

A comparative study of GdAlO_3 perovskite prepared by the sol–gel method using different complexing agents

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This paper presents on the results of the sol–gel preparation of the microcrystalline gadolinium aluminate (GdAlO_3 , GAP) ceramics at slightly different synthetic conditions. Metal ions generated by dissolving the starting materials of metals in the diluted acetic acid were complexed by different complexing agents (natural and synthetic tartaric acids, 1,2-ethanediol, citric acid, ethanolamine) to obtain the precursors for the GAP. In the sol–gel processing different starting gadolinium materials such as gadolinium nitrate or gadolinium oxide were also employed. Phase transformations, composition and microstructural features in the gels and polycrystalline samples were studied by powder X-ray diffraction analysis (XRD), infrared spectroscopy (IR) and scanning electron microscopy (SEM).

Key words: aluminates, perovskites, gadolinium, ceramics, sol–gel synthesis

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INTRODUCTION

Ceramics based on $\text{Ln}_2\text{O}_3\text{-M}_2\text{O}_3$ (Ln – lanthanide element; M – Al or Fe) combination are promising materials for optical, magnetic, electronic and structural applications [1–7]. The perovskite aluminates doped with a lanthanide element offers the advantages of longer lifetimes and higher polarized cross sections with respect to most of other oxide matrices, and are useful as a host for solid-state lasers, luminescence systems and window materials for a variety of lamps.

Transition metal perovskites are usually considered to be the most promising multiferroic materials. There exist hundreds of magnetic and ferroelectric perovskites. A good collection is presented in the tables compiled by Goodenough and Longo [8]. Related ceramic materials are currently being incorporated into automobile catalytic converters, they also are promising substrates for the epitaxy of thin oxide films that can be potentially used as buffer layers for the epitaxial growth of various perovskite-type films such as high tempera-

ture superconductors, ferroelectrics and colossal magnetoresistance oxides. Gadolinium compounds are widely used in the preparation of phosphors for colour TV tubes. About 1% of gadolinium in iron, chromium and related alloys improves the workability and resistance to high temperatures and oxidation. Since gadolinium is ferromagnetic, it can be used as a magnetic component in different sensing devices. For example, gadolinium aluminate is currently under development as a candidate material for the neutron absorption and control rod applications [9–14].

The wide applications of gadolinium oxides have induced the search for suitable processes for their preparation. Over the last few decades, the sol–gel techniques have been used to prepare a variety of mixed-metal oxides [15–18]. In these sol–gel processes good quality of the oxide products was expected primarily due to the purity of the used precursor materials and chemical homogeneity obtained by synthesis [19, 20]. The sol–gel methods based on the molecular precursors have a cutting edge over the other solution routes because they allow chemical interactions among the initial mixtures of precursor species favouring the evo-

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lution of a solid-state structure at the atomic level. Therefore, the sol-gel process is used to obviate the experimental difficulties and chemical inhomogeneity associated with a conventional ceramic processing. In the ideal situation, the homogeneity in an amorphous gel, which under the subsequent pyrolysis yields the comp-lex oxide directly, provided that segregation and partial crystallization can be prevented. In this paper, we are presenting the results of a systematic study of the sol-gel synthetic approach to pure gadolinium aluminate (GdAlO₃, GAP) using different complexing agents. In order to prevent a partial crystallization of the metal salts, we chose complexing agents which contained a various number of hydroxo and/or carboxyl groups, namely, natural and synthetic tartaric acids, 1,2-ethan-ediol, citric acid and ethanolamine. The results illustrate the significance of the selection of the complex-ing agent to be used in the low-temperature synthesis of such type ceramics.

