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Preparation and characterization of nanoscale lutetium aluminium garnet (LuAG) powders doped by Eu^{3+}

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Abstract

Nanoscale powders of $Lu_3Al_5O_{12}$:Eu were synthesized by a standard precipitation process using $(NH_4)HCO_3$. Characterisation of the nanocrystalline particles was done with respect to particle morphology and luminescence spectra. The mean particle diameter was reduced by means of a dispersing additive during the precipitation process. A procedure was developed to gain particles in the particle size range of 20–50 nm. Additionally, the reactivity of the precipitated precursor could be enhanced to such an extent that phase transformation into the garnet phase takes place at 900 °C. The optical properties of the doped nanoscale lutetium garnet are identical with microscale powders. Eu^{3+} doped nanoscale lutetium garnet showed quantum efficiencies up to 40%.

Keywords: Co-precipitation; Lutetium aluminium garnet (LuAG); Nanoscale particles; Rare earth doping; Optical properties

Introduction

Lutetium aluminium garnet $Lu_3Al_5O_{12}$ (LuAG) is as $Y_3Al_5O_{12}$ (YAG) a widely applied optical host material for luminescent powders, ceramics, and single crystals. Rare earth doped LuAG and YAG found application in IR Lasers, phosphor converted LEDs, X-ray detectors and field emission displays [1–4]. The wide application range of RE doped garnets is due to their high mechanical and radiation stability, wide band gap, and excellent radiation conversion efficiency for many rare earth dopants. Eu^{3+} doped LuAG is due to the wide optical band gap of LuAG, viz. 6.1 eV, of potential interest as a red emitter in Xe excimer discharge lamps and plasma displays.

Industrial manufacturing of LuAG und YAG powder is done by a conventional mix and fire procedure, i.e. by blending the rare earth oxides RE_2O_3 ($RE = Y, Lu$) with Al_2O_3 in a molar ratio of 3:5 and subsequent annealing between 1600 and 1700 °C for several hours. This process yields microscale particles having a mean diameter of 1–10 μm.

Nanoscale particles of YAG can be e.g. obtained by precipitation processes, in which the pH of an aqueous solution is homogeneously enhanced to obtain hydroxides of Al^{3+} and the trivalent rare earth cations. For the pH enhancement the application of ammonium hydrogen carbonate has been claimed, whereby this led to garnet particles with a mean diameter of about 100–200 nm [5].

Due the high surface area of these fine garnet particles, they are very useful for the synthesis of transparent ceramics [6–10]. Alternatively, YAG and LuAG nanoparticles can be gained via pyrolysis of organic precursors or by the well-known sol–gel process [11,12].

The goal of this work was to reduce the particle size of Eu^{3+} doped LuAG particles from 200 nm down to 20–50 nm, which is of interest for the preparation of transparent phosphor layers or ceramics. To this end, doped LuAG

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particles were made according to a precipitation process based on the addition of $(NH_4)HCO_3$ to an aqueous solution of the cations as known from literature [1], which led to 200 nm particles. In the framework of this work the standard process was modified by changing the solvent and by application of dispersing additives, to obtain much smaller particles.

Experimental section

The synthesis of all doped LuAG samples was done by the following procedure: 7.5 mmol $LuCl_3 \cdot 6H_2O$ (Aldrich 99.9%), 12.5 mmol Aluminium(III)chlorid Hexahydrat (Aldrich 99%) and the respective dopant ($EuCl_3 \cdot 6H_2O$ (5%) or $PrCl_3 \cdot 6H_2O$ (1%)) are dissolved in a mixture of 20 ml deionized water and 30 ml 2-propanol (Merck 99.5%).

The solution was filled into a dropping funnel and drop wisely added to a solution of 90 mmol $(NH_4)HCO_3$ (Aldrich 99%), 350 ml 2-propanol and 50 ml deionized water. To restrict the particle growth 0.06 g polyacrylic acid (Aldrich $M_w \approx 100\,000$ 35 (G/G) in water) as a dispersing agent was added. During the whole precipitation process the pH value of the solution was adjusted to 8 by the addition of a conc. NH_4OH solution.

The clear solution became whitish and the precipitate was separated by filtration, washed several times by a 2-propanol/water (1:1) mixture and finally dried at 140 °C. The dried precursor was typically annealed at 900 °C for 3 h.

