Structural and vibrational properties of phase-pure monoclinic NdLuO₃ interlanthanides synthesized from nanostructured precursors

Júlia C. Soares^a, Kísla P.F. Siqueira^a, Roberto L. Moreira^b, Anderson Dias^{a,*}

^a Departamento de Química, Universidade Federal de Ouro Preto, Campus Morro do Cruzeiro, ICEB II, Ouro Preto, MG, 35400-000, Brazil

^b Departamento de Física, ICEx, Universidade Federal de Minas Gerais, C.P. 702, Belo Horizonte, MG, 30123-970, Brazil

ARTICLE INFO

Article history:

Received 8 December 2015

Received in revised form

17 February 2016

Accepted 30 March 2016

Available online 1 April 2016

Keywords:

Ceramics

Electron microscopy

Nanomaterials

Raman spectroscopy

Rare-earth

ABSTRACT

Phase-pure monoclinic NdLuO₃ interlanthanides were successfully synthesized from hydrothermal-derived precursors. LuO(OH) and Nd(OH)₃ materials were firstly obtained by hydrothermal synthesis at 250 °C, for 24 h. X-ray diffraction, micro-Raman spectroscopy, scanning and transmission electron microscopies were employed to investigate the thermal behavior of these precursors and NdLuO₃ interlanthanide up to 1600 °C. It was observed that LuO(OH) and Nd(OH)₃ were converted to cubic lanthanide oxides below 1000 °C. Cubic Nd₂O₃ has changed to the monoclinic structure at 1000 °C, followed by reaction with cubic Lu₂O₃ at 1400 °C to produce monoclinic NdLuO₃. Phase-pure monoclinic (C2/m space group, #12) interlanthanide was then produced at 1600 °C for the first time, as confirmed by all the employed techniques. Phonon modes were additionally determined and assigned for this monoclinic structure.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

LnLn'O₃ mixed oxides, known as interlanthanide materials, have recently received an enormous scientific and technological interest because of their outstandingly complex structures toward promising microwave-related, magnetic, and optical applications [1–5]. These interlanthanides are frequently interpreted as mixtures of simple binary sesquioxides of trivalent lanthanides, which also exhibit intricate crystal chemistry and can be found in at least three different modifications ranging from cubic fluorite-type (C-type), hexagonal (A-type), to monoclinic (B-type) polymorphs, with very remarkable properties [6–11]. In the last decades, many works have been devoted to investigate a large number of trivalent lanthanide combinations in order to obtain potentially ordered ternary mixed-lanthanide phases by systematically substituting smaller ions into lower coordination sites and larger ions into higher coordination sites [1–4,12,13]. These attempts revealed a systematic occurrence of order-disorder phenomena in many ternary interlanthanide combinations, which can be advantageous from the perspective of doping (in disordered materials) or from the point of view of the

polymorphism (in ordered materials). However, all compositions deserve investigation towards a complete assessment of structure-property relationships, where different lanthanide ions lead to diverse crystal structures.

The present work focuses the ternary lanthanide oxide NdLuO₃, firstly studied by Schneider and Roth [14] and again reported by Berndt et al. [15] as a new material fifteen years later. Both papers did not presented any x-ray diffraction (XRD) data nor further evidence for their findings, only reporting either a mixture of monoclinic and cubic phases after heat treatments at 1650 °C for 6 h [14] or a mixture of 50% of the perovskite phase (orthorhombic) in combination with monoclinic and cubic phases after solid-state reactions of coprecipitated hydroxides at 1250 °C [15]. Su et al. [16] proposed the synthesis of many ternary lanthanide oxides, including NdLuO₃, by using for the first time high pressure and high temperature methods. Although no XRD was presented, the authors claimed a phase-pure NdLuO₃ in a perovskite form at 1200 °C and 40 kbar. More recently, Dubok et al. [13] reported the electrophysical properties of interlanthanide oxides, and NdLuO₃ appeared as belonging to a C-type structure after coprecipitation of hydroxides followed by thermal decomposition and sintering at high temperatures. Bharathy et al. [12] presented a nice structure map for all known ternary lanthanide oxides in the literature, which shows that NdLuO₃ is

* Corresponding author.

E-mail address: anderson_dias@iceb.ufop.br (A. Dias).

known, but its structure has not been reported by X-ray or neutron diffraction techniques. In fact, in their introduction, Barathy et al. [12] mentioned NdLuO₃ as studied by Berndt et al. [15], Ito et al. [3] and Su et al. [16]. Unfortunately, Ito et al. [3] did not presented any result for this interlanthanide.