EXPERIMENTAL

Preparation of gels

Gadolinium aluminate (GdAlO₃, GAP) ceramic samples were synthesized by the aqueous sol-gel method. The gels were prepared using stoichiometric amounts of analytical-grade Gd(NO₃)₃·6H₂O or Gd₂O₃ as Gd³⁺ raw materials and Al(NO₃)₃·9H₂O as Al³⁺ source. For the preparation of the samples by the sol-gel process, gadolinium nitrate or gadolinium oxide respectively were first dissolved in 50 mL of 0.2 mol/L CH₃COOH at 65 °C. To this solution aluminium nitrate dissolved in 50 mL of distilled water was added, and the resulting mixture was stirred for 1 h at the same temperature. In the following step, natural or synthetic tartaric acids or 1,2-ethanediol, or citric acid, or ethanolamine, or their mixtures as complexing agents were added to the reaction solution. After concentrating the solutions by a slow evaporation at 65 °C under stirring, the Gd-Al-O sols turned into white transparent gels. Oven-dried (100 °C) gel powders were ground in an agate mortar and pre-heated for 3 h at 800 °C in air. Since the gels were very combustible, a slow heating rate (~3–4 °C min⁻¹) especially between 100 and 400 °C was found to be essential. After the intermediate grinding in an agate mortar, the powders were additionally sintered in air for 10 h at 1000 °C.

Characterization techniques

The infrared spectra in the range of 4000–400 cm⁻¹ were recorded on an EQUINOX 55/S/NIR FTIR spectrometer. The samples were prepared as KBr pellets. X-ray diffraction measurements of the powder were performed at room temperature on a Stoe-Cie Powder Diffraction System STADI P diffractometer operating with a Mo K_α radiation. A scanning electron microscope (SEM) DSM 962 was used to study the surface morphology and microstructure of the ceramic samples.

RESULTS AND DISCUSSION

The Gd-Al-O precursor gel powders prepared using gadolinium nitrate as gadolinium source as well as natural and synthetic tartaric acids as complexing agents in the sol-gel process were calcined and sintered at 1000 °C. The XRD patterns of the obtained GAP ceramics are shown in Fig. 1.

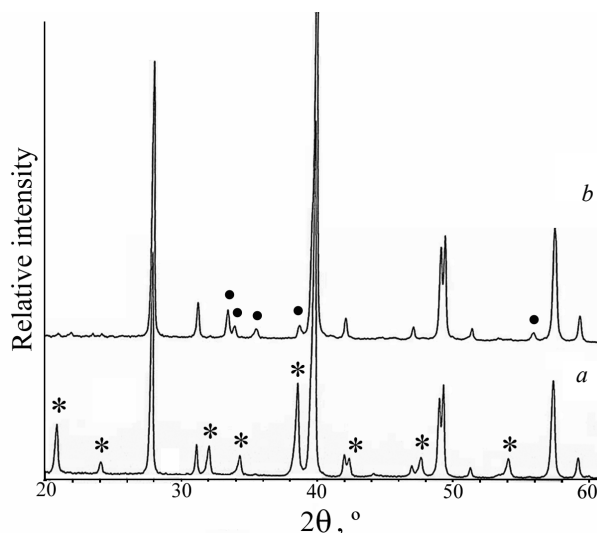


Fig. 1. X-ray diffraction patterns of a GdAlO₃ ceramic sample prepared using gadolinium nitrate as a gadolinium source and natural tartaric acid (a) or synthetic tartaric acid (b) as complexing agents in the sol-gel processing. The impurity phases are marked: * – Gd₃Al₅O₁₂, • – Gd₂O₃

The XRD pattern of the ceramic material prepared using natural tartaric acid as a complexing agent is presented in Fig. 1a. The XRD data confirm GdAlO₃ to be the main crystalline component. However, the formation of the impurity phases was also evident. For example, the diffraction lines at $2\theta \approx 20.9^\circ, 24.1^\circ, 32^\circ, 34.3^\circ, 38.5^\circ, 42.3^\circ, 47.6^\circ, \text{ and } 54.1^\circ$ could be attributed to the phase of Gd₃Al₅O₁₂. Figure 1b shows the X-ray diffraction pattern of the ceramic sample synthesized using synthetic tartaric acid as a complexing agent. The diffraction lines assignable to the perovskite crystal structure at $2\theta \approx 27.8^\circ, 31.1^\circ, 39.7^\circ, 42.0^\circ, 46.9^\circ, 48.9^\circ, 49.2^\circ, 51.3^\circ, 57.3^\circ \text{ and } 59.2^\circ$ are well pronounced in the XRD pattern. However, there are diffraction lines attributable to the impurity phase Gd₂O₃.

