

Sol-Gel Synthesis of Nanocrystalline LaAlO₃-M₂O₃ (M = La, Al) and Nd:LaAlO₃-M₂O₃ Composite Materials via “Phase Metathesis” Route

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A sol-gel method based on *in-situ* generation of mixed-metal chelates by complexing metal ions with 1,2-ethanediol in aqueous media has been developed to prepare pure and neodymium-doped nanocrystalline perovskite lanthanum aluminate (LaAlO₃, LAP and Nd: LaAlO₃, Nd:LAP) dispersed within alumina and lanthanum oxide matrix. The X-ray diffraction (XRD) patterns of the powders sintered at 1000 °C showed the formation of highly crystalline composite materials. This temperature is the lowest temperature reported for the synthesis of such type composite ceramics. A homogeneous distribution of neodymium in the LAP lattice of LAP-M₂O₃ (M = Al, La) composite was achieved in all dopant concentrations investigated. The phase transformations, composition and micro-structural features in the polycrystalline samples were studied by XRD analysis, IR spectroscopy, and scanning electron microscopy (SEM). The quality of the resulting products (homogeneity, crystallization temperature, grain size, grain size distribution, *etc.*) is discussed.

Keywords: composite materials, aluminates, LaAlO₃, Al₂O₃, La₂O₃, sol-gel synthesis.

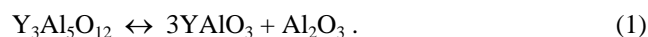
1. INTRODUCTION

The development of innovative multi-functional advanced materials should have a major impact in future applications. Ceramics based on Ln₂O₃-Al₂O₃ (Ln – lanthanide element) combination are promising materials for optical, electronic and structural applications [1 – 5]. The perovskite yttrium aluminate (YAlO₃, YAP) doped with lanthanide element offers advantages of longer lifetimes and higher, polarized cross sections with respect to most of other oxide matrix [6], and is useful as host for solid-state lasers, luminescence systems and window materials for a variety of lamps [7]. LaAlO₃ (LAP) and related materials are currently being incorporated into automobile catalytic converters [8]. LaAlO₃ is promising substrate for the epitaxy of thin oxide films and has potential use as buffer layer for the epitaxial growth of various perovskite-type films such as a high temperature superconductors, ferro-electrics and colossal magnetoresistance oxides [9, 10].

Owing to such wide and diverse application potential of aluminates-based ceramics, new routes for the synthesis of pure and homogeneously doped different metal-mixed aluminates are highly desirable. It has been demonstrated that the sol-gel process offers considerable advantages such as better mixing of the starting materials and excellent chemical homogeneity in the final product. Moreover, the molecular level mixing and the tendency of partially hydrolyzed species to form extended networks facilitate the structure evolution thereby lowering the crystallization temperature [11 – 15].

The unique properties of most of the mixed-cation oxide ceramics depend largely on impurities or dopants. Such complex oxides with the perovskite structure also demonstrate an impressive range of electrical, optical and magnetic properties. In the Y₂O₃-Al₂O₃ system, depending

on the synthesis conditions the formation of different phases such as Y₃Al₅O₁₂, YAlO₃ and Y₄Al₂O₉ (YAM) usually takes place [16]. This feature is often considered as serious problem during preparation of single-phase YAG. Sometimes these transient intermediate phases (YAP, YAM) could be fully converted to garnet phase by higher temperatures or by longer annealing time. For example, recently MacKenzie and Kemmitt [17] concluded that diffusion of Al to YAlO₃ could be controlled effectively by temperature. On the other hand, the formation of impurity phases may be attributed to the metastable decomposition of YAG into several phases [18]:



It has been reported that when Al₂O₃ and Y₂O₃ reactants were heated below 1600 °C, Y₃Al₅O₁₂ could not be obtained as a single phase but co-exists with YAlO₃ and Al₂O₃ [19]. Such a situation has initiated the present work, motivating us to elaborate a novel synthetic approach for the preparation of composite material LaAlO₃-M₂O₃ (M = La, Al) using “phase metathesis” approach.

