Synthesis and evolution of crystalline garnet phases in $\text{Y}_3\text{Al}_{5-x}\text{In}_x\text{O}_{12}$

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Abstract. In the present work the sinterability and microstructural evolution of mixed-metal $\text{Y}_3\text{Al}_{5-x}\text{In}_x\text{O}_{12}$ ($0 \leq x \leq 2$) (YAING) garnet powders synthesized by an aqueous sol-gel process were investigated. The synthesized samples were characterized by X-ray powder analysis (XRD). It was demonstrated that the formation of $\text{Y}_3\text{Al}_{5-x}\text{In}_x\text{O}_{12}$ garnets proceeds only within narrow substitutional range. Scanning electron microscopy was used to study the morphology and microstructure of the ceramic samples.

1. Introduction

Phosphors are composed of an inert host lattice and an optically excited activator, typically a 3d or 4f electron metal. Oxide phosphors were found to be suitable for field emission display (FED), vacuum fluorescent display (VFD), electroluminescent (EL) devices and plasma panel display (PDP) devices. The compound $3\text{Y}_2\text{O}_3\cdot5\text{Al}_2\text{O}_3$ commonly called as yttrium aluminium garnet (Y$_3$Al$_5$O$_{12}$, YAG), adopts the cubic garnet structure and when doped with a transition metal or lanthanide element, YAG is an important solid-state laser material widely used in luminescence systems, window materials for a variety of light sources, and for fiber-optic telecommunication systems. The rare-earth-doped YAG oxides are also widely applied as phosphors in cathode-ray tubes, field emission, vacuum fluorescent and electroluminescent displays and as scintillators in x-ray and positron emission tomographs. Rare-earth doped YAG materials are currently attracting attention due to their high luminescence efficiency under several types of radiation. Besides, with lanthanide elements as activators yttrium aluminium garnet matrix shows emissions which spread from the near infra-red to the UV range of the electromagnetic spectrum [1–3]. Moreover, YAG ceramics are a variety of potential advanced structural materials in view of high creep and oxidation resistance at high temperature and low heat conductivity.

The specific luminescence properties of metal oxide ceramics are highly sensitive to the dopant concentration and host stoichiometry [4–6]. It is well known, that physical properties of garnets are very dependent not only on the nature and concentration of dopants, but also on the phase purity. The YAG crystal has several disadvantages, however, it is hard to fabricate in a large size and with high...
concentration of lanthanide. All these disadvantages have limited its application so as to exclude large-size solid-state lasers. Compared with the single crystal form, polycrystalline YAG ceramics have excellent possibilities for future application because of their advantages, such as low cost, short preparation time, ease manufacture, high doping, scalability and etc. In the Y_2O_3-Al_2O_3 system, however, depending on the synthesis conditions the formation of different phases such as Y_3Al_5O_12, YAlO_3 (YAP) and Y_4Al_2O_9 (YAM) usually takes place [6–10]. This feature is often considered as a serious problem during preparation of single-phase YAG. Besides, the optical properties of YAG are dependent on the crystal size and crystal size distribution, and on processing conditions. For example, different morphology was determined for the lanthanide-doped YAG samples synthesized by different methods [11–15].

Moreover, the phosphors host materials have proven to be of great importance as well. The matrix should possess good chemical, mechanical, thermal, optical characteristics and properties [16]. For example, transition metal and rare-earth element ions have demonstrated lasing action in a wide variety of host crystals [17, 18]. Despite the YAG matrix possesses excellent thermal and optical properties, however, in recent years considerable effort has been devoted to the development and preparation for the new host materials. On the other hand, one of the most important host for the luminescence materials remains garnet structure compounds. As was mentioned, they have good thermal and optical properties, and additionally they are chemically stable and mechanically hard. Recently we have synthesized different mixed-metal garnets having different stoichiometries of Sc^{3+}, Al^{3+}, and Ga^{3+} (Y_3Sc_2Al_1Ga_2O_{12} (YSAGG-212), Y_3Sc_1Al_3Ga_1O_{12} (YSAGG-131), Y_3Sc_2Al_3O_{12} (YSAG), and Y_3Al_5Ga_2O_{12} (YAGG)) by an aqueous sol-gel method [19–23]. Some of the advantages of the proposed sol-gel synthesis technique, e.g. a low sintering temperature (1000 °C) of garnet samples, an excellent homogeneity and control of stoichiometry, high phase purity, were also demonstrated in this study. Moreover, the adopted aqueous sol-gel method is inexpensive and thus appropriate for the large-scale production of new materials.

