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Sol-Gel Synthesis of Nanocrystalline $LaAlO_3$-M_2O_3 (M = La, Al) and Nd:$LaAlO_3$-M_2O_3 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 ($LaAlO_3$, LAP and Nd: $LaAlO_3$, 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-M_2O_3 (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, $LaAlO_3$, Al_2O_3, La_2O_3, sol-gel synthesis.

1. INTRODUCTION

The development of innovative multi-functional advanced materials should have a major impact in future applications. Ceramics based on Ln_2O_3-Al_2O_3 (Ln – lanthanide element) combination are promising materials for optical, electronic and structural applications [1 – 5]. The perovskite yttrium aluminate ($YAlO_3$, 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]. $LaAlO_3$ (LAP) and related materials are currently being incorporated into automobile catalytic converters [8]. $LaAlO_3$ 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, ferroelectrics 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 Y_2O_3-Al_2O_3 system, depending on the synthesis conditions the formation of different phases such as $Y_3Al_5O_{12}$, $YAlO_3$ and $Y_4Al_2O_9$ (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 $YAlO_3$ 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]:

$$Y_3Al_5O_{12} \leftrightarrow 3YAlO_3 + Al_2O_3 . \quad (1)$$

It has been reported that when Al_2O_3 and Y_2O_3 reactants were heated below 1600 °C, $Y_3Al_5O_{12}$ could not be obtained as a single phase but co-exists with $YAlO_3$ and Al_2O_3 [19]. Such a situation has initiated the present work, motivating us to elaborate a novel synthetic approach for the preparation of composite material $LaAlO_3$-M_2O_3 (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 $La(NO_3)_3$, $Al(NO_3)_3 \cdot 9H_2O$ and Nd_2O_3 as starting materials. The nominal molar ratio of La : Al = 3 : 5, corresponding to the stoichiometrical composition for $La_3Al_5O_{12}$ 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 CH_3COOH 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; $1.25 \cdot 10^{-5}$ 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 (~3 °C min^{-1} – 4 °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 $CuK\alpha_1$ 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 °C – 1000 °C. IR spectra of the $La_3Al_5O_{12}$ samples sintered at different temperatures are presented in Fig. 1.

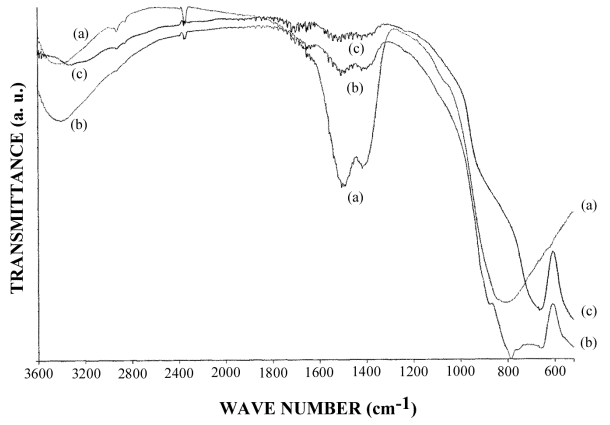

Fig. 1. IR spectra of La-Al-O precursor gel samples annealed at: a – 800 °C; b – 900 °C; c – 1000 °C

IR spectra of all three samples calcined at different temperatures from 800 °C to 1000 °C contain a broad band at 3310 cm^{-1} – 3435 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 cm^{-1} – 700 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 cm^{-1} – 700 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 ($Y_3Al_5O_{12}$, $Y_3Fe_5O_{12}$, $Y_3Sc_xAl_{5-x-y}Ga_yO_{12}$) contain several intense peaks in the range of 900 cm^{-1} – 500 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.