2. EXPERIMENTAL

The ceramic samples were synthesized by an aqueous sol-gel method. The gels were prepared using stoichiometric amounts of analytical-grade La(NO₃)₃, Al(NO₃)₃·9H₂O and Nd₂O₃ as starting materials. The nominal molar ratio of La:Al = 3:5, corresponding to the stoichiometrical composition for La₃Al₅O₁₂ was used. In the sol-gel process lanthanum nitrate (2.4369 g; 0.0075 mol) was first dissolved in 50 ml of 0.2 M CH₃COOH at 60 °C. To this solution, aluminium nitrate (4.6892 g; 0.0125 mol) dissolved in 50 ml of distilled water was added and the resulting mixture was stirred for 2 h at the same temperature. For the preparation of Nd-doped samples the appropriate amount of neodymium oxide (1 % Nd ⇒ 0.0042 g; 1.25·10⁻⁵ mol; 3 % Nd ⇒ 0.0126 g;

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$3.75 \cdot 10^{-5}$ mol; and 5 % Nd \Rightarrow 0.0210 g; $6.25 \cdot 10^{-5}$ mol) dissolved in 50 ml 0.2 M CH_3COOH at 60°C was added and the resulting mixture was stirred for 1 h at the same temperature. In a following step, 1,2-ethanediol (2 ml) as complexing agent was added to the above solutions. After concentrating the solutions by slow evaporation at 65°C under stirring the La-Al-O or Nd:La-Al-O acetate-nitrate-glycolate sols turned into white transparent gels. The oven dried (100°C) gel powders were ground in an agate mortar and preheated for 3 h at 600°C in air. Since the gels are very combustible, slow heating ($\sim 3^\circ\text{C min}^{-1} - 4^\circ\text{C min}^{-1}$) especially between 100°C and 400°C was found to be essential. After an intermediate grinding in an agate mortar the La-Al-O powders were additionally sintered for 10 h at 800°C , 900°C , and 1000°C in air. The Nd:La-Al-O powders (with 1 % Nd, 3 % Nd, and 5 % Nd were sintered for 10 h at 1000°C in air.

The X-ray powder diffraction (XRD) studies were performed on a Siemens diffractometer operating with $\text{CuK}\alpha_1$ radiation. The infrared (IR) spectra were recorded as KBr pellets on a BioRad FTIR-165 spectrometer. Scanning electron microscope (SEM) JEOL JSM-35 was used to study the morphology and microstructure of the ceramic samples.

3. RESULTS AND DISCUSSIONS

To obtain nanocrystalline LaAlO_3 , LAP composite and to check for the exact calcination temperature for the formation of the LAP- M_2O_3 ceramics the Ln-Al-O precursor gels were calcined in air at various temperatures in the range $800^\circ\text{C} - 1000^\circ\text{C}$. IR spectra of the $\text{La}_3\text{Al}_5\text{O}_{12}$ samples sintered at different temperatures are presented in Fig. 1.

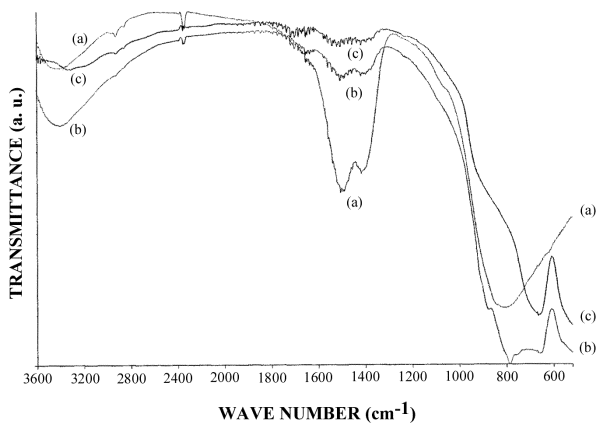


Fig. 1. IR spectra of La-Al-O precursor gel samples annealed at: a – 800°C ; b – 900°C ; c – 1000°C

