

Sol gel synthesis of multiphase lanthanum oxycarbonate and langasite thin films.

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Precursors of lanthanum oxide and of (3La₂O₃, 5Ga₂O₃, SiO₂) system were first elaborated then thermally decomposed into polycrystalline lanthanum oxide and langasite La₃Ga₅SiO₁₄. The as prepared lanthanum oxide powder was then hydrated and carbonated to give hydroxycarbonates: thermal decomposition of these complex system La₂O_{3-x}(OH)_y(CO₃)_z was studied by Fourier Transform infrared spectroscopy. Spin coating process applied to these precursors was optimized to elaborate thin films of lanthanum oxycarbonate La₂O₂CO₃, lanthanum oxide La₂O₃ and langasite, on silicium substrates (Si-(001)). Thin films are partly textured. Making use of same spin coating process, multiphase thin films of langasite covered with La₂O₃ particles were obtained.

Keywords: thin films, sol-gel growth, lanthanum carbonate, X-ray diffraction

I. Introduction

The general aim of this study was to associate catalytic and piezoelectric materials reacting with different gases at variable temperatures, susceptible to be involved in miniaturized systems for gas detection. Presently, we deal with coupling of hydrated carbonated lanthanum oxide, and langasite La₃Ga₅SiO₁₄ (LGS). Single crystals of langasite [1 - 4] were extensively studied as piezoelectric materials at high temperature: they present high piezoelectric performances, at least up to 1000°C. At high temperature, the stable La₂O₃ phase is a good catalyst for methane conversion into CO₂ and H₂O [5, 6]. Under environmental conditions, this lanthanum oxide is subjected to phase modification into hydroxycarbonates La₂O_{3-x}(OH)_y(CO₃)_z presently noted LHC, with x, y, z fractions depending on environmental conditions (temperature, H₂O, CO₂). In previous works [7, 8, 9], such modified La₂O₃ phases were already described and commented.

These two types of materials might be coupled in gas sensors working at variable high temperatures, to separately detect water, CO₂ and methane gases. Presently, we try to separately synthesize thin films of basic La₂O₃, La₂O₂CO₃ and La₃Ga₅SiO₁₄ phases. In a further step, these materials might be coupled to develop new surface or bulk acoustic devices (SAW, BAW technologies) for multifunctional gas sensors working at variable high temperatures to detect different gases.

II. Characterizations.

To identify crystallized phase formation in polycrystalline samples, X-ray diffraction patterns

were recorded on a Siemens-Brucker D5000 equipment, working in a classical θ -2 θ coupled mode, with copper X-ray source ($\lambda=1.5406 \cdot 10^{-10}$ m), Soller slides, a secondary monochromator and a rotating sample holder. The patterns were recorded with a 2 θ step of 0.02° and 26 seconds per step. To analyze thin films, a low angle configuration was used: the X-ray beam irradiated the thin film plane with a fixed low θ angle of 7°. Calculations of crystallographic parameters were performed from classical least mean square refinement approaches (Fullproof program [10]).

A Philips XL 30 scanning electron microscopy (SEM) equipment was used to image thin layers (back scattering electrons) and perform local EDS analyses. To characterize intermediate species formed during thermal decomposition of lanthanum hydroxycarbonates (noted as LHC), Fourier Transform Infrared (FTIR) spectroscopy was carried out at 25°C on samples initially stabilized at various temperatures (ranging between 25 and 600°C). Transmittance spectra were recorded using FTIR Mattson UNICAM spectrometer, in the wavelength range 2.5 to 25 μ m (wavenumbers: $\nu = 400$ to 4000 cm⁻¹). The samples were KBr pellets having 1 wt. % of phases, compacted at 4 kbar, in dry conditions to avoid additional hydration and carbonation of samples.

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III. Precursors and thermal treatments.

III.1. Lanthanum oxide and hydroxycarbonates.

