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Crystal structure of fluorite-related Ln_3SbO_7 (Ln=La–Dy) ceramics studied by synchrotron X-ray diffraction and Raman scattering

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ABSTRACT

Ln_3SbO_7 (Ln=La, Pr, Nd, Sm, Eu, Gd, Tb and Dy) ceramics were synthesized by solid-state reaction in optimized conditions of temperature and time to yield single-phase ceramics. The crystal structures of the obtained ceramics were investigated by synchrotron X-ray diffraction, second harmonic generation (SHG) and Raman scattering. All samples exhibited fluorite-type orthorhombic structures with different oxygen arrangements as a function of the ionic radius of the lanthanide metal. For ceramics with the largest ionic radii (La–Nd), the ceramics crystallized into the *Cmcm* space group, while the ceramics with intermediate and smallest ionic radii (Sm–Dy) exhibited a different crystal structure belonging to the same space group, described under the *Ccmm* setting. The results from SHG and Raman scattering confirmed these settings and ruled out any possibility for the non-centrosymmetric $C222_1$ space group describing the structure of the small ionic radii ceramics, solving a recent controversy in the literature. Besides, the Raman modes for all samples are reported for the first time, showing characteristic features for each group of samples.

1. Introduction

Ceramics of general formula Ln_3MO_7 (where Ln^{3+} is a lanthanide element and M is Os^{5+}, Re^{5+}, Ru^{5+}, Mo^{5+}, Ir^{5+}, Sb^{5+}, Nb^{5+} or Ta^{5+}) have been intensively studied because of their interesting photocatalytic activity [1], dielectric [2,3], and magnetic properties [4–7]. These materials present an ordered, defective fluorite-type structure, which was described by Hinatsu et al. [6], as follows: The unit cell for oxides has the general formula $M_4^{4+}O_8$, in which the four tetravalent metal ions are replaced by three trivalent ions (Ln) and one pentavalent ion (M), thus creating one oxygen vacancy per fluorite cell. Owing to the significant differences between the ionic radii of the Ln^{3+} and M^{5+}, cation ordering occurs on the metal sites and the oxide-vacancy orders on the anion sites.

A variety of crystal structures has been proposed for the Ln_3MO_7 ceramics, as a direct consequence of the great number of chemical combinations that is possible between the lanthanide ions and the element M (Ta, Nb, Sb, Mo) [1–7]. Also, the processing conditions can contribute to produce different crystallographic structures; for example, several polymorphic modifications can be achieved through temperature changes [5,6,8,9]. Since the physical properties are strictly dependent on the crystalline phase, it is important to determine the correct crystal structure for the produced ceramics before designing any possible application. The first structure determination for these ceramics was reported by Rossell [10], who proposed the *Cmcm* space group to describe the La_3NbO_7 crystal phase. However, the *Pnma* space group was later employed by Kahn-Harari et al. [11] to describe the crystal structure of this compound. In the literature, the *Cmcm* space group has been often used to describe the crystal structure of several members of the Ln_3MO_7 family: Ln_3RuO_7 (Ln=La–Eu) [6,12–15], Ln_3ReO_7 (Ln=Pr, Nd, Sm–Tb) [16,17], Ln_3OsO_7 (Ln=Pr, Nd, Sm–Gd) [18–20], Ln_3TaO_7 (Ln=La–Nd) [5,21], Ln_3IrO_7 (Ln=Pr, Nd, Sm, Eu) [9,22,23], Pr_3NbO_7 [21] and Ln_3SbO_7 (Ln=La–Nd) ceramics [6,7,21]. For Ln_3TaO_7 (Ln=Y, Sm–Ho) [5] and Ln_3MoO_7 (Ln=La–Nd, Sm, Eu) ceramics [24,25], the $C222_1$ and $P2_12_12_1$ space groups were previously described, respectively. Besides, the $Fm\overline{3}m$ space group was found for Ln_3TaO_7 (Ln=Ho–Lu) [5,6] and Ln_3NbO_7 (Ln=Dy–Lu) ceramics [4,6]. The $C222_1$ space group was also employed to describe the structure of Ln_3NbO_7 with intermediate

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ionic radii *Ln* (*Ln*=Sm–Tb), while the *Pnma* space group was proposed for the larger ionic radii ceramics (*Ln*=La, Pr, Nd) [4]—in agreement with previous work by Kahn-Harari et al. [11].