In the present work, for the first time to our knowledge, the sinterability and microstructural evolution of mixed-metal Y_{3Al_5-xIn_x}O_{12} (YAING) garnet powders in the range of 0 ≤ x ≤ 5 synthesized by an aqueous sol-gel process have been investigated. Moreover, this paper extends current investigation, focusing on the determination of the substitutional limit (replacement of Al^{3+} by In^{3+}) in Y_{3Al_5-xIn_x}O_{12}.

2. Experimental
The Y-Al(In)-O precursor gels were prepared using stoichiometric amounts of analytical-grade Y_2O_3, Al(NO_3)_3·9H_2O and In(NO_3)_3·5H_2O as starting materials. In the sol-gel process yttrium oxide (0.00375 mol) was first dissolved in 100 ml of 0.2 M CH_3COOH. A clear solution of yttrium acetate was obtained after stirring for 10 h at 65 °C in a beaker covered with a watch glass. To this solution, aluminium nitrate (Y_3Al_5O_{12}, YAG), or indium nitrate (Y_3In_5O_{12}, YING), or the mixtures of aluminium nitrate and indium nitrate (Y_3Al_5-xIn_xO_{12}, YAING) (0.0125 mol) dissolved in 50 ml of distilled water were added and the resulting mixture was stirred for 3 h at the same temperature. In a following step, 2 ml of 1,2-ethanediol as complexing agent was added to the solutions. After concentrating the solutions by slow evaporation at 65 °C under stirring the Y-Al-O, Y-In-O or Y-Al-In-O acetate-nitrate-glycolate sols turned into white transparent gels. The gel powders were ground in an agate mortar and preheated for 2 h at 800 °C in air. After an intermediate grinding in an agate mortar the powders were additionally sintered for 10 h at different temperatures (from 800 °C up to 1200 °C) in air. The flow chart of the sol-gel synthesis of yttrium aluminium indium garnets is presented in Figure 1.

The synthesized samples were characterized by X-ray powder analysis (XRD) performed with a Siemens D-5000 powder diffractometer equipped with a conventional X-ray tubes (CuKα1 radiation (λ = 1.54060 Å), power conditions (40 kV/30 mA)) or with a Stoe-Cie transmission diffractometer STADI P operating with a Ge monochromatized Co radiation (λ = 1.788965 nm), power conditions
(40 kV/30 mA) and equipped with a PSD detector. Scanning electron microscope (SEM) EVO 50 XVP was used to study the morphology and microstructure of the ceramic samples.

Figure 1. A schematic diagram of the steps involved in the sol-gel process used for the preparation of Y₃Al₅₋ₓInₓO₁₂ ceramics.

3. Results and Discussion
In the first part of experimental investigations, to obtain crystalline garnets the appropriate Y-Al-O, Y-In-O and Y-Al-In-O precursor gels were calcined and sintered at 1000 °C in air. The X-ray diffraction patterns for the non-substituted YAG and YING samples are shown in Figure 2. As seen, sintering at 1000 °C produced single-phase Y₃Al₅O₁₂ garnet [2, 7, 14, 20, 24, 25]. Sintering at 1000 °C of Y-In-O gel, however, produced fully crystallized single-phase perovskite yttrium indate (YInO₃, YINP; PDF [25-1172]) and no traces of Y₃In₅O₁₂ have formed. Therefore we can conclude that by heat treatment of the Y-In-O precursor gel powders at 1000 °C the formation of mixture of 3YInO₃ : In₂O₃ (indium oxide possibly amorphous) instead of the single Y₃In₅O₁₂ garnet phase occurs.

