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Sol–gel synthesis of nanosized $Y_3Sc_{2.5}Ga_{2.5}O_{12}$ garnet

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The nanosized yttrium scandium gallium garnet $Y_3Sc_{2.5}Ga_{2.5}O_{12}$ (YSGG) was synthesized by an aqueous sol–gel route.

The discovery of advanced oxide phosphors with multiple superior qualities for display applications remains a difficult problem. Specific luminescence properties are highly sensitive to the host material, changes in dopant composition and host stoichiometry. The matrix of phosphors should possess good chemical, mechanical, thermal and optical characteristics.[1–5] Transition and rare-earth metal ions have demonstrated a lasing action in various host crystals. For example, rare-earth aluminium garnets have attracted considerable attention as host crystals for near-infrared solid-state lasers and optoelectronics devices.[6–9] Among the compounds that can incorporate transition metals or lanthanides, several scandium- and gallium-based materials were also elaborated.[10–15]

Recently, we reported on the synthesis of substituted yttrium aluminium garnets: $Y_3Sc_2AlGa_2O_{12}$, $Y_3ScAl_3GaO_{12}$, $Y_3Sc_2Al_3O_{12}$ and $Y_3Al_3Ga_2O_{12}$.[16–18] The XRD patterns of the powders sintered at 1000 °C showed the formation of monophasic garnet material except in the case of $Y_3Sc_{2.5}Ga_{2.5}O_{12}$ (YSGG). Moreover, it was demonstrated that the increase in the scandium content from $x = 2.0$ to $x = 3.0$ in $Y_3Sc_xGa_{5-x}O_{12}$ destabilizes the garnet phase, presumably due to the large ionic radius of Sc^{3+}.[19]

Sol–gel techniques have been used to prepare mixed-metal oxides. In these sol–gel processes, good quality of the oxide products was expected primarily due to the purity of precursor materials and chemical homogeneity obtained from the synthesis route. The molecular level mixing and the tendency of partially hydrolysed species to form extended networks facilitate the structure evolution thereby lowering the crystallisation temperature of multicomponent metal oxide ceramics. Moreover, the usefulness of the sol–gel process in the synthesis of materials comprising nanoscale architectures is beyond doubt.[20–24] The aim of this study was to synthesize nanocrystalline $Y_3Sc_{2.5}Ga_{2.5}O_{12}$ garnet using an aqueous sol–gel process.

The Y–Sc–Ga–O precursor gels were prepared using stoichiometric amounts of the following analytical grade reagents: yttrium oxide (Y_2O_3), scandium oxide (Sc_2O_3) and gallium nitrate [$Ga(NO_3)_3$]. In the sol–gel process, yttrium oxide was first dissolved in 0.2 M AcOH. Since Sc_2O_3 is insoluble in acetic acid, it was initially dissolved in hot nitric acid and evaporated to dryness. A clear solution of yttrium acetate was obtained after stirring for 1 h at 90 °C in a beaker covered with a watch glass. To this solution, gallium nitrate dissolved in distilled water and scandium oxide dissolved in dilute nitric acid were added. The resulting mixture was stirred for 3 h at the same temperature. Next, 2 ml of 1,2-ethanediol as a complexing agent was added with continuous stirring to the above solutions. After concentrating the solutions by slow evaporation (~8 h) at 65 °C in an open beaker under stirring, the Y–Sc–Ga–O acetate–nitrate–glycolate sols turned into transparent gels. The oven dried (110 °C) gel powders were ground in an agate mortar, placed in alumina crucibles and burned for 2 h at 800 °C in air (heating rate of 1 K min^{-1}). After an intermediate grinding in an agate mortar, the powders were additionally sintered for 10 h at 1000 °C (heating rate of 4 K min^{-1}) in air at ambient pressure.

The X-ray diffraction (XRD) studies were carried out on a Rigaku D/max-2000 X-ray powder diffractometer using CuKα radiation (λ = 1.5408 Å). The size and morphology of the product were characterized by scanning electron microscopy (SEM, AMARY 1910FE, USA) at 15 kV. The energy dispersive X-ray (EDX) analysis was performed, in a vacuum, in the specimen chamber of an EVO 50 EDX coupled scanning electron microscope. TEM images were taken on a JEOL 200CX transmission electron microscope under a working voltage of 160 kV.

To obtain the yttrium scandium gallium garnet phase $Y_3Sc_{2.5}Ga_{2.5}O_{12}$ (YSGG), the Y–Sc–Ga–O precursor gels were calcined and sintered at 1000 °C in air. The X-ray diffraction pattern for the calcined gel powders and sintered for 10 h at 1000 °C is shown in Figure 1. According to XRD analysis fully crystallized oxide $Y_3Sc_{2.5}Ga_{2.5}O_{12}$ with a well pronounced garnet crystal structure was formed. Almost all single lines are indexed, and only three unindexed lines at $2\theta \approx 21.4$, 24.8 and 30.5 could be observed. The most intense lines are (420) – 100%, (422) – 32.2%, and (640) – 27.4%. Thus, the XRD data confirm $Y_3Sc_{2.5}Ga_{2.5}O_{12}$ to be the main crystalline component after the annealing of Y–Sc–Ga–O precursor gels at 1000 °C.

