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Influence of annealing temperature on the phase purity, crystallinity and optical properties of $Y_3Sc_2Ga_3O_{12}$ prepared by different methods

Jiri Pinkas

Faculty of Natural Sciences, Masaryk University Brno, Kotlarska 2, CZ-61137 Brno, Czech Republic

Edita Garškaitė,

Aldona Beganskienė,

Giedrė Nenartavičienė and

Aivaras Kareiva*

Faculty of Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

Mixed-metal garnet ($Y_3Sc_2Ga_3O_{12}$, YSGG) samples were prepared by: (i) sol–gel, (ii) semi–sol–gel, and (iii) solid state reaction methods. In all the cases, precursor powders were calcined for 10 h at 800 °C in air, ground in an agate mortar and heated again for 10 h at different temperatures in the range of 1000–1400 °C in air atmosphere. The synthesized samples were characterized by X-ray powder diffraction analysis and scanning electron microscopy. It was demonstrated that monophasic $Y_3Sc_2Ga_3O_{12}$ garnet could be obtained at 1000 °C using the sol–gel technique and at 1200 °C using the semi–sol–gel route.

Key words: mixed-metal garnets, YSGG, optical materials, sol–gel process

INTRODUCTION

Garnets, both natural and synthetic, form a wide range of compounds which are closely related in their structure, chemical and physical properties. Garnets containing transition metals and rare-earths carry many important technological uses as magnetic materials, phosphor materials employed in solid state lasers and television screens, computer memories and in many other devices such as microwave optical elements [1–4].

Yttrium aluminium garnet ($Y_3Al_5O_{12}$, YAG) is one of the most popular garnet having excellent structural and optical properties. Since the discovery of lasing in ruby, which is Cr-doped Al_2O_3, the search of new solid-state laser materials with diverse properties such as lasing ability at new wavelengths, broad tunability near infrared (NIR) and high efficiency, still is an important task for material scientists. The rare-earth-doped YAG oxides are also widely applied as phosphors in cathode-ray tubes (projection TV sets), field emission, vacuum fluorescent, and electroluminescent displays and as scintillators in X-ray and positron emission tomographs [5–9].

Moreover, phosphor host materials have proven to be of great importance as well. The matrix should possess good chemical, mechanical, thermal, optical characteristics and properties [10, 11]. For example, transition metal and rare-earth element ions have demonstrated the lasing action in a wide variety of host crystals. Among the compounds that can incorporate transition metals or lanthanides, several scandium and gallium based materials were elaborated [12–16]. The main purpose of this study was to synthesize and characterize a ternary mixed-metal – yttrium-scandium-gallium ($Y_3Sc_2Ga_3O_{12}$, YSGG) garnet compound using three different synthesis routes: (i) sol–gel, (ii) semi–sol–gel, and (iii) solid state reaction methods.

EXPERIMENTAL

In the sol–gel process, yttrium oxide was first dissolved in 0.2 M CH_3COOH by stirring the mixture for 10 h at 55–60 °C in a beaker covered with a watch-glass. To this solution, a mixture of scandium and gallium nitrates dissolved in distilled water was added and the resulting mixture was stirred for 3 h at the same temperature. In the following step, 1,2-ethanediol as a complex-

* Corresponding author. E-mail: aivaras.kareiva@chf.vu.lt

ing agent was added to the above solution. The acidic medium (pH ~5) prevented the flocculation of metal hydroxides in the mixtures and no adjustment of pH was necessary. After concentrating the solution by slow evaporation at 60–70 °C under stirring, the Y-Sc-Ga-O acetate-nitrate-glycolate solution turned into a white transparent gel. The oven-dried (100–120 °C) gel became light brown due to the initial decomposition of nitrates. The gel powders were ground in an agate mortar and preheated for 10 h at 800 °C in air. After the intermediate grinding the powders were additionally sintered for 10 h at 1000 °C in air.