Among all Ln_3MO_7 ceramics reported in the literature, a few studies have been carried out for *M*=Sb as pentavalent cation. In a pioneer work in the seventies, a series of Ln_3SbO_7 ceramics with *Ln*=Nd, Sm–Yb and Y were reported by Nath as belonging the pyrochlore ($Fd\overline{3}m$) structure [26]. Later on, Vente et al. proposed a fluorite related *Cmcm* group for Pr_3SbO_7 [21]. Then, Fennell et al. [27] proposed the $C222_1$ space group for Dy_3SbO_7 and Ho_3SbO_7. Recently, Hinatsu et al. [7] determined the *Cmcm* space group for *Ln*=La, Pr, Nd and $C222_1$ for *Ln*=Nd–Lu. However, Fu and Ijdo reported a critical, detailed study for all these structures and presented an alternative setting of the *Cmcm* space group, namely *Ccmm*, instead of $C222_1$, for Ln_3SbO_7 ceramics containing intermediate-sized lanthanides [28]. It can be concluded from this brief review that the proposed crystalline structures of Ln_3SbO_7 ceramics are still controversial. Concerning the conflicting structures reported in the literature, the description within the *Cmcm* space group has also been proposed for other Ln_3MO_7 ceramics by neutron diffraction [12,13,21], X-ray powder diffraction [4–7,9,17,18,28], as well as by X-ray single crystal diffraction [29]. In the case of the $C222_1$ space group, only studies using X-ray powder diffraction were reported [7].

In this context, the present paper intends to contribute to the elucidation of the possible crystal structure of Ln_3SbO_7 ceramics (*Ln*=La–Dy, exception of Ce and Pm), by reporting on our results of Raman scattering, second harmonic generation and synchrotron X-ray powder diffraction (SXRD). A similar methodology was previously applied by our group to solve structural conflicts for many materials [30–33].

2. Experimental

Ln_3SbO_7 ceramics were synthesized by using Ln_2O_3 (*Ln*=La, Nd, Sm, Eu, Gd, and Dy; >99.9% Sigma-Aldrich), Pr_6O_{11}, Tb_4O_7 (>99.9% Sigma-Aldrich) and Sb_2O_5 (>99.9% Sigma-Aldrich) as starting materials through solid-state reaction. All lanthanides used in this work were heat treated at 900 °C overnight before being employed for the synthesis. Stoichiometric amounts were weighed and mixed with a mortar and pestle. For the synthesis of La_3SbO_7 and Dy_3SbO_7 samples, an excess amount of about 200% weight of antimony oxide was added to ensure formation of Ln_3SbO_7 ceramics. For the synthesis of these ceramics, the conventional solid-state processing was employed in temperatures ranging from 1300 °C to 1500 °C, and times up to 15 h. After synthesis, diluted nitric acid (0.1 M) was employed to remove unreacted Gd_2O_3 and Tb_4O_7, which could be present in Gd_3SbO_7 and Tb_3SbO_7 ceramics, respectively. Then, the resulting products were washed in distilled water followed by drying at 80 °C.

SXRD measurements were taken in the superconducting wiggler XDS beamline of the Brazilian Synchrotron Laboratory, LNLS, with λ=0.65319 Å. The optical path of the beam upstream the sample position included a water-cooled Pt-coated vertically collimating mirror, a LN_2-cooled double Si(1 1 1) crystal monochromator with sagittal focusing and a Pt-coated vertically focusing mirror, yielding a highly monochromatic beam with dimensions of $2.0(H)\times 0.17(V)$ mm^2 full width at half maximum (FWHM) at the sample position. The samples were mounted in flat-plane $\theta/2\theta$ geometry with a spinning axis perpendicular to the sample surface to optimize grain statistics. The diffraction profiles were taken in the vertical scattering plane using a 0.3 mm slit located 0.80 m away from the sample followed by a highly-oriented pyrolitic graphite analyzer and a high-throughput $LaBr_3$ scintillator detector in the 2θ arm. This mounting resulted in high-resolution and low-background powder diffraction profiles, with typical Bragg peak widths of $\sim$0.02° FWHM at low angles, and maximum peak heights of $\sim 10^5$ counts against a background level of $\sim 10^2$ counts. The measurements were performed in the range 4–90°2θ, covering $\sim$2000 Bragg reflections, with a step size of 0.008°2θ. Rietveld refinements were performed using the GSAS+EXPGUI program [34].