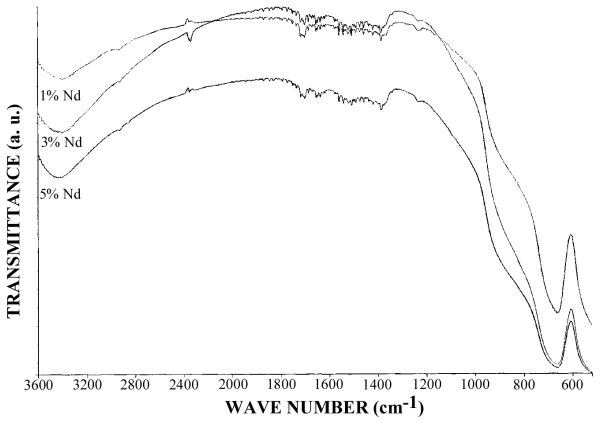

Fig. 2. IR spectra of Nd-doped La-Al-O precursor gel samples annealed at 1000 °C

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.

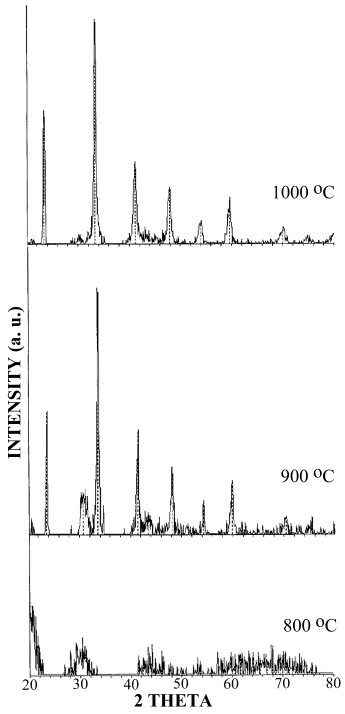

Fig. 3. Powder X-ray diffraction patterns of the La-Al-O precursor gel samples annealed at different temperatures

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 $2\theta = 30° - 40°$ and $2\theta = 55° - 65°$ reach maximum height around $2\theta \approx 20°$, 30°, 44°, 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 $La_2O_2CO_3$ [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 $2\theta = 33.3°$ (100 %), $2\theta = 23.4°$ (59.4 %), and $2\theta = 41.2°$ (34.7 %). Thus, $La_3Al_5O_{12}$ 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:

$$1.5\ La_2O_3 + 2.5\ Al_2O_3 \rightarrow La_3Al_5O_{12} \quad (2)$$

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

$$1.5\ La_2O_3 + 2.5\ Al_2O_3 \rightarrow LaAlO_3 + La_2O_3 + 2\ Al_2O_3 \quad (3)$$

or by *"phase metathesis"* reaction:

$$La_3Al_5O_{12} \leftrightarrow LaAlO_3 + La_2O_3 + 2\ Al_2O_3\ . \quad (4)$$

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

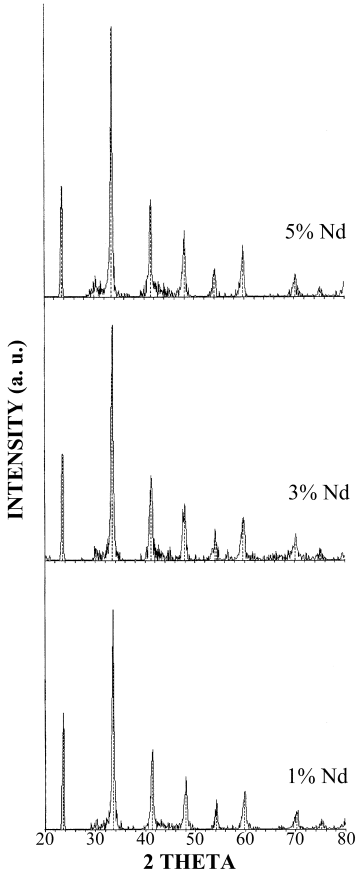

Fig. 4. Powder X-ray diffraction patterns of Nd-doped La-Al-O precursor gel samples annealed at 1000 °C

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 $2\theta = 33.5°$ (100 %), $2\theta = 23.5°$ (53.1 %), and $2\theta = 41.3°$ (33.2 %) for 1 % Nd-doped sample; at $2\theta = 33.4°$ (100 %), $2\theta = 23.5°$ (45.2 %), and $2\theta = 41.2°$ (32.7 %) for 3 % Nd-doped sample; and at $2\theta = 33.4°$ (100 %), $2\theta = 23.5°$ (39.6 %), and $2\theta = 41.3°$ (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.