Lanthanum oxide was first prepared via a sol gel route. An aqueous solution of lanthanum nitrate was first prepared by adjusting the pH with NH_4OH addition (final pH = 10). After agitation during one hour, a gel was formed, then intensely washed in distilled water to eliminate the residual $(\text{NH}_4)^+$ ions. The gel was finally dried at 80°C , during 24 hours. The obtained pulp was milled then heated at 300°C during 3 hours. The final step was a heating process at 750°C during 3 hours. To avoid hydration and carbonation by environmental water and CO_2 , this phase had to be stocked under neutral (N_2) atmosphere. The obtained powder was identified as being the La_2O_3 pure phase: the hexagonal crystal cell parameters were refined from Fullproof analysis [10]: $a = 3.937$ (1); $c = 6.129$ (1). These parameters were quite similar to the parameters of JCPDS standard 73-2141.

To obtain hydroxycarbonates, the as prepared La_2O_3 powder (in initial dry form) was placed in environmental conditions of storage during 12 hours, at a given temperature of 25°C (climatic chamber at 20°C , relative humidity 90 %, $0.03\ \text{CO}_2$ vol. %). During this period, La_2O_3 powder was progressively hydrated and carbonated to give a complex system in which residual grain core was La_2O_3 basic oxide and grain surface was hydroxycarbonate noted $\text{La}_2\text{O}_{3-x}(\text{OH})_y(\text{CO}_3)_z$. Then, the samples were thermally decomposed at various temperatures, during 6 hours, and studied by Fourier transform spectroscopy at 25°C . Initial

hydroxycarbonate sample and seven samples were obtained at eight stabilization temperatures: a) $T = 25^\circ\text{C}$ (initial sample); b) $T = 300^\circ\text{C}$; c) $T = 350^\circ\text{C}$; d) $T = 400^\circ\text{C}$; e) $T = 450^\circ\text{C}$; f) $T = 500^\circ\text{C}$; g) $T = 550^\circ\text{C}$; h) $T = 600^\circ\text{C}$. Figure 1 reports the FTIR spectra of the eight samples.

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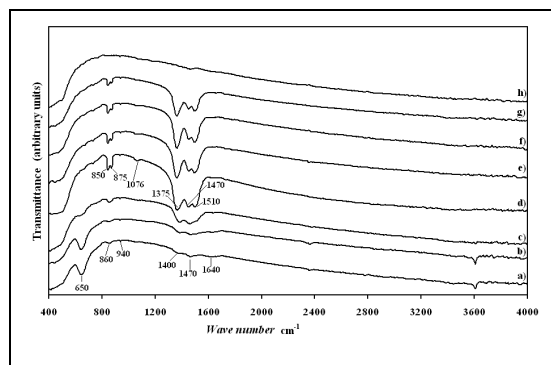


Figure 1: Fourier Transform Infrared Spectroscopy (at 25°C) of LHC thermally treated samples:

a) $T = 25^\circ\text{C}$; b) $T = 300^\circ\text{C}$; c) $T = 350^\circ\text{C}$; d) $T = 400^\circ\text{C}$; e) $T = 450^\circ\text{C}$; f) $T = 500^\circ\text{C}$; g) $T = 550^\circ\text{C}$; h) $T = 600^\circ\text{C}$.

In environmental conditions, the initial (a) sample is characterized by vibration bands of $\text{La}(\text{OH})_3(\text{H}_2\text{O})_n$ phase with frequencies of 650, 1640 et 3600 cm^{-1} associated with O--H bonds. Small bands at 2350-2360 cm^{-1} are observed: they are linked to weakly bound CO_2 species. Bands at 860, 1400, 1470 cm^{-1} might be associated with surface CO_3^{2-} carbonate species. The 940 cm^{-1} frequency band should be linked to La--O bonds.

From 350°C, the intensities of these OH bands decrease (elimination of water) and a major fact is observed: the progressive growth of bands associated with CO_3^{2-} ions at 850, 1076, 1375-1470, 1510 cm^{-1} [7, 8].

At 400°C, the OH bands completely vanish and carbonate bands appear at 1375-1470 cm^{-1} : this clearly can be ascribed to decomposition of lanthanum hydroxide into La_2O_3 [7, 8] and growth of new carbonate phase: $\text{La}_2\text{O}_3\text{CO}_3$.