In the semi–sol–gel method, only the Y-Sc-O precursor was synthesized by the sol–gel route, and finally mixed with $Ga(NO_3)_3$ in the further annealing stage. The obtained precursor powders were calcined for 10 h at 800 °C in air, ground in the agate mortar and heated again for 10 h at different temperatures in the range of 1000–1200 °C in air atmosphere. During the solid state reaction synthesis, the stoichiometric mixture of the starting materials (yttrium oxide, scandium and gallium nitrates) was carefully ground in the agate mortar. The obtained physical mixture was also annealed for 10 h at different temperatures in the range of 1000–1400 °C in air atmosphere.

The synthesized samples were characterized by X-ray powder analysis (XRD) performed with a Stoe STADI P powder diffractometer using $CuK\alpha_1$ radiation. A scanning electron microscope (SEM) CAM SCAN S4 was used to study the morphology and microstructure of the ceramic samples. The optical transmission measurements of the garnet samples were carried out using an SF-26 spectrophotometer at room temperature with a fused-quartz glass substrate inserted into the reference beam path of the spectrophotometer.

RESULTS AND DISCUSSION

The X-ray diffraction pattern for the sol–gel derived YSGG sample annealed at 1000 °C is shown in Fig. 1. Evidently, all diffraction lines observed in Fig. 1 could be attributed to the $Y_3Sc_2Ga_3O_{12}$ garnet phase [15, 17]. The X-ray diffraction patterns for the YSGG sample synthesized by the semi–sol–gel method and annealed at 1000 °C and 1200 °C for 10 h are shown in Fig. 2. It is clearly seen from Fig. 2 that the observed reflections in the XRD pattern of the sample annealed at 1000 °C are very weak and are not attributable to the garnet phase. Therefore, the obtained material was additionally annealed for 10 h at 1200 °C (Fig. 2, bottom). As it can be seen, this XRD pattern is very similar to that shown in Fig. 1. Thus, we can conclude that using the semi–sol–gel route the monophasic $Y_3Sc_2Ga_3O_{12}$ garnet could be obtained only at the higher temperature (1200 °C) in comparison with the sol–gel technique.

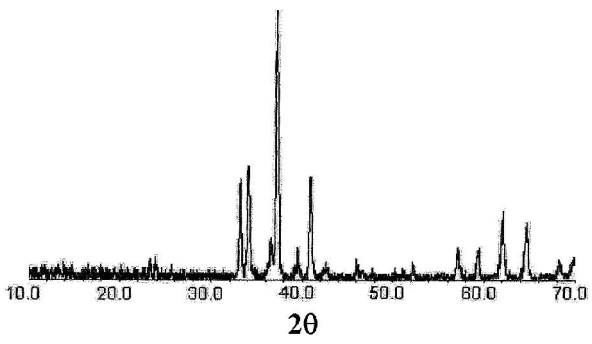

Fig. 1. XRD pattern of YSGG ceramic sample obtained by the sol–gel method and annealed at 1000 °C for 10 h

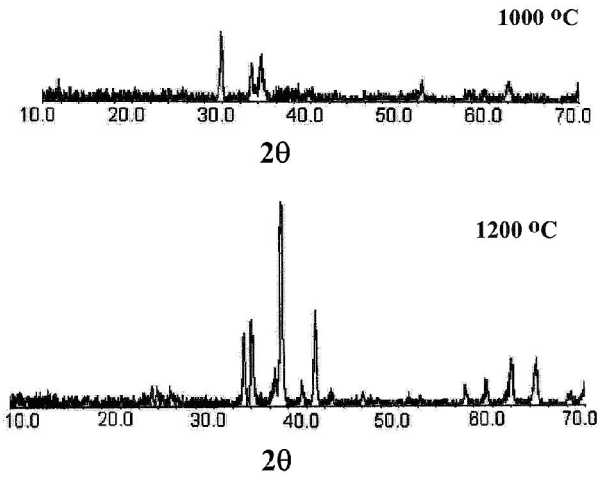

Fig 2. XRD patterns of YSGG ceramic samples obtained by the semi–sol–gel method and annealed at 1000 °C (*top*) and 1200 °C (*bottom*) for 10 h

