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Sol-gel preparation and characterization of perovskite gadolinium aluminates

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The paper reports on the results concerning the sol-gel preparation of the nanocrystalline non-substituted and Sr-substituted gadolinium aluminate ($GdAlO_3$, GAP) ceramics at slightly varying conditions of synthesis. The metal ions, generated by dissolving starting materials of metals in the diluted acetic acid were complexed by 1,2-ethanediol to obtain precursors for the non-substituted and Sr-substituted GAP. In the sol-gel processing different starting gadolinium materials such as gadolinium nitrate or gadolinium oxide were employed. The influence of the temperature and the amount of substituent on the phase purity of GAP was also investigated. Phase transformations, composition and micro-structural features in the gels and polycrystalline samples were studied by thermal analysis, powder X-ray diffraction analysis, infrared spectroscopy and scanning electron microscopy.

Key words: *aluminate; perovskite; ceramics; aqueous sol-gel process*

1. Introduction

Ceramics based on the Ln_2O_3–Al_2O_3 system (Ln – lanthanide element) are promising materials for optical, electronic and structural applications [1–3]. Perovskite aluminates doped with a lanthanide element offer advantages of longer lifetimes and higher, polarized cross sections with respect to most other oxide matrices, and are useful as hosts for solid-state lasers, luminescence systems and window materials for a variety of lamps. For example, gadolinium aluminate is currently under development as candidate material for the neutron absorption and control rod applications. Related ceramic perovskite materials are currently being incorporated into automobile catalytic

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converters, are also promising substrates for the epitaxy of thin oxide films having potential use as buffer layers for the epitaxial growth of various perovskite-type films such as high temperature superconductors, ferroelectrics, piezoelectrics and colossal magnetoresistance oxides. Some perovskites also exhibit very large electric permittivities [4–9].

The unique properties of most of the mixed-cation oxide ceramics depend largely on the impurities or dopants. Such complex oxides with the perovskite structure also demonstrate an impressive range of electrical, optical and magnetic properties. These properties of perovskites can be tuned by substituting cations at both sites. For instance, recently a strong photoluminescence was obtained without luminance temperature-degradation in the mixed alkaline earth substituted lanthanide aluminates or lanthanide doped alkaline earth aluminates [10, 11, 12–15]. Strontium atoms can substitute into the perovskite $LnAlO_3$ structure possibly for the lanthanide cation [16].

In the context of doped materials, the incorporation of homogeneously distributed nanosized secondary phases in a host matrix, which can be realized by the molecular level fabrication of new materials, is of significant interest. Over the last few decades, the sol-gel techniques have been used to prepare a variety of mixed-metal oxides [17–21]. In this paper, we present results of a systematic study of aqueous sol-gel synthetic approach to pure $GdAlO_3$ and Sr-substituted gadolinium aluminates $Gd_{1-x}Sr_xAlO_{3-\delta}$. The results illustrate the influence of starting materials, annealing temperature and strontium concentration on the phase purity and crystallinity of the end products.

2. Experimental

2.1. Preparation of gels

Gadolinium aluminate and gadolinium–strontium aluminate ceramic samples were synthesized by the sol-gel method. The gels were prepared using stoichiometric amounts of analytical-grade $Gd(NO_3)_3\cdot 6H_2O$ ($GdAlO_3$, sample I; $Gd_{0.9}Sr_{0.1}AlO_3$, sample II; $Gd_{0.75}Sr_{0.25}AlO_3$, sample III; $Gd_{0.5}Sr_{0.5}AlO_3$, sample IV; $Gd_{0.25}Sr_{0.75}AlO_3$, sample V) or Gd_2O_3 ($GdAlO_3$, sample VI; $Gd_{0.9}Sr_{0.1}AlO_3$, sample VII; $Gd_{0.75}Sr_{0.25}AlO_3$, sample VIII) as Gd^{3+} raw materials. Strontium acetate $Sr(CH_3COO)_2$ and aluminium nitrate $Al(NO_3)_3\cdot 9H_2O$ have been used as Sr^{2+} and Al^{3+} sources, respectively. For the preparation of unsubstituted samples by the sol-gel process, gadolinium nitrate or gadolinium oxide were first dissolved in 50 cm^3 of 0.2 mol/dm^3 CH_3COOH at 65 °C. To this solution, aluminium nitrate dissolved in 50 cm^3 of distilled water was added and the resulting mixture was stirred for 1 h at the same temperature. For the preparation of Sr-substituted samples an appropriate amount of strontium acetate dissolved in 50 cm^3 of 0.2 mol/dm^3 CH_3COOH at 65 °C was added and the resulting mixtures were stirred for 1 h at the same temperature. Then 1,2-ethanediol (2 cm^3) as complexing agent was added to the reaction solutions. After concentrating the solutions by a slow evaporation at 65 ºC under stirring, the Gd–Al–O or Gd(Sr)–Al–O acetate–nitrate–glycolate sols turned into white transparent gels. The oven dried (100 ºC) gel powders were ground in an agate mortar and preheated for 3 h at 800 ºC in air. Since the gels are very combustible, a slow heating rate (~ 3–4 ºC·min^{-1}), especially between 100 ºC and 400 ºC was found to be essential. After an intermediate grinding in an agate mortar, the powders were additionally sintered in air for 10 h at 800 ºC (samples VII and VIII) and at 1000 ºC (the remaining samples).