The X-ray diffraction patterns of the GdAlO₃ ceramics prepared using gadolinium oxide as a gadolinium source and the same complexing agents (natural and synthetic tartaric acids) are shown in Fig. 2.

According to the XRD analysis, sintering of the Gd-Al-O precursor gel obtained using Gd₂O₃ as a starting material and natural tartaric acid as a complexing agent, produced fully crystalline single-phase GdAlO₃ ceramics. As it can be seen from Fig. 2a, all diffraction peaks in

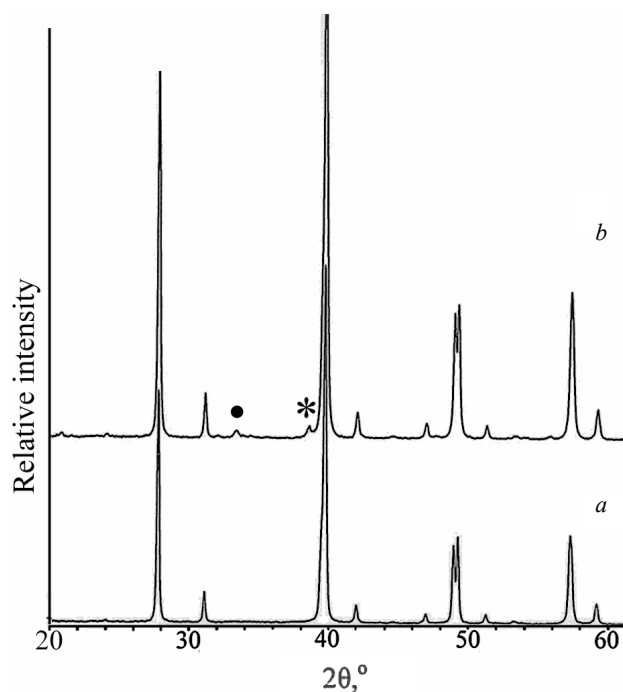


Fig. 2. X-ray diffraction patterns of a GdAlO_3 ceramic sample prepared using gadolinium oxide as a gadolinium source and natural tartaric acid (a) or synthetic tartaric acid (b) as complexing agents in the sol-gel processing. The impurity phases are marked: * – $\text{Gd}_3\text{Al}_5\text{O}_{12}$, • – Gd_2O_3

this XRD spectrum could be attributed to the perovskite crystal structure of GdAlO_3 (PDF [46–395]).

However, in the case when synthetic tartaric acid was used as a complexing agent, along with perovskite gadolinium aluminate the formation of the impurity phases such as Gd_2O_3 (PDF [43–1014]) and $\text{Gd}_3\text{Al}_5\text{O}_{12}$ (PDF [32–383]) is evident (see Fig. 2b). These results allow us to conclude that gadolinium nitrate is not the best starting material for the sol-gel synthesis of perovskite gadolinium aluminate.

The IR spectra for these two samples prepared using Gd_2O_3 as a gadolinium source as well as natural and synthetic tartaric acid as complexing agents were recorded. The obtained IR results are virtually consistent with the crystallization process observed by the XRD measurements. Fig. 3 shows the IR spectra of GdAlO_3 ceramics prepared by calcinations of the above mentioned Gd-Al-O gel precursors for 10 h at 1000 °C.

The broad bands centered around 3428 cm^{-1} and 1640 cm^{-1} are assigned to the H-O-H stretching modes and bending vibrations of the free or adsorbed water, respectively [21]. Both spectra of the synthesized samples contain a sharp peak at 1395 cm^{-1} . However, the nature of this absorbance still is not clear. Strong bands at 660 cm^{-1} and 465 cm^{-1} could be attributed to the M-O stretching frequencies which are characteristic vibrations of perovskite structure compounds [13, 22, 23].

The X-ray diffraction patterns of the GdAlO_3 ceramics prepared using 1,2-ethanediol, citric acid and a mixture of citric acid and ethanolamine as complexing agents in the sol-gel processing are shown in Fig. 4.