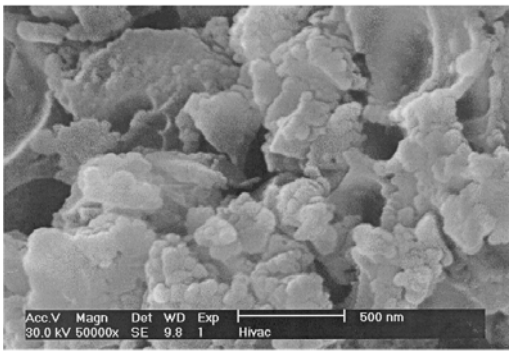

Fig. 5. Scanning electron micrograph of the La-Al-O precursor gel sample sintered at 800 °C

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

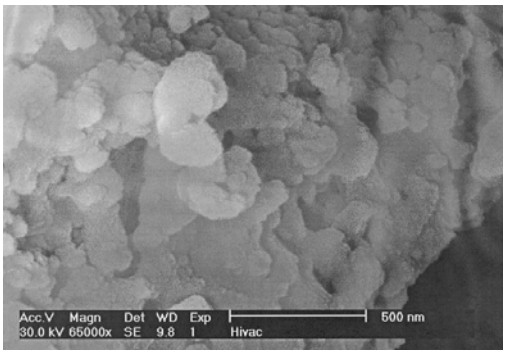

Fig. 6. Scanning electron micrograph of the La-Al-O precursor gel sample sintered at 900 °C

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).

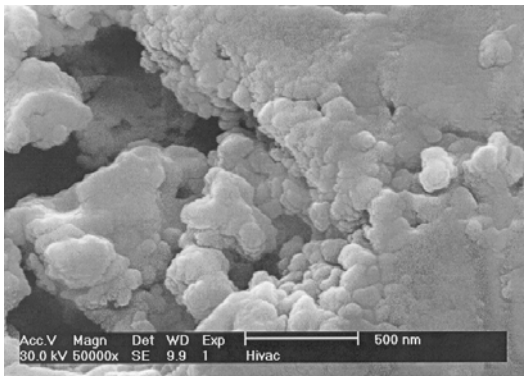

Fig. 7. Scanning electron micrograph of the La-Al-O precursor gel sample sintered at 1000 °C

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.

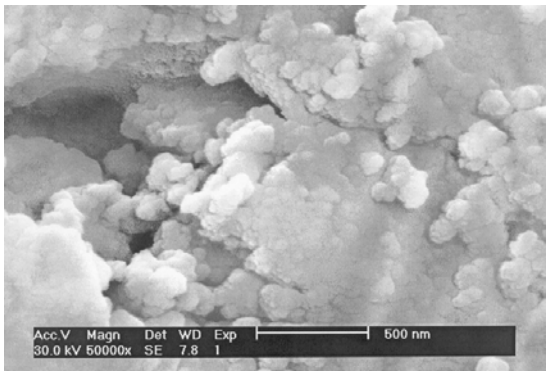

Fig. 8. Scanning electron micrograph of 3 % Nd-doped La-Al-O precursor gel sample sintered at 1000 °C

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-M_2O_3 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: $LaAlO_3$-M_2O_3 ceramic composites.