IR spectra of all three samples calcined at different temperatures from 800°C to 1000°C contain a broad band at $3310\text{ cm}^{-1} - 3435\text{ cm}^{-1}$. The intensities of these bands, which can be assigned to the adsorbed water during the exposure of dried powder to air [20, 21], remain almost unchanged with calcination temperature. In all three spectra the peaks at ca. 2340 cm^{-1} are well pronounced, arising from the adsorption of carbon dioxide from atmosphere. The IR spectrum of sample annealed at 800°C

exhibits two bands at 1506 cm^{-1} and 1418 cm^{-1} , assignable to the ionic carbonates [22]. Also, there is a broad band ($880\text{ cm}^{-1} - 700\text{ cm}^{-1}$), assigned to the characteristic metal-oxygen vibrations in the ceramic samples [23]. The carbonate peaks in the IR spectra of La-Al-O sample persist to 900°C , but with lower intensity than before (see Figure 1, b). Furthermore, the broad band in the region of $880\text{ cm}^{-1} - 700\text{ cm}^{-1}$ for the sample sintered at 900°C is replaced by several bands at 877 , 785 , and 734 cm^{-1} , indicating a multiphase character of the synthesized product. Heating to 1000°C again gives only one absorption line at around 665 cm^{-1} . This band, however, is not characteristic absorption line for the garnet structure compound. It is well known that IR spectra of the garnet samples ($\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Y}_3\text{Fe}_5\text{O}_{12}$, $\text{Y}_3\text{Sc}_x\text{Al}_{5-x-y}\text{Ga}_y\text{O}_{12}$) contain several intense peaks in the range of $900\text{ cm}^{-1} - 500\text{ cm}^{-1}$. And these bands are characteristic for YAG, YIG or YSAGG structures and could be attributable to the stretching mode of the tetrahedral units present in the garnet structure [20, 24]. Thus, according to the stretching frequencies observed the formation of crystalline LAG by proposed synthesis routes possibly does not proceed. Besides, IR spectrum of sample calcined at 1000°C does not show any band attributable to the carbonates.

To demonstrate the suitability and versatility of our sol-gel synthesis method to the preparation of doped oxide ceramics, we also evaluate here the above mentioned synthetic approach for the preparation of Nd-doped La-Al-O ceramics. As was already mentioned, the Nd-doped La-Al-O precursor gel powders having different concentrations of Nd (1 %, 3 %, and 5 %) were sintered for 10 h at 1000°C in air. The IR spectra of the neodymium-doped La-Al-O samples are presented in Fig. 2.

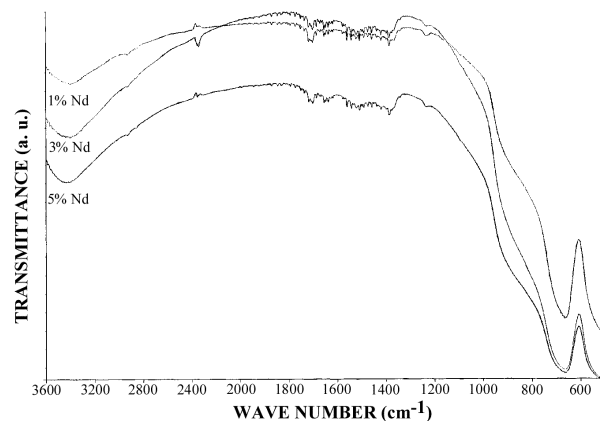


Fig. 2. IR spectra of Nd-doped La-Al-O precursor gel samples annealed at 1000°C

In all of the cases, IR spectra found to be identical regardless of neodymium doping level. Moreover, these three spectra, consequently and the origin of the peaks are almost the same as presented in Fig. 1. Evidently, the absorption band at 665 cm^{-1} which is hardly attributable to the stretching mode of the tetrahedra in the garnet structure is present in all IR spectra of Nd-doped ceramics. Despite this broad absorption band in the same wavenumber region is not typical Al-O vibrations for the garnet structure compounds, all IR spectra of the heat treated neodymium-doped samples show only IR frequencies corresponding to

M-O vibrations. Taking into account the similarity of the IR spectra of samples investigated and observation that each IR spectrum of the heated neodymium-doped La-Al-O sample shows only one typical absorption band, the homogeneous distribution of Nd in the oxide ceramics could be suggested.