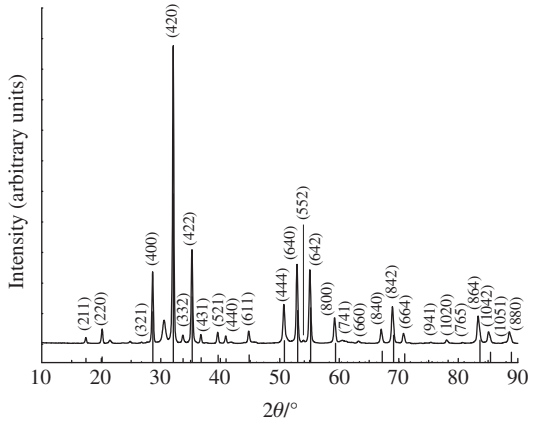

Figure 1 X-ray diffraction pattern of $Y_3Sc_{2.5}Ga_{2.5}O_{12}$ ceramic samples synthesized at 1000 °C. The vertical lines represent the XRD pattern of $Y_3Sc_{1.43}Ga_{3.57}O_{12}$ [PDF 77-1063].

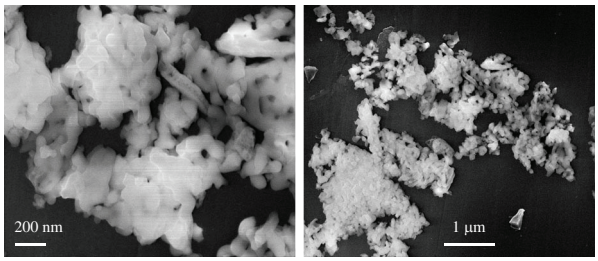

Figure 2 SEM micrographs of YSGG sample sintered at 1000 °C at two magnifications: 50 kX (right) and 150 kX (left).

The morphological properties of synthesized ceramics were characterized by SEM and TEM measurements. Figure 2 exhibits surface features of a YSGG sample synthesized at 1000 °C. Figure 2 shows that the synthesis product consists of clustered nanograins made up of several tiny crystallites with a defined structure. The SEM micrographs show that the YSGG solids are composed of spherical grains. Individual particles seem to be nearly nanosized crystals with an average particle size of less than 100 nm. Moreover, the SEM images also show a sinter-neck of few nano-YSGG particles, which have different orientation to each other. Very well pronounced agglomeration of the nanoparticles indicates a good connectivity between the grains.

The average metal ratios determined by energy dispersive X-ray analysis, in the end product powders correspond to the metal stoichiometry consistent with the YSGG phase and no component segregation or non-ideal stoichiometries, at the micrometer level, were observed in any parts of the sample. The average metal ratios in the YSGG sample was found to be Y:Sc:Ga = 37.4(5):31.2(5):31.4(4), which is in a good agreement, within the standard deviations of the distributions, with the starting composition Y:Sc:Ga = 37.50:31.25:31.25. Using these data, the approximate chemical formula $Y_{3.0(3)}Sc_{2.5(3)}Ga_{2.5(2)}O_{12}$ of synthesized garnet could be suggested.

The TEM investigations confirmed the high quality of the synthesis product. Analogous conclusions from TEM measurements could be drawn, as was indicated by SEM investigations. The TEM image of the YSGG sample is shown in Figure 3, which revealed agglomerated grains. The TEM image shows dispersed crystallites of YSAGG ceramic of nearly uniform size. Moreover, Figure 3 shows the fusion of small YSAGG crystallites to form dumbly shaped particles, which grow further to form clusters of grains. The clustering tendency of the particles in the sol–gel synthesis may be due to the decomposition (> 900 °C) of yttrium oxycarbonate or the traces of the 'unburned' complexing agents (which may function as a binder).

Selected-areas electron diffraction (ED) photographs were also obtained. The crystalline character could be easily determined from the ED image for the YSGG sample, which is also presented in Figure 3. The dimensions and symmetries of all the main reflections agreed with the cubic unit cell of garnet phase. No any streakings are visible in the electron diffraction pattern, which indicates that point or planar defects are absent in the structure of synthesized garnet.

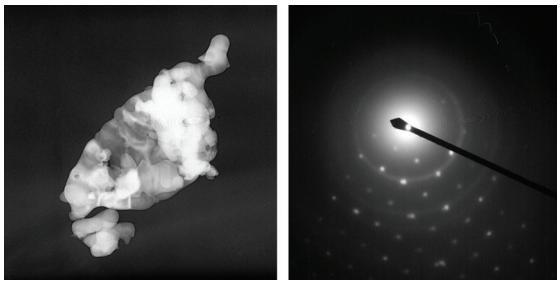

Figure 3 TEM micrograph at magnification 75 kX (left) and selected-area ED photograph (right) of YSGG sample sintered at 1000 °C.

Thus, using an aqueous sol–gel method, the yttrium–scandium–gallium mixed-metal $Y_3Sc_{2.5}Ga_{2.5}O_{12}$ (YSGG) garnet was prepared. The XRD results clearly revealed the formation of almost monophasic garnet material. The morphological characterization using SEM and TEM showed the formation of a highly agglomerated nanocrystalline sample of a nearly uniform size (< 100 nm).

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