The synthesis procedures employed to produce binary and even ternary lanthanide oxides vary enormously, either as single crystals, ceramic powders or films. The standard solid-state reaction remains the major processing route for these materials [2,4], although other non-conventional methods are currently applied, such as reverse-strike coprecipitation [17], mechanochemical [18], thermal decomposition [5,6,13,19–21], sol-gel processing [22–24], combustion synthesis [25], molecular beam epitaxy technique [26,27], and hydroxide fluxes [12]. The hydrothermal technology is currently applied by our research group to synthesize nanostructured materials with technological interest [28–34]. In our previous investigations, crystal chemistry and morphology are monitored and controlled by choosing the appropriate feed chemistry and processing conditions during hydrothermal syntheses of nanostructured precursors [28–34]. By using experimental setups with fully-controlled temperature-pressure-time-pH environments, potentially reactive materials can be produced in mild, reliable and reproducible conditions [28–34]. These processing parameters have decisive influence on the crystal structure, purity, ordering degree, particle size and morphology of the resulting materials [35,36]. It is well known that these features determine the performance of the materials, which lead us to conclude that the investigation of their processing conditions becomes very important in this context.

In view of that, this work introduces the hydrothermal processing route for the synthesis of phase-pure monoclinic NdLuO₃. Based on the available literature discussed above, it seems that all attempts to produce phase-pure NdLuO₃ failed. Thus, this paper reports the thermal behavior of nanostructured hydrothermally-derived precursors (hydroxides and oxy-hydroxides), which was monitored by XRD, Raman spectroscopy, scanning and transmission electron microscopies. Our procedures allowed us to synthesize, for the first time, phase-pure NdLuO₃ interlanthanide belonging to the monoclinic C2/m (#12) space-group. Moreover, in order to expand the knowledge of this material, the complete set of non-polar phonon modes for the monoclinic NdLuO₃ was determined and assigned for the first time, with appropriate use of polarized micro-Raman scattering tools on sintered samples.

2. Experimental section

Stoichiometric amounts of Nd(NO₃)₃·6H₂O and Lu₂O₃ (Sigma-Aldrich, purity >99.9%) were used as starting materials. Lutetium oxide was firstly treated with HNO₃ 65% to produce a mother solution of lutetium nitrate, according to the chemical reaction:

Neodymium nitrate hydrate was then introduced and mixed to this mother solution followed by adding of NaOH (10 mol/L) until the pH reach values above 13 under vigorous stirring. The resulting solutions were loaded into stainless steel Parr® autoclaves equipped with pressure and temperature controllers. The reaction vessels were heated at 10 °C min⁻¹ up to the processing temperature and its corresponding saturated vapor pressure (250±1 °C and 580 ± 2 psi) for 24 h. After synthesis, the obtained precursors were washed with distilled water in order to remove any remaining Na⁺ ion and dried at 70 °C. The general chemical reaction for the synthesis of the precursors can be written as:

Following, the materials were calcined (air atmosphere) in the temperature range 800–1600 °C for fixed times of 2 h in order to investigate their thermal behavior. For sintering, cylindrical pucks of about 5 mm height and 12.5 mm diameter were produced by applying a pressure of 150 MPa in samples previously treated at 1200 °C. The obtained pucks were then sintered in a conventional oven (air atmosphere) at 1600 °C, for 8 h.

In the sequence, the structural properties were investigated by x-ray diffraction (XRD) using a Shimadzu D-6000 diffractometer with graphite monochromator and a nickel filter in the range of 10–60°2θ (15 s/step of 0.02°2θ), operating with FeKα radiation (λ = 0.1936 nm), 40 kV and 20 mA (the results were automatically converted to CuKα radiation for data treatment and manipulation). The lattice parameters were determined by the software MDI Jade 9.0. The vibrational properties were studied by micro-Raman spectroscopy in back-scattering configuration by using an Olympus confocal microscope (100 × objective) attached to a Horiba/Jobin-Yvon LABRAM-HR spectrometer (equipped with 600 and 1800 grooves/mm diffraction gratings). The 632.8 nm line of a He–Ne laser (maximum effective power of 6 mW at the surface of each sample) was used as exciting line and a Peltier-cooled charge coupled device (CCD) detected the scattered light. An edge filter was employed to stray light rejection (Rayleigh line). In order to avoid any kind of crystallization due to laser exposition, very low intensities were employed, besides lens with low magnification and defocused laser, when possible. Accumulation times of typically 20 collections of 10 s were employed with spectral resolution better than 1 cm⁻¹. The resulting spectra were corrected by the Bose-Einstein thermal factor besides individual baseline subtractions.

Morphological and structural features of the samples were also investigated by electron microscopy. A Quanta FEG 3D (FEI) field-emission scanning electron microscope (FESEM) equipped with energy-dispersive spectrometer (EDS) was employed to analyze the morphology and chemical features of the NdLuO₃-derived materials (applied voltages varied from 5 to 30 kV). Images were taken in both detection modes, i.e., secondary (SE) and backscattered (BSE) electrons, in order to differentiate the precursors and final materials. High-resolution transmission electron microscopy (HRTEM) was carried out to investigate the crystalline aspects of the nano-powders in a Tecnai G2-20 (FEI) transmission microscope (applied voltage of 200 kV). Selected area electron diffraction (SAED) patterns were obtained for all samples in order to characterize their polycrystalline nature.