The X-ray diffraction patterns for the YSGG samples synthesized by the solid state reaction method and annealed at different temperatures for 10 h are shown in Fig. 3. The diffraction lines observed for the sample synthesized at 1000 °C (Fig. 3, top) could be attributed mainly to the individual metal oxide phases (at $2\theta \approx$ 24.3°, 26.3° and 52.2°to Y_2O_3; at $2\theta \approx$ 31.8°, 32.6° and 40.5° to Sc_2O_3; at $2\theta \approx$ 36.6°, and 37.9° to Ga_2O_3). These results allow us to conclude that the solid state reaction does not proceed at 1000 °C. The solid state reaction was also performed at 1200 °C. From the X-ray diffraction pattern for the YSGG sample synthesized by the solid state reaction method and annealed at 1200 °C for 10 h (Fig. 3, middle), however, no traces of the garnet phase were determined. With the further increase of the temperature up to 1400 °C, a few not intensive diffraction lines in the ranges of 2θ ~32–~42° and ~60–~70° (see Fig. 3, bottom) could be attributed to the crystalline $Y_3Sc_2Ga_3O_{12}$ phase. However, the coexistence of other predominating crystalline phases is obvious.

The main morphological features of the $Y_3Sc_2Ga_3O_{12}$ sample obtained by the sol–gel technique are presented in Fig. 4. As it can be seen, during the sol–gel synthesis mainly plate-like crystals of a size of 0.5–3 μm

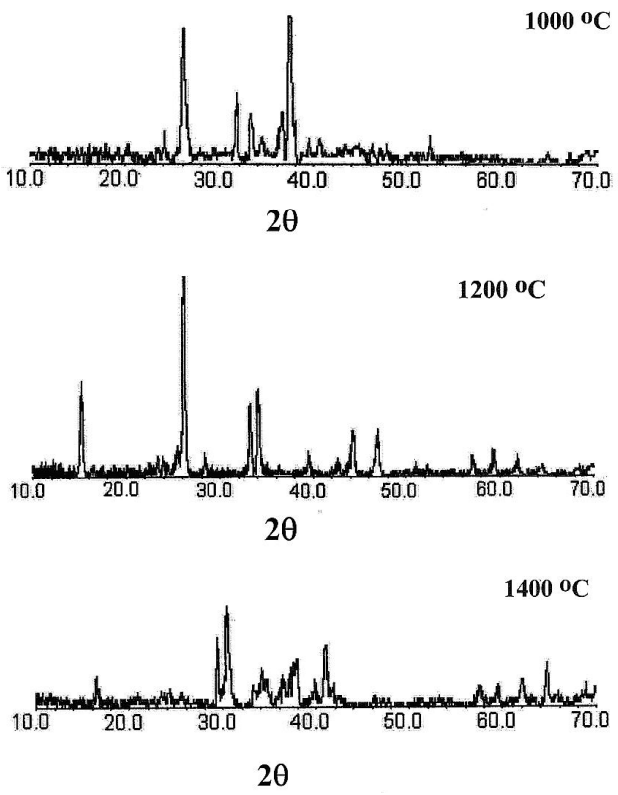

Fig. 3. XRD patterns of YSGG ceramic samples obtained by the solid state reaction method and annealed at 1000 °C (*top*), 1200 °C (*middle*) and 1400 °C (*bottom*) for 10 h