2.2. Characterization techniques

Thermal decomposition processes of the precursor gels were studied in air atmosphere by thermogravimetric and differential thermal analyses (TGA and DTA, respectively) using a Setaram TG-DSC12 apparatus at a heating rate 10 ºC·min^{-1}. The infrared spectra in the range of 4000–400 cm^{-1} were recorded on an EQUINOX 55/S/NIR FTIR spectrometer. Samples were prepared as KBr pellets. Powder X-ray diffraction measurements were performed at room temperature on a Stoe-Cie Powder Diffraction System STADI P diffractometer operating with a CuK$_\alpha$ radiation. Scanning electron microscope (SEM) DSM 962 was used to study the surface morphology and microstructure of the ceramic samples.

3. Results and discussion

3.1. Thermal analysis of precursor gels

The main requirement for the sol-gel approach is to achieve a high level of precursor homogeneity to produce a homogeneous end product – ceramic oxide material. It is well known that thermal characterization of synthesized samples is important both for the control of the reaction process and for the properties of materials obtained. In this context, thermal analysis is a versatile aid to monitor preparative studies. The mechanism of the thermal decomposition in flowing air of Gd(Sr)–Al–O precursor gels was studied by TGA/DTA measurements. The TGA/DTA profiles for the precursor gel samples I, II and III are shown in Fig. 1.

All TGA curves show a three-step decomposition of the gel precursor to form the ceramic material. The initial weight loss below 175 °C observed in all TGA curves (~5–6%, Fig. 1) is due to the evaporation of water and solvent molecules as indicated by broad endothermic peaks on the DTA curves in this region. The temperature ranges of three main weight losses (175–400 °C, 400–805 °C and 805–1000 °C) are also very similar in the synthesized gel samples. The first two and most significant decomposition steps can be attributed to the pyrolysis and combustion of organic compounds and the degradation of intermediate species formed during the gelation process. This observation is corroborated by well-resolved exotherms in the DTA curves at approximately 400–500 °C. The final weight loss (~3–4%, Fig. 1) on the TGA curves of the gel samples was observed in the temperature range of 805–1000 ºC.

