

Samarium-Substitution Effects in Sol-Gel Derived Yttrium Aluminium Garnet

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In this study, yttrium aluminium garnet (YAG) powders substituted by samarium were prepared by simple an aqueous sol-gel method using aluminium nitrate nonahydrate, yttrium oxide, samarium oxide as the starting materials and ethane-1,2-diol as complexing agent. The powders annealed at 1000 °C in air were characterized by X-ray diffraction (XRD) analysis, infrared spectroscopy (IR) and scanning electron microscopy (SEM). It was demonstrated, however, that the total substitution of yttrium by samarium does not proceed in the YAG. Pure cubic garnet phase was formed only at low concentration of samarium. With further substitution, the main part of garnet phase transformed in to the perovskite samarium aluminate phase.

Keywords: Yttrium Aluminium Garnet, YAG, Samarium, Substitution Effects, Characterization.

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1. INTRODUCTION

Yttrium aluminium garnet ($Y_3Al_5O_{12}$, YAG) has the garnet structure, excellent chemical stability, high temperature creep resistance and good optical properties [1]. Neodymium doped yttrium aluminium garnet (Nd:YAG) is one of the most important laser materials. Crystals are available from different commercial suppliers with dopant concentration up to 2.5 at % [2]. Differently doped an un-doped YAG nanopowders were synthesized by means of microwave assisted citrate gel process at a reduced calcinations temperature, by co-precipitation, by chelate-polymerization and many other methods. The obtained results using these new methodologies were compared with those conventional heat treatments [3]. When garnet phase is doped with samarium, cerium or europium, secondary phases like perovskite ($YAlO_3$, YAP) and hexagonal ($YAlO_3$, YAH) have been observed.

Over the last few decades, the sol-gel techniques have been used to prepare a variety of mixed-metal oxides, nanomaterials and nanoscale architectures, nanoporous oxides, organic-inorganic hybrids [4-7]. It has been demonstrated that the sol-gel process offers considerable advantages such as better mixing of the starting materials and excellent chemical homogeneity in the final product. Moreover, the molecular level mixing and the tendency of partially hydrolyzed species to form extended networks facilitate the structure evolution thereby lowering the crystallization temperature. Recently for the preparation of different garnets and other mixed-metal oxides we elaborated an aqueous glycolate sol-gel processing route [8-10].

Several lanthanide aluminium garnets (i.e., $Ce_3Al_5O_{12}$, $Pr_3Al_5O_{12}$, $Nd_3Al_5O_{12}$, $Sm_3Al_5O_{12}$) has not been synthesized so far, to the best our knowledge. Rare earth aluminium garnets ($RE_3Al_5O_{12}$) were reported to be thermodynamically stable with RE = Gd – Lu. Garnet structures with larger rare earth ions (Sm, Eu) are metastable, in favour of the competing perovskite type. Besides, the garnet phase does not exist for the lighter rare earth elements. Garnets with

RE = Sm and Eu were reported only as side phases from autoclave reactions in 1,4-butanediol at temperatures around 300 °C [11]. Thus, $Sm_3Al_5O_{12}$ garnet phase is not synthesized and characterized so far. However, theoretically some substitution of Y^{3+} by Sm^{3+} at dodecahedral sites in YAG structure could be possible since the values of ionic radii of these elements differ marginally. Therefore, the main aim of this study was for the first time to investigate samarium substitution effects in $Y_{3-x}Sm_xAl_5O_{12}$ garnet structure compound synthesized using an aqueous sol-gel processing route.

