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INSTITUTE OF CHEMISTRY, CENTER FOR PHYSICAL SCIENCES
AND TECHNOLOGY

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SOL-GEL SYNTHESIS AND CHARACTERIZATION OF
LANTHANIDE ALUMINIUM GARNETS

Summary of doctoral dissertation

Physical sciences, Chemistry (03 P)

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VILNIAUS UNIVERSITETAS
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRO CHEMIJOS
INSTITUTAS

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LANTANOIDŲ ALIUMINIO GRANATŲ SINTEZĖ
ZOLIŲ-GELIŲ METODU IR APIBŪDINIMAS

Daktaro disertacija
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1. INTRODUCTION

The development and application of advanced materials is a very important task of today's information society. Garnet crystal structure compounds because of their specific physical and chemical properties are widely used in information technology, manufacturing of solid-state lasers and optical equipments, medical equipments and many other areas. Therefore, these materials because of their unique properties and characteristics are of high interest so far.

The yttrium aluminium garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$, YAG) doped with a transition metal or lanthanide ions, is an important solid-state laser material which is widely used in fluorescent systems and optical fiber telecommunications systems. In addition, recently the YAG doped with various transition metal ions (Cr^{4+} , Co^{2+} and V^{3+}) has been applied as passive Q-switch crystals. The YAG oxides are also widely applied as phosphors in cathode-ray tubes (projection TV settings), electroluminescent and vacuum fluorescent displays and positron emission tomographs. Besides, the yttrium aluminium garnet is characterized by a relatively high mechanical strength and high temperature creep resistance.

The rare earth (RE) garnets are also potential materials which have high mechanical stability like that of YAG. The rare earth garnets are also used as laser and phosphor materials. Lutetium aluminium garnet ($\text{Lu}_3\text{Al}_5\text{O}_{12}$, LuAG) is widely applied as optical host material for luminescent powders or single crystals. Rare earth doped LuAG has found applications in IR lasers, phosphor converted LEDs, X-ray detectors and field emission displays. The literature highlights that LuAG proves to be a promising host structure for scintillating materials. So, the synthesis and study of lanthanide aluminium garnets is relevant and contemporary issue. New, reliable, cost-effective and simple methods of synthesis should be developed for creating materials which can be used in modern technologies. The sol-gel technology, due to its apparent advantages of fine homogeneity, high reactivity of starting materials, low sintering temperature and lower costs, is a promising method for the preparation of garnet crystal structure. Therefore, the aim of this study was to synthesize various multiple materials having garnet crystal structure using an aqueous sol-gel method. Lanthanide aluminium garnets have never been synthesized using sol-gel method and some of them are not synthesized so far. It proves that this doctoral thesis is an original study.

The aim of the research was to synthesize and study various lanthanide aluminium garnets using an aqueous sol-gel method. For this reason there were formulated tasks as follows:

1. For the first time to use the sol-gel method to synthesize lanthanide (Ce, Pr, Nd, Tb, Dy, Ho, Er, Tm, Yb, Lu) aluminium garnets.
2. To characterize these sol-gel derived garnets using different characterization techniques.
3. To study the effect of yttrium substitution by neodymium in yttrium aluminium garnet.
4. To study the effect of yttrium substitution by samarium in yttrium aluminium garnet.

Statements for defence

The results of the investigations let us defend the most important statements:

1. The sol-gel method is suitable, effective and economical method to synthesize single-phase polycrystalline $Tb_3Al_5O_{12}$ (TbAG); $Dy_3Al_5O_{12}$ (DyAG); $Ho_3Al_5O_{12}$ (HoAG); $Er_3Al_5O_{12}$ (ErAG); $Tm_3Al_5O_{12}$ (TmAG); $Yb_3Al_5O_{12}$ (YbAG); $Lu_3Al_5O_{12}$ (LuAG) garnet structure compounds, which are characterized by high level of homogeneity.
2. Ce-Al-O, Pr-Al-O and Nd-Al-O acetate-glycolate gels can not be used for the synthesis of cerium aluminium garnet $Ce_3Al_5O_{12}$, praseodymium aluminium garnet $Pr_3Al_5O_{12}$ and neodymium aluminium garnet $Nd_3Al_5O_{12}$ using the same synthesis parameters. Instead of presumable lanthanide (Ce, Pr, Nd) aluminium garnets the samples consisted of cerium oxide (CeO_2) and alumina (Al_2O_3) phases (in cases of cerium), or in cases of neodymium and praseodymium, the formation of perovskite $NdAlO_3$ and $PrAlO_3$ phases took place.
3. When Nd and Sm are introduced in $Y_3Al_5O_{12}$, the garnets phases $Y_{3-x}Nd_xAl_5O_{12}$ and $Y_{3-x}Sm_xAl_5O_{12}$ can be synthesized at 1000 °C only when Nd or Sm concentrations are suitable. When Nd and Sm concentration is up to 2.5 at % multiphasic materials are formed. When Nd and Sm concentration is higher, neodymium and samarium perovskite aluminates are formed instead of garnet structure compounds.

2. EXPERIMENTAL

2.1. Materials and reagents

For the sol-gel synthesis stoichiometric amounts of Y_2O_3 , $[NH_4]_2[Ce(NO_3)_6]$, Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Tb_4O_7 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , Lu_2O_3 , $Al(NO_3)_3 \cdot 9H_2O$ as starting compounds, ethane-1,2-diol ($HOCH_2CH_2OH$) as complexing agent, all of them analytical grade, were used.

2.2 Methods of synthesis

Nd, Dy, Ho, Er, Tm, Yb and Lu acetates were prepared by dissolving the corresponding lanthanide 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. However, terbium and praseodymium oxide were found not soluble in acetic acid. Therefore, these oxides were dissolved in 65% nitric acid at the same temperature. $[NH_4]_2[Ce(NO_3)_6]$ was dissolved in 100 ml of distilled water. Then, aqueous solution of aluminium nitrate nonahydrate (25 ml) was added to above solutions. The resulting mixtures were stirred at 60–65 °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 60–70 °C until they turned into transparent gels. The gels were dried in an oven at 105 °C for 10 h. The resulting gel powders were ground in an agate mortar and heated in air at 800 °C for 4 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 temperatures (800–1200 °C) for 10 h.

Yttrium-neodymium aluminium garnet ($Y_{3-x}Nd_xAl_5O_{12}$, YNdAG) ($x = 0.1, 0.25, 0.35, 0.5, 0.6, 0.7, 0.8, 1.5, 2, 2.5, 3$) and yttrium-samarium aluminium garnet ($Y_{3-x}Sm_xAl_5O_{12}$, YSmAG) ($x = 0.1, 0.15, 0.25, 0.5, 0.75, 1, 1.5, 2, 2.5, 3$) samples were synthesized by an aqueous sol-gel method. Y, Nd and Sm acetates were prepared by dissolving the corresponding lanthanide 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 nonahydrate (25 ml) was added to above solution. Neodymium acetate or samarium acetate was added to initial mixture. The resulting mixtures were stirred at 60–65 °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 60-70 °C until they turned into transparent gels. The gels were dried in an oven at 105 °C for 10 h. The resulting gel powders were ground in an agate mortar and heated in air at 800 °C for 4 h by slow temperature elevation (~ 3–4 °C min⁻¹). After grinding in an agate mortar, the powders were further sintered in air at 1000 °C for 10 h.

2.3. Characterization and techniques

The XRD studies were performed on a Philips Xpert diffractometer (CuK α 1 radiation; $\lambda = 1.5406 \text{ \AA}$) (for Ce₃Al₅O₁₂, Pr₃Al₅O₁₂, Nd₃Al₅O₁₂, Tb₃Al₅O₁₂, Dy₃Al₅O₁₂ and Er₃Al₅O₁₂), Bruker AXE D8 Focus Diffractometer, LynxEye detector (CuK α radiation; $\lambda = 1.5406 \text{ \AA}$) (for Ho₃Al₅O₁₂, Tm₃Al₅O₁₂, Yb₃Al₅O₁₂ and Lu₃Al₅O₁₂). IR spectra were recorded with Perkin–Elmer FT-IR Spektrum BX II or Bruker EQUINOX 55/S/NIR FTIR spectrometers. Scanning electron microscopes CAM SCAN S4 (for Ce₃Al₅O₁₂, Pr₃Al₅O₁₂, Nd₃Al₅O₁₂, Tb₃Al₅O₁₂, Dy₃Al₅O₁₂ and Er₃Al₅O₁₂), FE-SEM Zeiss Ultra 55, In-Lens detector (for Ho₃Al₅O₁₂, Tm₃Al₅O₁₂, Yb₃Al₅O₁₂ and Lu₃Al₅O₁₂) were used to study the morphology and microstructure of the ceramic samples.

3. RESULTS AND DISCUSSION

3.1. Sol gel synthesis and characterization of lanthanide (Tb, Dy, Ho, Er, Tm, Yb, Lu) aluminium garnets

The synthesis of lanthanide (Tb, Dy, Ho, Er, Tm, Yb, Lu) aluminium garnets via simple aqueous sol–gel method has been suggested. For the first time Tb₃Al₅O₁₂, Dy₃Al₅O₁₂, Ho₃Al₅O₁₂, Er₃Al₅O₁₂, Tm₃Al₅O₁₂, Yb₃Al₅O₁₂ and Lu₃Al₅O₁₂ compounds were synthesized using sol-gel method.