3. Results and discussion

Fig. 1 presents XRD pattern and Raman spectrum obtained for a stoichiometric mixture of the precursors hydrothermally synthesized at 250 °C. The results showed that Nd(OH)₃ and LuO(OH) were produced and may be indexed according to the ICDD (International Committee for Diffraction Data) cards #00-006-0601 and #01-072-0928, respectively (Fig. 1a). Fig. 1b presents the Raman spectrum for this mixture of precursors at room temperature. As it can be seen, a set of relatively broad Raman modes in the region 100–950 cm⁻¹ corresponds to the LuO(OH) and Nd(OH)₃ vibrations. The bands related to LuO(OH) occur below 200 cm⁻¹ and at around 410, 660 and 830 cm⁻¹, while the modes related to neodymium hydroxide occur at 297 and 371 cm⁻¹ [20]. In the sequence, the thermal evolution aiming to the production of phase-

Fig. 1. (a) XRD pattern and (b) Raman spectrum for an equimolar mixture of the hydrothermally-synthesized Nd(OH)_3 and LuO(OH) precursors. In (b), the main bands for each phase are indicated in different colors. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

pure monoclinic NdLuO_3 from hydrothermal-derived precursors was studied in the temperature range 800–1600 °C. Morphological and structural aspects of the precursors were investigated by FESEM and HRTEM. Fig. 2a shows a FESEM image where nanosized, agglomerated particles can be observed for the precursors synthesized by hydrothermal processing at 250 °C, for 24 h. As it can be seen, two different morphologies are present and could be associated after chemical analyses (EDS) with the precursors obtained after synthesis. LuO(OH) exhibits tabular, faceted particles (easily identified by a circle in Fig. 2a), while Nd(OH)_3 shows nanostructured, heavily agglomerated particles (identified by an arrow in Fig. 2a). Fig. 2b shows representative HRTEM images obtained in Nd(OH)_3 precursor hydrothermally synthesized at 250 °C, in which nanosized, well-dispersed tabular particles can be visualized. For this sample, the interplanar spacing was computed to be about 3.19 Å, which correspond to the (110) plane of the $P6_3/m$ hexagonal space group.

Fig. 3 shows the XRD results for the samples thermally treated for 2 h at selected temperatures (800, 1000, 1200, 1400 and 1600 °C). At temperatures below 1000 °C, the precursors have converted to lanthanide oxides according to the ICDD cards #00-

Fig. 2. (a) FESEM image for the precursors obtained by hydrothermal synthesis at 250 °C, for 24 h. LuO(OH) tabular particles are identified by a circle, while Nd(OH)_3 particles are indicated by an arrow; (b) HRTEM images for the Nd(OH)_3 . Tabular, faceted particles are shown (left image) with interplanar spacing at 3.19 Å, corresponding to the (110) plane of the $P6_3/m$ hexagonal space group (right image).

021-0579 (Nd_2O_3) and #01-072-6366 (Lu_2O_3). These oxides belong to the $Ia\bar{3}$ (#206) space group (cubic fluorite-type phase) and can be visualized as phase-pure materials at 800 °C in Fig. 3b with lattice parameters $a = 10.96$ Å for Nd_2O_3 and $a = 10.39$ Å for Lu_2O_3 . At 1000 °C, cubic Nd_2O_3 changed (see Fig. 3b) to monoclinic neodymium oxide, $C2/m$ space-group (#12), according to the ICDD card #01-076-7416, with lattice parameters $a = 14.12$ Å, $b = 3.63$ Å, $c = 8.80$ Å and $\beta = 100.2^\circ$. This result was unexpected, since a hexagonal structure (space group $P\bar{3}m1$) is frequently found for pure Nd_2O_3 [20,37,38]. At 1200 °C, a mixture of pure monoclinic Nd_2O_3 and cubic Lu_2O_3 phases can be observed. At this temperature and above, Fig. 3b shows clearly the chemical reaction and crystal phase evolutions, since it focuses on the range 25–35°2 θ , where the most important changes in the diffraction patterns of Fig. 3a occur. In Fig. 3b, each peak could be identified in agreement with ICDD cards of previously published works [5,17,39,40]. At 1400 °C, the NdLuO_3 interlanthanides become visible as a monoclinic phase ($C2/m$ space group, #12) together with residual cubic lutetium oxide. Finally, heat treatment at 1600 °C produced phase-pure monoclinic NdLuO_3 , whose identification and assignment could only be accomplished by comparing its XRD pattern with that observed for the LaYO_3 material (ICDD card #70-3117) [39].