have formed. A high level of agglomeration is also evident. The SEM image of the $Y_3Sc_2Ga_3O_{12}$ sample obtained by the semi–sol–gel technique is shown in Fig. 5. In the case of the semi–sol–gel synthesis, the plate-like crystals have formed as well. However, the formation of much larger crystallites (5–16 μm) is evident. This could be associated with the higher annealing temperature (1200 °C) used in the semi–sol–gel preparation of $Y_3Sc_2Ga_3O_{12}$. Moreover, in some cases these large crystals have been covered with a differently shaped particulate matter. The SEM image of the ceramic sample obtained by the solid state reaction method is shown in Fig. 6. The SEM investigations revealed the formation of very large crystallites within the synthesis products when the solid state reaction approach was used for the preparation of the garnet. Besides, smaller particles of irregular size and shape could be easily observed on the surface of these large crystals. The SEM results also confirm that although the solid state reaction synthesis was performed at 1400 °C, a multiphasic material instead of the single phase YSGG has formed. In short, it was demonstrated that the monophasic $Y_3Sc_2Ga_3O_{12}$ garnet could be obtained at 1000 °C using the sol–gel technique and at 1200 °C using the semi–sol–gel route, however, for the solid state reaction route the temperature of 1400 °C is too low to obtain the YSGG phase.

The transmittance spectra of the $Y_3Sc_2Ga_3O_{12}$ samples were measured at room temperature in the range of 200–1200 nm. Fig. 7 demonstrates the transmission

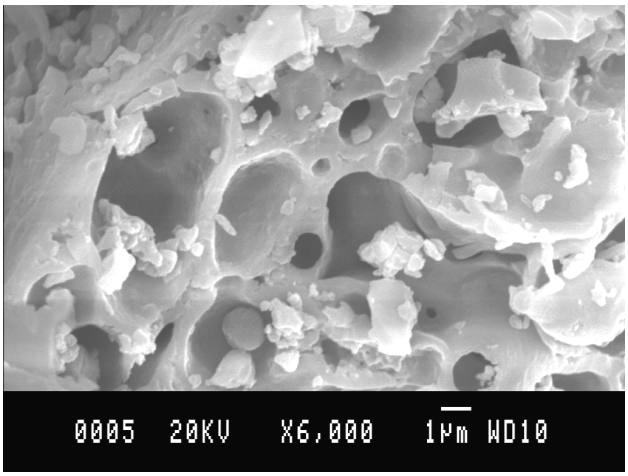

Fig. 4. SEM micrograph of YSGG ceramic sample obtained by the sol–gel method and annealed at 1000 °C for 10 h

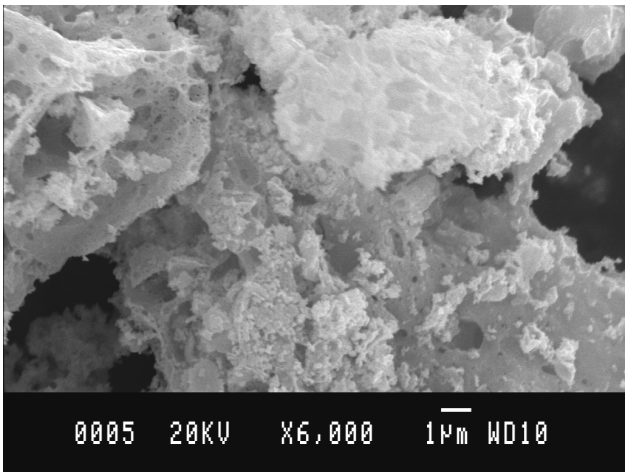

Fig. 5. SEM micrograph of YSGG ceramic sample obtained by the semi–sol–gel method and annealed at 1200 °C for 10 h

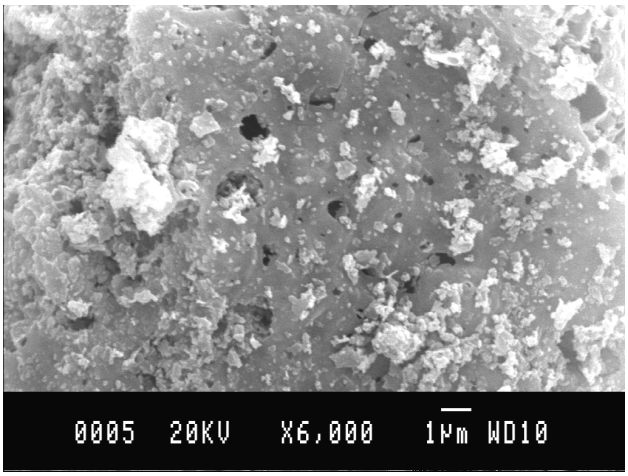

Fig 6. SEM micrograph of synthesis product obtained by the solid state reaction method and annealed at 1400 °C for 10 h