3.1.1 XRD characterization of lanthanide (Tb, Dy, Ho, Er, Tm, Yb, Lu) aluminium garnets

In the first part, the Tb–Al–O, Dy–Al–O, Ho–Al–O, Er–Al–O, Tm–Al–O, Yb–Al–O and Lu–Al–O precursor gels were calcined at 800 °C for 5 h and finally annealed at 1000 °C for 10 h. The X-ray diffraction patterns of the Tb–Al–O, Dy–Al–O and Er–Al–O precursor gels annealed at 1000 °C are shown in Fig. 1. The XRD results presented in Fig. 1a revealed that Tb–Al–O ceramics obtained at 1000 °C consists of one

crystalline phase: terbium aluminium garnet ($\text{Tb}_3\text{Al}_5\text{O}_{12}$). The obtained XRD pattern is in a good agreement with the reference data for $\text{Tb}_3\text{Al}_5\text{O}_{12}$ (PDF [17–735]).

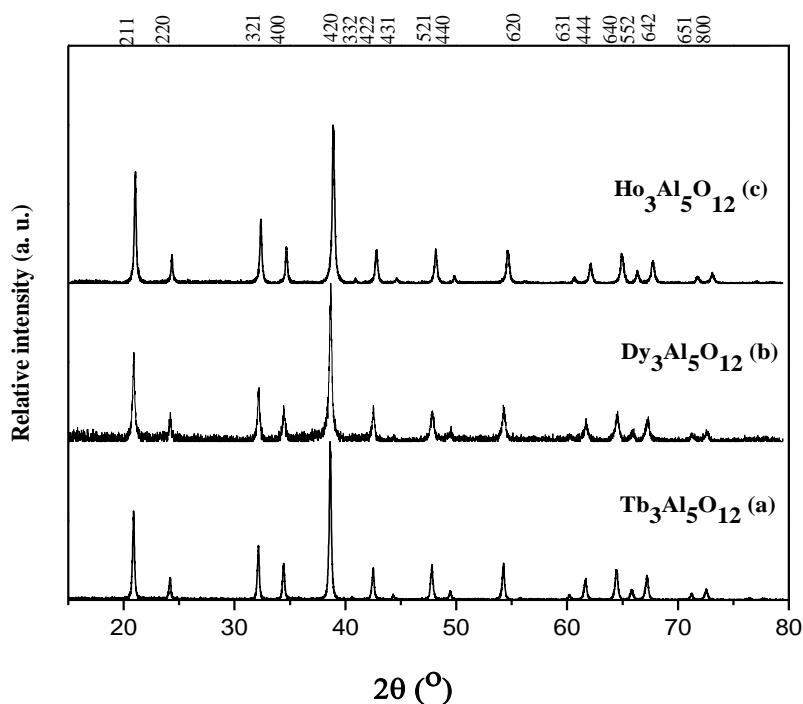


Fig. 1. XRD patterns of $\text{Tb}_3\text{Al}_5\text{O}_{12}$ (a), $\text{Dy}_3\text{Al}_5\text{O}_{12}$ (b) and $\text{Ho}_3\text{Al}_5\text{O}_{12}$ (c) ceramic powders, synthesized by sol–gel method and annealed at $1000\text{ }^\circ\text{C}$ for 10 h.

Fig. 1b reveals that only one dysprosium aluminium garnet $\text{Dy}_3\text{Al}_5\text{O}_{12}$ phase (ICSD [00-022-1093]) was also obtained after calcination of precursors at $1000\text{ }^\circ\text{C}$. In the case of the holmium aluminium system, the analogous results were obtained. In Fig. 1c the X-ray diffraction pattern of the final holmium aluminium ceramic sample annealed at $1000\text{ }^\circ\text{C}$ is presented. The XRD pattern proves the formation of the cubic holmium aluminium garnet ($\text{Ho}_3\text{Al}_5\text{O}_{12}$). Evidently, the obtained XRD pattern is in good agreement with the reference data for $\text{Ho}_3\text{Al}_5\text{O}_{12}$ (ICSD [00-076-0112]).

The X-ray diffraction patterns of the Er–Al–O, Tm–Al–O, Yb–Al–O and Lu–Al–O precursor gels annealed at $1000\text{ }^\circ\text{C}$ are shown in Fig. 2. The XRD results presented in Fig. 2a revealed that ceramics obtained at $1000\text{ }^\circ\text{C}$ consists of one crystalline phase of erbium aluminium garnet ($\text{Er}_3\text{Al}_5\text{O}_{12}$). The obtained XRD pattern is in a good agreement with the reference data for $\text{Er}_3\text{Al}_5\text{O}_{12}$ (PDF [32–12]). Fig. 2b reveals that only one thulium aluminium garnet $\text{Tm}_3\text{Al}_5\text{O}_{12}$ phase was obtained after calcinations of precursors

at 1000 °C (ICSD [04-001-9712]). Fig. 2c is the X-ray diffraction pattern of the final Yb–Al–O ceramic powders annealed at 1000 °C. Evidently, the obtained XRD pattern is in good agreement with the reference data for Yb₃Al₅O₁₂ (ICSD [00-023-1476]). Fig. 2d shows XRD pattern of monophasic Lu₃Al₅O₁₂ phase. All indexed lines have been assigned to the pure polycrystalline Lu₃Al₅O₁₂ phase (ICSD [04-001-9996]).

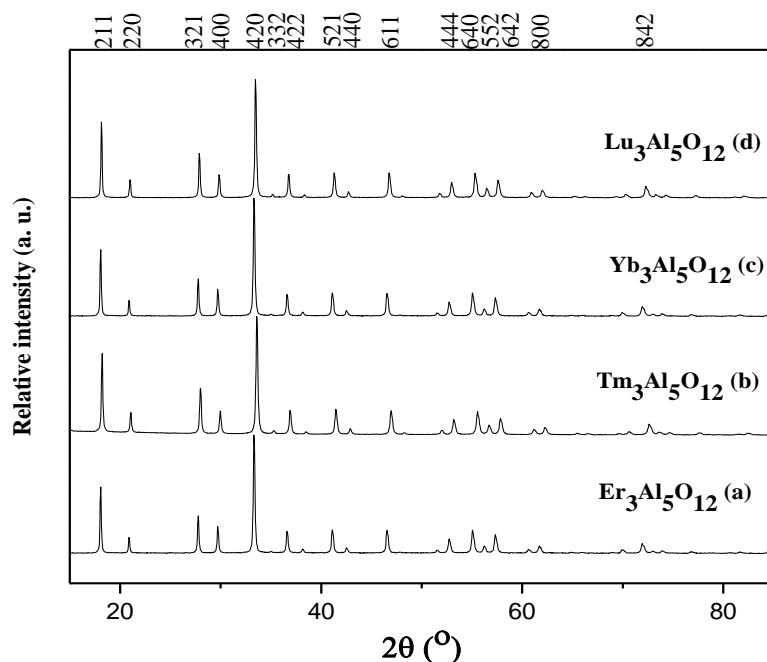
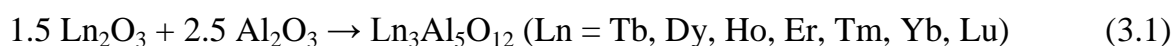


Fig. 2. XRD patterns of Er₃Al₅O₁₂ (a), Tm₃Al₅O₁₂ (b), Yb₃Al₅O₁₂ (c) and Lu₃Al₅O₁₂ (d) ceramic powders, synthesized by sol–gel method and annealed at 1000 °C for 10 h.

The solid state reactions expressed by Eqs. (3.1) proceed completely at 1000 °C, which is rather low temperature for such type of ceramics.



Therefore, the optimum temperature for the formation of Tb₃Al₅O₁₂, Dy₃Al₅O₁₂, Ho₃Al₅O₁₂, Er₃Al₅O₁₂, Tm₃Al₅O₁₂, Yb₃Al₅O₁₂ and Lu₃Al₅O₁₂ garnets is 1000 °C.

3.1.2 IR characterization of lanthanide (Tb, Dy, Ho, Er, Tm, Yb, Lu) aluminium garnets

All seven IR spectra of $\text{Tb}_3\text{Al}_5\text{O}_{12}$, $\text{Dy}_3\text{Al}_5\text{O}_{12}$, $\text{Ho}_3\text{Al}_5\text{O}_{12}$, $\text{Er}_3\text{Al}_5\text{O}_{12}$, $\text{Tm}_3\text{Al}_5\text{O}_{12}$, $\text{Yb}_3\text{Al}_5\text{O}_{12}$ and $\text{Lu}_3\text{Al}_5\text{O}_{12}$ garnets are very similar. The representative IR spectra are shown in Fig. 3. The most important feature is that several intensive bands are determined in the region of $900\text{--}450\text{ cm}^{-1}$, which may be attributed to the stretching modes of the isolated $[\text{AlO}_4]$ tetrahedra and $[\text{AlO}_6]$ octahedra in the garnet structure, i.e. these bands correspond to the formation of crystalline TbAG, DyAG, HoAG, ErAG, TmAG, YbAG, and LuAG.

