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Effect of annealing on luminescence of Eu^{3+} - and Sm^{3+} -doped Mg_2TiO_4 nanoparticles

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ABSTRACT

This work explores the influence of annealing temperature on the structure and luminescence of 2 at% Eu^{3+} and 1 at% Sm^{3+} -doped Mg_2TiO_4 nanopowders produced via Pechini-type polymerized complex route. Mg_2TiO_4 samples were annealed at 7 different temperatures (400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 650 °C and 700 °C) to determine the temperature range in which cubic inverse spinel structure is stable and to follow the changes of material luminescence properties. X-ray diffraction revealed that crystallization of both Eu^{3+} and Sm^{3+} -doped Mg_2TiO_4 nanopowders starts at 400 °C, and that Sm^{3+} -doped Mg_2TiO_4 starts to decompose at 650 °C, while Eu^{3+} doped Mg_2TiO_4 starts to decompose at 700 °C. Samples annealed at higher temperatures show higher crystallinity and larger crystallite size. Mg_2TiO_4 powder annealed at 600 °C is composed of ~5 nm size nanoparticles agglomerated in micron-size and dense chunks. The emission spectra of nanoparticles are composed of emissions from defects in Mg_2TiO_4 host and characteristic emissions of Eu^{3+} ($^5\text{D}_0 \rightarrow ^7\text{F}_j$) and Sm^{3+} ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_j$) ions. The stronger emission and longer emission decays are observed with samples annealed at high temperatures. In the case of the Eu^{3+} ions emission intensity increased one order of magnitude between samples annealed at 400 °C and 650 °C.

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1. Introduction

Over the past two decades nanostructured materials, with properties quite different from corresponding bulk materials, have turned into a class of their own. In recent years, an increased number of investigations have been performed on rare earth (RE) doped nanocrystals. Because of the small particle size nanocrystalline materials doped with rare earth ions exhibit optical properties that differ from their bulk counterparts [1–4]. These differences are expected due to: the confinement effects on the vibrational spectra of nanocrystals, the increased role of the impurity ions at the surface whose optical properties are modified by the disorder at the surface, and the alteration of the electronic bands of the matrix. Meltzer et al. [5] reported stronger luminescence emission in nanocrystalline materials compared to bulk ones and modification of radiative lifetimes. It was shown that doping uniformity and phase purity are easier to achieve in nanomaterials. Literature results also indicate that crystallites of nanoscale dimensions may lead to a higher stability of some cubic phases

[6,7]. Internal scattering in nanomaterial is reduced as the size of the particles is much smaller than the wavelength of the visible light. Because of the reduced energy transfer between identical or non-equivalent emission centers, concentration quenching occurs at higher RE concentrations in nanoparticles than in the bulk materials.

Magnesium orthotitanate (Mg_2TiO_4) is widely used as heat resistor, dielectric for microwave technology, capacitor for temperature compensation and as refractory material [8]. Magnesium titanates are usually synthesized by high-temperature solid state reaction at ~1400 °C giving powders with relatively large, non-uniform particles [9–12]. With wet chemical methods, reaction temperatures required for Mg_2TiO_4 formation could be reduced. To date, Mg_2TiO_4 particles were successfully synthesized via a sol–gel, coprecipitation, polymeric precursor method and the peroxide route [8,13–17]. With these methods particles were fabricated at 1300 °C for 8 h (~4 μm) [8], 1000 °C for 3 h [13], 600 °C for 1 h [14] and 560 °C [15]. Mg_2TiO_4 particles (~40 nm) were obtained using the peroxide route at 550 °C for 8 h [16], and the smallest particles of about ~5 nm (Mn^{4+} doped Mg_2TiO_4) are obtained using Pechini-type polymerized complex route [17].

In order to obtain Mg_2TiO_4 nanopowder we used a Pechini-type polymerized complex route, based on polyesterification between

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citric acid (CA) and ethylene glycol (EG). An important aspect of this approach is using mixed metal–CA complex with stoichiometric Mg:Ti ratio of 2:1, rather than a simple mixture of individual metal–CA complexes. In this way, due to local mixing of constituting atoms, Mg₂TiO₄ particles could be obtained at low temperatures [18]. Additionally, reduction of the particle size could be achieved by the introduction of small quantities of trivalent RE³⁺ ions (here Eu³⁺ and Sm³⁺) into Mg₂TiO₄ host. Replacement of Mg²⁺ with Eu³⁺ (or Sm³⁺) ions leads to charge imbalance that is compensated by forming cation vacancies. The presence of vacancies leads to the increase of lattice defects, unit cell distortion, decrease in short-range ordering and consequently particle size reduction.

The aim of this work is to investigate the structure and luminescence of Eu³⁺ and Sm³⁺ in Mg₂TiO₄ nanocrystals annealed at different temperatures. For this purpose, mixed metal–CA complex method is used for the synthesis of Mg₂TiO₄ nanoparticles. We wanted to determine the temperature range in which cubic inverse spinel structure is stable and to systematically examine the influence of annealing temperature on the structure, emission intensity and emission decay of the nanoparticles.

