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Abstract
LaYbO₃ is a highly distorted perovskite with orthorhombic structure. However, its exact space group has been a matter of debate. Both the polar $Pna2_1$ and the centrosymmetric $Pnma$ space groups, with $Z = 4$, have been proposed to describe its structure at room temperature. In this work we present optical spectroscopic investigations by Raman scattering and infrared reflectivity of LaYbO₃ ceramics sintered at 1600 °C. The results allowed us to propose a new centrosymmetric $Cmcm$ space group for this compound, and to show which phonons give the main contributions to its dielectric constant and quality factor at microwave frequencies.

1. Introduction

The rapid evolution of wireless telecommunication and satellite broadcasting leads the research on new materials with relatively high dielectric permittivity (ε' ranging from 20 to 80), high unloaded quality factors ($Q_u \ldots f \sim 20\,000$ GHz) and low temperature coefficient of variation of the resonance frequency (τ_f). These requirements satisfy the needs of miniaturization, selectivity and thermal stability of the devices, respectively [1].

We are now interested in the ceramic material LaYbO₃. This interlanthanide oxide crystallizes in a distorted perovskite structure; nevertheless, its crystal structure has been the subject of debate and controversy. The polar $Pna2_1$ space group, with atomicity $Z = 4$, was first proposed to describe its structure [2]. Thus, this system would belong to a family that includes CdTiO₃, GdFeO₃ and NaTaO₃ crystals [2, 3]. However, GdFeO₃ and NaTaO₃ were later described as belonging to a different orthorhombic space group, the

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centrosymmetric *Pnma* one, with the same atomicity ($Z = 4$) [4, 5]. This structure has been proposed more recently as being the correct one for LaYbO$_3$, from Rietveld analysis of x-ray diffractograms [6].

The microwave (MW) dielectric response of any material is determined by the behaviour of its polar phonon modes (intrinsic contributions, depending on the crystalline structure) together with extrinsic contributions coming from space charges, domain walls and imperfections linked to the sample morphology. Then, in order to investigate the potential of a given material to MW applications (resonators or filters), the knowledge of its polar phonons is mandatory. Thus, we have decided to determine the phonon modes of LaYbO$_3$ by measuring its phonon spectrum by Raman and infrared spectroscopies. The results should also allow us to contribute to the debate on the crystalline structure of this system. As it will be shown by group theory analysis, the results revealed that the correct space group would be different from those previously proposed. If this is the case, it is possible to determine the complete set of phonon modes of the material, and then the intrinsic dielectric losses and polarization of the system in the MW region.

2. Experimental details

LaYbO$_3$ ceramics were prepared by using the conventional mixed oxide route. The starting materials were high-purity grade La$_2$O$_3$ and Yb$_2$O$_3$ powders, weighed according to the required equimolar ratio and mixed by ball milling in n-propanol for 20 h. The dried slurries were calcined in air at 1400 °C. Purity and crystallinity were determined by x-ray diffraction. The calcined powders were finely milled and shaped into pellets under isostatic pressure of 200 MPa. The green compacts were fired at 1600 °C for 4 h in air, using controlled heating and cooling rates of 5 and 3 °C min^{-1}, respectively. The final sample dimensions were 10 mm diameter and 8 mm thickness. The obtained ceramics were dense, showing experimental densities above 97% of their theoretical densities. The dielectric properties at MW frequencies were measured by the resonant post (Hakki and Courtney) method using a network analyser (model 8720D, Hewlett-Packard, Palo Alto, CA) [7, 8]. Silver cavities were used to measure the temperature coefficient of the resonance frequency. The results showed ε_r, τ_f and $Q_u \cdot f$ values of 16.1, -22 ppm K^{-1} and 20 500 GHz (at 11 GHz), respectively. Its negative τ_f makes it suitable for combining with materials having a positive τ_f, such as alkaline earth titanates.