According to the previous literature discussed above, perovskite-like NdLuO_3 interlanthanides can be formed as a stable

Fig. 3. XRD patterns exhibiting the thermal behavior for samples produced in the temperature range 800–1600 °C (from bottom to top). (a) General XRD patterns in the 10–60°2 θ range, and (b) particular view in the region 25–35°2 θ with identification of all observed phases for better visualization.

phase [15,16]. In fact, the structural stability and formability of perovskite materials are based on the so-called tolerance factor (t), a criterion proposed by Goldschmidt through the relationship [41]:

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)}, \quad (3)$$

where R_A , R_B and R_O are the ionic radii of A, B and oxygen in the general formula ABO_3 . In an ideal cubic perovskite structure, the tolerance factor is equal to the unity. Lower t values could occur, which means that distorted structures would be present. It is

currently accepted that almost all perovskites have t values ranging from 0.75 to 1.00. However, the tolerance factor is a necessary but not a sufficient condition for the formation of perovskite structures. The Goldschmidt's criterion neglects the influence of the coordination number on the effective ionic radii, and was debated by the literature by years without a definitive solution. For $NdLuO_3$, the tolerance factor could be calculated as 0.7847, which indicates that this material could be produced in a (highly distorted) perovskite phase, even if one considers this value in the border for the traditional perovskite atomic arrangement. In this work, the phase behavior followed by our $NdLuO_3$ was quite different: the hydro-thermal precursors were converted to monoclinic Nd_2O_3 and cubic Lu_2O_3 at 1200 °C, followed by a chemical reaction at higher temperatures allowing the production of phase-pure monoclinic ($C2/m$, #12) materials at 1600 °C. Fig. S1 (Supplementary Material) presents XRD data for the phase-pure monoclinic $NdLuO_3$ together with its Miller indexes for the monoclinic $C2/m$ space group. In a

Fig. 4. Raman spectra (100–1000 cm^{-1} range) showing the thermal evolution (800–1600 °C) of the samples produced from hydrothermally-processed precursors at 250 °C. The main bands for each phase are indicated in different colors. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Micro-Raman spectra for the $NdLuO_3$ sample in the spectral region 50–1200 cm^{-1} . Experimental data are in open circles, whereas the fitting curve is represented by a red line. Green lines represent the phonon modes adjusted by Lorentzian curves. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Phonon frequencies, FWHM and assignment of the *gerade* modes determined from the adjustment of the Raman experimental data by Lorentzian curves, for the phase-pure monoclinic NdLuO₃.

Band	Frequency (cm ⁻¹)	FWHM (cm ⁻¹)	Assignment
1	65.7	5	A _g
2	96.5	19	A _g
3	110.5	6	B _g
4	123.6	14	A _g
5	168.4	11	A _g
6	181.1	16	A _g
7	200.2	19	A _g
8	218.4	18	B _g
9	265.9	43	B _g
10	306.0	52	A _g
11	338.5	47	B _g
12	381.7	43	B _g
13	408.7	42	A _g
14	439.9	27	A _g
15	486.9	9	B _g
16	572.2	36	A _g
17	595.2	29	B _g
18	702.3	56	A _g
19	815.2	48	A _g
20	840.0	40	A _g
21	953.4	17	A _g

previous publication [39], Yamamura et al. studied the synthesis of monoclinic LaYO₃ and their results were employed in the present work to indexing our NdLuO₃ samples, since no XRD pattern for this material in the monoclinic phase could be found in the literature. The lattice parameters were determined as $a = 14.08 \text{ \AA}$, $b = 3.54 \text{ \AA}$, $c = 8.67 \text{ \AA}$ and $\beta = 101.3^\circ$ for the monoclinic $C2/m$ space group, according to the equation [42]:

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right). \quad (4)$$

It is important to highlight that conventional solid-state reaction using neodymium oxide with lutetium oxide at 1600 °C did not result in a phase-pure monoclinic NdLuO₃. Fig. S1 also presents XRD results for conventionally-synthesized materials by solid-state reaction. We can note the presence of both unreacted Lu₂O₃ and Nd₂O₃ in the final product obtained throughout solid-state reaction.

The thermal behavior of hydrothermally treated precursors for the synthesis of NdLuO₃ was also monitored by micro-Raman scattering. Fig. 4 presents selected spectra for the samples sequentially treated at 800 °C, 1000 °C, 1400 °C and 1600 °C. The spectrum for the samples heat treated at 800 °C is quite similar to those obtained by Ubaldini and Carnasciali [20] for lutetium and neodymium cubic oxides. The strongest bands for these materials are located, respectively, at 338 and 390 cm⁻¹. For the samples prepared at 1000 °C, we can also observe the strongest band related to the Lu₂O₃ (390 cm⁻¹) together with vibrational modes associated with monoclinic Nd₂O₃.²⁰ These additional modes are also reported for the same crystal structure by Mele et al. [5], for Nd₂O₃–Gd₂O₃ mixed system, Martel et al. [43], for Sm₂O₃, and Heiba et al. [22], for Dy_{2-x}Ho_xO₃ ($x > 0.4$). At 1400 °C, monoclinic NdLuO₃ can now be observed, in accordance with Tompsett et al. [17], particularly in the frequency range 350–500 cm⁻¹. Although some secondary phases (lanthanide oxides) are still present, as verified by XRD and discussed previously, in the range 350–500 cm⁻¹ a broad group of Raman modes could be assumed as a fingerprint of the monoclinic $C2/m$ (#12) space group, as previously proposed for the LaGdO₃ material [17] and for the (Gd_{0.5}Nd_{0.5})₂O₃ system [3].

