

SYNTHESES AND CHARACTERISATION OF Gd₃Al₅O₁₂ AND La₃Al₅O₁₂ GARNETS

Edita GARSKAITE^{a1}, Natalija DUBNIKOVA^{a2}, Arturas KATELNIKOVAS^{a3}, Jiri PINKAS^b and Aivaras KAREIVA^{a4,*}

^a Department of General and Inorganic Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania; e-mail: ¹ edita.garskaite@chf.vu.lt, ² natalija.dubnikova@chf.vu.lt, ³ arturas.katelnikovas@chf.vu.lt, ⁴ aivaras.kareiva@chf.vu.lt

^b Department of Inorganic Chemistry, Masaryk University, Kotlářská 2, CZ-61137 Brno, Czech Republic; e-mail: jpinkas@chemi.muni.cz

Received September 16, 2006

Accepted December 11, 2006

A sol-gel method based on in situ generation of mixed-metal chelates by complexing metal ions with ethane-1,2-diol in aqueous media has been elaborated to prepare lanthanide-ion containing garnets, Gd₃Al₅O₁₂ (GAG) and La₃Al₅O₁₂ (LAG). XRD patterns of the powders sintered at 1 000 °C revealed the formation of monophasic GAG. However, LAG does not form under the same experimental conditions. The phase composition of the samples was characterised by IR spectroscopy. Microstructural features of the polycrystalline garnets were studied by SEM.

Keywords: Gadolinium aluminium garnet; GAG; Lanthanum aluminium garnet; LAG; Sol-gel processes; Material science; XRD; SEM.

Garnets, both natural and synthetic, form a wide range of compounds which are closely related by their structure and chemical and physical properties. Garnets containing transition and rare-earth metals have many important technological applications such as magnetic and phosphorescent materials employed in solid-state lasers and TV screens, computer memories and in many devices such as microwave optical elements¹⁻⁴.

Yttrium aluminium garnet (Y₃Al₅O₁₂, YAG) with excellent structural and optical properties is one of the most popular garnets. Since the discovery of ruby laser, which is Cr-doped Al₂O₃, the search for new solid-state laser materials with diverse properties such as laser ability at new wavelengths, broad tunability in to the near infrared (NIR) region and high efficiency, has been an important task for material scientists. Rare-earth-doped YAG oxides are also widely used in cathode-ray tubes (projection TV sets), field

emission, vacuum fluorescent and electroluminescent displays and as scintillators in X-ray and positron emission tomographs⁵⁻⁹.

The phosphorescent host materials have proven to be of great importance as well. The matrix should have good chemical, mechanical, thermal and optical characteristics and properties^{10,11}. For example, the laser action of transition and rare-earth metal ions has been demonstrated in a wide variety of host crystals. Among them, several scandium- and gallium-based materials were prepared¹²⁻¹⁶.

Physical properties of crystalline materials are well known to depend strongly on the phase purity, narrow distribution of grain size and high crystalline homogeneity. In the last few years, there has been a growing interest in this field in developing new preparative techniques for nanocrystalline garnet powders¹⁷⁻²³. The sol-gel technology, due to its apparent advantages of fine homogeneity, high reactivity of starting materials, easier composition control, lower sintering temperature and lower costs, is a most promising method for preparation of nanostructured YAG ceramics²⁴⁻²⁶. The main aim of this study was to synthesise and characterise lanthanide (Gd and La) substituted yttrium aluminium garnet (YAG) compounds using an aqueous sol-gel processing route.

EXPERIMENTAL

Synthetic Procedure

In the aqueous sol-gel process, the following materials were used: Gd₂O₃ (99.99%, Aldrich), La₂O₃ (99.99%, Merck), Al(NO₃)₃·9H₂O (99.99%, Aldrich), acetic acid (98%, Lachema, Czech Republic) and ethane-1,2-diol (99%, Merck).