Next, the same aqueous sol-gel synthesis method has been applied for the preparation of mixed-metal garnets Y₃Al₅₋ₓInₓO₁₂ obtained by substituting part of aluminium by indium. We attempted to synthesize three samples with different nominal compositions of Y₃Al₂In₃O₁₂, Y₃Al₂,₅In₂,₅O₁₂ and Y₃Al₁In₂O₁₂. Figure 3 shows the XRD patterns for the products obtained by calcinations of Y-Al-In-O precursor gels at 1000 °C and 1200 °C. According to XRD data the variation of temperature from 1000 °C to 1200 °C does not influence the phase composition of the end products.
Figure 2. XRD patterns of Y-Al-O and Y-In-O acetate-nitrate-glycolate gels annealed at 1000 °C.

Figure 3. XRD patterns of Y-Al-In-O acetate-nitrate-glycolate gels with different stoichiometry of metals $Y_3Al_2In_3O_{12}$ (a), $Y_3Al_{2.5}In_{2.5}O_{12}$ (b) and $Y_3Al_In_2O_{12}$ (c) and annealed at 1000 °C (left) and 1200 °C (right).
Moreover, Figure 3a clearly exhibits that no formation of mixed-metal oxide $\text{Y}_3\text{Al}_2\text{In}_3\text{O}_{12}$ occurs at both annealing temperatures. With higher amount of $\text{In}^{3+}$ the perovskite phase is predominant in the synthesis product. The formation of mixed $\text{Y}_3\text{Al}_x\text{In}_{5-x}\text{O}_{12}$ garnets is problematic also at lower substitutional level of indium (see Figure 3 b and c). As could be observed for the $\text{Y}_3\text{Al}_3\text{In}_2\text{O}_{12}$ and $\text{Y}_3\text{Al}_{2.5}\text{In}_{2.5}\text{O}_{12}$ systems, only traces of garnet phase compounds have formed during the heat treatment of Y-Al-In-O acetate-nitrate-glycolate precursor gels. However, even in the case of $x = 2$, the sol-gel synthesis gave mixture of perovskite and garnet phases.

After the preliminary experiments we decided to investigate the influence of the concentration of dopant and annealing temperature on the formation of $\text{Y}_3\text{Al}_{5-x}\text{In}_x\text{O}_{12}$ in more detail. For this, the low concentrations of indium have been selected, i.e. the formation of $\text{Y}_3\text{Al}_{5-x}\text{In}_x\text{O}_{12}$ garnet structure compounds was investigated in the substitutional range of $1.75 \leq x \leq 0.75$. The X-ray diffraction patterns for the YAING samples having low concentration of indium and synthesized at 1000 °C are shown in Figure 4.

![Figure 4. XRD patterns of $\text{Y}_3\text{Al}_{5-x}\text{In}_x\text{O}_{12}$ garnet structure compounds with different $x$.](image)