The spectrum for the calcined sample at 1600 °C (Fig. 4, top)

shows the Raman-active modes for the phase-pure NdLuO₃. In this monoclinic $C2/m$ space group, there are six formula units per unitary cell ($Z = 6$) [5,44]. Four oxygen ions and three lanthanide ions occupy the 4i Wyckoff position with C_s symmetry ($2A_g \oplus B_g \oplus A_u \oplus 2B_u$), and one oxygen ion sites on an $2b$ position with C_{2h} symmetry ($A_u \oplus 2B_u$). Based on these occupation sites, the site-group method of Rousseau et al. [45] was applied to obtain the following representation of the Raman-active modes (*gerade*) at the Brillouin-zone center:

$$\Gamma_{\text{RAMAN}} = 14A_g(xx, yy, zz, xy) \oplus 7B_g(xz, yz). \quad (5)$$

According to this model, one would expect to observe up to 21 first-order Raman modes in the spectrum of NdLuO₃ sample treated at 1600 °C (beside 24 infrared bands, $8A_u(y) \oplus 16B_u(x,z)$). However, the spectrum of this sample showed in Fig. 4 presents relatively broad peaks and does not allow one to visualize more than 10 bands. Therefore, in order to resolve the superimposed phonon modes, peak fitting procedures were required. The Raman spectrum for this sample was then fitted by Lorentzian curves and the results are presented in Fig. 5. The experimental data are in open circles and the fitting curve is presented by a red line. The results showed that 21 Raman modes were required for the fitting (green curves), in perfect agreement with the theoretical predictions. Based on this fitted spectrum, the frequencies and full-width at half maxima (FWHM) for all bands were determined for our phase-pure monoclinic NdLuO₃ and are presented in Table 1.

The Raman spectrum depicted in Fig. 5 could represent a fingerprint of the NdLuO₃ interlanthanides with monoclinic $C2/m$ structure. In addition, as already mentioned, 21 Raman-active modes were expected, with the following distribution in terms of the irreducible representations (i.r.) of the C_{2h}^3 point group: $14A_g \oplus 7B_g$ [2,22,44]. In order to corroborate our findings and assign these non-polar *gerade* modes to their respective i.r., additional experiments were carried out by using polarized micro-Raman spectroscopy. For this study, a ceramic sample was sintered at 1600 °C for 8 h. These processing conditions were employed because the goal was to obtain ceramics with large grains in order to get suitable polarized micro-Raman spectra. It is well known that the inelastic scattered light intensities due to the Raman effect are

Fig. 6. Polarized micro-Raman scattering for the sintered NdLuO₃. Parallel (//) and cross-polarized (⊥) configurations are indicated in red and blue lines, respectively. The relative strengthening of the A_g modes in the parallel configuration are accompanied by the relative weakening of the B_g modes (indicated in blue). Conversely, B_g modes are favored by crossed light configuration, for the same sample position (particular grain size orientation). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. FESEM images for samples obtained at different conditions. (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1400 °C and (e) 1600 °C.

proportional to the square of the elements of the polarizability tensor (second-order tensor). Then, the base functions of the i.r. that are Raman-active have quadratic forms, i.e., they transform like the product of the Cartesian coordinates (*e.g.*, *xx*, *xy*, *xz*, *yy*, *etc.*). For single crystals, we take benefit of the crystal symmetry to assign the lattice vibrations to the different i.r. [45,46]. However, in the case of the ceramics, although the group-theory predictions remain valid, the symmetries of the modes are generally mixed up due to the random orientation of the crystalline grains. In this work, we have used a confocal microscope with an objective of magnification of 100×, which allows the selection of observation regions smaller

than the grain sizes (scattering volumes of *circa* 1 μm³). However, we do not know anything about the crystallographic axes of these grains, which have also random orientation throughout the sample. By measuring the micro-Raman spectra of NdLuO₃ sintered sample with polarized light (Fig. 6), we observed that for some grains the spectra of parallel (red line) and crossed light (blue line) become quite different. We can observed the relative strengthening of the totally symmetric 14A_g modes in the parallel configuration (because these modes are particularly observed for *xx*, *yy* and *zz* configurations of polarizer and analyzer), accompanied by the relative weakening of the 7B_g modes, which are favored by crossed

Fig. 8. HRTEM images for the phase-pure monoclinic NdLuO₃ produced at 1600 °C. Thick samples were the result of the solid-state reactions that occurred at this temperature (left image). Interplanar spacing of 3.13 Å corresponds to the (111) plane of the monoclinic *C2/m* space group (right image). The inset shows the SAED pattern for this sample, in which the aligned spots confirm its monoclinic structure.

light configuration (selected only for *xz* and *yz* configurations). These crossed-polarized *B_g* modes are indicated in blue in Fig. 6. Therefore, we could assign all the 21 Raman-active *gerade* modes as belonging to the *A_g* and *B_g* symmetries, as also presented in Table 1. These results are in complete agreement for the proposed monoclinic *C2/m* (#12) space group for our phase-pure NdLuO₃.