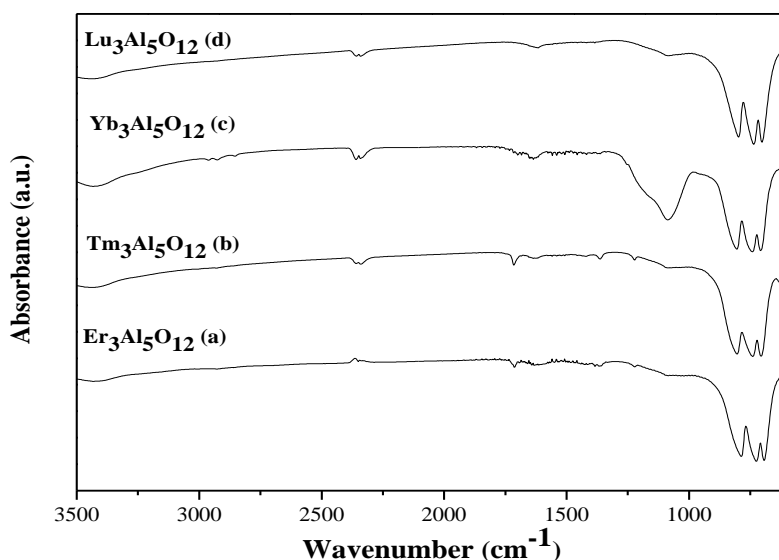


Fig. 3. IR spectra of $\text{Er}_3\text{Al}_5\text{O}_{12}$ (a), $\text{Tm}_3\text{Al}_5\text{O}_{12}$ (b), $\text{Yb}_3\text{Al}_5\text{O}_{12}$ (c) and $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (c) ceramic powders, synthesized by sol-gel method and annealed at $1000\text{ }^\circ\text{C}$ for 10 h.

Broad absorption bands arising from O-H stretching and bending vibration of water due to the exposure of the sample to atmosphere occur at ~ 3500 and $\sim 1600\text{ cm}^{-1}$. Bands at ca. 2350 cm^{-1} belong to carbon dioxide from atmosphere. Thus, the observed M-O vibrations which in view of the earlier reports are characteristic Al-O stretching frequencies let us to conclude, that the IR results are consistent with crystallization process observed by XRD measurements. The negligible difference between the synthesized samples is the nature of lanthanide cation in the dodecahedral positions. However, the ionic radii of Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} and Lu^{3+} are comparable, and differ only from 0.92 \AA for Tb^{3+} to 0.86 \AA for Lu^{3+} . As a result, the IR spectra in the

investigated region of monophasic $Tb_3Al_5O_{12}$, $Dy_3Al_5O_{12}$, $Ho_3Al_5O_{12}$, $Er_3Al_5O_{12}$, $Tm_3Al_5O_{12}$, $Yb_3Al_5O_{12}$ and $Lu_3Al_5O_{12}$ powders are comparable as well.

3.1.3 SEM characterization of lanthanides (Tb, Dy, Ho, Er, Tm, Yb, Lu) aluminium garnets

Fig. 4 representative SEM micrographs of Ho–Al–O and Tm–Al–O precursor gels calcined at 800 °C for 5 h. As seen, the calcinations products contain differently shaped crystallites along with agglomerated cloudy amorphous particles. These results indicate that all synthesis products obtained at 800 °C are multiphasic independently on the nature of lanthanide ion.

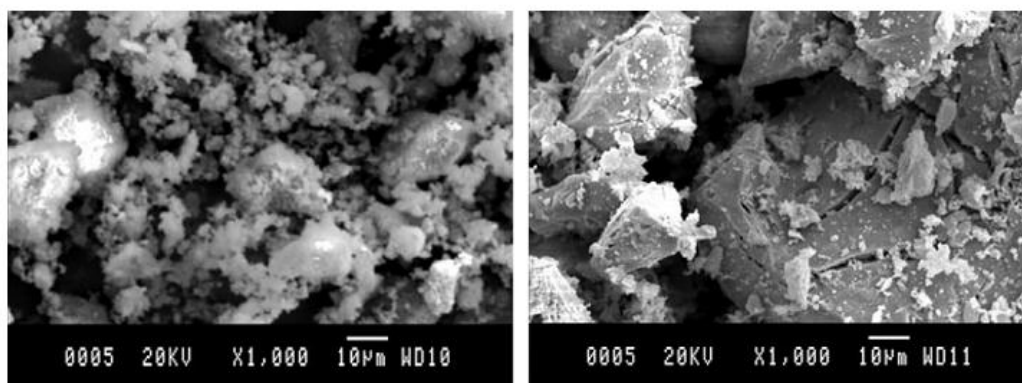


Fig. 4. SEM micrographs of Ho–Al–O (at left) and Tm–Al–O (at right) precursor gels calcined at 800 °C for 5 h.

Fig. 5 shows the representative SEM micrograph of $Yb_3Al_5O_{12}$ powders synthesized at 1000 °C for 10 h.

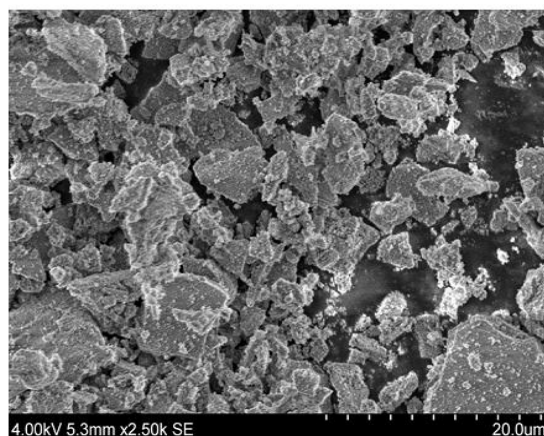


Fig. 5. SEM micrograph of the $Yb_3Al_5O_{12}$ garnet.

The SEM results show, that most of the lanthanide aluminium garnet samples consist of plate-like particles in size of 0.5–8 μm , however, some of them are close to nanometer dimensions. This observation suggests that the LnAG crystallites obtained at 1000 $^{\circ}\text{C}$ are homogeneous, having wide particle size distribution. Slightly different microstructure was observed for $\text{Lu}_3\text{Al}_5\text{O}_{12}$. It is clear, that many large plate-like particles (about 5–20 μm) are packed with extremely fine powders.

3.2. Sol gel synthesis and characterization of lanthanide (Ce, Pr, Nd) aluminium garnets

In this part an aqueous sol-gel method was proposed for the preparation of the lanthanide (Ce, Pr, Nd) aluminium garnets $\text{Ce}_3\text{Al}_5\text{O}_{12}$, $\text{Pr}_3\text{Al}_5\text{O}_{12}$, $\text{Nd}_3\text{Al}_5\text{O}_{12}$.

3.2.1 XRD characterization of lanthanide (Ce, Pr, Nd) aluminium garnets

The Ce-Al-O, Pr-Al-O and Nd-Al-O precursor gels were calcined at 800 $^{\circ}\text{C}$ for 5 h and finally annealed at 1000 $^{\circ}\text{C}$ for 10 h. The X-ray diffraction pattern of the Ce-Al-O precursor gel annealed at 1000 $^{\circ}\text{C}$ is shown in Fig. 6.

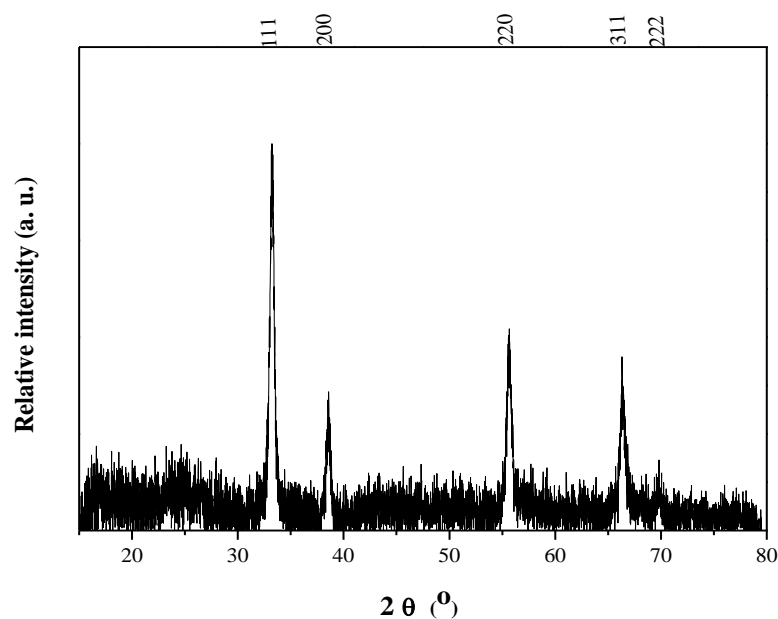
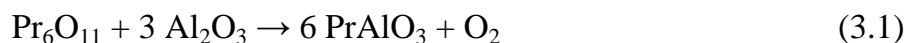


Fig. 6. XRD pattern of the cerium aluminium gel, synthesized by sol-gel method and annealed at 1000 $^{\circ}\text{C}$ for 10 h.

Surprisingly, the XRD pattern testifies the formation of poor crystalline CeO₂ (PDF [34-394]) and, probably, amorphous aluminium oxide (Al₂O₃). Even no traces of Ce₃Al₅O₁₂ could be detected in the XRD pattern.