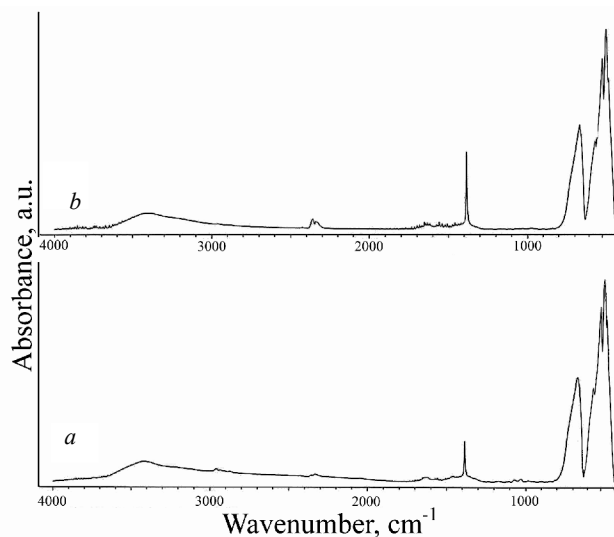


Fig. 3. Infrared spectra of a GdAlO_3 ceramic sample prepared using gadolinium oxide as gadolinium source and natural tartaric acid (a) or synthetic tartaric acid (b) as complexing agents in the sol-gel processing

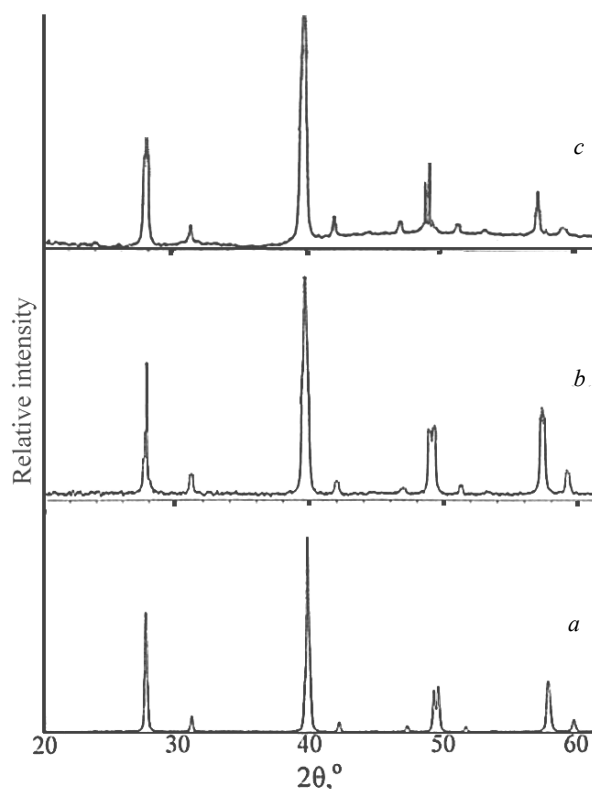


Fig. 4. X-ray diffraction patterns of a GdAlO_3 ceramic sample prepared using gadolinium oxide as gadolinium source and 1,2-ethanediol (a), citric acid (b), or a mixture of citric acid and ethanolamine (c) as complexing agents in the sol-gel processing

According to the XRD analysis, all three diffraction patterns show the formation of fully crystalline single-phase GdAlO_3 ceramic samples. All diffraction lines in

these XRD spectra could be attributed to the GdAlO₃ phase having the perovskite crystal structure (PDF [46–395]). Thus, we can conclude that the three complexing agents (natural tartaric acid, 1,2-ethanediol and citric acid) as well as the mixture of citric acid and ethan-olamine are suitable complexing reagents for the sol-gel preparation of GAP.

The most interesting results were obtained when we used double mixtures of the natural tartaric acid and 1,2-ethanediol or citric acid and 1,2-ethanediol in the sol-gel process. The XRD patterns of the ceramic samples prepared using these two combinations of complexing agents are shown in Fig. 5.