The thermal behavior of all samples was examined in their morphological, chemical and structural aspects by FESEM and HRTEM. Fig. 7 presents a sequence of FESEM images (backscattered electrons) for samples obtained under different conditions. Fig. 7a–e shows representative FESEM images for samples obtained at 800, 900, 1000, 1400 and 1600 °C. It was observed a general increase in their particle sizes; in particular, the morphologies due to LuO(OH) and Nd(OH)₃ precursors presented and discussed in Fig. 2 were changed above 800 °C (Fig. 7a–c) due to their conversion into lanthanide oxides. EDS analyses showed that Lu and Nd are still in opposite corners, which means that a chemical reaction between these precursors was not in progress. Above 900 °C (Fig. 7b and c), it is expected that some changes can occur since XRD data verified a phase transformation for Nd₂O₃, from cubic to monoclinic. However, the morphology had no significant changes above 900 °C, except for a further increase in the particle size. Fig. 7d and e presents the morphology of the samples obtained at 1400 °C and 1600 °C, which exhibit features of materials where some solid-state reaction cannot be neglected. Hard, compacted agglomerates can be seen, which indicate that a chemical reaction between the hydrothermally-derived precursors have now occurred. In fact, EDS analyses indicate that it is no longer possible to discern between lutetium and neodymium along the samples.

Fig. 8 presents HRTEM images for the phase-pure monoclinic NdLuO₃ produced at 1600 °C. It was observed that thick samples dominate the scenario, which were the result of the solid-state reactions that occurred at this temperature (left image). The interplanar spacing was determined to be about 3.13 Å, corresponding to the (111) plane of the monoclinic *C2/m* space group (right image). The inset in Fig. 8 shows the SAED pattern for the sample obtained at 1600 °C, in which spots observed in well-aligned samples confirm their monoclinic structure.

4. Conclusions

In this work, phase-pure monoclinic NdLuO₃ was synthesized

for the first time from nanostructured hydrothermally-derived precursors. Aqueous solutions of lutetium and neodymium nitrates were hydrothermally treated at 250 °C for 24 h in order to produce nanostructured LuO(OH) and Nd(OH)₃ precursors. The thermal behavior of this interlanthanide material was investigated by XRD, micro-Raman spectroscopy and electron microscopy (FESEM and HRTEM). It was observed that the starting materials were converted to cubic lanthanide oxides below 1000 °C. Cubic Nd₂O₃ has changed to the monoclinic structure at 1000 °C, followed by reaction with Lu₂O₃ at 1400 °C to produce monoclinic NdLuO₃. Phase-pure monoclinic *C2/m* space group was obtained only at 1600 °C, as verified by XRD, Raman spectroscopy and HRTEM. In order to validate our results, polarized micro-Raman scattering was also employed to probe the phonon modes in sintered NdLuO₃. All the 21 non-polar vibrational modes predicted by group theory calculations for the *C2/m* space group were identified and assigned, which also confirmed the production of phase-pure NdLuO₃ interlanthanides at 1600 °C.

Acknowledgements

The authors acknowledge the financial support from CAPES, CNPq, FINEP and FAPEMIG. The Center of Microscopy at the Universidade Federal de Minas Gerais (<http://www.microscopia.ufmg.br>) is also acknowledged for providing the equipment and technical support for experiments involving electron microscopy.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jallcom.2016.03.291>.

References

- [1] R.L. Moreira, A. Feteira, A. Dias, Raman and infrared spectroscopic investigation on the crystal structure and phonon modes of LaYbO₃ ceramics, *J. Phys. Condens. Matter* 17 (2005) 2775–2781.
- [2] Y. Sharma, S. Sahoo, A.K. Mishra, P. Misra, S.P. Pavunny, A. Dwivedi, S.M. Sharma, R.S. Katiyar, Structural phase transition of ternary dielectric SmGdO₃: evidence from angle-dispersive X-ray diffraction and Raman spectroscopic studies, *J. Appl. Phys.* 117 (2015) 094101.
- [3] K. Ito, K. Tezuka, Y. Hinatsu, Preparation, magnetic susceptibility, and specific heat on interlanthanide perovskites ABO₃ (A=La–Nd, B=Dy–Lu), *J. Solid State Chem.* 157 (2001) 173–179.