Fig. 7 represents the X-ray diffraction pattern of the Pr–Al–O precursor gel annealed at 1000 °C. Evidently, the formation of perovskite praseodymium aluminate (PrAlO₃, PAP) phase and amorphous aluminium oxide (Al₂O₃) instead of Pr₃Al₅O₁₂ takes place. Also, the same results were observed in the case of neodymium. Only formation of perovskite neodymium aluminate has been determined. The obtained X-ray diffraction patterns are in a good agreement with the reference data for PrAlO₃ (PDF [29–76]) and NdAlO₃ (PDF [29–56]). From the above results we can conclude that the Pr₃Al₅O₁₂ and Nd₃Al₅O₁₂ phases have not formed by heat treatment of the precursor gel powders. The final ceramic product consists of other crystalline phases. For instance:



“Phase metathesis” reactions (Eqs. 3.3 and 3.4) may also occur:

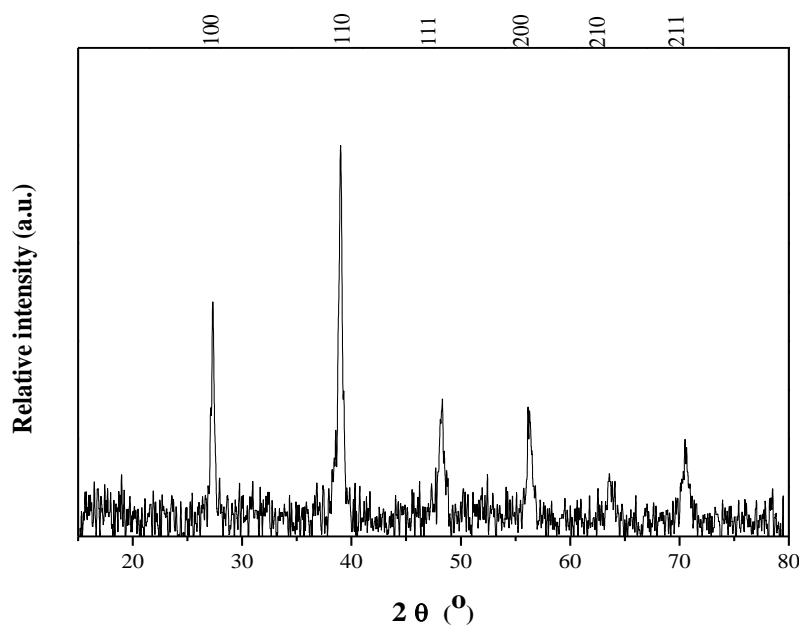
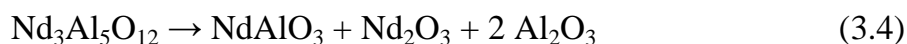


Fig. 7. XRD pattern of the praseodymium aluminium gel, synthesized by sol–gel method and annealed at 1000 °C for 10 h.

The Ce-Al-O, Pr-Al-O and Nd-Al-O precursor gels were also calcined for 10 h at 800 and 1200 °C. Again, the results obtained from the XRD patterns showed no formation even traces of garnet phases. Therefore, we can conclude that by heat treatment of the Ce-Al-O, Pr-Al-O and Nd-Al-O precursor gel powders in the temperature region of 800–1200 °C the formation of CeO₂:Al₂O₃, LnAlO₃:Al₂O₃ or LnAlO₃:Ln₂O₃:2Al₂O₃ (Ln=Pr, Nd) mixtures occurs instead of the single Ce₃Al₅O₁₂, Pr₃Al₅O₁₂ and Nd₃Al₅O₁₂ garnet phases.

3.2.2 IR characterization of lanthanide (Ce, Pr, Nd) aluminium garnets

The IR spectra of ceramic materials obtained after the calcinations of the Ce-Al-O, Pr-Al-O and Nd-Al-O gels are shown in Fig. 8. The synthesized ceramics show several intense broad bands. Strong absorption bands arising from O–H stretching and bending vibration of water due to the exposure of the sample to the atmosphere occur at ~3500 and ~1600 cm⁻¹, respectively.

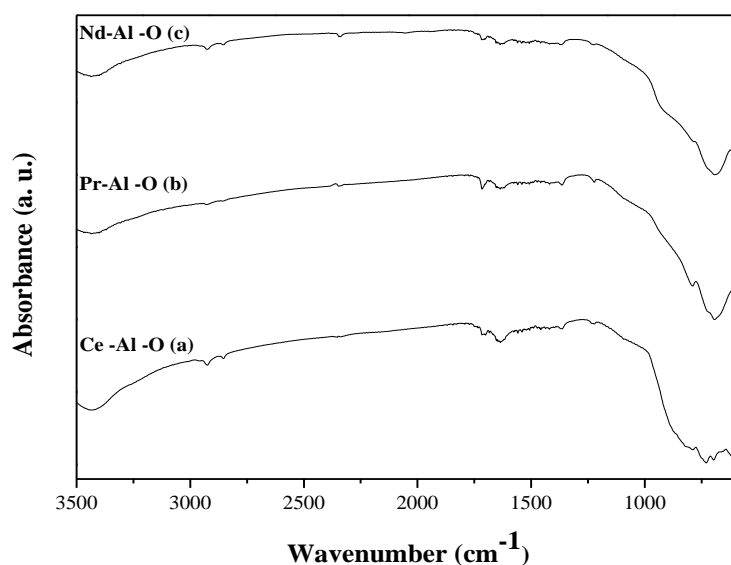


Fig. 8. IR spectra of the obtained products by annealing cerium aluminium (a), praseodymium aluminium (b) and neodymium aluminium (c) gel precursors at 1000 °C.

Importantly, in Figs. 8(b), (c) in the 1300–400 cm⁻¹ fingerprint region, two sharp bands were present at 664 and 455 cm⁻¹. These are typical metal-oxygen (Al–O)

absorptions for the perovskite-type compounds. Evidently, the character of this region of IR spectrum for cerium aluminium sample (see Fig. 8(a)) is a little different. This is associated with fact that during annealing of cerium aluminium precursor gel at 1000 °C only separate oxides (CeO_2 and Al_2O_3) have formed and no traces of perovskite CeAlO_3 compound were observed. Therefore, the IR results absolutely support the conclusions made by XRD measurements.

3.2.3 SEM characterization of lanthanides (Ce, Pr, Nd) aluminium garnets

Representative scanning electron micrographs of the Ce–Al–O gel sample calcined at 1000 °C is shown in Fig. 9. Individual particles seem to be submicrosized plate-like crystals and they partially fused to form hard agglomerates. Moreover, these agglomerates are covered with differently shaped smaller particles. Thus, we can conclude that obtained ceramics consists of two separate phases, possibly CeO_2 and Al_2O_3 . A progressive change in morphology is evident for the heat treated praseodymium aluminium and neodymium aluminium specimens. Apparently, the particles were formed with more pronounced agglomeration, indicating good connectivity between the grains which is characteristic feature for ceramic composite material.

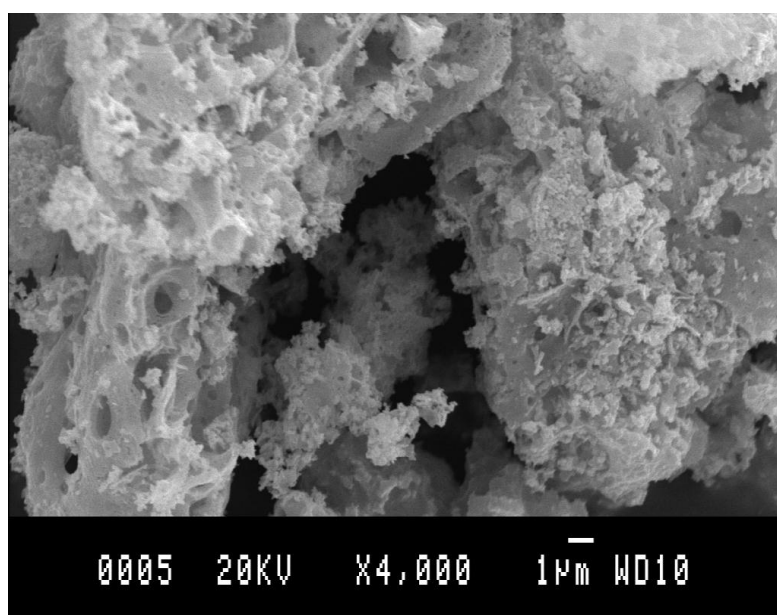


Fig. 9. SEM micrograph of the cerium aluminium ceramics synthesized at 1000 °C.

3.3 Sol-gel synthesis and characterization of Nd^{3+} substituted yttrium aluminium garnet ($\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$) and Sm^{3+} substituted yttrium aluminium garnet ($\text{Y}_{3-x}\text{Sm}_x\text{Al}_5\text{O}_{12}$)

In this part will be examined neodymium and samarium substitution effects in $\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ and $\text{Y}_{3-x}\text{Sm}_x\text{Al}_5\text{O}_{12}$ compounds ($x = 0.1, 0.15, 0.25, 0.35, 0.5, 0.6, 0.7, 0.75, 0.8, 1, 1.5, 2, 2.5, 3$) obtained by sol-gel technique.