Gd and La acetates were prepared by dissolving the corresponding oxides in 2×10^{-1} M acetic acid (100 ml). Clear solutions were obtained after stirring at 60–65 °C for 10 h in beakers covered with a watch-glass. Then, aqueous solution of aluminium nitrate (25 ml) was added. The resulting mixture was stirred at 65 °C for 1 h, followed by dropwise addition of ethane-1,2-diol (2 ml) upon vigorous stirring. The resulting sols were mixed at the same temperature for another 1 h and then concentrated by slow solvent evaporation at 65 °C until they turned into transparent gels. The gels were dried in an oven at 110 °C for 1 d. The resulting gel powders were ground in an agate mortar and heated in air at 800 °C for 5 h by slow temperature elevation ($\sim 3\text{--}4$ °C min⁻¹). After grinding in an agate mortar, the powders were further sintered in air at different high temperatures for 10 h. Longer duration of annealing was used in the separate experiments.

Characterisation

X-ray powder diffraction (XRD) measurements were performed with a Stoe STADI P diffractometer, using CuK α_1 radiation and nickel filters. Infrared spectra of samples in KBr pellets were recorded with a Bruker Equinox 55/S/NIR FTIR spectrometer (resolution 1 cm⁻¹).

Morphological characterization of the samples was carried out on a Joel 820 scanning electron microscope. To avoid charging, samples were slightly coated with Au/Pd.

RESULTS AND DISCUSSION

X-ray Powder Diffraction Analysis

In the first part, the Gd-Al-O and La-Al-O precursor gels were calcined at 800 °C for 5 h and finally annealed at 1 000 °C for 10 h. The X-ray diffraction pattern of the Gd-Al-O precursor gel annealed at 1 000 °C is shown in Fig. 1. The XRD results reveal that Gd-Al-O ceramics obtained at 1 000 °C consists of two crystalline phases: gadolinium aluminium garnet (Gd₃Al₅O₁₂, GAG) and gadolinium aluminate perovskite (GdAlO₃, GAP). The XRD pattern is in a good agreement with the reference data for Gd₃Al₅O₁₂ (PDF [32-383]) and GdAlO₃ (PDF [46-395]). In the case of the La-Al-O system, however, different results were obtained. Figure 2 is the X-ray diffraction pattern of the final La-Al-O ceramic sample annealed at 1 000 °C. The XRD pattern testifies to the formation of the perovskite lanthanum aluminate (LaAlO₃, LAP) phase instead of LAG, which occurs at this temperature. The obtained XRD pattern is in a good agreement with the reference data for LaAlO₃ (PDF [31-22]). It can be seen that the degree of crystallinity of the ultimate LAP ceramics is very poor. No other crystalline phase was detected. Due to the poor crystallinity of the LAP phase, the

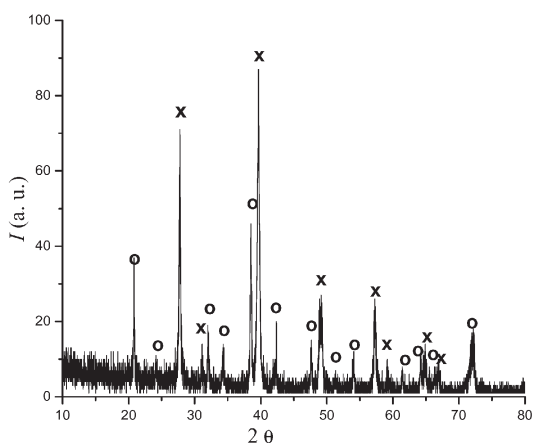


FIG. 1

XRD pattern of the ceramics obtained by calcination of the Gd-Al-O precursor gel at 1 000 °C for 10 h. The peaks denoted with ○ and × belong to Gd₃Al₅O₁₂ and GdAlO₃ phases, respectively

expected Al_2O_3 diffraction lines may be overlapped by the background pattern of the final product. Eventually, the formed alumina phase is amorphous.