For temperatures higher than 550°C, the sole bands at 940 and 456 cm^{-1} , characteristic of La -O vibrations are visible: the unique La_2O_3 phase is stable.

III.2. Langasite precursors.

Standard LGS powder. In a previous work, Shou-Qi Wang and Satoshi Uda [11] described a series of samples belonging to the LGS system, close to the nominal LGS composition. They clearly showed that LGS was an incongruent-melting compound and established a phase diagram. As a first step, we elaborated standard LGS ceramics from a specific solid-state reaction optimized after a series of thermal and grinding cycles. Pellets having stoichiometric composition ($2\text{L}+5\text{G}+\text{S} \rightarrow \text{La}_3\text{Ga}_5\text{SiO}_{14}$) were thermally treated at 950°C during 5 hours, with heating and cooling rates of 5°C/min. In these conditions, we limited evaporation of some melt components and migrations of phases (Ga_2O_3 and SiO_2). After cooling, pellets were ground then compacted and reheated up to 1200°C, with heating rate of 5°C/min. The final sample was heated during 6 hours at 1200°C, then cooled with the same rate, and maintained under dry conditions.

To clearly identify LGS phase from X-ray diffraction, we used the specific Rietveld procedure [10] to refine all atom coordinates and cell parameters (hexagonal setting, P 321 space group). The resulting refined atom coordinates and cell parameters $a = 8.1694$ (4) Å and $c = 5.0938$ (4) Å were in good agreement with literature results [12, 13, 14].

Sol gel LGS route. To prepare a precursor for thin film deposition, we investigated a new sol gel route. A first solvent was prepared. Ethanol, tetraethyl ortho-silicate ($\text{TEOS} = (\text{C}_2\text{H}_5)_4\text{SiO}_4$) and nitric acid were mixed, and the pH was adjusted to pH=1. Two aqueous solutions of lanthanum and gallium nitrate precursors were prepared in room conditions. The solution of lanthanum nitrate was first diluted into

the first solvent, and, just after, the gallium nitrate solution was added to this intermediate solution, provoking the formation of a white gel. The as prepared mixture was dried at 80°C during 6 hours, and a first powder was finally obtained. The solid precursor was compacted at a pressure of 4 kbars and heated at 950°C for ten hours. The X-ray diffraction analysis (classical powder analysis) of the obtained ceramics showed that LGS was formed at 950°C, as being the major phase, instead of 1200°C for our own solid state reaction: however, residues of LaGaO_3 and SiO_2 were observed. After grinding the powder and applying identical thermal treatments at 950°C, the proportion of these residues strongly decreased. Figure 2 reports the first step of LGS precursor thermal treatment giving a major LGS phase with residues.

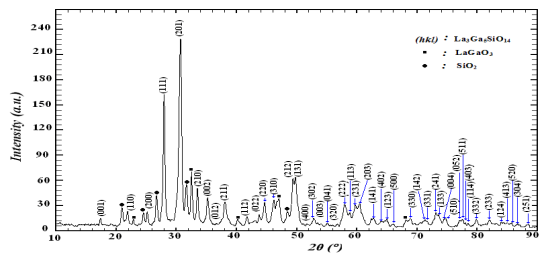


Figure 2: X-ray diffraction of LGS and residual phases, obtained from sol gel route (first heating cycle); (hkl) Miller indices of LGS phase are reported.

IV. Elaborations of thin films.

Thin films of La_2O_3 . To prepare thin films of La_2O_3 or LGS, a specific chemical route was experimented using a spin coating deposition process. The previously prepared lanthanum “sol” was used to form thin layers of La_2O_3 on a silicium substrate having (001) crystal orientation. Such substrates are commonly used in microelectronics applications. Drops of this solution were deposited on the substrate, placed on the rotating plate of the spin coating equipment. It was necessary to optimize the spin coating process: the optimized final conditions were a speed of 1500 revolutions per minute (rpm), an acceleration up to 2000 rpm/s, a deposition time of 15 s, and a drop volume of 10 μl .