The Raman spectra of the light scattered by the crystals were collected in back-scattering configuration by using a Olympus microscopy attached to a Jobin-Yvon LabRam-HR spectrometer. The 632.1 nm line of a He–Ne laser (12.5 mW) was used as exciting line and the detection was done by an LN$_2$-cooled CCD detector. The spectral resolution was better than 2 cm^{-1} and the accumulation times were typically 20 collections in 10 s. All the spectra were divided out by the Bose factor [9] before being fitted by a sum of Lorentzian lines. For the infrared reflectivity measurements, we used a BOMEM-DA8 Fourier-transform infrared spectrometer, equipped with a fixed-angle specular reflectance accessory (external incidence angle of 11.5°). In the mid-infrared region (500–4000 cm^{-1}), the spectra were recorded using a SiC (Globar) source, a Ge-coated KBr beamsplitter, and a liquid-nitrogen-cooled HgCdTe detector. In the far-infrared range (50–600 cm^{-1}), we used the same source, but a 6 μm coated Mylar Hypersplitter® and a liquid-helium-cooled silicon bolometer. The measurements were performed under vacuum (10^{-4} bar), at 4 cm^{-1} of spectral resolution, with 64 scans. As reference spectrum we used a 'rough' mirror, obtained by coating a thin gold film onto one of the sample surfaces. This mirror mimics the surface, correcting the spectrum by reducing the losses by diffusion of the light.
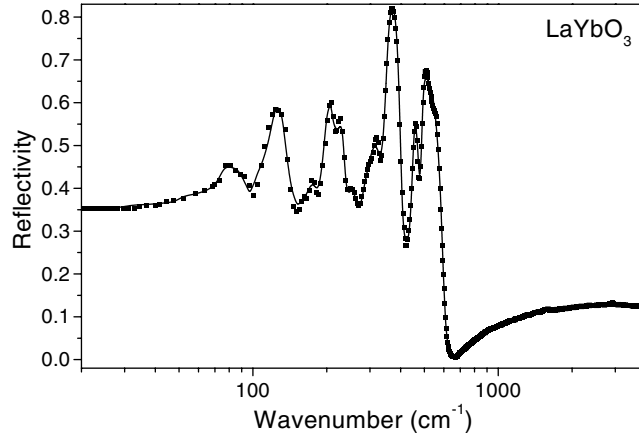
Figure 1. Measured (square symbols) and adjusted (solid curve) infrared reflectance spectra for a LaYbO$_3$ ceramic.

3. Results

3.1. Infrared reflectance

The infrared reflectance spectrum of LaYbO$_3$ is presented in figure 1. This spectrum has been analysed by using the four-parameter semi-quantum model [10], using a non-linear least-squares program [11]. According to this model, the infrared phonon contribution to the complex dielectric function $\varepsilon(\omega)$ is given by

$$\varepsilon(\omega) = \varepsilon_\infty \prod_{j=1}^{N} \frac{\Omega_{j,\mathrm{LO}}^2 - \omega^2 + i\omega\gamma_{j,\mathrm{LO}}}{\Omega_{j,\mathrm{TO}}^2 - \omega^2 + i\omega\gamma_{j,\mathrm{TO}}}, \tag{1}$$

where ε_∞ is the dielectric constant due to the electronic polarization contribution; $\Omega_{j,\mathrm{LO}}(\Omega_{j,\mathrm{TO}})$ and $\gamma_{j,\mathrm{LO}}(\gamma_{j,\mathrm{TO}})$ are the frequency and damping of the jth longitudinal (transverse) optical modes, respectively. N is the number of polar phonons. At quasinormal incidence, the dielectric function is related to the optical reflectance R by the Fresnel formula:

$$R = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2. \tag{2}$$

Equations (1) and (2) were used to fit the experimental data and the results are also presented in figure 1, as a solid curve. Then, we could obtain the wavenumbers and widths of the transverse (TO) and longitudinal (LO) infrared modes, which are listed in table 1. We note firstly that 13 infrared modes were discerned for this material. We will discuss this feature in detail, compared with group theory predictions, later, after presenting the Raman results. Once the infrared modes are determined, the oscillator strengths of the individual jth TO modes can be obtained by

$$\Delta\varepsilon_j = \frac{\varepsilon_\infty}{\Omega_{j,\mathrm{TO}}^2} \frac{\prod_k \left(\Omega_{k,\mathrm{LO}}^2 - \Omega_{j,\mathrm{TO}}^2 \right)}{\prod_{k \neq j} \left(\Omega_{k,\mathrm{TO}}^2 - \Omega_{j,\mathrm{TO}}^2 \right)}. \tag{3}$$

Table 1. Dispersion parameters calculated from the fit of the infrared reflectance spectrum of LaYbO$_3$. The positions (Ω) and damping constants (γ) are given in cm^{-1}.

$\Omega_{j,\text{TO}}$	$\gamma_{j,\text{TO}}$	$\Omega_{j,\text{LO}}$	$\gamma_{j,\text{LO}}$	$\Delta\varepsilon_j$	$10^6 \tan\delta_j/\omega$
88.5	10.9	90.4	12.9	0.857	72.7
125.6	10.5	138.2	31.5	3.066	124.4
177.5	20.2	181.4	20.8	0.593	23.2
201.1	12.6	202.0	43.2	0.121	2.2
231.2	16.3	236.2	14.1	0.709	13.2
263.4	33.2	266.7	23.3	0.443	12.9
314.0	50.7	331.4	35.1	2.708	84.9
351.5	17.7	403.9	27.3	2.108	18.4
417.2	47.9	429.6	44.5	0.206	3.5
449.6	21.6	464.0	75.7	0.356	2.3
479.4	119.8	479.8	26.3	0.033	1.0
487.1	18.4	599.7	39.8	0.671	3.2
673.7	148.9	677.9	130.5	0.019	0.4

| $\varepsilon_\infty = 4.51$ | | | $\varepsilon_O = 16.40$ | | |

Now, the static (infrared) dielectric constant, which corresponds to the intrinsic MW dielectric constant, can be obtained by adding the oscillator strengths over all modes, i.e.,

$$\varepsilon_O = \varepsilon_\infty + \sum_{j=1}^{N} \Delta\varepsilon_j. \tag{4}$$