In order to prove whether higher calcination temperatures influence the formation of GAG and LAG phases, the precursor gels were also annealed at $1\,200\text{ °C}$ for 10 h. The obtained XRD pattern of the GAG ceramics annealed at higher temperature is shown in Fig. 3. The main phase in this case is

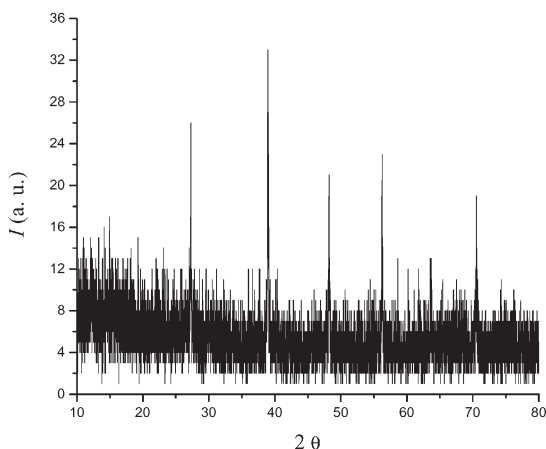


FIG. 2

XRD pattern of the LaAlO_3 ceramics obtained by calcination of the La-Al-O precursor gel at $1\,000\text{ °C}$ for 10 h

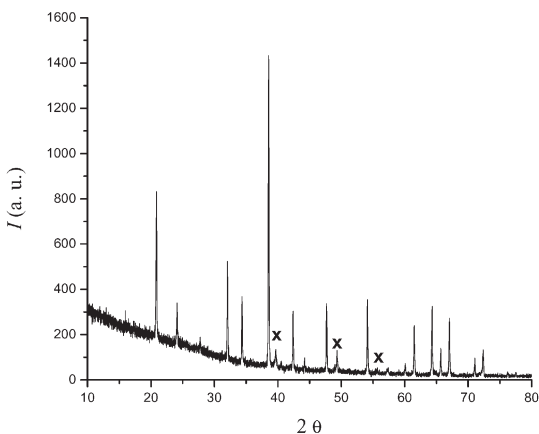


FIG. 3

XRD pattern of the $\text{Gd}_3\text{Al}_5\text{O}_{12}$ ceramics obtained by calcination of the Gd-Al-O precursor gel at $1\,200\text{ °C}$ for 10 h. The peaks denoted with \times belong to the minor GdAlO_3 phase

Gd₃Al₅O₁₂ and only a small amount (~8%) of the GdAlO₃ is formed. On the other hand, the XRD pattern of the La-Al-O gel precursor annealed at 1 200 °C was almost identical to that presented in Fig 2. We can conclude that the higher temperature did not promote the formation of the LAG phase.

After the preliminary experiments we decided to investigate the influence of the annealing time and temperature on the formation of GAG and LAG in more detail. The Gd-Al-O and La-Al-O precursor gels were calcined in steps at 600, 700, 800, 900 and twice at 1 000 °C for 10 h. The gradual formation of the Gd₃Al₅O₁₂ phase is shown in Fig. 4. The formation of the GAG phase starts already at ~800 °C. The phase purity of the polycrystalline Gd₃Al₅O₁₂ ceramics improved when the sample was annealed at 900 °C. The XRD pattern of the ceramics annealed twice at 1 000 °C clearly shows the formation of the single Gd₃Al₅O₁₂ phase.

Figure 5 shows the XRD pattern of monophasic Gd₃Al₅O₁₂, the values of 2θ ranging between 10 and 130°. All indexed lines have been assigned to the pure polycrystalline Gd₃Al₅O₁₂ phase. The characteristic lines are (in °): 2θ = 17.88 (78.38%), 20.69 (49.21%), 27.49 (55.67%), 29.44 (45.81%), 33.01 (100%), 36.27 (43.14%), 40.73 (45.05%), 42.12 (31.42%), 46.13 (42.80%), 51.07 (29.51%), 52.25 (35.20%), 54.55 (39.36%), 55.7 (31.8%), 56.8 (37.11%), 60.06 (28.78%), 61.12 (29.13%), 71.24 (30.66%), 86.42 (28.40%).