4. CONCLUSIONS

The sinterability and microstructal evolution of $LaAlO_3$-M_2O_3 (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 $LaAlO_3$-M_2O_3 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 $LaAlO_3$-M_2O_3 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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REFERENCES

1. **Kennedy, B. J., Howard, C. J., Prodjosantoso, A. K., Chakoumakos, B. C.** Neutron Powder Diffraction Study of the Rhombohedral to Cubic Phase Transition in the Series $La_{1-x}Pr_xAlO_3$ *Applied Physics A Materials Science Processing* 74 2002: pp. S1660 – S1663.
2. **Jancar, B., Suvorov, D., Valant, M. Drazic, G.** Characterization of $CaTiO_3$-$NdAlO_3$ Dielectric Ceramics *Journal of the European Ceramic Society* 23 2003: pp. 1391 – 1400.
3. **Zylberberg, J., Ye, Z. G.** Improved Dielectric Properties of Bismuth-Doped $LaAlO_3$ *Journal of Applied Physics* 100 2006: article number 086102.
4. **Cizauskaite, S., Reichlova, V., Nenartaviciene, G., Beganskiene, A., Pinkas, J., Kareiva, A.** Sol-gel Preparation and Characterization of Gadolinium Aluminate *Materials Chemistry and Physics* 102 2007: pp. 105 – 110.
5. **Berchmans, L. J., Angappan, S., Visuvasam, A., Kumar, K. B. R.** Preparation and Characterization of $LaAlO_3$ *Materials Chemistry and Physics* 109 2008: pp. 113 – 118.
6. **Malinowski, M., Piramidowicz, R., Frukacz, Z., Chadeyron, G., Mahiou, R., Joubert, M. F.** ,Spectroscopy and Upconversion Processes in $YAlO_3$:Ho^{3+} Crystals *Optical Materials* 12 1999: pp. 409 – 423.
7. **Yada, M., Ohya, M., Machida, M., Kijima, T.** Synthesis of Porous Yttrium Aluminium Oxide Templated by Dodecyl Sulphate Assemblies *Chemical Communications* 18 1998: pp. 1941 – 1942.
8. **Atwood, D. A., Yearwood, B. C.** The Future of Aluminium Chemistry *Journal of Organometallic Chemistry* 600 2000: pp. 186 – 197.
9. **Nieminen, M., Sajavaara, T., Rauhala, E., Putkonen, M., Niinistö, L.** Surface-controlled Growth of $LaAlO_3$ Thin Films by Atomic Layer Epitaxy *Journal of Materials Chemistry* 11 2001: pp. 2340 – 2345.
10. **Tall, P. D., Coupeau, C. Rabier, J.** Identation-Induced Twinning in $LaAlO_3$ Single Crystals: An Atomic Force Microscopy Study *Scripta Materiala* 49 2003: pp. 903 – 908.
11. **Livage, J., Henry, M. Sanchez, C.** Sol-Gel Chemistry of Transition Metal Oxides *Progress in Solid State Chemistry* 18 1988: pp. 259 – 341.
12. **Brinker, C. J., Scherer, G. W.** Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, Academic Press, London, 1990.
13. **Cushing, B. L., Kolesnichenko, V. L., Connor, C. J. O'.** Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles *Chemical Reviews* 104 2004: pp. 3893 – 3946.
14. **Katelnikovas, A., Barkauskas, J., Ivanauskas, F., Beganskiene, A. Kareiva, A.** Aqueous Sol-Gel Synthesis Route for the Preparation of YAG: Evaluation of Sol-Gel Process by Mathematical Regression Model *Journal of Sol-Gel Science and Technology* 41 2007: pp. 193 – 201.
15. **Mackenzie, J. D., Bescher, E. P.** Chemical Routes in the Synthesis of Nanomaterials Using the Sol-Gel Process *Accounts of Chemical Research* 40 2007: pp. 810 – 818.