Taking into account the previous thermal decomposition analysis of hydrated carbonated La_2O_3 powders, two types of thermal treatments were applied: the first one (A sample) consisted in heating the thin layer on its substrate, at 600°C during 3 hours, and the second one (B sample) consisted in heating the sample at 750°C during 3 hours. The La_2O_3 thin films prepared at 600°C and at 750°C were analyzed by X-ray diffraction, with fixed low angle configuration. Figure 3a reports XRD data for a standard La_2O_3 powder placed in dry conditions. These data will be used to discuss the diffraction data of thin films. Figure 3 b and 3c report the diffraction patterns of thin films

respectively heated at 600°C and 750°C. On figure 3b and 3c, strong Bragg peaks of oriented (001) silicium substrate are observed. On Figure 3b, the two major phases La_2O_3 and $\text{La}_2\text{O}_2\text{CO}_3$ are clearly identified (according to our standard and JCPDS references). On Figure 3c, the unique La_2O_3 phase is identified, and the carbonate phase is not observable, which is due to high temperature treatment. Cell parameters of both phases were determined (with large standard deviations). The La_2O_3 phase was hexagonal with $a = 3.94 \pm 0.01 \text{ \AA}$, $c = 6.14 \pm 0.02 \text{ \AA}$ and the $\text{La}_2\text{O}_2\text{CO}_3$ phase was monoclinic (close to orthorhombic system) with $a = 4.07 \pm 0.01 \text{ \AA}$, $b = 13.56 \pm 0.03 \text{ \AA}$, $c = 4.06 \pm 0.01 \text{ \AA}$ and $\beta = (a, c) = 90.9^\circ$.

From Bragg peak intensity analyses, it was observed that the La_2O_3 grains were partly oriented with (h00) preferential orientations: this showed that the crystallographic directions (00l) of the La_2O_3 hexagonal crystals were more or less aligned in the substrate plane.

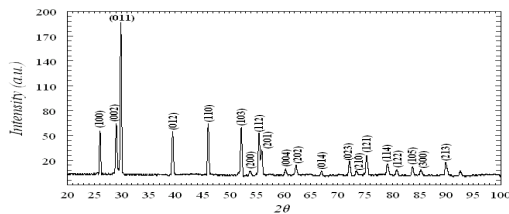


Figure 3a: Standard La_2O_3 sample, powder synthesized from sol gel route and maintained in dry conditions.

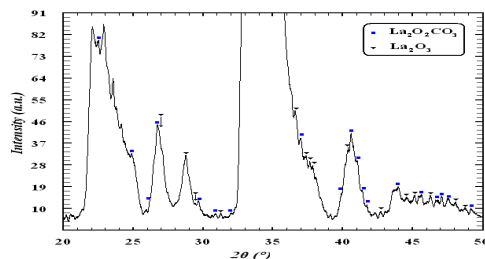
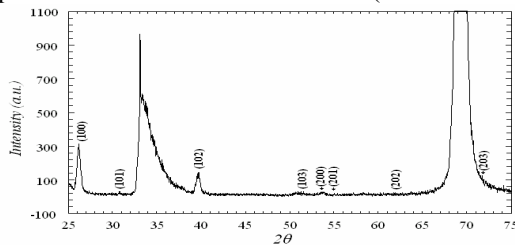


Figure 3b: thin film heated at 600°C: mixed system ($\text{La}_2\text{O}_2\text{CO}_3 + \text{La}_2\text{O}_3$). On each pattern, strong Bragg peaks of Si substrate are visible (close to $35^\circ 2\theta$



angles and $69.5^\circ 2\theta$ angles).

Thin films of Langasite. The LGS precursor obtained from sol gel route described above was first diluted in ethanol. Drops of this solution were deposited on the Si substrate. The spin coating process was optimized: the optimized conditions were a speed of 2500 rpm, with acceleration up to Figure 3c: thin film heated at 750°C: La_2O_3 unique phase. On each pattern, strong Bragg peaks of Si substrate are visible (close to $35^\circ 2\theta$ angles and $69.5^\circ 2\theta$ angles).