The same experiment was performed with the La-Al-O precursor gel. Figure 6 reveals again that no La₃Al₅O₁₂ phase appears at temperatures up

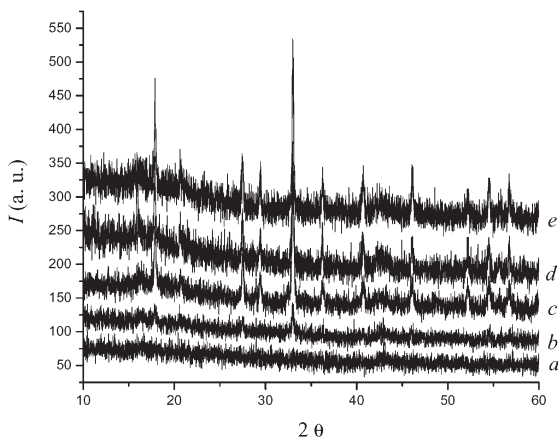


FIG. 4

XRD patterns of the Gd₃Al₅O₁₂ ceramic samples annealed at different temperatures (in °C): *a* 600, 10 h; *b* 800, 10 h; *c* 900, 10 h; *d* 1 000, 10 h; *e* 1 000, 20 h

to 1 000 °C, independent of the increased annealing time. Instead of the LAG phase, pure lanthanum aluminate perovskite was obtained at 900 °C.

Infrared Spectroscopy

IR spectroscopy was used as additional tool for the structural characterisation of the precursor gels and ceramic materials obtained by the aqueous

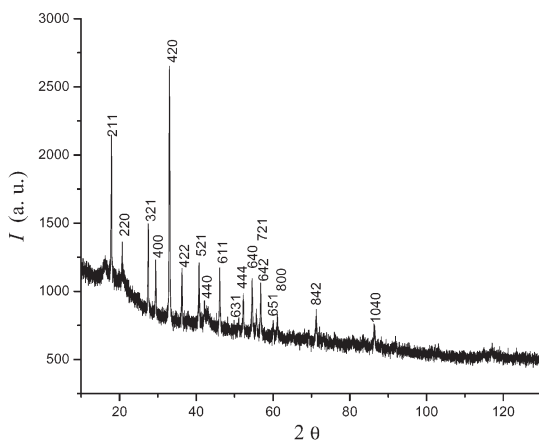


FIG. 5
XRD pattern of the $Gd_3Al_5O_{12}$ ceramic sample annealed at 1 000 °C for 20 h

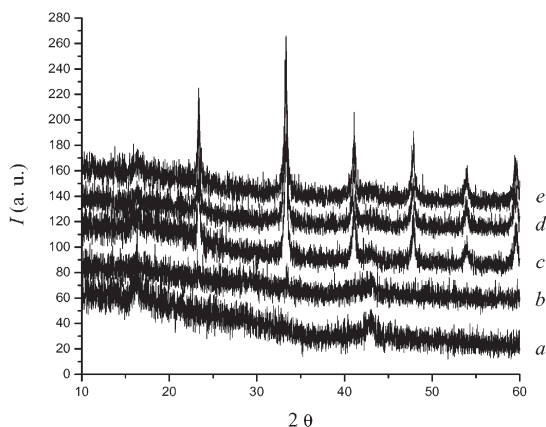


FIG. 6
XRD patterns of the La-Al-O precursor gel samples annealed at different temperatures (in °C): *a* 600, 10 h; *b* 800, 10 h; *c* 900, 10 h; *d* 1 000, 10 h; *e* 1 000, 20 h

sol-gel method. The IR spectrum of the Gd-Al-O precursor gel is shown in Fig. 7. The two broad bands in the region 1 650–1 370 cm⁻¹ can be assigned to vibrations of NO₃⁻, CH₂OH and COOH groups²⁷. Crystallisation water in the precursor gel absorbs at 3 438 cm⁻¹. Another broad absorption band due to M-O vibrations²⁸ occurs at lower wavenumbers (950–450 cm⁻¹).