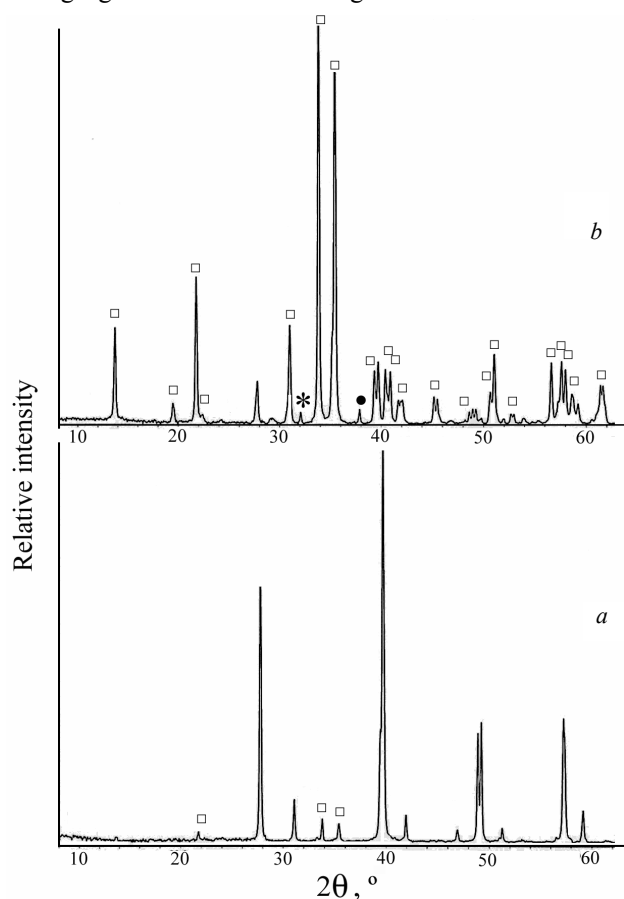


Fig. 5. X-ray diffraction patterns of a GdAlO₃ ceramic sample prepared using gadolinium oxide as a gadolinium source and mixture of natural tartaric acid and 1,2-ethanediol (a) or mixture of citric acid and 1,2-ethanediol (b) as complexing agents using in the sol-gel processing. The impurity phases are marked: * – Gd₃Al₅O₁₂, • – Gd₂O₃, □ – Gd₄Al₂O₉

It turned out that the use of double mixtures of the complexing agents gave the opposite results. In the case of the mixture of natural tartaric acid and 1,2-ethanediol (see Fig. 5a.), the diffraction lines at $2\theta \approx 21.8^\circ$, 33.7° and 35.4° could be attributed to the Gd₄Al₂O₉ phase. When the mixture of citric acid and 1,2-ethanediol was used in the sol-gel synthesis (Fig. 5b), the main phase determined was Gd₄Al₂O₉, and the side phases were GdAlO₃, Gd₂O₃ and Gd₃Al₅O₁₂. So, the question why

individual complexing agents are suitable for the sol-gel preparation of a single phase GdAlO₃, while their double mixtures can not be successfully used, is still pending.

The textural properties of the same calcined powders were investigated by SEM, from which the grain size and typical morphologies were obtained. Scanning electron micrographs of the samples prepared using gadolinium oxide as a gadolinium source and natural tartaric acid, 1,2-ethanediol and citric acid as complexing agents in the sol-gel processing are shown in Fig. 6.