3.3.1 XRD characterization of Nd^{3+} substituted yttrium aluminium garnet ($\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$) and Sm^{3+} substituted yttrium aluminium garnet ($\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$)

The Y-Nd-Al-O and Y-Sm-Al-O precursor gels were calcined at $800\text{ }^{\circ}\text{C}$ for 5 h and finally annealed at $1000\text{ }^{\circ}\text{C}$ for 10 h. Representative XRD patterns of the compounds ($\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ ($x = 0.1, 0.25, 0.35, 0.5$)) obtained using the sol-gel synthesis are shown in Fig.10. The XRD results presented in Fig. 10 revealed that all samples consists of one crystalline garnet phase. In the case of the compounds with higher amount of neodymium $\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ ($x = 0.6, 0.7, 0.8$), the analogous results were obtained. The only mixed-metal garnet $\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ phases were determined.

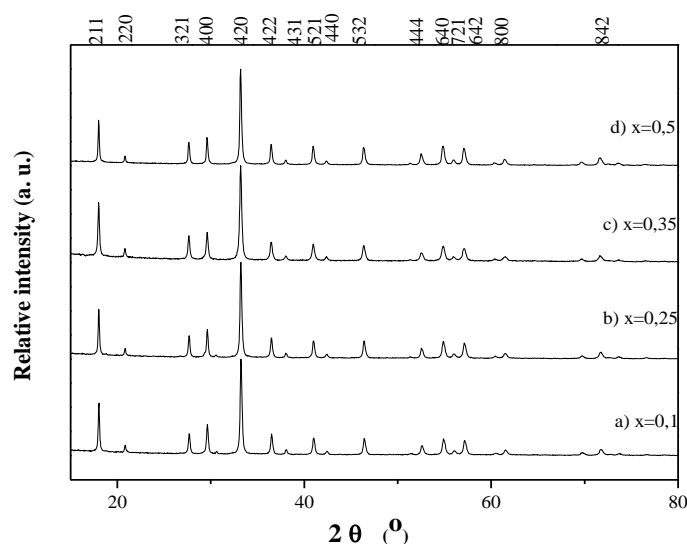


Fig. 10. XRD patterns of $\text{Y}_{2.9}\text{Nd}_{0.1}\text{Al}_5\text{O}_{12}$ (a), $\text{Y}_{2.75}\text{Nd}_{0.25}\text{Al}_5\text{O}_{12}$ (b), $\text{Y}_{2.65}\text{Nd}_{0.35}\text{Al}_5\text{O}_{12}$ (c) and $\text{Y}_{2.5}\text{Nd}_{0.5}\text{Al}_5\text{O}_{12}$ (d) ceramic powders synthesized by sol-gel method and annealed at $1000\text{ }^{\circ}\text{C}$ for 10 h.

However, in the case of $Y_{1.5}Nd_{1.5}Al_5O_{12-\delta}$ and $Y_1Nd_2Al_5O_{12-\delta}$ compounds the XRD pattern showed the formation of biphasic synthesis products. Despite, the garnet phase predominates in the sample the trace of the secondary phase of $NdAlO_3$ (NAP) (ICSD [00-039-0487]) could be also detected.

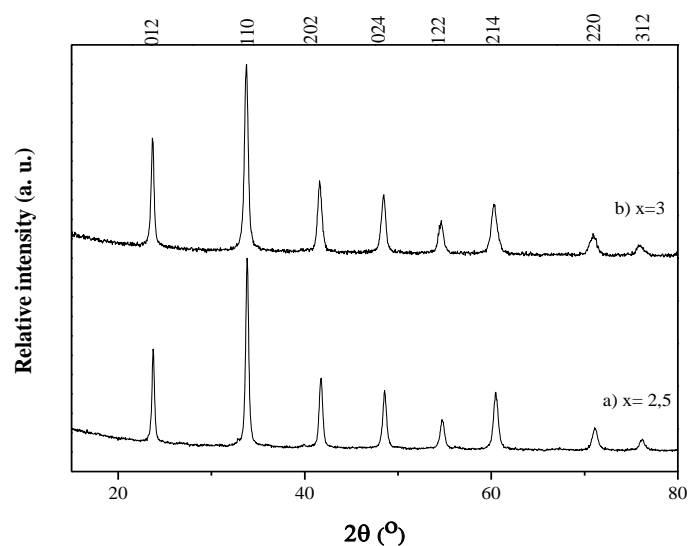


Fig. 11. XRD patterns of $Y_{0.5}Nd_{2.5}Al_5O_{12}$ (a) and $Nd_3Al_5O_{12}$ ceramic powders synthesized by sol-gel method and annealed at $1000\text{ }^{\circ}C$ for 10 h.

Fig. 11 shows the X-ray diffraction patterns of the $Y_{0.5}Nd_{2.5}Al_5O_{12}$ and $Nd_3Al_5O_{12}$ compounds synthesized using the same synthesis parameters. As seen from Fig. 11, the formation of perovskite neodymium aluminate ($NdAlO_3$) phase instead of garnet proceeds in both cases.

Representative XRD patterns of the samarium substituted compounds $Y_{3-x}Sm_xAl_5O_{12}$ ($x = 0.1, 0.15, 0.25$) obtained using the sol-gel synthesis route and calcined at $1000\text{ }^{\circ}C$ for 10 h are given in Fig. 12. The XRD results presented in Fig. 12 revealed that all samples consists of one garnet crystalline phase. In the case of the compounds $Y_{3-x}Sm_xAl_5O_{12}$ ($x = 0.5, 0.75, 1$), the analogous results were obtained. Fig. 13 shows the X-ray diffraction patterns of the compounds with nominal composition of $Y_{1.5}Sm_{1.5}Al_5O_{12}$, $Y_1Sm_2Al_5O_{12}$ and $Y_{0.5}Sm_{2.5}Al_5O_{12}$. Again, garnet phase is predominate in the samples, and only traces of the secondary phase of $SmAlO_3$ (SAP) (ICSD [00-046-0394]) could be also detected. However, during the synthesis of $Sm_3Al_5O_{12}$ compound pure perovskite samarium aluminate phase instead of $Sm_3Al_5O_{12}$ has formed.

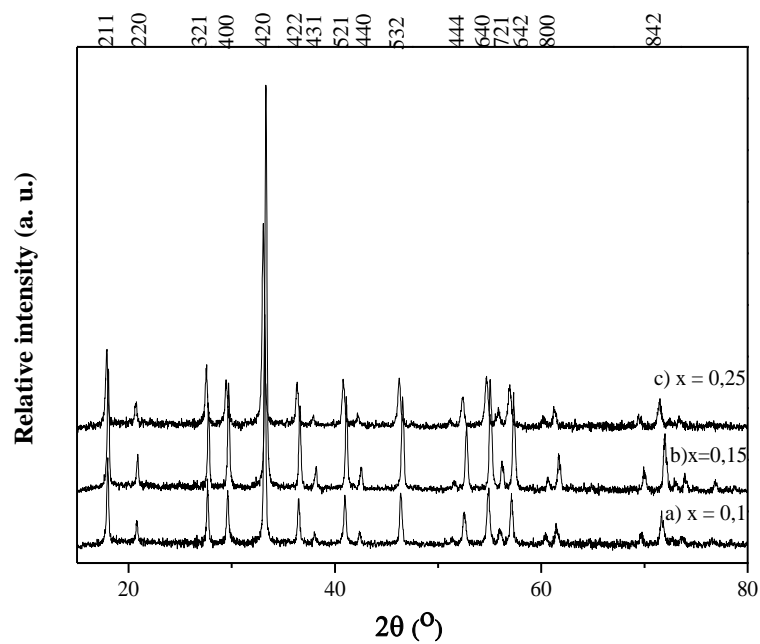


Fig. 12. XRD patterns of $Y_{2.9}Sm_{0.1}Al_5O_{12}$ (a), $Y_{2.85}Sm_{0.15}Al_5O_{12}$ (b) and $Y_{2.75}Sm_{0.25}Al_5O_{12}$ (c) ceramic powders synthesized by sol-gel method and annealed at $1000\text{ }^\circ\text{C}$ for 10 h.

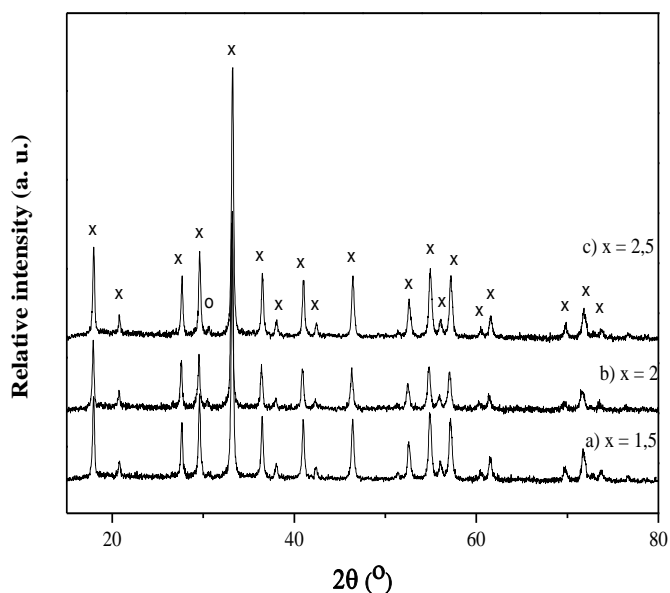


Fig. 13. XRD patterns of $Y_{1.5}Sm_{1.5}Al_5O_{12}$ (a), $Y_1Sm_2Al_5O_{12}$ (b) and $Y_{0.5}Sm_{2.5}Al_5O_{12}$ (c) ceramic powders synthesized by sol-gel method and annealed at $1000\text{ }^\circ\text{C}$ for 10 h.