The IR spectrum of the La-Al-O precursor gel (Fig. 8) is very similar to that of the Gd-Al-O gel, suggesting the same functional groups are present

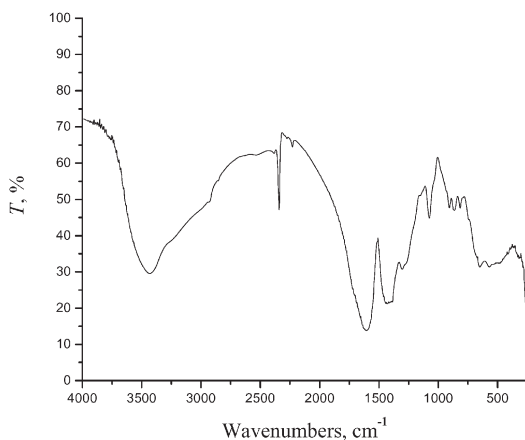


FIG. 7
IR spectrum of the Gd-Al-O precursor gel dried at 110 °C for 1 d

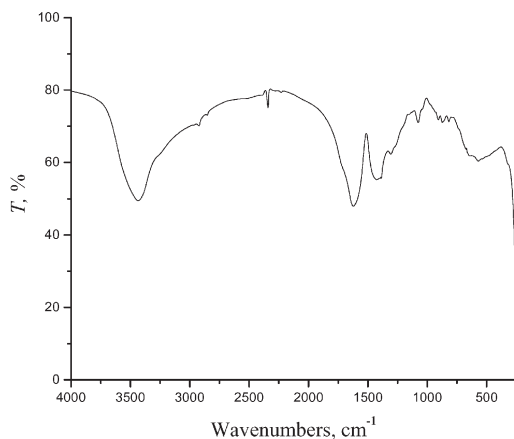


FIG. 8
IR spectrum of the La-Al-O precursor gel dried at 110 °C for 1 d

in both samples. The recorded IR spectra permit to conclude that both Gd-Al-O and La-Al-O gels were of high quality and the proposed sol-gel preparative technique is highly reproducible.

The ceramic materials obtained after the calcinations of the Gd-Al-O and La-Al-O gels were also characterised by IR spectroscopy. The IR spectra of the $\text{La}_3\text{Al}_5\text{O}_{12}$ and $\text{Gd}_3\text{Al}_5\text{O}_{12}$ samples obtained after annealing at 1 000 °C for 20 h are shown in Figs 9 and 10, respectively. The La-Al-O ceramics shows several intense broad bands. Strong absorption bands arising from O-H stretching and bending vibrations of water due to the exposure of the sample to atmosphere occur at 3 438 and 1 640 cm^{-1} , respectively. Importantly, in the 1 300–400 cm^{-1} fingerprint region, two sharp bands were present at 664 and 435 cm^{-1} , which are typical metal–oxygen absorptions for the perovskite-type compounds^{28–30}.

The IR spectrum of the Gd-Al-O sample annealed at 1 000 °C (Fig. 10) shows that the envelope of two broad absorption bands in the region 800–400 cm^{-1} in preceding Fig. 9 is well resolved into several narrow absorption bands. According to the literature data, this pattern corresponds to the metal–oxygen vibrations in the tetrahedral garnet structure^{31–33}. Therefore, the IR results support the conclusions made on grounds of the XRD measurements.

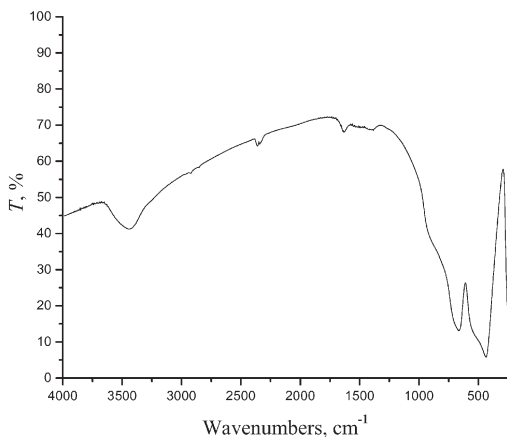


FIG. 9

IR spectrum of the La-Al-O gel sample annealed twice at 1 000 °C for 10 h

SEM Measurements

The scanning electron microscopy (SEM) proved to be a valuable technique for morphological characterisation of ceramic samples. Figure 11 shows a SEM image of the Gd-Al-O sample annealed at 1 000 °C. While some of the particles appear to reach the nanometer size, many of them are close to or even exceed micrometer dimensions. This observation suggests that the