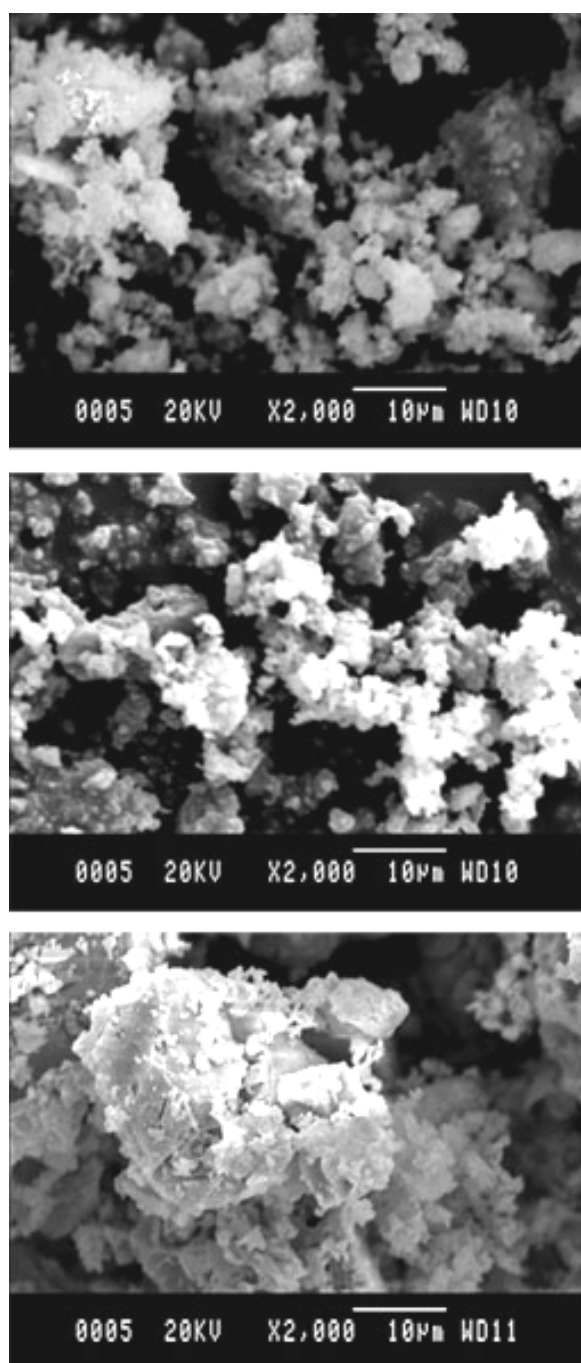


Fig. 6. Scanning electron micrographs of the GdAlO₃ ceramic sample prepared using gadolinium oxide as a gadolinium source and natural tartaric acid (top), 1,2-ethanediol (middle) and citric acid (bottom) as complexing agents in the sol-gel processing