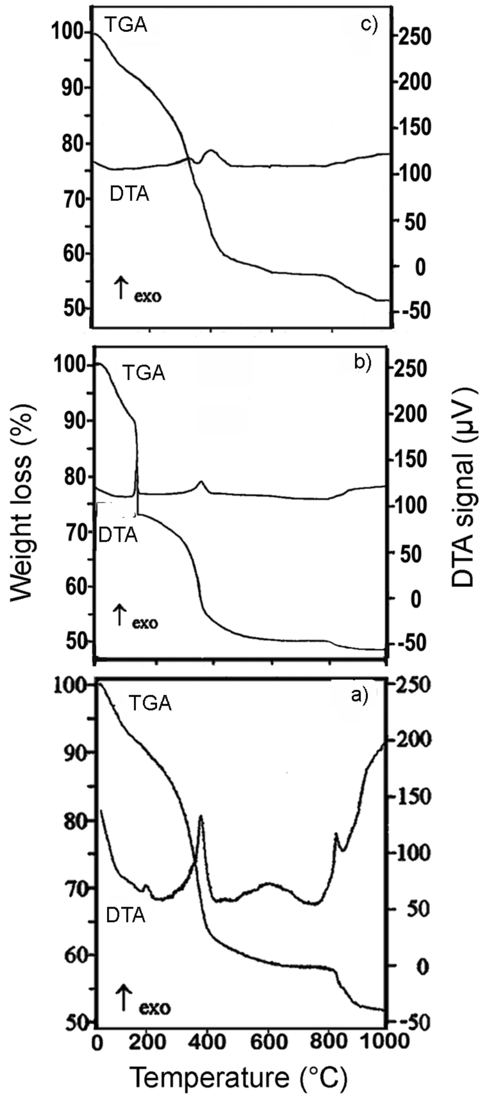

Fig. 1. TGA and DTA profiles of the Gd–Sr–Al–O precursor gels prepared using gadolinium nitrate in the sol-gel processing: a) 0% Sr, b) 10% Sr, c) 25% Sr. The heating rate was 5 ºC·min^{-1}

Furthemore, the thermal decomposition behaviour is associated with weak exothermic effects in the DTA curves. These peaks probably correspond to the decomposition and simultaneous solid-state reaction of the intermediate oxycarbonates $Gd_2O_2CO_3$ or $Al_2O_2CO_3$ to the mixed-metal oxides [3, 21, 26]. According to the thermal analysis data the crystallisation of $GdAlO_3$ ceramic oxides could vary from 800 to 1000 ºC. Therefore, the final annealing temperature of 800–1000 ºC for the preparation of GAP phase was selected.

3.2. Powder X-ray diffraction studies

The Gd(Sr)–Al–O precursor gel powders prepared using gadolinium nitrate in the sol-gel processing were calcined and sintered at 1000 °C. The XRD patterns of the obtained GAP ceramics derived from the Gd(Sr)–Al–O precursor gels (samples I–V) are shown in Fig. 2.

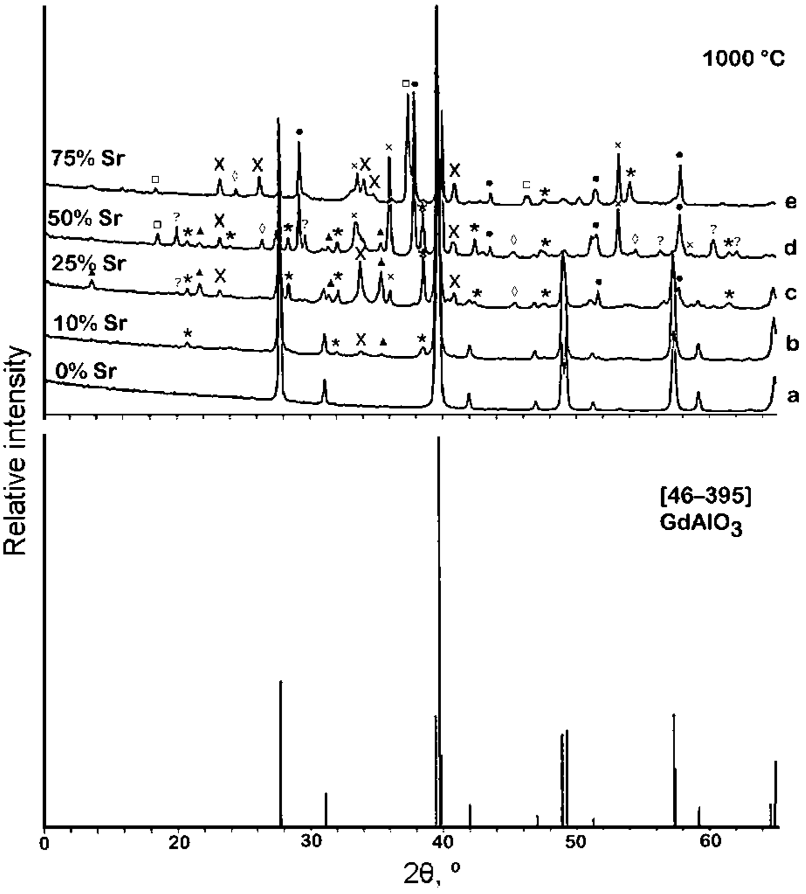

Fig. 2. X-ray diffraction patterns of: a) GdAlO$_3$, b) Gd$_{0.9}$Sr$_{0.1}$AlO$_3$, c) Gd$_{0.75}$Sr$_{0.25}$AlO$_3$, d) Gd$_{0.5}$Sr$_{0.5}$AlO$_3$, e) Gd$_{0.25}$Sr$_{0.75}$AlO$_3$ ceramics prepared using gadolinium nitrate in the sol-gel processing. Schematic presentation of the XRD pattern of GdAlO$_3$ from JCPDS is presented at the bottom. The impurity phases: × – SrAl$_4$O$_7$, ▲ – Gd$_4$Al$_2$O$_9$, ◊ – Sr$_4$Al$_2$O$_7$, X – SrAl$_2$O$_4$, * – Gd$_3$Al$_5$O$_{12}$, □ – Sr$_3$Al$_2$O$_6$, ● – SrGdAlO$_4$, ? – unidentified phases