- [4] J. Blanus, N. Jovic, T. Dzomic, B. Antic, A. Kremenovic, M. Mitric, V. Spasojevic, Magnetic susceptibility and ordering of Yb and Er in phosphors Yb,Er:Lu₂O₃, Opt. Mater. 30 (2008) 1153–1156.
- [5] P. Mele, C. Artini, A. Ubaldini, G.A. Costa, M.M. Carnasciali, R. Masini, Synthesis, structure and magnetic properties in the Nd₂O₃-Gd₂O₃ mixed system synthesized at 1200°C, J. Phys. Chem. Solids 70 (2009) 276–280.
- [6] P. Mele, C. Artini, R. Masini, G.A. Costa, A. Hu, N. Chikumoto, M. Murakami, Synthesis and superconductive characterisation of RuSr₂NdxGd_{1-x}Cu₂O₈ compounds (x=0, 0.09, 0.18, 0.35), Phys. C 391 (2003) 49–54.
- [7] D.Y. Chung, E.H. Lee, Microwave-induced combustion synthesis of Ce_{1-x}SmxO_{2-x/2} powder and its characterization, J. Alloys Compd. 374 (2004) 69–73.
- [8] C. Peng, Z. Zhang, Nitrate–citrate combustion synthesis of Ce_{1-x}GdxO_{2-x/2} powder and its characterization, Ceram. Int. 33 (2007) 1133–1136.
- [9] H. Yang, H. Wang, H.M. Luo, D.M. Feldman, P.C. Dowden, R.F. Depaula, Q.X. Jia, Structural and dielectric properties of epitaxial Sm₂O₃ thin films, Appl. Phys. Lett. 92 (2008) 062905.
- [10] J. Hao, Y.W. Li, J.S. Wang, C.L. Ma, L.Y. Huang, R. Liu, Q.L. Cui, G.T. Zou, J. Liu, X.D. Li, Experimental determinations of the high-pressure crystal structures of Ca₃N₂, J. Phys. Chem. C 114 (2010) 16750–16755.
- [11] G. Azimi, R. Dhiman, H. Kwon, A. Paxson, K. Varanasi, Hydrophobicity of rare-earth oxide ceramics, Nat. Mater. 12 (2013) 315–320.
- [12] M. Bharathy, A.H. Fox, S.J. Mugavero, H.-C. zur Loye, Crystal growth of inter-lanthanide LaLn'O₃ (Ln'=Y, Ho-Lu) perovskites from hydroxide fluxes, Solid State Sci. 11 (2009) 651–654.
- [13] V.A. Dubok, V.V. Lashneva, Y.N. Kryuchkov, Electrophysical properties of oxide interlanthanides and solid solutions based on them, Glass Ceram. 60 (2003) 115–117.
- [14] S.J. Schneider, R.S. Roth, Phase equilibria in systems involving the rare-earth oxides. Part II. Solid state reactions in trivalent rare-earth oxide systems, J. Res. NBS 64A (1960) 317–332.
- [15] U. Berndt, D. Maier, C. Keller, New A^{III}B^{III}O₃ interlanthanide perovskite compounds, J. Solid State Chem. 13 (1975) 131–135.
- [16] W. Su, D. Wu, X. Li, X. Ma, J. Zhou, Z. Qian, Y. Wang, W. Liu, Z. Ge, An investigation using high-pressure synthesis of double-rare-earth oxides of ABO₃-composition, Physica 139 & 140B (1986) 658–660.
- [17] G.A. Tompsett, R.J. Philips, N.M. Sammes, A.M. Cartner, Characterisation of LaGdO₃ by X-ray powder diffraction and Raman spectroscopy, Solid State Commun. 108 (1998) 655–660.
- [18] T. Tsuzuki, W.T.A. Harrison, P.G.J. McCormick, Synthesis of ultrafine gadolinium oxide powder by mechanochemical processing, J. Alloys Compd. 281 (1998) 146–151.
- [19] C. Artini, G.A. Costa, R. Masini, Study of the formation temperature of mixed LaREO₃ (RE=Dy, Ho, Er, Tm, Yb, Lu) and NdGdO₃ oxides, J. Therm. Anal. Calorim. 103 (2011) 17–21.
- [20] A. Ubaldini, M.M. Carnasciali, Raman characterization of powder of cubic RE₂O₃ (RE=Nd, Gd, Dy, Tm, and Lu), Sc₂O₃ and Y₂O₃, J. Alloys Compd. 454 (2008) 374–378.
- [21] B. Antic, A. Kremenovic, M. Vucinic-Vasic, Z. Dohcevic-Mitrovic, A.S. Nikolic, M. Gruden-Pavlovic, B. Lancar, A. Meden, Composition related properties of (Yb,Y)₂O₃ nanoparticles synthesized by controlled thermal degradation of AA complexes, Mater. Chem. Phys. 122 (2010) 386–391.
- [22] Z.K. Heiba, M.B. Mohamed, H. Fuess, XRD, IR, and Raman investigations of structural properties of Dy_{2-x}Ho_xO₃ prepared by sol gel procedure, Cryst. Res. Technol. 47 (2012) 535–540.
- [23] Z.K. Heiba, L. Arda, Y.S. Hascicek, Structure and microstructure characterization of the mixed sesquioxides (Gd_{1-x}Yb_x)₂O₃ and (Gd_{1-x}Ho_x)₂O₃ prepared by sol-gel process, J. Appl. Cryst. 38 (2005) 306–310.