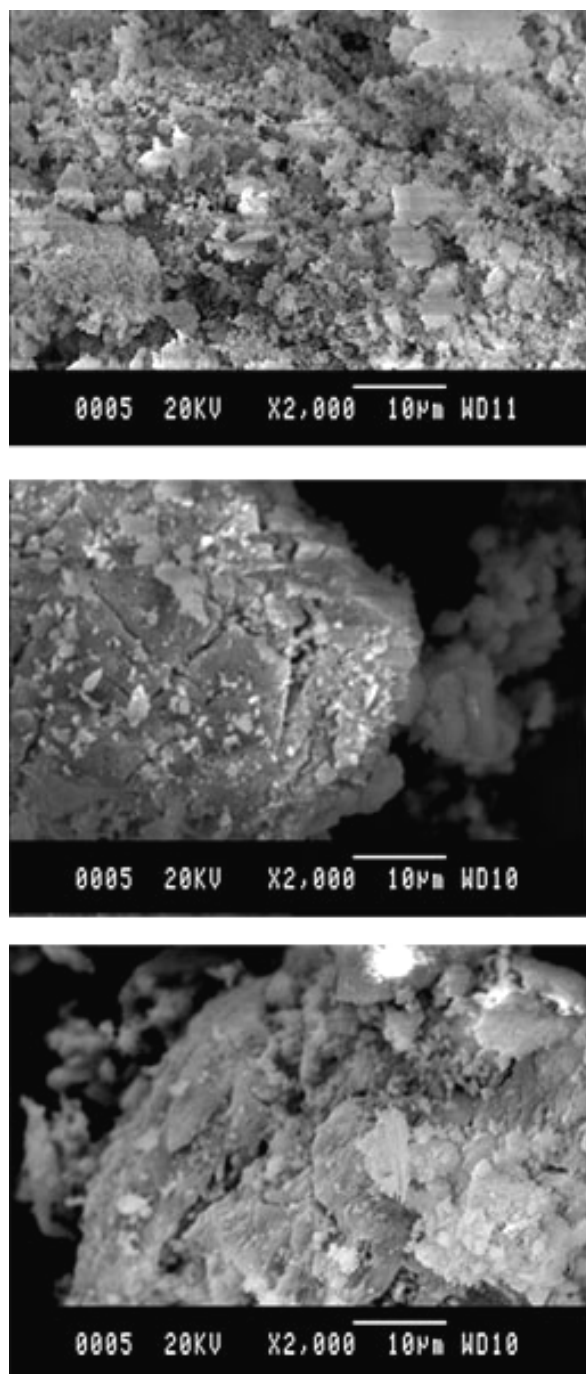


Fig. 7. Scanning electron micrographs of a GdAlO_3 ceramic sample prepared using gadolinium oxide as a gadolinium source and mixtures of citric acid and ethanolamine (top), citric acid and 1,2-ethanediol (middle) and natural tartaric acid and 1,2-ethanediol (bottom) as complexing agents in the sol-gel processing

An almost identical microstructure was obtained when tartaric acid and 1,2-ethanediol were used in the synthesis process. Individual particles seemed to be micro-sized volumetric plate-like crystals and they were partially fused to form hard agglomerates. Besides, the plate-like grains coexist with spherically shaped particles. When citric acid was used, the synthesized solids were composed of larger grains with a less regular shape.

Fig. 7 shows the SEM images of the samples obtained when the mixtures of complexing agents were used in the sol-gel processing.

The SEM picture of the single-phase GAP prepared using a mixture of citric acid and ethanolamine shows very small crystals with the particle size less than 3–5 μm with its morphology similar to that observed for the ceramics prepared using only citric acid. Evidently, the microstructure of the GAP oxide ceramic samples obtained using the mixtures of citric acid and 1,2-ethanediol or natural tartaric acid and 1,2-ethanediol as complexing agents consisted of a large-grained matrix with clusters of small grains. The SEM micrographs of these two specimens revealed the formation of inhomogeneous mixed-metal oxides, and the formation of a continuous network of crystallites is evident.

CONCLUSIONS

From the present study it could be concluded that the formation of perovskite GdAlO_3 ceramics during the sol-gel synthesis depends on the nature of the starting materials and complexing agents. The monophasic GdAlO_3 was obtained when gadolinium oxide as a gadolinium source and natural tartaric acid, 1,2-ethanediol, citric acid or a mixture of citric acid and ethanolamine as complexing agents were used in the sol-gel processing. However, the formation of GAP did not proceed at the same synthesis conditions when gadolinium nitrite as a gadolinium source and synthetic tartaric acid or the mixtures of citric acid and 1,2-ethanediol or natural tartaric acid and 1,2-ethanediol as complexing agents were used in the sol-gel processing. The present study also demonstrates the versatility of the solution method to yield a monophasic GAP sample at a low sintering temperature (1000 $^\circ\text{C}$) when compared to the temperature required for the solid-state synthesis (>1400–1600 $^\circ\text{C}$).

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**Sigutė Čižauskaitė, Gintarė Špakauskaitė,
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**PEROVSKITINIO GdAlO₃, SINTETINTO
ZOLIŲ-GELIŲ METODU NAUDOJANT SKIRTINGUS
KOMPLEKSINIUS REAGENTUS, APIBŪDINIMAS**

S a n t r a u k a

Šiame darbe zolių-gelių metodu vandeniniuose tirpaluose, naudojant pradinėmis medžiagomis gadolinio nitratai ar gadolinio oksidą bei skirtingus su metalų jonais kompleksus sudarančius reagentus, susintetinti Gd-Al-O geliai. Iškaitinus šiuos gelius 1000°C temperatūroje, vienfazis gadolinio aluminatas (GdAlO₃), pasižymintis perovskito kristaline struktūra, buvo gautas, kai zolių-gelių procese buvo naudotas Gd₂O₃ bei tam tikri kompleksuojantys reagentai, būtent natūrali vyno rūgštis, 1,2-etandiolis, citrinų rūgštis bei citrinų rūgšties ir etanolamino mišinys. Gauti junginiai apibūdinti infraraudonosios spektroskopijos, rentgeno spindulių difrakcinės analizės bei skleidžiamosios elektroninės mikroskopijos metodais.