16. **Harlan, C. J., Kareiva, A., MacQueen, D. B., Cook, R., Barron, A. R.** Yttrium-Doped alumoxanes: A *Chimie Douce* route to $Y_3Al_5O_{12}$ (YAG) and $Y_4Al_2O_9$ (YAM) *Advanced Materials* 9 1997: pp. 68 – 71.
17. **MacKenzie, K. J. D., Kemmitt, T.** Evolution of Crystalline Aluminates from Hybrid Gel-Derived Precursors Studied by XRD and Multinuclear Solid-State MAS NMR. II. Yttrium-Aluminium Garnet, $Y_3Al_5O_{12}$ *Thermochimica Acta* 325 1999: pp. 13 – 18.
18. **Wang, S., Akatsu, T., Tanabe, Y., Yasuda, E.** Phase Compositions and Microstructural Characteristics of Solidified Al_2O_3-Rich Spinel Solid Solution/YAG Composite *Journal of the European Ceramic Society* 20 2000: pp. 39 – 43.
19. **Roy, S., Wang, L., Sigmund, W., Aldinger, F.** Synthesis of YAG Phase by a Citrate-nitrate Combustion Technique *Materials Letters* 39 1999: pp. 138 – 141.
20. **Vaqueiro, P., Lopez-Quintela, M. A.** Synthesis of Yttrium Aluminium Garnet by the Citrate Gel Process *Journal of Materials Chemistry* 8 1998: pp. 161 – 163.
21. **Schrader, B.** Infrared and Raman Spectroscopy. Methods and Applications, VCH, Weinheim, 1995.
22. **Nakamoto, K.,** Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1986.
23. **Baranauskas, A., Jasaitis, D., Kareiva, A.** Characterization of Sol-gel Process in the Y-Ba-Cu-O Acetate-Tartrate System Using IR Spectroscopy *Vibrational Spectroscopy* 28 2002: pp. 263 – 275.
24. **Muliuoliene, I., Mathur, S., Jasaitis, D., Shen, H., Sivakov, V., Rapalaviciute, R., Beganskiene, A., Kareiva, A.** Evidence of the Formation of Mixed-Metal Garnets via Sol-Gel Synthesis *Optical Materials* 22 2003: pp. 241 – 250.
25. **Callender, R. L., Harlan, C. J., Shapiro, N. M., Jones, C. D., Callahan, D. L., Wiesner, M. R., MacQueen, D. B., Cook, R., Barron, A. R.** Aqueous Synthesis of Water-Soluble Alumoxanes: Environmentally Benign Precursors to Alumina and Aluminum-Based Ceramics *Chemistry of Materials* 9 1997: pp. 2418 – 2433.
26. **Choy, J.-H., Han, Y.-S., Kim, J.-T., Kim, Y.-H.** Citrate Route to Ultra-Fine Barium Polytitanates with Microwave Dielectric-Properties *Journal of Materials Chemistry* 5 1995: pp. 57 – 63.
27. **Chemlal, S., Larbot, A., Persin, M., Sarrazin, J., Sghyar, M., Rafiq, M.** Cobalt Spinel $CoAl_2O_4$ via Sol-Gel Process: Elaboration and Surface Properties *Materials Research Bulletin* 35 2000: pp. 2515 – 2523.
28. **Gülgün, A., Putlayev, V., Rühle, M.** Effects of Yttrium Doping Alpha Alumina: I. Microstructure and Microchemistry *Journal of American Ceramic Society* 82 1999: pp. 1849 – 1856.
29. **Hashemi, T., Brinkman, A. W., Wilson, M. J.** Preparation, Sintering and Electrical Behaviour of Cobalt, Nickel and Zinc Germanate *Journal of Materials Science* 28 1993: 2084 – 2088.
30. **Niou, C. S., Ma, Y. T., Li, W. P., Javadpour, J., Murr, L. E.** Preparation of Superconducting $YBa_2Cu_3O_{7-x}$ Powders by a Solution Technique *Journal of Materials Science: Materials in Electronics* 3 1992: pp. 181 – 186.