According to the XRD analysis, fully crystallized single-phase oxide GdAlO$_3$ with well pronounced perovskite crystal structure has formed (Fig. 2a) (JCPDS file 46-395). The XRD pattern of the sample II (ceramic material with 10% of strontium) is presented in Fig. 2b. The XRD data confirm Gd$_{0.9}$Sr$_{0.1}$AlO$_{3-x}$ to be the main crystalline component. However the formation of certain amount of impurity phases was already detected. The diffraction lines at $2\theta \approx 22.8^{\circ}$, 32.1° and 38.6° could be attributed to the $Gd_3Al_5O_{12}$ phase, at $2\theta \approx 33.8^{\circ}$ to the $SrAl_2O_4$, and at $2\theta \approx 35.5^{\circ}$ to the $SrGd_2O_4$. Figure 2c shows the X-ray diffraction pattern of the ceramic sample III with nominal composition of $Gd_{0.75}Sr_{0.25}AlO_{3-\delta}$. The diffraction lines assigned to the perovskite crystal structure at $2\theta \approx 27.5^{\circ}$, 31.1°, 39.2°, 42.1°, 46.9°, 49.0°, 51.3°, 57.4° and 59.3° are well pronounced in the diffractogram. However, the intensities of diffraction lines corresponding to the impurity phases such as $Gd_4Al_2O_9$, $Gd_3Al_5O_{12}$ and $Sr_3Al_2O_6$ are much more intensive than those observed for the previous sample. On further increasing the Sr content, the formation of perovskite aluminate seems to be problematic. The impurity phases ($SrGdAlO_4$ and $SrAl_2O_4$) are already the dominating component formed during the synthesis of $Gd_{0.25}Sr_{0.75}AlO_{3-\delta}$ ceramics (Fig. 2e).

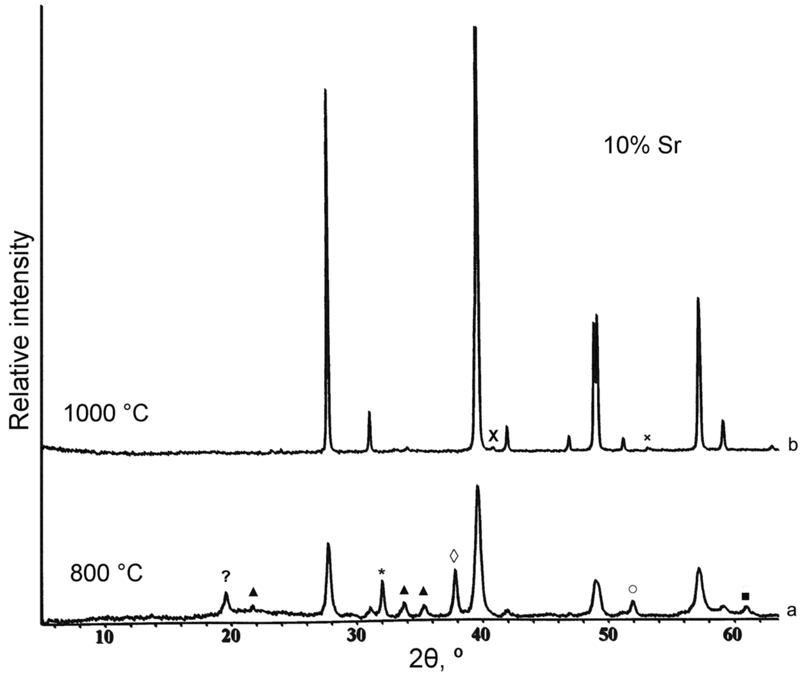

Fig. 3. X-ray diffraction patterns of $Gd_{0.9}Sr_{0.1}AlO_3$ ceramics prepared using gadolinium oxide in the sol-gel processing at various temperatures: a) 800 °C, and b) 1000 °C. The impurity phases: × – $SrAl_4O_7$, ▲ – $Gd_4Al_2O_9$, ◊ – $Sr_4Al_2O_7$, X – $SrAl_2O_4$, * – $Gd_3Al_5O_{12}$, ○ – $SrGd_2O_4$, ■ – $GdAl_{11}O_{18}$, ? – unidentified phases

