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Solvothermal synthesis of Eu^{3+}-doped holmium aluminum garnet

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Eu^{3+}-doped holmium aluminum garnet ($Ho_3Al_5O_{12}$, HoAG) has been synthesized by a solvothermal method and annealed at various temperatures. The X-ray diffraction patterns confirmed that single-phase HoAG was obtained already at 220 °C.

The yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) doped with transition metal or lanthanide ions is an important solid-state laser material used in luminescence systems and window materials for light sources and fiber-optic telecommunication systems. The YAG oxides also find broad application 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.[1–6]

The solid-state reaction route is a widely used method for the preparation of powders from a mixture of starting oxides or carbonates. Various wet-chemical methods, which include combustion, co-precipitation, hydrothermal, spray pyrolysis, sol-gel, solvothermal and emulsion synthesis, have been developed and successfully employed in the low-temperature production of phase-pure YAG, yttrium gallium garnet and yttrium iron garnet powders and related systems.[7–9]

Here, we report the first synthesis of Eu^{3+}-doped holmium aluminum garnet $Ho_3Al_5O_{12}:Eu^{3+}$ by a solvothermal method at a low temperature.†

The synthesized samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and dynamic light scattering (DLS) measurements.‡

Figure 1 shows that the product obtained at 220 °C (20 h heating) is well-crystallized, and all diffraction lines could be attributed to a holmium aluminum garnet (PDF [04-001-9715]) crystalline phase. To investigate the influence of temperature on the phase purity and crystallinity of $Ho_3Al_5O_{12}:Eu^{3+}$, the products were additionally heated at higher temperatures for 4 h. Interestingly, the XRD pattern of the HoAG sample additionally heated at 500 °C for 4 h is almost identical to that of the specimen just synthesized in an autoclave. With the further heating of HoAG at higher temperatures (1000 °C for 10 h and 1200 °C for 4 h), the intensity of the HoAG diffraction peaks increases and the full-width at half-maximum decreases due to the growth of particles and improved crystallinity of the samples.

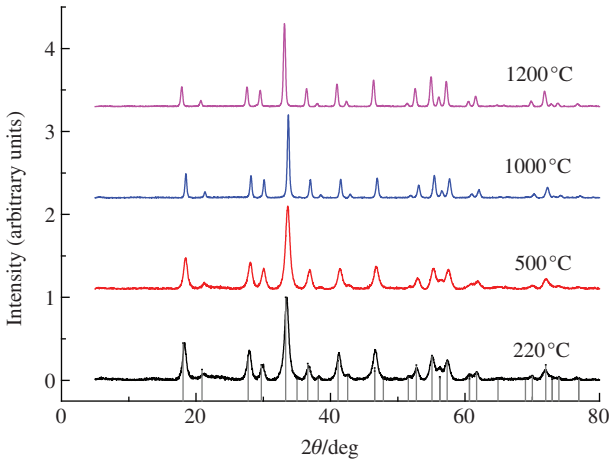

Figure 1 XRD patterns of solvothermally derived holmium aluminum garnet powders calcined at different temperatures.

As can be seen in Figure 2, solvothermally synthesized $HoAG:Eu^{3+}$ garnet samples are also monophasic compounds. Apparently, europium does not affect the formation of a garnet structure up to a concentration of 5%. No new peaks or/and shifted peaks could be determined in the XRD patterns of different Eu^{3+}-doped holmium aluminum garnets.

The particle size and particle size distribution in $Ho_3Al_5O_{12}$ garnets synthesized at 220 °C and annealed at different temperatures were examined by DLS. Figure 3 demonstrates high influence of annealing temperature on the particle size of HoAG. Indeed, the nanoparticles of HoAG (~100 nm) with a narrow particle size distribution were formed during solvothermal synthesis at 220 °C. The particles of ~220 nm in size formed after heating the solvothermally obtained sample at 500 °C. With increasing the heating temperature to 1000 °C, the largest fraction of HoAG was composed of ~410 nm particles. The largest particles were determined for the HoAG sample annealed at 1200 °C. Thus, the particle size of HoAG synthesized using a solvothermal

† For the preparation of $HoAG:Eu^{3+}$, $Al(NO_3)_3·9H_2O$ (99.99%), $Ho(NO_3)_3·5H_2O$ (99.99%) and $Eu(NO_3)_3·6H_2O$ (99.99%) were used as starting materials. First, an aluminum, holmium and europium solution was obtained by dissolving metal nitrates in 50 ml of deionized water. The resulting mixture was stirred until substances fully dissolved. Second, ethane-1,2-diol ($HOCH_2CH_2OH$) was added to the above solution with vigorous stirring. The aluminum, holmium and europium hydroxides were precipitated by dropwise addition of an excess of a 10% ammonia solution under vigorous stirring. The precipitates were repeatedly centrifuged and washed with distilled water to remove residual ammonia. The washed hydroxides were dispersed in ethane-1,2-diol and then placed in an autoclave with a Teflon liner. The autoclave was heated to 220 °C and maintained at this temperature for 20 h. The obtained powders were centrifuged and repeatedly washed with ethanol solution, dried in air at 80 °C and then annealed at different temperatures for 4 h.