4500 rpm/s, deposition time of 20 s, and drop volume of 20 μl . The following heating cycle was also adapted: a first thermal plateau at 120°C was applied during 2 hours to evaporate the solvent, then a second thermal plateau was fixed at 950°C during 3 hours to obtain phase crystallization.

The diffraction pattern (Figure 4) was identified as being that of standard LGS phase, similar to the pattern of LGS powder described above. No accurate structural determination was possible because of weak intensities and specific profile due to low angle diffraction method. However, abnormal intensity attenuation was observed for (111) and (201) planes of the hexagonal structure (these Bragg peaks have the strongest intensities in the case of non oriented powder sample, see Figure 2). Correlatively, some (h00) peaks have strong relative intensities. This might be interpreted in terms of partial preferential orientation [100] of micro crystals, involving [001] crystal directions partly aligned in the plane of the Si substrate.

An additional effect was observed: the LGS Bragg peak profiles present a significant broadening linked to small particle sizes or small coherence lengths. As a first approach and having regard to limited experimental accuracy, we used the basic Scherrer model giving coherence length or crystal dimension as being $L = 0.9 \lambda / \Delta(2\theta) \cdot \cos(\theta)$: L allows evaluating mean grain sizes as a function of wavelength λ , angle broadening due to size effect $\Delta 2\theta$ (full width at half medium, FWHM), Bragg angle θ in radians. Using powder diffraction profiles of standard LGS sample, we obtained L values of about 35 - 40 nm, mainly for observable crystal directions [h00].

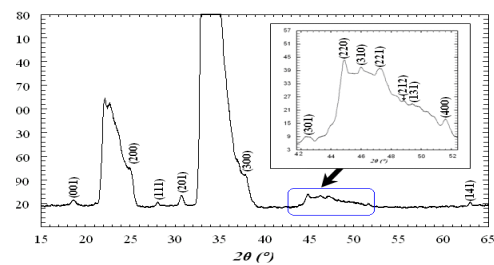


Figure 4: LGS thin film on silicium (001) substrate (spin coating process).

Figure 5 reports the BSE image of LGS film. The film was regularly formed of LGS grains having variable geometrical forms, with frequent rods or needle-like forms having lengths of 5 -10 microns and widths of 1-2 microns. This might be related to the observed attenuation of (111) Bragg peak intensity (see previous section): this should argue in favor of (00l) crystal axis lying in the silicium substrate plane.

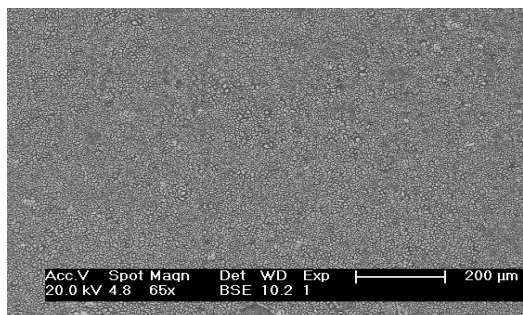


Figure 5: backscattering electron imaging of LGS first layer. Small rods are observed showing LGS specific crystallization with (001) axis lying in the substrate plane.

6. Conclusion

Thin films of La_2O_3 , $\text{La}_2\text{O}_3\text{-La}_2\text{O}_2\text{CO}_3$ multiphase system and LGS phases were successfully elaborated from a sol gel process associated with spin coating deposition. Depending on thermal treatment, it was possible to form either $\text{La}_2\text{O}_3 + \text{La}_2\text{O}_2\text{CO}_3$ mixed thin layers or pure La_2O_3 layers. La_2O_3 films present partial crystal orientation with c axis of hexagonal structure aligned in silicon (001) plane. These films with variable carbonate compositions might be involved in gas sensing systems, sensitive to several gases, including CO_2 gas. The microstructural modifications involved by deposition of LGS on La_2O_3 layers are now planned, electrical and catalytic analyses in presence of pollutant gas are now

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