These XRD measurements were recorded using Co radiation therefore the negligible shift in the $2\theta$ values is obviously seen. Interestingly, the XRD patterns of $\text{Y}_3\text{Al}_{4.25}\text{In}_{0.75}\text{O}_{12}$, $\text{Y}_3\text{Al}_{4.15}\text{In}_{0.85}\text{O}_{12}$, $\text{Y}_3\text{Al}_{4}\text{In}_1\text{O}_{12}$ and $\text{Y}_3\text{Al}_{3.85}\text{In}_{1.15}\text{O}_{12}$ garnets are almost identical to that of pure YAG. However, with increasing amount of indium in the composition of $\text{Y}_3\text{Al}_{5-x}\text{In}_x\text{O}_{12}$ ($x > 1.25$) the peaks observed at $2\theta \approx 23.8$ and $36.0$ ° attributable to the impurity phases already are seen. Moreover the characteristic reflections of garnet phase starts to vanish from the XRD pattern of $\text{Y}_3\text{Al}_{3.25}\text{In}_{1.75}\text{O}_{12}$. Thus, we can conclude that for the system of $\text{Y}_3\text{Al}_{5-x}\text{In}_x\text{O}_{12}$ the mean cationic radius at which still formation of garnet phase occurs seems to be in the range of 0.631-0.644 Å, which corresponds to the chemical compositions of $\text{Y}_3\text{Al}_{3.25}\text{In}_{1.75}\text{O}_{12}$ and $\text{Y}_3\text{Al}_{3}\text{In}_3\text{O}_{12}$, respectively. Of course, such conclusion could be done only if we assume that substitution at the octahedral sites occurs. Moreover, these results are in a good agreement with published previously for the $\text{Y}_3\text{Sc}_{5-x}\text{Ga}_x\text{O}_{12}$ system [21].
To check the exact temperature for the formation of mixed-metal garnet, the Y-Al-In-O precursor gels with the composition of $Y_3Al_{5-x}In_xO_{12}$ ($x = 1.0$) were calcined in steps at 800 °C, 850 °C, 900 °C, 950 °C, 1000 °C and 1050 °C for 10 h. The gradual formation of the $Y_3AlInO_{12}$ phase is shown in Figure 5.

![Figure 5. XRD patterns of $Y_3AlInO_{12}$ synthesized at different temperatures.](image)

The formation of the $Y_3AlInO_{12}$ phase starts already at ca 850 °C. The phase purity of the polycrystalline YAING ceramics improved when the sample was annealed at 900 °C. The XRD pattern of the ceramic sample annealed at 900 °C clearly shows the formation of the single $Y_3AlInO_{12}$ phase.

The textural properties of the calcined powders were investigated by SEM, from which the grain size and typical morphology were obtained. Scanning electron micrographs of the $Y_3Al_{4.75}In_{0.25}O_{12}$ and $Y_3AlInO_{12}$ garnets are shown in Fig. 6.

![Figure 6. SEM micrographs of $Y_3Al_{4.25}In_{0.75}O_{12}$ (left) and $Y_3AlInO_{12}$ (right) garnet samples synthesized at 1000 °C.](image)
The SEM pictures of Y$_3$Al$_{4.25}$In$_{0.75}$O$_{12}$ and Y$_3$Al$_{4}$In$_{1}$O$_{12}$ oxides show the formation of uniform plate-like crystals with particle size ranging from 1 μm to 3 μm. Besides, the SEM micrographs of the samples with lower amount of indium revealed that these volumetric plate-like grains are partially fused with low degree of crystallinity. Moreover, the both SEM images show a tendency of crystalline particles to form broad agglomerates.

The morphological features of indium-substituted samples with higher amount of indium were found to be rather similar. Figure 7 shows the scanning electron micrographs for the representative ceramic samples obtained by calcinations at 1000 °C Y-Al-In-O precursor gels which correspond to the nominal composition of Y$_3$Al$_{3.25}$In$_{1.75}$O$_{12}$ and Y$_3$Al$_{3}$In$_{2}$O$_{12}$.

![Figure 7. SEM micrographs of Y$_3$Al$_{3.25}$In$_{1.75}$O$_{12}$ (left) and Y$_3$Al$_{3}$In$_{2}$O$_{12}$ (right) garnet samples synthesized at 1000 °C.](image)

The typical scanning electron micrograph of YAING samples with higher amount of indium consists of crystalline particles forming ~10-20 μm sized highly porous agglomerates. Additionally, the SEM micrographs presented in Figure 7 show that these volumetric plate-like crystallites are covered with spherical particles or particulate matter which could be attributable to the impurity phases.