The results from IR spectroscopy were found to be consistent with crystallization process observed by the XRD measurements. The X-ray diffraction patterns for the calcined gel powders and sintered for 10 h at 800 °C – 1000 °C are shown in Fig. 3.

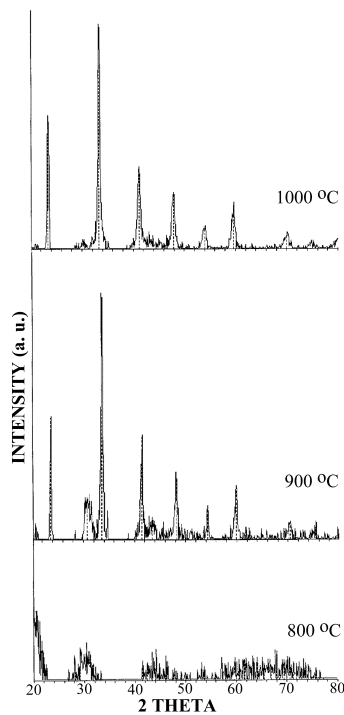
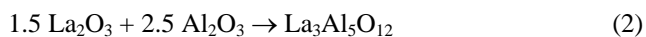


Fig. 3. Powder X-ray diffraction patterns of the La-Al-O precursor gel samples annealed at different temperatures

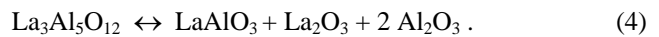
As seen, the powders remain essentially amorphous to X-rays for calcination temperatures of up to 800 °C. The pattern for the product obtained at 800 °C only indicates an unidentified several amorphous humps, which $2\theta = 30^\circ - 40^\circ$ and $2\theta = 55^\circ - 65^\circ$ reach maximum height around $2\theta \approx 20^\circ, 30^\circ, 44^\circ,$ and 67° . When heated above 800 °C, the samples fully crystallize, and the obtained phases depend on synthesis temperature. By 900 °C crystalline perovskite lanthanum aluminate (LAP) had begun to form as a major phase, although the peaks at 2θ values of 30.8° , and 43.5° indicate the coexistence of impurity phases, such as γ -alumina and $\text{La}_2\text{O}_2\text{CO}_3$ [23, 25]. Sintering at 1000 °C produced fully crystallized three phases, LaAlO_3 , Al_2O_3 and La_2O_3 . The most intensive lines could be detected at $2\theta = 33.3^\circ$ (100 %), $2\theta = 23.4^\circ$ (59.4 %), and $2\theta = 41.2^\circ$ (34.7 %). Thus, $\text{La}_3\text{Al}_5\text{O}_{12}$ phase has not formed by heat treatment of the precursor gel powders. The solid state reaction expressed by Eq. 2 does not proceed at 1000 °C:



Therefore, the possible formation of ceramic composite schematically could be described by the following reaction:



or by “*phase metathesis*” reaction:



The XRD patterns of the Nd:LAP- La_2O_3 - Al_2O_3 ceramics are shown in Fig. 4.

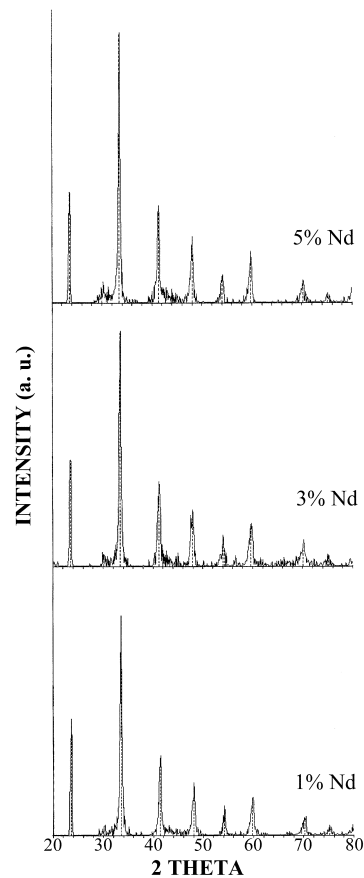


Fig. 4. Powder X-ray diffraction patterns of Nd-doped La-Al-O precursor gel samples annealed at 1000 °C