3.3.2 IR characterization of Nd^{3+} substituted yttrium aluminium garnet ($\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$) and Sm^{3+} substituted yttrium aluminium garnet ($\text{Y}_{3-x}\text{Sm}_x\text{Al}_5\text{O}_{12}$)

Representative IR spectra of the $\text{Y}_{3-x}\text{Sm}_x\text{Al}_5\text{O}_{12}$ ($x = 0.1, 0.15, 0.25$) and $\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ ($x = 0.1, 0.25, 0.35, 0.5$) samples are shown in Figs. 14 and 15.

As was expected, all IR spectra are very similar. The most important feature is that several intensive bands are determined in the region of $950\text{-}450\text{ cm}^{-1}$, which may be attributed to the stretching modes of the isolated $[\text{AlO}_4]$ tetrahedral and $[\text{AlO}_6]$ octahedral in the garnet structure.

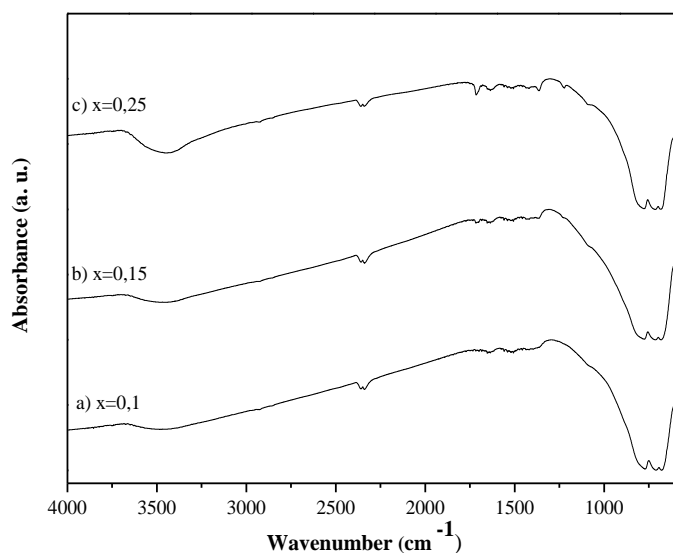


Fig. 14. IR spectra of $\text{Y}_{2.9}\text{Sm}_{0.1}\text{Al}_5\text{O}_{12}$ (a), $\text{Y}_{2.85}\text{Sm}_{0.15}\text{Al}_5\text{O}_{12}$ (b) and $\text{Y}_{2.75}\text{Sm}_{0.25}\text{Al}_5\text{O}_{12}$ (c) ceramic powders synthesized by sol-gel method and annealed at $1000\text{ }^{\circ}\text{C}$ for 10 h.

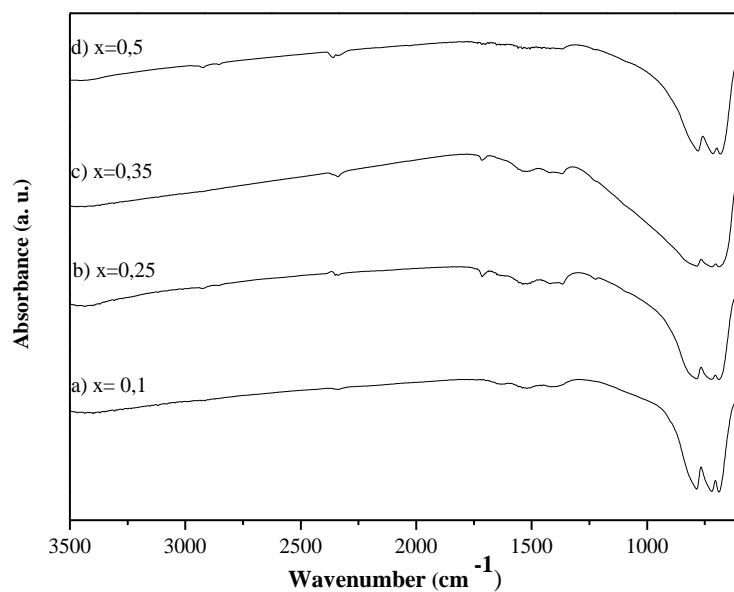


Fig. 15. IR spectra of $Y_{2.9}Nd_{0.1}Al_5O_{12}$ (a), $Y_{2.75}Nd_{0.25}Al_5O_{12}$ (b), $Y_{2.65}Nd_{0.35}Al_5O_{12}$ (c) and $Y_{2.5}Nd_{0.5}Al_5O_{12}$ (d) ceramic powders synthesized by sol-gel method and annealed at $1000\text{ }^{\circ}\text{C}$ for 10 h.

The IR spectra of the $Y_{3-x}Nd_xAl_5O_{12}$ ($x = 2.5, 3$) samples are shown in Fig. 16.

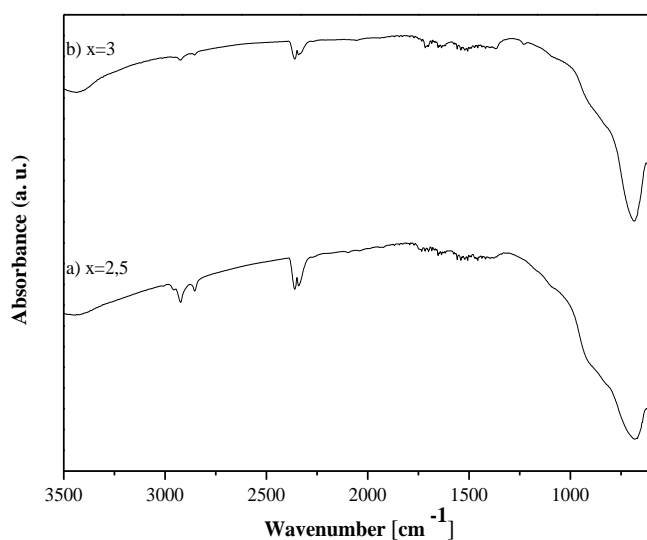


Fig. 16. IR spectra of $Y_{0.5}Nd_{2.5}Al_5O_{12}$ (a) and $Nd_3Al_5O_{12}$ (b) ceramic powders synthesized by sol-gel method and annealed at $1000\text{ }^{\circ}\text{C}$ for 10 h.

Both IR spectra are very similar. Importantly, only two sharp bands were present at 664 cm^{-1} and 455 cm^{-1} in the spectra, which are typical metal-oxygen absorptions for the perovskite-type compounds.

3.3.3 SEM characterization of Nd^{3+} substituted yttrium aluminium garnet ($\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$) and Sm^{3+} substituted yttrium aluminium garnet ($\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$)

Figs. 17 and 18 show the representative morphology of synthesized at $1000\text{ }^\circ\text{C}$ for 10 h powders of $\text{Y}_{2.9}\text{Nd}_{0.1}\text{Al}_5\text{O}_{12}$ and $\text{Y}_{2.75}\text{Sm}_{0.25}\text{Al}_5\text{O}_{12}$ samples, respectively.

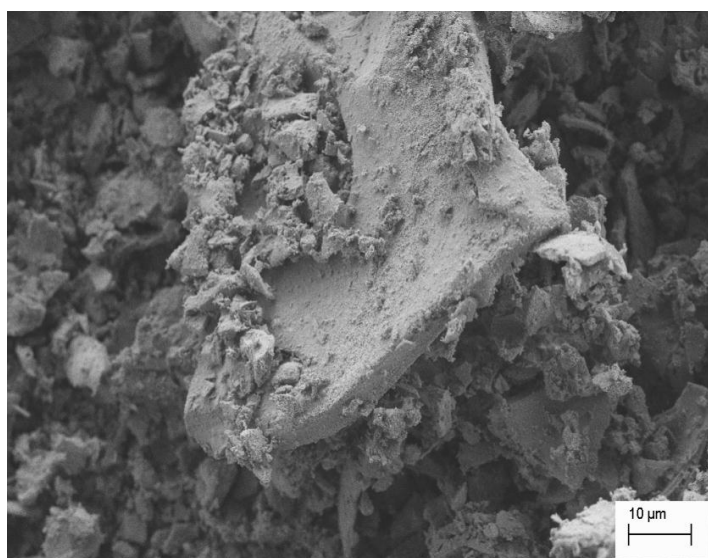


Fig. 17. SEM micrograph of $\text{Y}_{2.9}\text{Nd}_{0.1}\text{Al}_5\text{O}_{12}$ ceramics synthesized at $1000\text{ }^\circ\text{C}$.

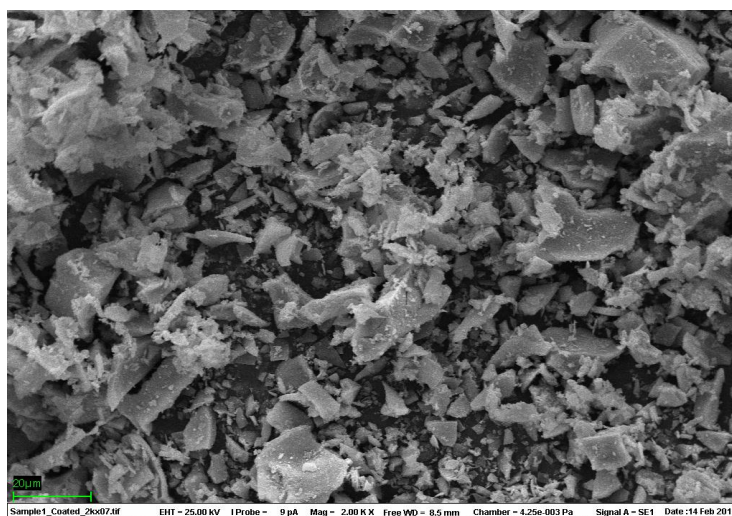


Fig. 18. SEM micrograph of $\text{Y}_{2.75}\text{Sm}_{0.25}\text{Al}_5\text{O}_{12}$ ceramics synthesized at $1000\text{ }^\circ\text{C}$.