As was already mentioned, one of the goals of this study was to investigate the influence of nature of starting material used as gadolinium source on the sinterability and phase purity of the end ceramics. Again, according to the XRD analysis, the synthesized at 1000 °C non-substituted compound was a single-phase gadolinium aluminate ($GdAlO_3$). Next, the influence of sintering temperature on the quality of Sr-substituted gadolinium aluminates was also estimated. The X-ray diffraction patterns of the $Gd_{0.9}Sr_{0.1}AlO_{3-x}$ (sample VII) ceramics prepared using gadolinium oxide in the sol-gel processing and annealed at various temperatures are shown in Fig. 3. Many different impurity phases in the X-ray diffraction pattern of the sample annealed at 800 °C could be detected (Fig. 3a). Apparently, this temperature of synthesis is too low for the preparation of monophasic GAP. The diffraction lines assiged to the perovskite crystal structure at $2\theta \approx 27.5^\circ, 31.1^\circ, 39.2^\circ, 42.1^\circ, 46.9^\circ, 49.0^\circ, 51.3^\circ, 57.4^\circ$ and 59.3° are well pronounced in the X-ray diffraction pattern of the sample annealed at higher temperature (1000 °C, Fig. 3b).

The X–ray diffraction patterns of the $Gd_{0.75}Sr_{0.25}AlO_{3-x}$ (sample VIII) ceramics prepared using gadolinium oxide in the sol-gel processing at various temperatures are shown in Fig. 4.

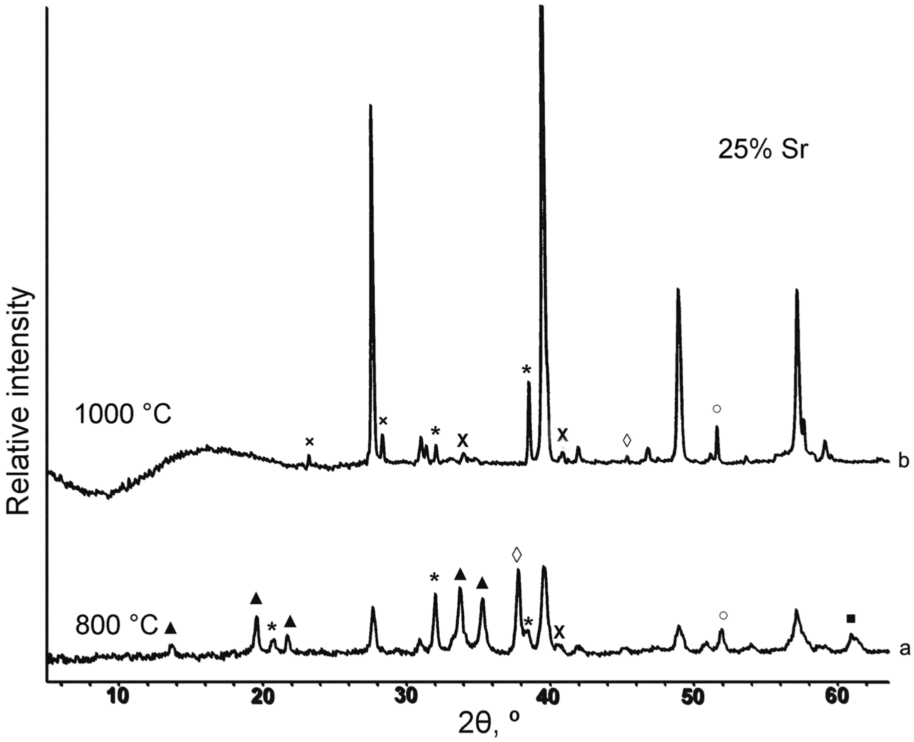

Fig. 4. X-ray diffraction patterns of $Gd_{0.75}Sr_{0.25}AlO_3$ ceramics prepared using gadolinium oxide in the sol-gel processing at various temperatures: a) 800 °C, and b) 1000 °C. The impurity phases: × – $SrAl_4O_7$, ▲ – $Gd_4Al_2O_9$, ◊ – $Sr_4Al_2O_7$, X – $SrAl_2O_4$, * – $Gd_3Al_5O_{12}$, ○ – $SrGd_2O_4$, ■ – $GdAl_{11}O_{18}$