‡ The XRD patterns were recorded on a Siemens D5000 diffractometer with CuKα radiation (using a step of 0.05° 2θ and 2.5 s per step). Morphological characterization was performed on a JEOL 7100F field emission scanning electron microscope. Particle size distributions of aqueous suspensions of the powders were measured with a Malvern Zetasizer Nano ZS analyzer.

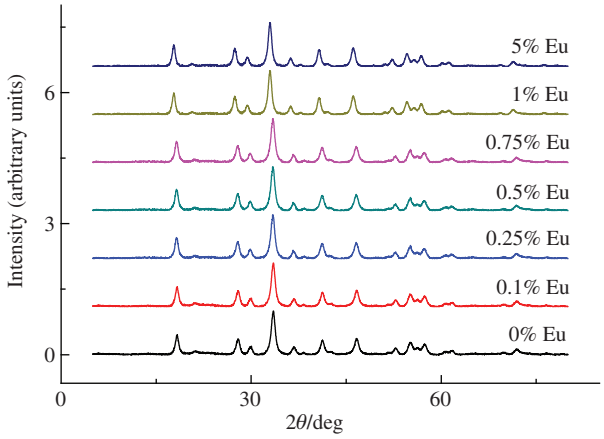

Figure 2 XRD patterns of HoAG samples doped with different amount of europium ions and synthesized by a solvothermal method at 220 °C for 20 h.

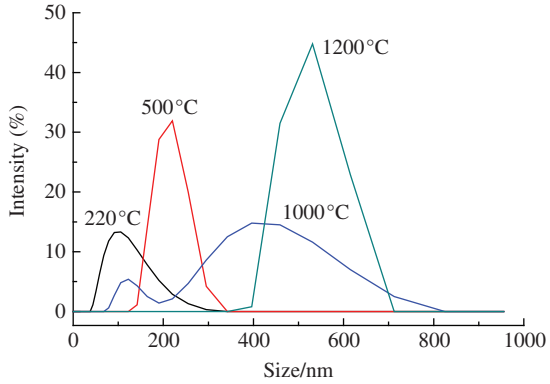

Figure 3 Particle size distribution of HoAG samples obtained at different temperatures.

method monotonically increases from 100 to 600 nm with annealing temperature. The particle size distribution also becomes broader with increasing the heating temperature.

The textural properties of HoAG powders were investigated by SEM, from which the grain size and typical morphologies were obtained. Scanning electron micrographs of the HoAG and HoAG : Eu^{3+} samples are shown in Figure 4.

The SEM results are in a good agreement with those obtained by DLS measurements. The even increase in particle size of HoAG with the heating temperature is evident. As synthesized at 220 °C HoAG is composed mainly of well-distributed fine spherical grains (less than 100 nm). The SEM image of the HoAG : Eu^{3+} sample annealed at 500 °C looks very similar at first glance; however, the connectivity between grains is less pronounced. The HoAG and HoAG : Eu^{3+} specimens annealed at 1200 °C are obviously composed of largest and agglomerated spherical particles. It is known that the use of phosphors with spherical particles should increase screen brightness and improve resolution because of the lower scattering of the evolved light and a higher packing density as compared to the irregularly shaped particles obtained by other conventional methods.[6]

Thus, the sinterability and microstructural evolution of holmium aluminum garnet $Ho_3Al_5O_{12}$ and europium-doped

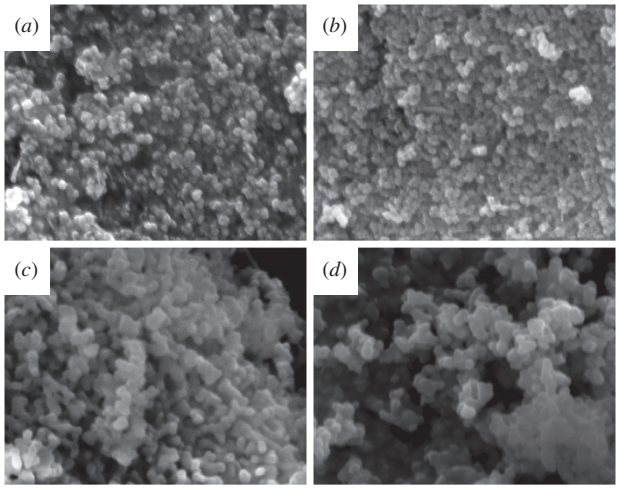

Figure 4 SEM micrographs of (*a*) HoAG synthesized at 220 °C, (*b*) HoAG : 0.25% Eu^{3+} annealed at 500 °C, (*c*) HoAG annealed at 1200 °C and (*d*) HoAG : 0.25% Eu^{3+} annealed at 1200 °C.

$Ho_3Al_5O_{12}$: Eu^{3+} garnets synthesized by a solvothermal method were investigated. It was concluded from the XRD data that monophasic $Ho_3Al_5O_{12}$ and $Ho_3Al_5O_{12}$: Eu^{3+} nanocrystalline garnets can be easily synthesized at 220 °C using the proposed solvothermal approach. The amount of europium did not affect the formation of garnet structure up to a concentration of 5%. The crystallinity of garnets significantly increased on the additional annealing of specimens at 1000 and 1200 °C. Based on DLS measurements it was determined that the particle size of HoAG samples monotonically increased from 100 nm (as-synthesized) to about 600 nm (annealed at 1200 °C). The SEM results showed that HoAG synthesized by a solvothermal method was composed mainly of well-distributed fine spherical grains (less than 100 nm).

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