In the case of $Y_{3-x}Nd_xAl_5O_{12}$ ($x = 0.1, 0.25, 0.35, 0.5, 0.6, 0.7, 0.8$) and $Y_{3-x}Sm_xAl_5O_{12}$ ($x = 0.1, 0.15, 0.25, 0.5, 0.75, 1$) ceramics samples, most of the plate-like particles have formed to reach the size of 1-20 μm . However, some of them are close to nanometre dimensions. These nanograins show tendency to form larger agglomerates. The SEM results also suggests that obtained at 1000 $^{\circ}\text{C}$ garnet crystallites are homogeneous, having wide particle size distribution.

Figs. 19 and 20 shows the surface features of the $Y_{0.5}Nd_{2.5}Al_5O_{12}$ and $Y_1Sm_2Al_5O_{12}$ powders calcined at 1000 $^{\circ}\text{C}$.

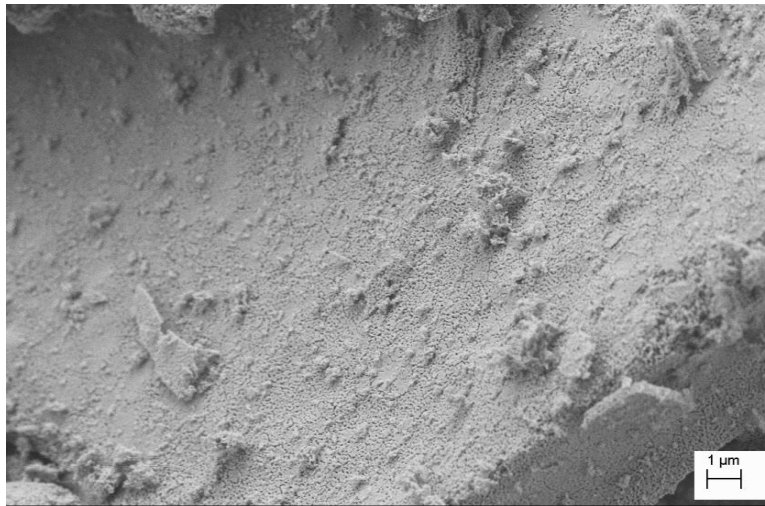


Fig. 19. SEM micrograph of $Y_{0.5}Nd_{2.5}Al_5O_{12}$ ceramics synthesized at 1000 $^{\circ}\text{C}$.

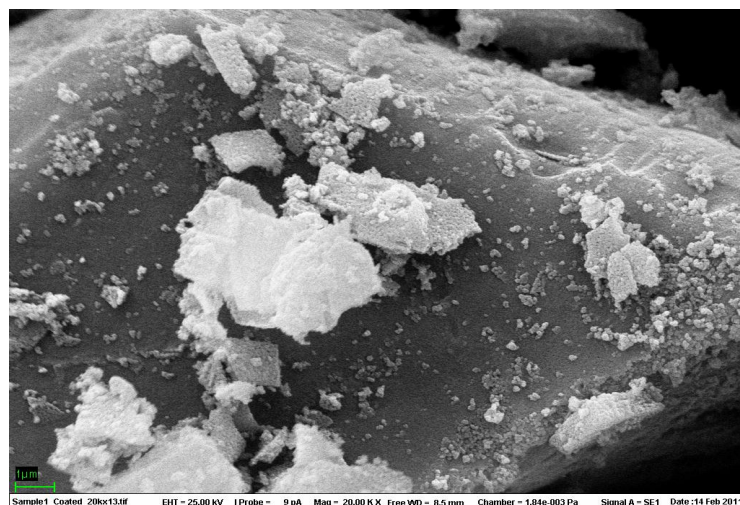


Fig. 20. SEM micrograph of $Y_1Sm_2Al_5O_{12}$ ceramics synthesized at 1000 $^{\circ}\text{C}$.

As seen, with increasing amount of substituent the particles formed with more pronounced agglomeration, indicating good connectivity between the grains. Again, the microstructure of multiphasic ceramics samples consisted of large-grained matrix and several of small grains. So, we can conclude that the surface microstructure of the sol-gel derived compounds in this study mostly is determined by used synthesis method.

Conclusions

1. For the first time Ce-Al-O, Pr-Al-O, Nd-Al-O, Tb-Al-O, Dy-Al-O, Ho-Al-O, Er-Al-O, Tm-Al-O, Yb-Al-O, Lu-Al-O, Y(Nd)-Al-O and Y(Sm)-Al-O acetate-nitrate-glycolate gels have been synthesized using environmentally friendly, economical and simple aqueous sol-gel method. They were used as starting materials for the synthesis of appropriate lanthanide aluminium garnets.
2. The results of X-ray diffraction analysis have indicated that single-phase terbium aluminium garnet ($\text{Tb}_3\text{Al}_5\text{O}_{12}$), dysprosium aluminium garnet ($\text{Dy}_3\text{Al}_5\text{O}_{12}$), holmium aluminium garnet ($\text{Ho}_3\text{Al}_5\text{O}_{12}$), erbium aluminium garnet ($\text{Er}_3\text{Al}_5\text{O}_{12}$), thulium aluminium garnet ($\text{Tm}_3\text{Al}_5\text{O}_{12}$), ytterbium aluminium garnet ($\text{Yb}_3\text{Al}_5\text{O}_{12}$) and lutetium aluminium garnet ($\text{Lu}_3\text{Al}_5\text{O}_{12}$) have been synthesized by annealing Tb-Al-O, Dy-Al-O, Ho-Al-O, Er-Al-O, Tm-Al-O, Yb-Al-O and Lu-Al-O precursor gels for 10 hours at 1000 °C, respectively. For the first time these garnet structure compounds were synthesized using sol-gel method. Moreover, these lanthanide aluminium garnets were synthesized at relatively low sintering temperature (1000°C).
3. It was demonstrated that cerium aluminium garnet $\text{Ce}_3\text{Al}_5\text{O}_{12}$, praseodymium aluminium garnet $\text{Pr}_3\text{Al}_5\text{O}_{12}$ and neodymium aluminium garnet $\text{Nd}_3\text{Al}_5\text{O}_{12}$ are not formed using the same synthesis conditions. X-ray diffraction analysis findings have indicated that synthesis products consist of: (a) cerium and aluminium oxides (CeO_2 and Al_2O_3); (b) aluminium oxide and perovskite praseodymium and neodymium aluminates (Al_2O_3 and PrAlO_3 or Al_2O_3 and NdAlO_3).
4. Neodymium substituted garnets $\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ have been synthesized using the same aqueous sol-gel method. The results of the X-ray diffraction analysis showed that

when small amounts of neodymium ($x = 0.1, 0.25, 0.35, 0.5, 0.6, 0.7, 0.8$) is introduced into yttrium position the single phase $Y_{3-x}Nd_xAl_5O_{12}$ garnets have formed and yttrium aluminium garnet lattice remains unchanged.

5. Samarium substituted garnets $Y_{3-x}Sm_xAl_5O_{12}$ were also synthesized using sol-gel method. The results of X-ray diffraction analysis showed the formation of single phase $Y_{3-x}Sm_xAl_5O_{12}$ garnets when small amounts of samarium ($x = 0.1, 0.15, 0.25, 0.5, 0.75, 1$) was introduced into yttrium position.

6. With further increasing amount of neodymium in $Y_{3-x}Nd_xAl_5O_{12}$ ($x = 1.5, 2$) compounds significant amount of side neodymium perovskite aluminate ($NdAlO_3$) phase has formed. However, when the concentration of samarium was reached the same level or even higher in $Y_{3-x}Sm_xAl_5O_{12}$ ($x = 1.5, 2, 2.5$) compounds, the phase composition of synthesis products changed marginally. Only small amount of perovskite samarium aluminate ($SmAlO_3$) phase was detected in the end products.

7. It was found that single-phase $NdAlO_3$ was formed during the sol-gel synthesis of mixed-metal compounds with nominal composition of $Y_{3-x}Nd_xAl_5O_{12}$ ($x = 2.5, 3$). Besides, it was determined, that single phase $SmAlO_3$ was formed only during synthesis of fully samarium substituted $Sm_3Al_5O_{12}$ garnet.

8. It was demonstrated that infrared spectroscopy is very effective method to determine compounds having garnet crystal structure. An interval from 950 to 450 cm^{-1} of IR spectrum can be successfully used as fingerprint to identify the formation of garnet crystal structure compounds.

9. The scanning electron microscopical characterization showed that the surface of majority of synthesized lanthanide aluminium garnets is composed of plate-like crystallites with various particle size (from several micrometers to $20\text{ }\mu\text{m}$).

