Previous works were able to define the symmetry of Raman-
active modes in rare-earth based manganites with double perovskite structure using polarized Raman spectroscopy [33–35]. In YCMO, the spectrum at 10 K is dominated by the commonly observed strong peak, observed at 634 cm$^{-1}$, which have been assigned to stretching vibrational mode of (Co/Mn)O$_6$, which is like a breathing mode, whose symmetry is $A_g$. At the central part of the spectrum, near the broad band at 543 cm$^{-1}$ and the sharp mode at 514 cm$^{-1}$, are expected several weak modes of $A_g$ and $B_g$ symmetries associated with octahedra antistretchings or bendings. Also, based on the reported polarized Raman spectra [32–35], the main modes observed at 634, 348, 307 and 272 cm$^{-1}$ can be assigned with $A_g$ symmetry, whereas the modes at 514 and 475 cm$^{-1}$ have $B_g$ symmetry.

Under temperature changes, as the sample was cooled down, a systematic increase in the Raman intensity was observed in both regions of the spectrum. Nevertheless, no remarkable changes were observed in the spectra, which is in agreement with the absence of structural phase transition in this temperature range (see Fig. 3(b) and (c)). The temperature dependence of the main wavenumber positions is shown in Fig. 4. We observe that at least two Raman-active modes show an evident softening near critical temperature $T_C = 80$ K. The position of these modes exhibit a deviation from the expected temperature dependence due to the purely anharmonic contribution, which was modeled by the Balkanski’s function [36], as

$$\omega(T) = \omega_0 - C \left[ 1 + \frac{2}{(e^{\frac{\theta}{k_B T}} - 1)} \right]$$  \hspace{1cm} (1)

where $C$ and $\omega_0$ are adjustable parameters, specific for each material and they are indicated as a red line in Fig. 4. This anomalous behavior is commonly associated to the renormalization of the phonons induced by the magnetic ordering due to a coupling between spin and phonons. However, while it is commonly observed only a single spin-phonon coupling in rare-earth based manganites with double perovskite structure when they are B-site ordered [13,16,34,35,37], in YCMO we have observed the spin-phonon coupling at least in two phonons, which is unconventional for double perovskites, where it is observed only in the stretching phonon. This multiple spin-phonon feature was confirmed by the relative Raman intensity of two modes in relation to the stretching one, which is shown in Fig. 5. We can see that the relative intensity of these modes decreases down to a minimum at the magnetic transition and turns to increase again for lower temperatures.

To understand the magnetostriction role in these couplings, we have investigated the dependence of the full-width-at-half-maximum (FWHM) of some selected modes, which is shown in Fig. 6. FWHM is related to the phonon lifetime and is not or slightly affected by magnetostriction features [22,38]. Although we can see a slight plateau between 80 and 40 K in the stretching mode’s FWHM, similar to that observed in Tb$_2$NiMnO$_6$ (TNMO) [13], this anomaly is very subtle. Also, the other phonons do not exhibit any anomaly. The absence of a remarkable anomaly on FWHM has been associated to spin-phonon coupling driven by magnetostriction effects, as it was observed in other yttrium-based multiferroics [2,39], in which magnetostriction effects due to the frustration behavior are common [40]. In addition, this result confirms the theoretical predictions by Density Functional Theory (DFT) about the E*-AFM state as the ground state, promoter of magnetostrictive properties of YCMO [41].

Also, according to a mean field approximation and considering nearest neighbor interaction, the spin-phonon coupling contribution to the stretching phonon position in perovskites is given by Ref. [17]:

$$\left|\frac{\Delta \omega_{ph}}{\omega_{ph}}\right|_{\text{street}} \propto \left(\frac{M(T)}{M_0}\right)^2$$  \hspace{1cm} (2)

In Fig. 7, we compare the position deviation, which is the spin-phonon contribution, of the symmetrical stretching phonon in relation to the square magnetization. We can see clearly that $\left|\Delta \omega_{ph}\right|$ does not fit $\left(\frac{M(T)}{M_0}\right)^2$ linearly, as it is shown in Fig. 7. In fact, $\left|\Delta \omega_{ph}\right|$ exhibits a squared dependence with the temperature.

This unconventional behavior exhibited by YCMO, compared to other double perovskites, can be associated to a competition between FM and AFM magnetic states due to their frustrated Ising spin chain ($E^*$-type) with $\uparrow \uparrow \downarrow \downarrow$ spin pattern [2,9,40,41]. Also, it can be associated to antisite disorder [30], that might lead to magnetic frustration due to the competing magnetic exchange interactions, Co$^{2+}$–O–Co$^{2+}$ (AFM), Mn$^{4+}$–O–Mn$^{4+}$ (AFM) and Co$^{2+}$–O–Mn$^{4+}$ (FM). Order-disorder effects are usual in samples of this compound because of the small difference in charge and ionic radii of the TM occupying the B sites [42]. Nevertheless, the sample studied here shows a large degree of cationic order, even if the presence of a
Fig. 4. Temperature dependence of (a) the typical Ag stretching mode, and (b–d) other main modes observed in YCMO. The red line denotes the expected mode position behavior under temperature changes obtained considering only the anharmonic model. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Temperature dependence of the normalized Raman intensities. The intensity of all present modes were calculated as a function of the intensity of the strongest mode at 634 cm\(^{-1}\).

Fig. 6. Temperature dependence of the Raman line widths (FWHM). The inset displays the curve that corresponds to peaks at 634 cm\(^{-1}\) that shows a slight slope change between 40 and 80 K.
small amount of antisite disorder (less than 10% [9]) can not be completely discarded and could also contribute to the observed anomaly [31]. Recently, neutron diffraction measurements have confirmed the coexistence of both ferromagnetic and antiferromagnetic interactions in YCMO [2], as it had also the case in the deeply investigated Lu$_2$MnCoO$_6$ compound [9]. A similar deviation from the mean field approximation model was observed in the La$_2$CoMnO$_6$ spin-phonon analysis [43]. Different value and signs of $\eta_j$’s can produce different contributions to the phonon renormalization induced by magnetic ordering, as observed for glassy Gd$_2$CoMnO$_6$ [44], which showed a phonon hardening at the magnetic transition, suggesting that the magnitude of the spin-phonon interaction at 80 K. However, other coupling, different from that usually mediated by magnetic ordering, as observed for glassy Gd$_2$CoMnO$_6$ [44], which showed a phonon hardening at the magnetic transition, suggesting that the magnitude of the spin-phonon interaction at 80 K. However, other coupling, different from that usually mediated by magnetic ordering, may be responsible for the stabilization of the E*-type magnetic structure (for instance a J

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