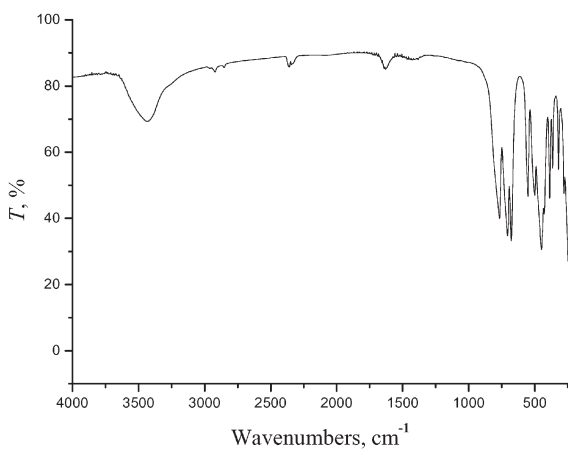


FIG. 10
IR spectrum of the Gd-Al-O gel sample annealed twice at 1 000 °C for 10 h. It corresponds to Gd₃Al₅O₁₂

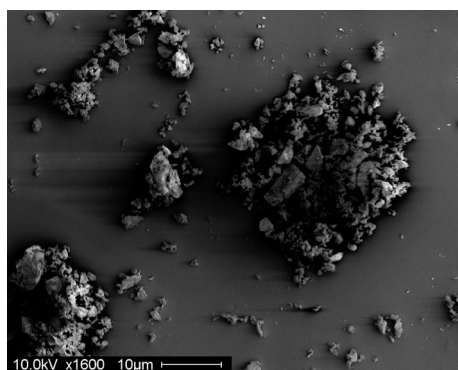


FIG. 11
SEM micrograph of the Gd₃Al₅O₁₂ ceramics synthesised at 1 000 °C

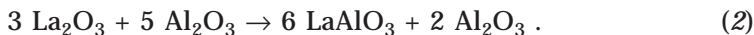
GAG crystallites obtained at 1 000 °C are not sufficiently homogeneous, having different shape and wide particle size distribution. Despite the irregular morphology of the garnet particles, it can also be observed that many large particles are packed with extremely fine powders.

Figure 12 shows the SEM image of the La-Al-O sample annealed at 1 000 °C. The ceramic material consists of irregularly shaped particles with pronounced agglomeration. It is apparent that micrograin networks are formed, keeping a glassy-like outline with no internal porosity. This feature indicates a good connectivity between the grains, which is characteristic for ceramic-ceramic composite materials³⁴⁻³⁶.

From the above results we can conclude that the $\text{La}_3\text{Al}_5\text{O}_{12}$ phase has not formed by heat treatment of the precursor gel powders. The solid state reaction expressed by Eq. (1) does not proceed in the temperature region 600–1 200 °C.



Instead, the final ceramic product consists of other crystalline phases:



Alternatively, the formation of the composite material is described by the following reaction:

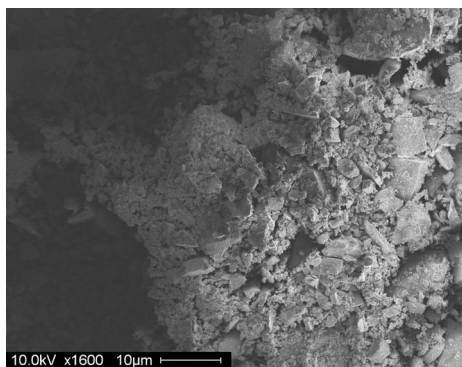
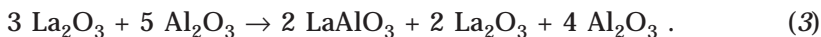
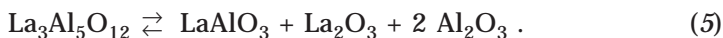