The List of Original Publications by the Author

Articles in Journals

1. **N. Dubnikova**, E. Garskaite, J. Pinkas, P. Bezdicka, A. Beganskiene, A. Kareiva. Sol-gel preparation of selected lanthanide aluminium garnets. *Journal of Sol-Gel Science and Technology*, 55 (2010) 213-219.

2. **N. Dubnikova**, E. Garskaite, A. Beganskiene, A. Kareiva. Sol-gel synthesis and characterization of sub-microsized lanthanide (Ho, Tm, Yb, Lu) aluminium garnets. *Optical Materials*, 33 (2011) 1179-1184.

Articles in Proceedings

3. **N. Dubnikova**, A. Kareiva, A. Beganskiene, E. Garskaite. Sol-gel synthesis route to the preparation of selected lanthanide aluminium garnets. *Proceedings of III International Interdisciplinary Technical Conference of Young Scientists. Modern Chemical and Physical Technologies*. Ed. W. Karpiuk and K. Wisniewski. Poznan, Poland (2010) 400-404.

Published Contributions to Academic Conferences

1. **N. Dubnikova**, J. Pinkas, P. Bezdicka, A. Beganskiene, A. Kareiva. The peculiarities of formation of lanthanide aluminium garnets. Conference "Chemistry and Technology of Inorganic Compounds". Kaunas, Lithuania, April 23, (2008) 9-10.
2. **N. Dubnikova**, E. Garskaite, J. Pinkas, P. Bezdicka, A. Kareiva. On the sol-gel preparation and characterization of lanthanide aluminium garnets. 5th International Conference on Sol-Gel Materials. Research, Technology, Applications, Trzebieszovice, Poland, June 1-5 (2008) 44.
3. **N. Dubnikova**, E. Garskaite, A. Beganskiene, A. Kareiva. On the preparation of $\text{Lu}_3\text{Al}_5\text{O}_{12}$, $\text{Yb}_3\text{Al}_5\text{O}_{12}$, $\text{Tm}_3\text{Al}_5\text{O}_{12}$ and $\text{Ho}_3\text{Al}_5\text{O}_{12}$ by an aqueous sol-gel method. The 11-th International Conference-School „Advanced Materials and Technologies“, Palanga, Lithuania, August 27–31 (2009) 70.
4. **N. Dubnikova**, E. Garskaite, A. Beganskiene, A. Kareiva. On the sol-gel preparation and characterization of $\text{Lu}_3\text{Al}_5\text{O}_{12}$, $\text{Yb}_3\text{Al}_5\text{O}_{12}$, $\text{Tm}_3\text{Al}_5\text{O}_{12}$ and $\text{Ho}_3\text{Al}_5\text{O}_{12}$. 9th National Lithuanian Conference „Chemistry 2009“. Vilnius, Lithuania, October 16 (2009) 19.

5. **N. Dubnikova**, E. Garskaite, A. Kareiva. Sol-gel synthesis and characterization of $Y_{3-x}Nd_xAl_5O_{12}$. Conference "Chemistry and Technology of Inorganic Compounds". Kaunas, Lithuania, April 21 (2010) 18-19.
6. **N. Dubnikova**, A. Kareiva, A. Beganskiene, E. Garskaite. Sol-gel synthesis route to the preparation of selected lanthanide aluminium garnets. III International Interdisciplinary Technical Conference of Young Scientists, Poznan, Poland, 19-21 May (2010).

The Publications Not Included in Doctoral Thesis

1. E. Garskaite, **N. Dubnikova**, A. Katelnikovas, J. Pinkas, A. Kareiva. Syntheses and characterisation of $Gd_3Al_5O_{12}$ and $La_3Al_5O_{12}$ garnets. *Collection Czechoslovak Chemical Communications*, 72 (2007) 321–333.

CURRICULUM VITAE

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LANTANOIDŲ ALIUMINIO GRANATŲ SINTEZĖ ZOLIŲ-GELIŲ METODU IR APIBŪDINIMAS

SANTRAUKA

Šiame darbe pirmą kartą buvo susintetinti Ce-Al-O, Pr-Al-O, Nd-Al-O, Tb-Al-O, Dy-Al-O, Ho-Al-O, Er-Al-O, Tm-Al-O, Yb-Al-O, Lu-Al-O, Y(Nd)-Al-O ir Y(Sm)-Al-O acetatiniai-nitratiniai-glikoliatiniai geliai zolių-gelių metodu vandeniniuose tirpaluose. Jie buvo panaudoti pradinėmis medžiagomis atitinkamų lantanoidų aliuminio granatų sintezei. Vienfaziai terbio aliuminio granatas ($Tb_3Al_5O_{12}$), disprozio aliuminio granatas ($Dy_3Al_5O_{12}$), holmio aliuminio granatas ($Ho_3Al_5O_{12}$), erbio aliuminio granatas ($Er_3Al_5O_{12}$), tulio aliuminio granatas ($Tm_3Al_5O_{12}$), iterbio aliuminio granatas

($\text{Yb}_3\text{Al}_5\text{O}_{12}$) ir liutecio aliuminio granatas ($\text{Lu}_3\text{Al}_5\text{O}_{12}$) buvo gauti, terbio jonų šaltiniu naudojant terbio oksidą, disprozio – disprozio oksidą, holmio – holmio oksidą, erbio – erbio oksidą, tulio – tulio oksidą, iterbio – iterbio oksidą, lutecio – liutecio oksidą, kompleksus sudarančiu reagentu 1,2-etandiolį. Tyrimų rezultatai parodė, kad šių lantanoidų aliuminio granatai gauti santykinai žemoje temperatūroje (1000°C). Zolių-gelių metodu sintetinant cerio aliuminio granatą ($\text{Ce}_3\text{Al}_5\text{O}_{12}$), prazeodimio aliuminio granatą ($\text{Pr}_3\text{Al}_5\text{O}_{12}$) ir neodimio aliuminio granatą ($\text{Nd}_3\text{Al}_5\text{O}_{12}$) ir atlikus tyrimus paaiškėjo, kad tose pačiose sintezės sąlygose jie nesusidaro. Rentgeno spindulių difrakcinės analizės rezultatai parodė, kad sintezės produktai, sintetinti 10 val. 1000°C temperatūroje, yra sudaryti iš: (a) cerio ir aliuminio oksidų (CeO_2 ir Al_2O_3), (b) iš aliuminio oksido bei perovskito kristalinės struktūros prazeodimio ir neodimio aluminatų (Al_2O_3 ir PrAlO_3 arba Al_2O_3 ir NdAlO_3). Zolių-gelių metodu susintetinus $\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ ir $\text{Y}_{3-x}\text{Sm}_x\text{Al}_5\text{O}_{12}$ granatus buvo tiriama, koks neodimio ir samario kiekis $\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ ir $\text{Y}_{3-x}\text{Sm}_x\text{Al}_5\text{O}_{12}$ junginiuose ($x = 0,1, 0,15, 0,25, 0,35, 0,5, 0,6, 0,7, 0,75, 0,8, 1, 1,5, 2, 2,5, 3$) dar nepakeičia YAG kristalinės gardelės. Tyrimų rezultatai parodė, kad į itrio aliuminio granatą itrio padėtyse įterpiant nedidelius neodimio ar samario kiekius ($x = 0,1, 0,15, 0,25, 0,35, 0,5, 0,6, 0,7, 0,75, 0,8, 1$), susidaro vienfaziai $\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ arba $\text{Y}_{3-x}\text{Sm}_x\text{Al}_5\text{O}_{12}$ granatai, ir itrio aliuminio granato kristalinė gardelė dar lieka nepakitusi. Tačiau didinant neodimio kiekį pakeistuose $\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ ($x = 1,5, 2$) junginiuose, atsiranda žymus kiekis pašalinės perovskitinio neodimio aluminato (NdAlO_3) fazės. Didinant samario kiekį pakeistuose $\text{Y}_{3-x}\text{Sm}_x\text{Al}_5\text{O}_{12}$ ($x = 1,5, 2, 2,5$) junginiuose, sintezės produktų fazinės sudėties pakitimai yra labai nežymūs. Atsiranda labai nežymus perovskito kristalinės struktūros samario aluminato (SmAlO_3) fazės kiekis. Dar labiau didinant neodimio kiekį pakeistuose $\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ ($x = 2,5, 3$) junginiuose, jau susidaro vienfasis NdAlO_3 . Tačiau įdomu pažymėti, kad tik sintetinant gryną $\text{Sm}_3\text{Al}_5\text{O}_{12}$, susidarė vienfasis SmAlO_3 . Parodyta, kad infraraudonosios spektroskopijos (IR) metodas taip pat yra efektyvus ir tikslus tyrimo metodas granato kristalinės struktūros keraminiam junginiam apibūdinti. IR spektro intervalas nuo 950 iki 450 cm^{-1} gali būti sėkmingai naudojamas operatyviam šios sandaros junginių susidarymui identifikuoti. Skleiziamosios elektroninės mikroskopijos (SEM) tyrimais įvertinti sintezės produktų paviršiaus morfologiniai ypatumai. Nustatyta, kad daugumos susintetintų lantanoidų aliuminio granatų ir daugiafazių sintezės produktų paviršius

sudarytas iš plokštuminių kristalitų, kurių dydis svyruoja plačiame intervale - nuo kelių mikrometrų iki 20 μm dydžio.