The first signs of crystallisation were observed, in all cases, at the same temperatures those required for undoped LAP composite ceramics. The most intensive lines could be detected at $2\theta = 33.5^\circ$ (100 %), $2\theta = 23.5^\circ$ (53.1 %), and $2\theta = 41.3^\circ$ (33.2 %) for 1 % Nd-doped sample; at $2\theta = 33.4^\circ$ (100 %), $2\theta = 23.5^\circ$ (45.2 %), and $2\theta = 41.2^\circ$ (32.7 %) for 3 % Nd-doped sample; and at $2\theta = 33.4^\circ$ (100 %), $2\theta = 23.5^\circ$ (39.6 %), and $2\theta = 41.3^\circ$ (34.0 %) for 5 % Nd-doped sample. Therefore, the sol-gel synthesis gave well-developed Nd-doped LAP- La_2O_3 - Al_2O_3 composite phase at 1000 °C and no formation of the crystalline dopant oxide Nd_2O_3 was observed.

The textural properties of the calcined powders were investigated by SEM, from which the grain size and typical morphologies were obtained. Scanning electron micrographs of the samples calcined at 800 °C, 900 °C, and 1000 °C are shown in Figures 5, 6, and 7, respectively. A progressive change in morphology is evident with increased calcination temperature. Fig. 5 shows the surface features of the powder calcined at 800 °C. Individual particles seem to be nano-sized plate-like crystals and they partially fused to form hard agglomerates.

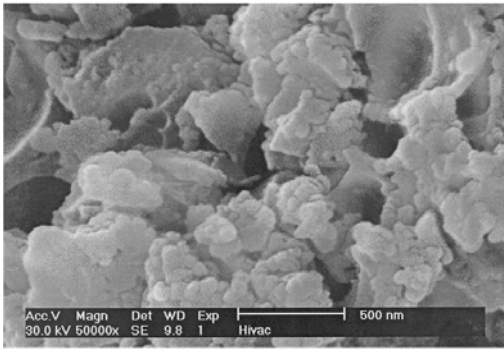


Fig. 5. Scanning electron micrograph of the La-Al-O precursor gel sample sintered at 800 °C

Fig. 6 shows the microstructure of the calcined powder at 900 °C.

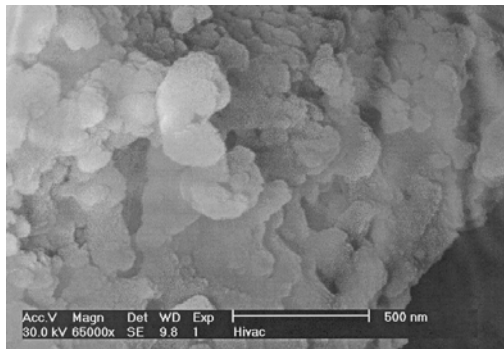


Fig. 6. Scanning electron micrograph of the La-Al-O precursor gel sample sintered at 900 °C

It can be seen from Fig. 6 that the synthesized solids are composed of grains with no regular shape. For example, the volumetric plate-like grains coexist with spherically shaped particles. Besides, these nearly round particles are slightly necked each other's, implying that grain growth takes place at this temperature [26]. It is interesting to note, however, that the particle size does not increase with firing temperature as usually is observed [27]. At 1000 °C, the sample consists of nearly spherical particles, with an average particle size of around 50 nm – 100 nm (see Fig. 7).