Second harmonic generation (SHG) measurements were also performed. SHG is only present in structures lacking inversion symmetry [35], hence this technique can be used to determine the presence of this symmetry operation. We have used a 140 fs Ti–Sapphire oscillator (Coherent Chameleon) with 80 MHz repetition tuned at 800 nm which is directed to a modified Olympus FV300 scanning laser microscope. The backscattered signal is then directed to a dichroic mirror and a thin band pass centered at second harmonic wavelength (400 nm) to completely remove the laser scattered light where the SH signal is detect by a photomultiplier tube. We have used an alpha-quartz crystal with the laser incidence parallel to the *c*-axis as a reference for this measurement. The second harmonic emission from alpha-quartz is clearly detectable, although this material posses weak second order susceptibility (0.3 pm/V) compared to other materials [35].

Raman spectra of the as-synthesized samples were collected in backscattering configuration by using two different instruments. An Horiba LABRAM-HR spectrometer was used with the 632.8 nm line of a helium–neon laser as excitation source (effective power of 6 mW at the sample's surface), diffraction gratings of 600 and 1800 grooves/mm, Peltier-cooled charge coupled device (CCD) detector, confocal Olympus microscope (100 × objective), and experimental resolution typically 1 cm^{-1} for 10 accumulations of 30 s. Appropriate interference filter for rejecting laser plasma lines, and edge filters for stray light rejection were used. Also, a Horiba T64000 spectrometer (80 × objective) equipped with the 488 nm line of an Ar$^+$ laser (4 mW at the sample's surface) and a LN_2-cooled CCD detector was used. In this case, the spectral resolution was better than 2 cm^{-1} and the accumulation were equally 10 collections of 30 s. All resulting spectra were corrected by Bose–Einstein thermal factor [36].

3. Results and discussion

Representative SXRD profiles of Ln_3SbO_7 for *Ln*=La and Eu are given in Fig. 1(b) and (a), respectively. For the large-size lanthanides (*Ln*=La and Pr), a good agreement between observed and calculated diffraction data was obtained using a single orthorhombic phase within the *Cmcm* space group (see Fig. 1(b)), such as reported previously for these ceramics [10]. A relatively large deviation of the unit cell parameters (*a*, *b*, *c*) with respect to the idealized ($2a_c$,$\sqrt{2}a_c$,$\sqrt{2}a_c$) cell derived from the cubic fluorite structure ($a_c\sim$5.4 Å) was noticed. An alternative structural refinement for *Ln*=La under the *Pnma* space group with a distinct choice of axes ($a\sim\sqrt{2}a_c$,$b\sim 2a_c$,$c\sim\sqrt{2}a_c$), such as reported for La_3NbO_7 [11] was performed, also yielding a good fit to our diffraction data (χ^2=17.0 and 17.6 for refinements under *Cmcm* and *Pnma* space groups, respectively). However, the extra Bragg reflections expected for *Pnma* and forbidden by the higher symmetry *Cmcm* space group could not observed, indicating *Cmcm* is indeed the most suitable space group for Ln_3SbO_7 with *Ln*=La and Pr.

For medium size lanthanides, *Ln*=Sm–Dy, another crystalline phase with a much smaller orthorhombic distortion is observed (see Fig. 1(a) for *Ln*=Eu). Following previous studies, we attempted structural refinements for *Ln*=Eu using two possible space groups, $C222_1$ [7,27] and *Ccmm* [28], both with ($a\sim 2a_c$, $b\sim\sqrt{2}a_c$,$c\sim\sqrt{2}a_c$) metrics. Details regarding these two models can