2. Experimental part

2.1. Synthesis of Eu³⁺(Sm³⁺)-doped Mg₂TiO₄ nanoparticles

For synthesis of 2 at% Eu³⁺ (or 1 at% Sm³⁺) doped Mg₂TiO₄ nanoparticles, titanium(IV) isopropoxide, magnesium(II) nitrate, citric acid and ethylene glycol were mixed in 1:2:5:20 molar ratio [18]. In the first step, titanium(IV) isopropoxide (Alfa Aesar, 97%) was dissolved in ethylene glycol (Lach-Ner, 99%) under constant magnetic stirring. Then citric acid (Kemika, 99.5%) was added to this solution and stirred until complete dissolution was achieved. Appropriate amounts of MgO (Alfa Aesar, 96%) and Eu₂O₃ (or Sm₂O₃) (Alfa Aesar, 99.9%) were dissolved in hot concentrated nitric acid, evaporated to dryness and joined with titanium(IV) isopropoxide/EG/CA mixture. After that, mixtures were stirred for 1 h at 60 °C until they became transparent, and further stirred at 130 °C for a few hours to promote polymerization, remove excess of solvents and subsequently transform to resin like form. In order to obtain black amorphous precursors, resins were fired at 350 °C for 30 min and ground to powders. The Eu³⁺ and Sm³⁺-doped precursor powders were calcined in 450 °C to 700 °C temperature range in order to obtain pure phase Mg₂TiO₄ nanoparticles. Finally, two sets of Mg₂TiO₄ samples were synthesized, one doped with 2 at% of trivalent Eu ions and one doped with 1 at% of trivalent Sm ions:

Set (I) 7 samples of Mg₂TiO₄ doped with 2 at% Eu³⁺ calcined at 400 °C for 4 h, 450 °C for 2 h and at 500 °C, 550 °C, 600 °C, 650 °C and 700 °C for 1 h.

Set (II) 7 samples of Mg₂TiO₄ doped with 1 at% Sm³⁺ ions calcined at same temperatures/time as Set I.

Samples obtained at 400 °C and 450 °C were additionally thermally treated for 4 and 2 h, respectively, since one hour was insufficient to remove all organic residuals. Rare earth doping concentrations are chosen arbitrarily, but according to the concentrations commonly used with oxide hosts.

2.2. Instruments and measurements

TG/DTA analysis was performed on the SETARAM SETSYS Evolution-1750 instrument. The Mg₂TiO₄ powder precursor (~10 to 15 mg), taken after gel firing at 350 °C for 30 min, was heated at 10 °C min⁻¹ heating rate, in air atmosphere (air flow 16 ml min⁻¹), from 30 °C to 1200 °C. Fourier transmission infrared

measurements were carried out on the Thermo Nicolet 380 FT-IR instrument, in reflection mode with a resolution of 4 cm⁻¹. X-ray diffraction measurements were performed using Rigaku SmartLab diffractometer. Diffraction data were recorded in a 2θ range from 15° to 120°, counting 0.7°/min in 0.02° steps. Microstructural characterization was done using a JEOL JSM-6610LV scanning electron microscope connected with an INCA energy-dispersion X-ray analysis (EDX) unit. An acceleration voltage of 20 kV was used for the analyses. Microstructure at a local level was analyzed by transmission electron microscopy using JEOL-JEM 2100 LaB₆ operated at 200 kV. Photoluminescence measurements were performed at room temperature on Fluorolog-3 Model FL3-221 spectrofluorimeter system (Horiba Jobin-Yvon), utilizing 450 W Xenon lamp as the excitation source for emission measurements and Xenon–Mercury pulsed lamp for lifetime measurements. The emission spectra were scanned in the range of wavelengths from 425 to 750 nm. The TBX-04-D PMT detector was used for both lifetime and steady state acquisitions. The line intensities and positions of the measured spectra were calibrated with a standard Mercury–Argon lamp. Photoluminescence measurements were performed on pellets prepared from the powders under a load of 5 T and without any additives.

3. Results and discussion

3.1. Thermal analysis (TG/DTA)

Thermal analysis was used to determine thermal decomposition behavior of the powder precursor obtained by ignition of Mg₂TiO₄:2 at% Eu³⁺ gel at 350 °C for 30 min. Results of TG/DTA analysis clarified the existence of three temperature regions (see Fig. 1): (i) first between room temperature and 300 °C where TG curve shows small weight loss (~5%); (ii) the second, marked weight loss indicated by TG (~65%) and the exothermic effect indicated by DTA, observed in the temperature range between 300 °C and 700 °C, may be related to the elimination of the residual organic compounds; and (iii) the third, after 700 °C when mass remains constant and there is no visible peak in DTA curve.

3.2. Fourier transform infrared spectroscopy (FT-IR)

The FTIR spectra of Mg₂TiO₄:2 at% Eu³⁺ gel, the precursor powder fired at 350 °C for 30 min, and of the powder obtained after calcination at 600 °C for 1 h, is shown in Fig. 2. Water

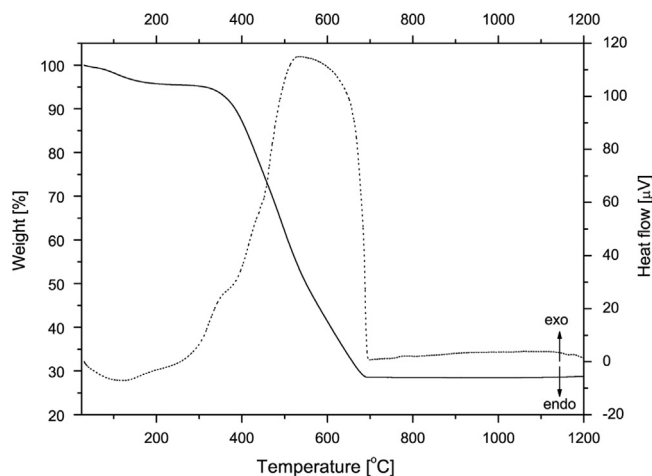


Fig. 1. Thermogravimetry (TG, solid line) and differential thermal analysis (DTA, dot line) curves for Mg₂TiO₄:2 at% Eu³⁺ powder precursor obtained by ignition of Mg₂TiO₄ gel at 350 °C for 30 min.

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