FIG. 12

SEM micrograph of the ceramics formed from the La-Al-O precursor gel annealed at 1 000 °C



“Phase metathesis” reactions (Eqs (4) and (5)) may also occur:



Therefore, heat treatment of the La-Al-O precursor gel powders at 1 000 °C leads to the formation of 3LaAlO₃:Al₂O₃ or LaAlO₃:La₂O₃:2Al₂O₃ mixtures (aluminium and lanthanum oxides, possibly amorphous) instead of the single La₃Al₅O₁₂ garnet phase.

CONCLUSIONS

The homogeneous Gd-Al-O precursor gels obtained by complexation of metal ions with ethane-1,2-diol in an aqueous medium were used for the low-temperature synthesis of single-phase gadolinium aluminium garnet (Gd₃Al₅O₁₂, GAG). The present study demonstrates the versatility of the solution method to yield a monophasic GAG sample at lower sintering temperatures (900–1 000 °C) when compared with the temperature required for the solid-state synthesis (>1 600 °C). Although several wet chemical techniques were employed for obtaining Gd₃Al₅O₁₂, the coexistence of other phases like GdAlO₃ and Gd₂Al₄O₉ was invariably observed below 1 000 °C. In the successful synthesis of the crystalline GAG phase, 900 °C was performed at the lowest reported temperature for the crystallisation of this material. However, the heat treatment of La-Al-O precursor gel powders at the same temperature leads to the formation 3LaAlO₃:Al₂O₃ or LaAlO₃:La₂O₃:2Al₂O₃ mixtures instead of the single La₃Al₅O₁₂ garnet phase. On the other hand, we have demonstrated for the first time the low-temperature sol-gel synthesis of a microscaled ceramic composite consisting of lanthanum aluminate perovskite (LaAlO₃, LAP) and metal oxides (Al₂O₃ and La₂O₃). Some of the advantages of the proposed sol-gel synthesis method, such as low sintering temperature (1 000 °C) of the LaAlO₃-M₂O₃ (M = Al, La) ceramic composite, excellent homogeneity and stoichiometry control, the high phase purity are also demonstrated in the present study.

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

E. Garskaite is grateful for the Lithuanian Science and Studies Foundation scholarship administered through the Ministry of Education, Youth and Sports of the Czech Republic. J. Pinkas gratefully acknowledges the financial support by the Grant Agency of the Czech Republic (203/04/0296) and the Ministry of Education, Youth and Sports of the Czech Republic (MSM0021622410).