The X-ray results confirm once again that the final annealing temperature should be higher than 800 °C. Besides, the XRD powder pattern shows formation of broad peaks; their poor intensities suggest that a considerable amount of the material is either amorphous or nanocrystalline [22]. Moreover, with increasing the strontium concentration the amount of impurity phases in the sample annealed at 1000 ºC (Fig. 4b) also increases. However, it is evident that upon using Gd_2O_3 as a starting material, the obtained GAP ceramics contain less amounts of impurities than those prepared using $Gd(NO_3)_3 \cdot 6H_2O$. We can thus conclude that for the preparation of GAP ceramics Gd_2O_3 instead of $Gd(NO_3)_3 \cdot 6H_2O$ should preferably be used as the starting material.

3.3. Infrared spectra

The results of the X-ray diffraction analysis are consistent with the crystallization process observed by the IR measurements. IR analysis of synthesized samples is important for the control of both the reaction process and of the properties of materials obtained. Figure 5 shows the IR spectra of Gd(Sr)–Al–O ceramics (samples VI–VIII) prepared by calcinations of gel precursors for 10 h at 1000 ºC.

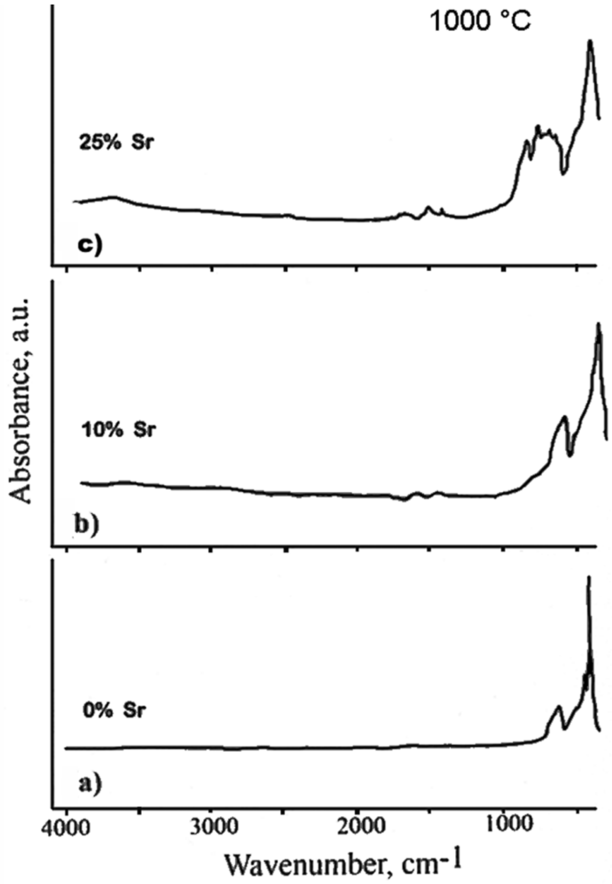

Fig. 5. Infrared spectra of: a) $GdAlO_3$, b) $Gd_{0.9}Sr_{0.1}AlO_3$, c) $Gd_{0.75}Sr_{0.25}AlO_3$ ceramics prepared at 1000 °C using gadolinium oxide in the sol-gel processing