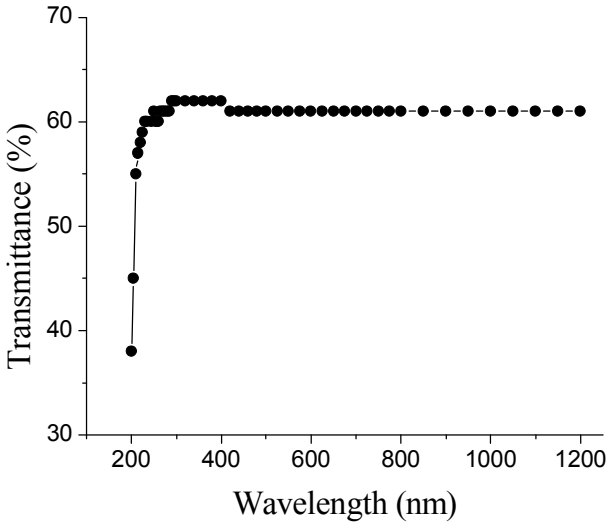

Fig. 7. The transmittance spectrum of $Y_3Sc_2Ga_3O_{12}$ garnet sample obtained by the sol–gel method and annealed at 1000 °C for 10 h

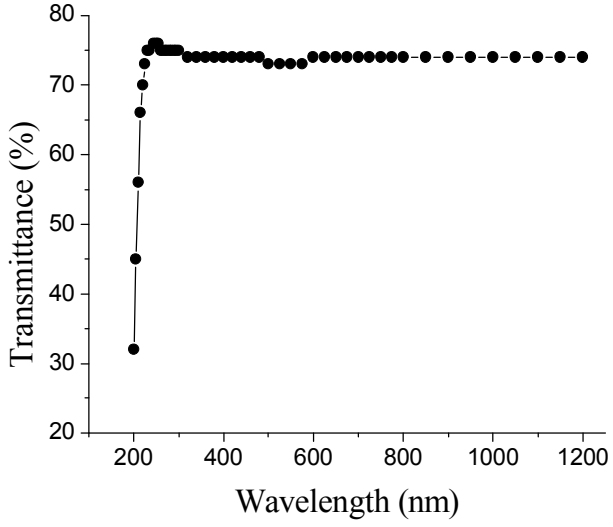

Fig. 8. The transmittance spectrum of $Y_3Sc_2Ga_3O_{12}$ garnet sample obtained by the semi–sol–gel method and annealed at 1200 °C for 10 h.

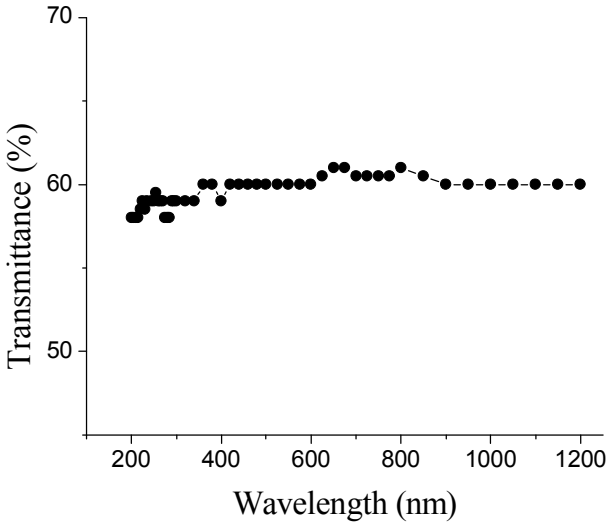

Fig. 9. The transmittance spectrum of ceramic sample obtained by the solid state reaction method and annealed at 1400 °C for 10 h