The formed phases in the synthesized powders were analyzed using an X-ray diffractometer (Philips APD 1700), whereby Cu–Kα-radiation (1.542 Å) for all measurements. Temperature dependent X-ray patterns were recorded by an X-ray diffractometer from PANalytical using a high temperature camera Anton Paar HTK16.

Reference data were taken from the PCPDFWIN database 2.0 of the JCPDS-ICDD. All powder samples were deposited as a thin layer on a silicon single crystal and measured between 10° and 90°. For temperature dependent measurements samples were fixed on a heatable platinum tape.

Determination of the particle morphology and size was done by scanning electron microscopy (SEM) using a Philips-FEI SEM XL30 with a tungsten field-emission cathode. To this end, the samples were fixed on a conducting pad mounted on an alumina waver, and subsequently coated by about 8 nm carbon.

Optical characterisation was done using a VUV spectrometer system. It consists of a Deuterium lamp, a vacuum monochromator and a refocusing unit evacuated by a directly flanged turbo drag pump. The remaining distance (a few centimetres) from the MgF_2 vacuum window to the sample position is under a constant flow of dry Nitrogen. The VUV excitation unit is fully integrated into the spectrofluorimeter system FL900 of Edinburgh Instruments. The detection branch of the spectrometer consists of a collecting optic, a monochromator and a photomultiplier tube (PMT) mounted in a Peltier cooled housing and driven in a single photon counting mode. A detailed description of the set-up is given in [14].

Results and discussion

(1) *LuAG phase formation from the precursor powders*

The precursors prepared from the metal chloride solution by the addition of ammonium hydrogen carbonate are white powders of lutetium hydroxycarbonate.

Fig. 1 displays the X-ray diffraction patterns of LuAG:Eu^{3+} annealed at different temperatures between 800 and 1100 °C for 30 min. It can be concluded that the powders are still amorphous at 800 °C, while the cubic garnet phase is formed at 900 °C.

The obtained diffraction patterns at and above 900 °C are in good agreement with the data reported in [15]. From the half width at full maximum of the peaks an average crystallite size of 20 nm (900 °C)–50 nm (1100 °C) can be derived according to the Debye–Scherrer formula, whereas the crystallite size increases with annealing temperature.

A comparison of the diffraction peaks of the here described LuAG:Eu^{3+}(5%) with undoped LuAG as depicted in Fig. 2 shows that the peaks are shifted towards smaller angles. This is in accordance to the incorporation of Eu^{3+} into the LuAG lattice, since the relatively large Eu^{3+} ions ($r = 120.6$ pm KZ 8) [13] replace the smaller Lu^{3+} ions ($r = 112$ pm KZ 8) [13]. This results in an increase of the lattice constant, e.g. from $Lu_3Al_5O_{12}$ (12.48 Å) to $Lu_3Al_5O_{12}$: Eu^{3+} (12.53 Å) and thus to the observed shift of the reflection peaks.

From the X-ray diffraction pattern in Fig. 2 the crystallite size could be derived by the Debye–Scherrer formula to 38 nm. This is in good agreement to the obtained particle size obtained by SEM photographs.

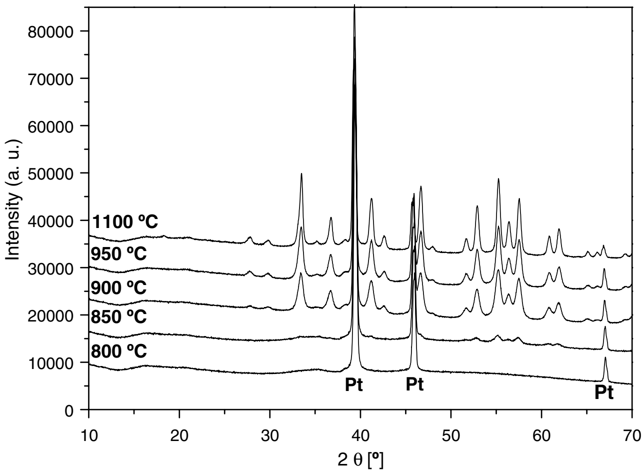

Fig. 1. XRD patterns of the precipitated LuAG:Eu precursor calcined at 800, 850, 900, 950 and 1100 °C on a platinum tape. The large peaks at 39.5°, 46° and 67° stem from the platinum.