2. EXPERIMENTAL PART

Yttrium aluminium garnet powders substituted by samarium $Y_{3-x}Sm_xAl_5O_{12}$, ($x = 0.1, 0.15, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5$ and 3.0) were prepared by simple an aqueous sol-gel method. In the aqueous sol-gel process, the following materials were used: Y_2O_3 (99.99%, Aldrich), Sm_2O_3 (99.99%, Aldrich), $Al(NO_3)_3 \cdot 9H_2O$ (99.99%, Aldrich), acetic acid (99.5%, Chempur, Poland) and ethane-1,2-diol (99%, Merck). Y and Sm acetates were prepared by dissolving the corresponding oxides in $2 \cdot 10^{-1}$ 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 the yttrium acetate solution. The mixture was stirred at 65 °C for 40 min and solution of samarium acetate was added. The resulting mixture was stirred at 65 °C for 1 h, followed by drop-wise addition of ethane-1, 2-diol (2 ml) upon vigorous stirring. The resulting sols were stirred 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 24 h. The resulting gel powders were ground in an agate mortar and heated in air at 800 °C for 5 h by slow temperature elevation ($\sim 3-4$ °C min^{-1}). After grinding in an agate mortar, the powders were further sintered in air at 1000 °C for 10 h.

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X-ray diffraction analysis (XRD) was performed on a Bruker AXE D8 Focus diffractometer with a LynxEye detector using Cu K_{α} radiation. Infrared spectra of samples in KBr pellets were recorded with a Bruker Equinox 55/S/NIR FTIR spectrometer (resolution 1 cm^{-1}). The particle size and morphology of the resultant $Y_{3-x}Nd_xAl_5O_{12}$ ($x = 0.1, 0.25, 0.35, 0.5, 0.6, 0.7, 0.8, 1.5, 2.0, 2.5,$ and 3.0) garnet powders were examined using FE-SEM Zeiss Ultra 55 field Mission scanning electron microscope with In-Lens detector.

3. RESULTS AND DISCUSSION

The XRD patterns of the samarium substituted compounds $Y_{3-x}Sm_xAl_5O_{12}$ ($x = 0.1, 0.15, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0,$ and 2.5) obtained using the sol-gel approach and calcined at $1000\text{ }^{\circ}\text{C}$ for 10 h revealed that the main crystalline component in the synthesis products is $Y_{3-x}Sm_xAl_5O_{12}$ ceramics. The obtained XRD patterns were in a good agreement with the reference data for $Y_3Al_5O_{12}$ (ICSD 00-033-0040). Fig. 1 shows the X-ray diffraction patterns of the representative compounds with nominal composition of $Y_{1.5}Sm_{1.5}Al_5O_{12}$, $Y_1Sm_2Al_5O_{12}$ and $Y_{0.5}Sm_{2.5}Al_5O_{12}$. The garnet phase is marked with ex.

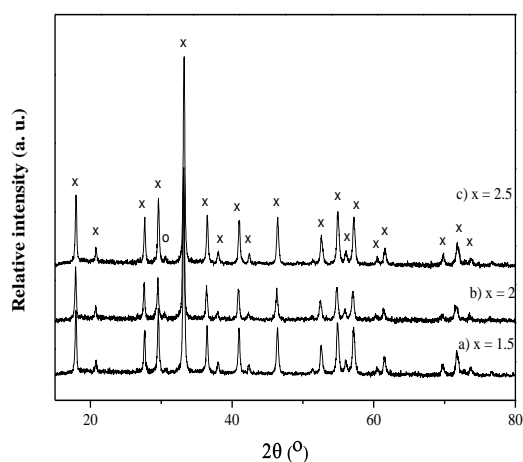


Fig. 1 – XRD patterns of $Y_{1.5}Sm_{1.5}Al_5O_{12}$ (a), $Y_1Sm_2Al_5O_{12}$ (b) and $Y_{0.5}Sm_{2.5}Al_5O_{12}$ (c) ceramic powders synthesized by sol-gel method and annealed at $1000\text{ }^{\circ}\text{C}$ for 10 h

Surprisingly, with full substitution of yttrium by samarium the formation only perovskite samarium aluminate $SmAlO_3$ (ICSD 00-046-0394) instead of samarium aluminium garnet was detected. From the obtained XRD results we can conclude that formation of crystalline garnet structure $Y_{3-x}Sm_xAl_5O_{12}$ proceeds than $x \leq 2.5$. It is hardly probable situation that the formation of $Sm_3Al_5O_{12}$ is prohibited thermodynamically at $1000\text{ }^{\circ}\text{C}$ and using ambient oxygen pressure. In view of the above, we can conclude that the formation of $Y_{3-x}Sm_xAl_5O_{12}$ phase is dependent on the molar ratio of yttrium and samarium, which influences the mean cationic radius of the composition.