4. Conclusions
We have demonstrated for the first time low-temperature synthesis (900 °C) of new mixed-metal garnets Y$_3$Al$_{5-x}$In$_x$O$_{12}$. It was also demonstrated that the formation of Y$_3$Al$_{5-x}$In$_x$O$_{12}$ garnets proceeds only within narrow substitutional range. The formation of a single-phase material depends on the chemical stoichiometry in the reaction system. The increase in the indium content from x = 1.75 to x = 2.0 destabilizes the garnet phase, presumably due to the large ionic radius of In$^{3+}$. The critical value of the mean cationic radius in the octahedral positions at which the substitutional effects occur was found to be in the range of 0.631-0.644 Å, which corresponds to the chemical compositions of Y$_3$Al$_{1.25}$In$_{0.75}$O$_{12}$ and Y$_3$Al$_{1}$In$_{1.95}$O$_{12}$, respectively. The SEM micrographs of Y$_3$Al$_{5-x}$In$_x$O$_{12}$ garnets showed the formation of high-agglomerated plate-like crystals with particle size ranging from 1 μm to 3 μm.

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References

[1] Lu C H, Hong H C and Jagannathan R 2002 J. Mater. Chem. 12 2525
[2] Pan Y, Wu M and Su Q 2004 J. Phys. Chem. Solids 65 845
[3] Caponetti E, Saladino M L, Martino D C, Pedone L, Enzo S, Russu S, Bettinelli M and Speghini A 2005 Nanopowd. Funct. Mater. Solid State Phenom. 106 7
[4] Leleckaitė A, Kareiva A, Bettentrup H, Jüstel T and Meyer H J 2005 Z. Anorg. Allg. Chem. 631 2987
[5] Potdevin A, Chadeyron G, Boyer D, Caillier B and Mahiou R 2005 J. Phys. D 38 3251
[6] Kasuya R, Isobe T and Kuma H 2006 J. All. Comp. 408-412 820
[7] Harlan C. J., A. Kareiva, D. B. MacQueen, R. Cook, A. R. Barron, Adv. Mater., 9 (1997) 68.
[8] Zhang X D, Xu G G, Wang J Y and Liu H 2005 Rare Met. Mater. Eng. 34 59
[9] Xu G, Zhang X, He W, Li H, Li H and Boughton R I 2006 Mater. Lett. 60 962
[10] Mathur S, Shen H, Veith M, Rapalaviciute R and Agne T 2006 J. Am. Ceram. Soc. 89 2027
[11] Pan Y, Wu M and Su Q 2004 Mater. Sci. Eng. B 106 251
[12] Zhou Y, Lin J, Yu M and Wang S 2004 J. All. Comp. 375 93
[13] Fu Y P 2006 J. All. Comp. 414 181
[14] Potdevin A, Chadeyron G, Boyer D and Mahiou R 2006 J. Mater. Sci. 41 2201
[15] Katelnikovas A, Barkauskas J, Ivanauskas F, Beganskiene A and Kareiva A 2007 J. Sol-Gel Sci. Techn. 41 193
[16] Fu Y P 2005 J. All. Comp. 402 233
[17] Ferrand B, Chambaz B and Couchaud M 1999 Opt. Mater. 11 101.
[18] De la Rosa E, Diaz-Torres L A, Salas P, Arredondo A, Montoya J A, Angeles C and Rodriguez R A 2005 Opt. Mater. 27 1793
[19] Muliuoliene I, Jasaitis D, Kareiva A, Blaschkowski B, Glaser J and Meyer H J 2003 J. Mater. Sci. Lett. 22 349
[20] Leleckaitė A and Kareiva A 2004 Opt. Mater. 26 123
[21] Garskaite E, Moravec Z, Pinkas J, Mathur S, Kazlauskas R and Kareiva A 2005 Philosophical Magazine Lett. 85 557
[22] Pinkas J, Garskaite E, Beganskiene A, Nenartaviciene G and Kareiva A 2006 Chemija 4 56
[23] Sakirzanovas S and Kareiva A 2007 Lithuanian J. Phys. 47 75
[24] Vaqueiro P and Lopez-Quintela M A 1998 J. Mater. Chem. 8 161
[25] Veith M, Mathur S, Kareiva A, Jilavi M, Zimmer M and Huch V 1999 J. Mater. Chem. 9 3069