REFERENCES

1. Lu C. H., Hsu W. T., Dhanaraj J., Jagannathan R.: *J. Eur. Ceram. Soc.* **2004**, *24*, 3723.
2. Batentschuk M., Osvet A., Schiering G., Klier A., Schneider J., Winnacker A.: *Radiat. Meas.* **2004**, *38*, 539.
3. Yen W. M.: *Opt. Mater.* **2005**, *27*, 1647.
4. Pari G., Mookerjee A., Bhattacharya A. K.: *Physica B (Amsterdam)* **2005**, *365*, 163.
5. Vaqueiro P., Lopez-Quintela M. A.: *J. Mater. Chem.* **1998**, *8*, 161.
6. Ganschow S., Klimm D., Reiche P., Uecker R.: *Cryst. Res. Technol.* **1999**, *34*, 615.
7. Kang Y. C., Lenggoro I. W., Park S. B., Okuyama K.: *J. Phys. Chem. Solids* **1999**, *60*, 1855.
8. Lu J., Prabhu M., Song J., Li C., Xu J., Ueda K., Kaminskii A. A., Yagi H., Yanagitani T.: *Appl. Phys. B: Lasers Opt.* **2000**, *71*, 469.
9. Zhou S., Fu Z., Zhang J., Zhang S.: *J. Lumin.* **2006**, *118*, 179.
10. Iida Y., Towata A., Tsugoshi T., Furukawa M.: *Vib. Spectrosc.* **1999**, *19*, 399.
11. Golubovic A., Nikolic S., Gajic R., Duric S., Valcic A.: *J. Serb. Chem. Soc.* **2002**, *67*, 291.
12. Vosegaard T., Massiot D., Gautier N., Jakobsen H. J.: *Inorg. Chem.* **1997**, *36*, 2446.
13. Ferrand B., Chambaz B., Couchaud M.: *Opt. Mater.* **1999**, *11*, 101.
14. Gaume R., Viana B., Derouet J., Vivien D.: *Opt. Mater.* **2003**, *22*, 107.
15. Muliuliene I., Mathur S., Jasaitis D., Shen H., Sivakov V., Rapalaviciute R., Beganskiene A., Kareiva A.: *Opt. Mater.* **2003**, *22*, 241.
16. Garskaite E., Moravec Z., Pinkas J., Mathur S., Kazlauskas R., Kareiva A.: *Philos. Mag. Lett.* **2005**, *85*, 557.
17. Harlan J., Kareiva A., MacQueen D. B., Cook R., Barron A. R.: *Adv. Mater.* **1997**, *9*, 68.
18. Lu C. H., Hong H. C., Jagannathan R.: *J. Mater. Chem.* **2002**, *12*, 2525.
19. Hreniak D., Streck W.: *J. Alloys Compd.* **2002**, *341*, 183.
20. Zhou Y., Lin J., Yu M., Wang S., Zhang H.: *Mater. Lett.* **2002**, *56*, 628.
21. Pan Y., Wu M., Su Q.: *J. Phys. Chem. Solids* **2004**, *65*, 845.
22. Hreniak D., Streck W., Mazur P., Pazik R., Zabkowska-Waclawek M.: *Opt. Mater.* **2004**, *26*, 117.
23. Kasuya R., Isobe T., Kuma H.: *J. Alloys Compd.* **2006**, *408–412*, 820.
24. Veith M., Mathur S., Kareiva A., Jilavi M., Zimmer M., Huch V.: *J. Mater. Chem.* **1999**, *9*, 3069.
25. Pan Y., Wu M., Su Q.: *Mater. Sci. Eng., B* **2004**, *106*, 251.
26. Potdevin A., Chadeyron G., Boyer D., Mahiou R.: *J. Mater. Sci.* **2006**, *41*, 2201.
27. Coates J. in: *Encyclopedia of Analytical Chemistry* (R. A. Meyers, Ed.). John Wiley & Sons Ltd., Chichester 2000.
28. Schrader B.: *Infrared and Raman Spectroscopy. Methods and Applications*. VCH, Weinheim 1995.

29. Higson S. P. J.: *Analytical Chemistry*. Oxford University Press, Oxford 2003.
30. Harding S. E., Chowdhry B.: *Protein-Ligand Interactions: A Practical Approach: Structure and Spectroscopy*. Oxford University Press, Oxford 2001.
31. McAloon B. P., Hofmeister A. M.: *Am. Mineral.* **1993**, 78, 957.
32. Vaqueiro P., Lopez-Quintela M. A.: *Chem. Mater.* **1997**, 9, 2836.
33. Leleckaite A., Kareiva A., Bettentrup H., Jüstel T., Meyer H.-J.: *Z. Anorg. Allg. Chem.* **2005**, 631, 2987.
34. Wang S., Akatsu T., Tanabe Y., Yasuda E.: *J. Eur. Ceram. Soc.* **2000**, 20, 39.
35. Mathur S., Veith M., Shen H., Lecerf N., Hufner S.: *Scr. Mater.* **2001**, 44, 2105.
36. Mitra N. K., Das S., Maitra S., Sengupta U., Basumajumdar A.: *Ceram. Int.* **2002**, 28, 827.