The IR spectra of $GdAlO_3$ and $Gd_{0.9}Sr_{0.1}AlO_3$ (see Fig. 5a and b, respectively) display only two frequencies at 660 and 465 cm^{-1} which are typical of the M–O (possibly Al–O stretching frequencies) vibrations in the perovskite structure compounds [23, 24, 25]. The IR spectrum of Sr-substituted $Gd_{1-x}Sr_xAlO_{3-\delta}$ sample with 25% substitutional level of Sr, however, indicates the atomic-level reorganization. The strong bands of 660 and 465 cm^{-1} are replaced by several bands which may be assigned to stretching modes of different polyhedra in the multiphasic oxide materials. Thus, the results of IR analysis indicate as well that when Sr concentration $x \geq 0.25$, the formation of multiphase crystalline products occurs. Besides, the spectra of strontium substituted ceramic samples show the presence of new peaks in the region of 1660–1390 cm^{-1}. Moreover, their intensities increase with increasing amount of strontium in the samples. The origin of these peaks is not very clear. It is known that typical carbonate vibrations are correspond to ~1470–1390 cm^{-1} (triply degenerated stretching mode) and ~880–850 cm^{-1} (doubly degenerated stretching mode) [24]. Thus, these additional bands probably may be assigned to metal carbonates formed as intermediates during high-temperature treatments. It is well known that aluminium carbonate ($Al_2(CO_3)_3$) decomposes at relatively low temperatures (~500 ºC) [26]. Therefore, the carbonate peaks in the IR spectra of doped $Gd_{1-x}Sr_xAlO_3$ ceramic samples may correspond to strontium carbonate ($SrCO_3$) and/or gadolinium oxycarbonate ($Gd_2O_2CO_3$). Because the intensity of the 1460 cm^{-1} peak is relatively weak, it is likely that very little carbonate was formed. However, the IR spectrum of undoped $GdAlO_3$ sample calcined at 1000 °C does not feature any characteristic carbonate bands [22, 25].

3.4. SEM analysis

Figure 6 shows SEM micrographs (back scattered electron (BSE) images) of synthesized $GdAlO_3$ and $Gd_{0.75}Sr_{0.25}AlO_3$ powders using gadolinium oxide in the initial stage of preparation. As seen from Fig. 6 (left), the broad distribution of light or dark regions in the SEM micrograph of $GdAlO_3$ specimen is absent. There-

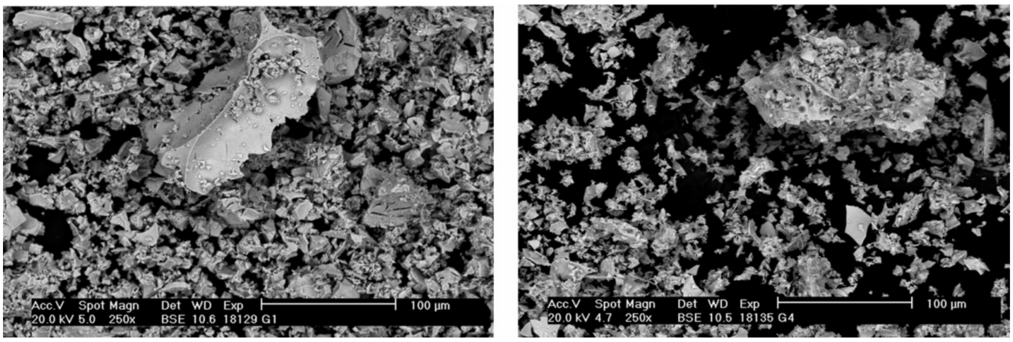

Fig. 6. Scanning electron micrographs in back scattering mode of $GdAlO_3$ (left) and $Gd_{0.75}Sr_{0.25}AlO_3$ (right) ceramics prepared using gadolinium oxide in the sol-gel processing. Magnification 250×

fore, the SEM image of the single-phase $GdAlO_3$ sample obtained using gadolinium oxide as starting material confirms that the most of the material is finely divided, i.e. the distribution of its chemical elements is highly uniform. Some individual particles seem to be plate-like crystals, most grains, however, are agglomerated having different shape and size ranging from ~5 µm to 30 µm. In the backscattered electron mode for the $Gd_{0.75}Sr_{0.25}AlO_3$ sample prepared using gadolinium oxide numerous light and dark regions are observed. Since the brightness of the specimen is highly inhomogeneous over the entire measuring area, the material is evidently composed of several phases.

4. Conclusions

Homogeneous gels in the Gd(Sr)–Al–O system were prepared by the complexation of metal ions with 1,2-ethanediol followed by a controlled hydrolysis and condensation in aqueous media. The obtained gels have been used for low-temperature synthesis of nano-scale gadolinium aluminate (GAP, $GdAlO_3$) and strontium substituted gadolinium aluminate ($Gd_{1-x}Sr_xAlO_{3-\delta}$) ceramics. The present study demonstrates the versatility of the solution method to yield a monophasic GAP sample at low sintering temperature (1000 ºC) when compared to the temperature required for the solid state synthesis (>1400–1600 °C). Furthermore, the Sr-substituted GAP ceramics (up to 25% of Sr) have also been successfully obtained by this method. In the view of the above results and the increasing importance of the nanomaterials, the nanocrystalline GAP and Sr-substituted GAP phases show a considerable application potential.

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