Representative IR spectra of the $Y_{3-x}Sm_xAl_5O_{12}$ ($x = 0.1, 0.15, 0.25$) samples are shown in Fig. 2. As was expected, all IR spectra are very similar. The most important feature is that several intensive bands are de-

termined in the region of $950\text{--}450\text{ cm}^{-1}$, which may be attributed to the stretching modes of the isolated $[AlO_4]$ tetrahedral and $[AlO_6]$ octahedral in the garnet structure [12].

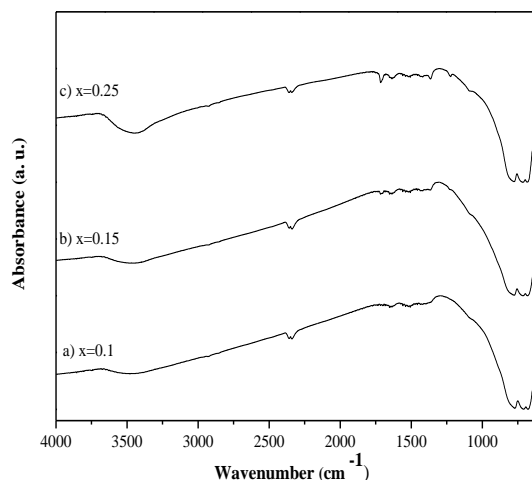


Fig. 2 – IR spectra of $Y_{2.9}Sm_{0.1}Al_5O_{12}$ (a), $Y_{2.85}Sm_{0.15}Al_5O_{12}$ (b) and $Y_{2.75}Sm_{0.25}Al_5O_{12}$ (c) ceramic powders synthesized by sol-gel method and annealed at $1000\text{ }^{\circ}\text{C}$ for 10 h

Fig. 3 shows the representative morphology of synthesized at $1000\text{ }^{\circ}\text{C}$ for 10 h powders of $Y_{2.75}Sm_{0.25}Al_5O_{12}$ sample.

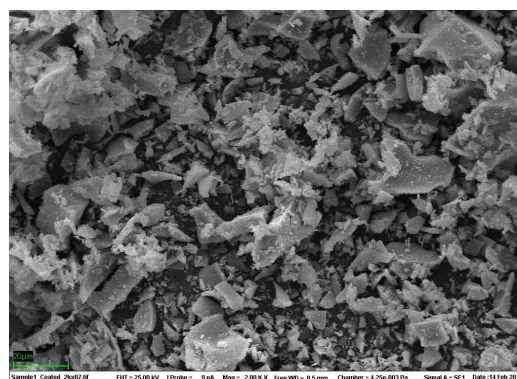


Fig. 3 – SEM micrograph of $Y_{2.75}Sm_{0.25}Al_5O_{12}$ ceramics synthesized at $1000\text{ }^{\circ}\text{C}$

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

4. CONCLUSIONS

Samarium substituted garnets $Y_{3-x}Sm_xAl_5O_{12}$ were 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. With further increasing amount of samarium in $Y_{3-x}Sm_xAl_5O_{12}$ ($x = 1.5, 2, 2.5$) compounds, the phase composition of synthesis prod-

ucts changed marginally. Only small amount of perovskite samarium aluminate (SmAlO_3) phase was detected in the end products. It was determined, however, that single phase SmAlO_3 was formed only during synthesis of fully samarium substituted $\text{Sm}_3\text{Al}_5\text{O}_{12}$ garnet. 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 garnet crystal structure. The scanning electron microscopical characterization showed that the surface of majority of synthesized samarium alumini-

um garnets is composed of plate-like crystallites with various particle size (from several micrometers to $20\text{ }\mu\text{m}$). The SEM results have showed that garnet solids are rather homogeneous and are characterized by high particle size distribution.

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