spectrum of the $Y_3Sc_2Ga_3O_{12}$ ceramic sample produced by the sol–gel method. As it can be seen from Fig. 7, the absorption edge for the $Y_3Sc_2Ga_3O_{12}$ sample could be detected at ~220 nm. In UV range the garnet sample shows a significant decrease of transmission, which is required for optical materials [18–21]. In the higher wavelength region the transmission is almost constant, i.e. not wavelength-dependent. Such garnet compound doped by a rare-earth element could have an excellent optical quality [22, 23]. Fig. 8 shows the optical transmission spectrum of the $Y_3Sc_2Ga_3O_{12}$ ceramic sample synthesized by the semi–sol–gel route. As it can be seen, the transmittance of YSGG prepared by the semi–sol–gel route is slightly higher than that of the mixed-metal garnet synthesized by the sol–gel method. Besides, the absorption edge for the $Y_3Sc_2Ga_3O_{12}$ ceramics synthesized by the semi–sol–gel route is slightly shifted to a higher wavelength (~230 nm). It seems that the intensity of transmittance and the position of absorption edge correlate with the crystal size of the garnets. On the other hand, this can be attributed to the difference in the grain growth in the specimens obtained by different synthetic techniques [24, 25]. An interesting fact is that the recorded transmission spectrum for the Y-Sc-Ga-O ceramic sample fabricated using the solid state reaction method (Fig. 9) shows that the transmittance is almost constant in the whole investigated wavelength region. Moreover, the absorption edge for this sample could be hardly determined. Finally, high phase purity, good mechanical properties, broad transparent range of $Y_3Sc_2Ga_3O_{12}$ garnet synthesized by the sol–gel and/or semi–sol–gel methods at 1000 °C and 1200 °C, respectively, make this compound an excellent candidate as a host material for advanced optical applications.

CONCLUSIONS

The present study demonstrates the versatility of the solution methods (sol–gel and semi–sol–gel) to yield monophasic mixed-metal $Y_3Sc_2Ga_3O_{12}$ garnet samples at the lower sintering temperature (1000 °C and 1200 °C, respectively) in comparison with the temperature required for the solid-sate synthesis (>1400°C). Some of the advantages of the sol–gel synthesis method, e.g. low sintering temperature (1000 °C) of $Y_3Sc_2Ga_3O_{12}$ ceramics, excellent homogeneity and control of stoichiometry, high phase purity are also demonstrated in the present study. Moreover, the proposed aqueous sol–gel method is inexpensive and thus appropriate for a large-scale production of new ceramic materials.

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Jiri Pinkas, Edita Garškaitė, Aldona Beganskienė, Giedrė Nenartavičienė, Aivaras Kareiva

SINTEZĖS TEMPERATŪROS ĮTAKA $Y_3Sc_2Ga_3O_{12}$ GRANATO, SINTETINTO SKIRTINGAIS METODAIS, FAZINIAM GRYNUMUI, KRISTALIŠKUMUI BEI OPTINĖMS SAVYBĖMS

S a n t r a u k a

Ištirta įvairių preparatyvinių metodų (zolių–gelių, semi–zolių–gelių ir kietafazių reakcijų) įtaka $Y_3Sc_2Ga_3O_{12}$ granato fazės susidarymo ypatumams. Parodyta, kad zolių–gelių metodu vienfazis $Y_3Sc_2Ga_3O_{12}$ granatas susidaro 1000 °C, o semi–zolių–gelių metodu – 1200 °C temperatūroje. Kietafazių reakcijų metodu $Y_3Sc_2Ga_3O_{12}$ granato nepavyko susintetinti net 1400 °C temperatūroje. Skleidžiamosios elektroninės mikroskopijos metodu ištirti sintezės produktų paviršiaus morfologiniai ypatumai. Buvo išmatuotas susintetintų junginių optinis pralaidumas 200–1200 nm srityje.