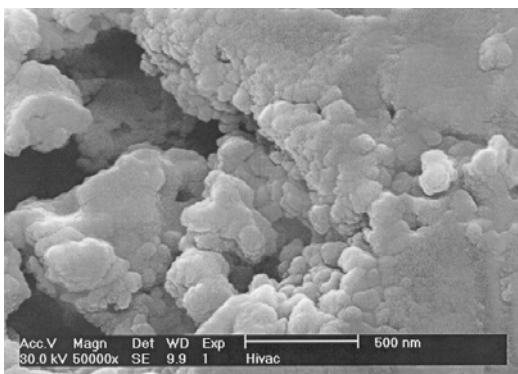


Fig. 7. Scanning electron micrograph of the La-Al-O precursor gel sample sintered at 1000 °C

At higher temperatures, it seems, particles were formed with more pronounced agglomeration, indicating good connectivity between the grains which is characteristic feature for ceramic composite material. Moreover, the

microstructure of LAP-metal oxides ceramic samples obtained at 900 °C and 1000 °C consisted of a large-grained matrix with clusters of small grains. The phenomena of clustering and texture in the similar samples were addressed in another publication [28].

It is interesting to note that almost identical microstructure was observed for all Nd-doped mixed-metal composites. Scanning electron micrograph of the representative sample with 3 % of Nd is shown in Fig. 8.

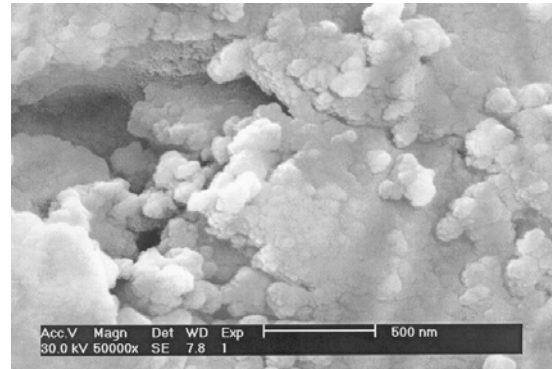


Fig. 8. Scanning electron micrograph of 3 % Nd-doped La-Al-O precursor gel sample sintered at 1000 °C

The SEM picture shows very small crystals with particle size ranging from 50 nm to 100 nm with morphology similar to that observed for non-doped ceramics. The SEM micrographs of all Nd-doped LAP-M₂O₃ specimens revealed the formation of very homogeneous mixed-metal oxides, and the formation of a continuous network of crystallites is evident. However, pores and voids can also be seen, which result probably from the escaping gases during calcination [29, 30]. The micrographs of Nd-doped LAP composites also showed highly agglomerated, uniform, and crystalline particles with smooth surfaces. Therefore, the proposed sol-gel technique appears to be very attractive way to make a high density, homogeneous nanosized Nd: LaAlO₃-M₂O₃ ceramic composites.

4. CONCLUSIONS

The sinterability and microstructural evolution of LaAlO₃-M₂O₃ (M = La, Al) composite powders synthesized by an aqueous sol-gel process were investigated in the present study. For the first time, to our knowledge, the novel “phase metathesis” synthetic route for the preparation of LAP in the metal oxides matrix has been suggested. We also showed, that this innovative approach offers a feasible way to obtain highly homogeneous lanthanide-doped nanoscaled ceramics with possible application as laser hosts. Some of the advantages of the proposed sol-gel synthesis method, e.g. low sintering temperature (1000 °C) of LaAlO₃-M₂O₃ ceramic composite, excellent homogeneity and control of stoichiometry, high phase purity, are also demonstrated in the present study. Besides, the present study demonstrates the versatility of aqueous sol-gel method to yield monophasic neodymium-doped LaAlO₃-M₂O₃ ceramic composite at low sintering temperature. Thus, the developed synthesis route offers unique opportunities for the synthesis of optical materials, since it is suited for the production of thin/thick films, monoliths

and fibers. Moreover, the proposed aqueous sol-gel method is inexpensive and thus appropriate for the large-scale production of new ceramic materials.

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