- [24] Z.K. Heiba, Y. Akin, W. Sigmund, Y.S. Hascicek, X-ray structure and microstructure determination of the mixed sesquioxides (Eu_{1-x}Yb_x)₂O₃ prepared by a sol-gel process, J. Appl. Cryst. 36 (2003) 1411–1416.
- [25] J.C. Panitz, J.C. Mayor, B. Grob, W. Durish, A Raman spectroscopic study of rare earth mixed oxides, J. Alloys Compd. 303–304 (2000) 340–344.
- [26] J. Wang, T. Liu, Z. Wang, E. Bugiel, A. Laha, T. Watahiki, R. Shayduk, W. Braun, A. Fissel, H.J. Osten, Epitaxial multi-component rare-earth oxide: a high-k material with ultralow mismatch to Si, Mater. Lett. 64 (2010) 866–868.
- [27] M. Paranthaman, D.F. Lee, A. Goyal, E.D. Specht, P.M. Martin, X. Cui, J.E. Mathis, R. Feenstra, D.K. Christen, D.M. Kroeger, Growth of biaxially textured RE₂O₃ buffer layers on rolled-Ni substrates using reactive evaporation for HTS-coated conductors, Supercond. Sci. Technol. 12 (1999) 319–325.
- [28] A. Dias, V.S.T. Ciminelli, Electroceramic materials of tailored phase and morphology by hydrothermal technology, Chem. Mater. 15 (2003) 1344–1352.
- [29] A. Dias, F.M. Matinaga, R.L. Moreira, Raman spectroscopy of (Ba_{1-x}Sr_x)(Mg_{1/3}Nb_{2/3})O₃ solid solutions from microwave-hydrothermal powders, Chem. Mater. 19 (2007) 2335–2341.
- [30] A. Dias, V.S.T. Ciminelli, F.M. Matinaga, R.L. Moreira, Raman scattering and X-ray diffraction investigations on hydrothermal barium magnesium niobate ceramics, J. Eur. Ceram. Soc. 21 (2001) 2738–2744.
- [31] K.P.F. Siqueira, R.L. Moreira, M. Valadares, A. Dias, Microwave-hydrothermal preparation of alkaline-earth-metal tungstates, J. Mater. Sci. 45 (2010) 6083–6093.
- [32] K.P.F. Siqueira, A. Dias, Incipient crystallization of transition-metal tungstates under microwaves probed by Raman scattering and transmission electron microscopy, J. Nanopart. Res. 13 (2011) 5927–5933.
- [33] A. Dias, F.M. Matinaga, R.L. Moreira, Vibrational spectroscopy and electron-phonon interactions in microwave-hydrothermal synthesized Ba(Mn_{1/3}Nb_{2/3})O₃ complex perovskites, J. Phys. Chem. B 113 (2009) 9749–9755.
- [34] A. Dias, R.L. Moreira, Production of Sr-deficient bismuth tantalates from microwave-hydrothermal derived precursors: structural and dielectric properties, J. Phys. Chem. Solids 68 (2007) 645–649.
- [35] M. Yoshimura, K. Byrappa, Hydrothermal processing of materials: past, present and future, J. Mater. Sci. 43 (2008) 2085–2103.
- [36] K. Byrappa, M. Yoshimura, Handbook of Hydrothermal Technology, William Andrew Publishing, New York, 2001.
- [37] M. Zinkevich, Thermodynamics of rare earth sesquioxides, Prog. Mater. Sci. 52 (2007) 597–647.
- [38] L. Eyring, in: K.A. Gschneider (Ed.), Handbook on the Physics and Chemistry of Rare Earths, 3, 1979, p. 337. Amsterdam, North Holland.
- [39] H. Yamamura, K. Yamazaki, K. Kakinuma, K. Nomura, The relationship between crystal structure and electrical conductivity in the LaY_{1-x}Ln_xO₃ (x=0.0–0.7), Solid State Ionics 150 (2002) 255–261.
- [40] N. Okita, A. Higashide, M. Saito, H. Yamamura, Structure transformation between perovskite-type and B-type rare earth structures, Procedia Eng. 36 (2012) 2–6.
- [41] H. Zhang, N. Li, K. Li, D. Xue, Structural stability and formability of ABO₃-type perovskite compounds, Acta Cryst. B63 (2007) 812–818.
- [42] S.R. Bathe, P.S. Patil, Electrochromic characteristics of pulsed spray pyrolyzed polycrystalline WO₃ thin films, Smart Mater. Struct. 18 (2009) 025004.
- [43] J.-F. Martel, S. Jandl, A.M. Lejus, B. Viana, D. Vivien, Optical crystal field study of Sm₂O₃ (C- and B-type), J. Alloys Compd. 275–277 (1998) 353–355.
- [44] J. Gouteron, D. Michel, A.M. Lejus, J. Zarembowitch, Raman spectra of lanthanide sesquioxide single crystals: correlation between A and B-type structures, J. Solid State Chem. 38 (1981) 288–296.
- [45] W. Hayes, R. Loudon, Scattering of Light by Crystals, Wiley, New York, 1978.
- [46] D.L. Rousseau, R.P. Bauman, S.P.S. Porto, Normal mode determination in crystals, J. Raman Spectrosc. 10 (1981) 253–290.