The values of ε_j, ε_O, and ε_∞ for LaYbO$_3$ are given in table 1, together with the phonon modes. Now, we remark that the intrinsic unloaded quality factor in the MW region, Q_u, can be calculated as the reciprocal of the dielectric loss tangent ($\tan\delta$), in the limit where $\Omega_{j,\text{TO}} \gg \omega$, which leads to

$$\tan\delta = \sum_j \tan\delta_j = \sum_j \omega \frac{\Delta\varepsilon_j \gamma_{j,\text{TO}}}{\varepsilon_O \Omega^2_{j,\text{TO}}}. \tag{5}$$

The low frequency dielectric constant and the calculated quality factor based on the adjusted infrared data were respectively $\varepsilon_O = 16.4$ and $Q_u \cdot f = 82\,800\,\text{GHz}$. The intrinsic (FTIR) ε_O is in good agreement with the MW measurements. However, the intrinsic $Q_u \cdot f$ is clearly higher than the extrinsic one (MW), showing that the dielectric losses at MW are mainly extrinsic. The actual sources of these losses are not clear yet and are under investigation.

3.2. Raman scattering

The Raman spectrum of LaYbO$_3$ is presented in figure 2(a). We observe now 12 well defined bands, whose positions and widths, after fitting, are summarized in table 2. Although the bands are relatively narrow, a direct comparison of the peak positions of the Raman and infrared bands is relatively complex. Instead, we can compare the Raman spectrum with the imaginary parts of ε and $1/\varepsilon = \eta$, which are presented in figure 2(b). These functions give, respectively, the characteristics (position, width and strength) of the transverse and longitudinal polar optical modes. For the systems belonging to centrosymmetric groups, Raman and infrared phonons are mutually exclusive, because the base functions of their representations have opposite parities, even or odd. Then, polar modes are only infrared active. Conversely, for polar groups, some or all polar modes are always seen in the Raman spectra, in a very close position to their infrared frequency (that can be the TO, the LO or an intermediate frequency). In figures 2(a) and (b)
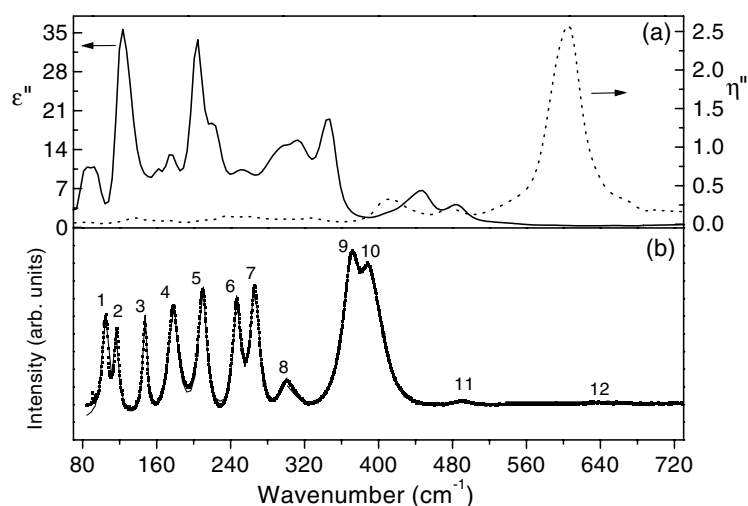
Figure 2. (a) Imaginary parts of the direct ($\varepsilon''(\omega)$, solid curve) and reciprocal ($\eta''(\omega)$, dashed curve) dielectric function, obtained from the adjustments of the infrared reflectance data of LaYbO$_3$ ceramic, and (b) the corresponding Raman spectrum (square symbols) fitted by a sum of Lorentzian lines (solid curve).

Table 2. Observed Raman modes for LaYbO$_3$. Positions and widths obtained from the adjustment of the experimental data by Lorentzian lines. γ is the full width at half maximum.

Peak	Ω (cm^{-1})	γ (cm^{-1})
1	104.5	8.9
2	117.0	5.0
3	147.2	5.0
4	178.1	12.0
5	209.7	10.0
6	246.8	9.1
7	266.1	11.0
8	301.0	14.9
9	369.8	18.3
10	390.4	31.4
11	490.5	20.2
12	649.2	67.8

the results show a relative independence of the Raman and infrared modes, favouring again a centrosymmetric structure, instead of a polar one. In the next section we use group theory tools to predict the number of active phonon modes in Raman and infrared spectra and compare with the experimental findings.

4. Group theory analysis and discussions

As pointed out above, LaYbO$_3$ has been described as belonging either to the *Pna*2$_1$ polar group (C$_{2v}^9$) or to the centrosymmetric *Pnma* one (D$_{2h}^{16}$), both with $Z = 4$. For the polar group all ions occupy 4a sites of general C$_1$ symmetry. Then, using the site group method of Rousseau *et al* [12] we can obtain the following distribution of the degrees of freedom in terms

of the irreducible representations (irs) of the C_{2v} point group

$$\Gamma = 15A_1 \oplus 15A_2 \oplus 15B_1 \oplus 15B_2. \qquad (6)$$

According to the character table of the C_{2v} point group, all irs are Raman active. Excluding the acoustic modes ($A_1 \oplus B_1 \oplus B_2$), we would expect 57 Raman modes and 42 IR bands ($14A_1 \oplus 14B_1 \oplus 14B_2$) for this group. Besides, all the IR modes are Raman active, so that the Raman spectrum alone would contain all the optical phonons of the system. These predictions are far from our experimental findings: the numbers of observed phonons is much lower than those predicted for both techniques; Raman and infrared modes are rather independent than coincident, as predicted.

Let us then try the centrosymmetric *Pnma* space group. In this case, Yb ions should occupy 4b Wyckoff sites of C_i symmetry, La and O(1) ions occupy 4c sites of C_s^{xz} symmetry and O(2) and O(3) occupy 8d sites of general C_1 symmetry. The site group method leads now to the following distribution of irs of the D_{2h} point group:

$$\Gamma = 7A_g \oplus 8A_u \oplus 5B_{1g} \oplus 10B_{1u} \oplus 7B_{2g} \oplus 8B_{2u} \oplus 5B_{3g} \oplus 10B_{3u}. \qquad (7)$$

Now, we would expect 24 Raman modes ($7A_g \oplus 5B_{1g} \oplus 7B_{2g} \oplus 5B_{3g}$) and 25 independent IR ones ($9B_{1u} \oplus 7B_{2u} \oplus 9B_{3u}$).

Although the independence of Raman and IR modes is compatible with experimental data, the number of predicted and observed modes is still different by a factor of two. This difference could be explained if the structure were more symmetric or if the number of motifs (Z) in the primitive cell were lower than that used. It is hard to imagine the first possibility because the x-ray results lead undoubtedly to an orthorhombic structure [2, 6]. However, the second possibility would hold for instance if the true crystal structure were not primitive. In this respect, it is interesting to investigate the face centred *Cmcm* space group (D_{2h}^{17}), with $Z = 4$ for the unitary cell, because its primitive cell has $Z = 2$ and also because this group has been described as that of β-LaYbS$_3$ and LaYbSe$_3$, whose chemical similarity with ours is evident [13].

According to the ion positions given by Mitchell *et al* for LaYbS$_3$ [13], in the *Cmcm* structure Yb ions occupy Wyckoff 4a sites of C_{2h}^{x} symmetry; La and S(2) ions the 4c sites of C_{2v}^{y} symmetry and the S(1) ions the 8f position of C_s^{yz} symmetry. The site group method now gives for the vibrational modes at the Brillouin zone centre

$$\Gamma = 4A_g \oplus 2A_u \oplus 3B_{1g} \oplus 6B_{1u} \oplus 1B_{2g} \oplus 6B_{2u} \oplus 4B_{3g} \oplus 4B_{3u}. \qquad (8)$$

Then, we note that for such a representation we would expect 12 Raman-active modes ($4A_g \oplus 3B_{1g} \oplus 1B_{2g} \oplus 4B_{3g}$) and 13 infrared ($5B_{1u} \oplus 5B_{2u} \oplus 3B_{3u}$) ones, in perfect agreement with our experimental results. This result, beside the complementary character of Raman and infrared modes, induces us to propose the *Cmcm* space group as the correct one for LaYbO$_3$.

5. Conclusions

We have performed Raman scattering and infrared reflectance spectroscopy analyses of the LaYbO$_3$ ceramics. The polar phonon modes allowed us to determine the intrinsic dielectric response at the MW region. The estimated value of ε_O agrees well with that measured directly at 11 GHz. Analyses by group theory for different space groups proposed for isomorphous materials showed that *Cmcm* would be the most likely group to describe our system. Assuming this group as the correct one, we can say that we have obtained the complete set of optical phonon modes of LaYbO$_3$.

Acknowledgments

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