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The crystal structure, vibrational and luminescence properties of the nanocrystalline $KEu(WO_4)_2$ and $KGd(WO_4)_2$:Eu^{3+} obtained by the Pechini method

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ABSTRACT

The luminescent nanocrystalline $KEu(WO_4)_2$ and $KGd_{0.98}Eu_{0.02}(WO_4)_2$ have been prepared by the Pechini method. X-ray diffraction, infrared and Raman spectroscopy as well as optical spectroscopy were used to characterise the obtained materials. The crystal structure of $KEu(WO_4)_2$ was refined in $I2/c$ space group indicating the isostructurality to $KGd(WO_4)_2$. The size of the crystalline grains depended on the annealing temperature, increasing with the increase of the temperature. The average size of crystallites of both crystals formed at 540 °C was about 50 nm. Vibrational spectra showed noticeable changes as a function of size due to, among others, phonon confinement effect. Luminescence studies did not reveal significant changes for the nanocrystallites with the lowest grain size in comparison with the bulk material. The differences observed in luminescence spectra in form of slight inhomogeneous broadening of the spectral lines and increase of the hypersensitive I_{0-2}/I_{0-1} ratio point to very low symmetry of Eu^{3+} ions and change of the polarisation of the local vicinities of Eu^{3+}. X-ray diffraction, vibrational and optical studies showed that the structure of the synthesised nanocrystalline $KEu(WO_4)_2$ and $KGd(WO_4)_2$:Eu is nearly the same as that found for the bulk material. The size-driven phase transitions were established for both compounds.

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1. Introduction

Rare-earth elements form a series of double isomorphous tungstates and molybdates with the general formula $K^{I}Ln^{III}(M^{VI}O_4)_2$, where Ln^{III} is a lanthanide ion and M^{VI} = Mo or W. These materials can be used as laser active media in which the emission properties are modified by the selection of the Ln^{3+} ion and by optimisation of its concentration. $KGd(WO_4)_2$ has been found to be especially promising material for a solid-state Raman laser application [1]. Well-characterised solid-state laser materials are evaluated for performance in optical refrigeration as well as radiation-balanced laser systems. It seems that, for such systems, $KY(WO_4)_2$ and $KGd(WO_4)_2$ are the most promising crystalline hosts for trivalent ytterbium ions [2].

Although properties of crystalline double tungstates and molybdates were a subject of numerous studies, functional electronic device demands the replacement or assembly of nanometre scale components into well-defined structures. In recent years, a rapid development of experiments with nanomaterials takes place due to their existing and future applications in various technological areas [3,4]. The materials with grain size less than 100 nm exhibit different optical, electrical, catalytic and mechanical properties than conventional microcrystalline specimens [5–8]. Therefore, processing techniques that allow production of large quantities of nanomaterials and a more precise control of chemical structures are important area of investigations. In order to examine the chemical and physical properties of nanomaterials, the alternative simple and cost-effective route is required. The Pechini process [9] is such polymeric precursor method known as versatile low temperature route. Among the advantages of this method are high efficiency, short time synthesis and the possibility to prepare complex compositions at a relatively low temperature.

According to the literature data, only three rare earth double tungstates, $NaLa(WO_4)_2$ and $KRE(WO_4)_2$ (RE = Gd and Yb), were prepared in nanocrystalline state so far [10,11]. In this paper, we shall focus attention on $KEu(WO_4)_2$ (KEW) and $KGd(WO_4)_2$:Eu (2 at wt%) (KGEW) prepared by Pechini method in order to investigate their optical properties and study the grain size dependence of their properties. Moreover, to our knowledge, both crystals were not structurally described.

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2. Experimental

2.1. Preparation of nanocrystalline powders

The $KEu(WO_4)_2$ and europium(III)-doped $KGd(WO_4)_2$ samples were prepared by the Pechini method. Europium nitrate $Eu(NO_3)_3 \cdot x5H_2O$ (Alfa Aesar, 99.99%), gadolinium nitrate $Gd(NO_3)_3 \cdot xH_2O$ (Alfa Aesar, 99.99%), potassium tungstate K_2WO_4 (Alfa Aesar, 99.5%) and ammonium metatungstate $(NH_4)_6W_{12}O_{41}$ (Fluka) were used as source of metallic cations. First, 1.46 mmol of the europium nitrate or 1.42 mmol of the gadolinium and 0.03 mmol of the europium nitrates and, separately, 0.72 mmol of the potassium and 0.18 mmol of the ammonium tungstates were dissolved in distilled water. Separately, 35 mmol of the citric acid was dissolved in distilled water in order to obtain the molar ratio of citric acid to total cations as 15:1. Next one-half of the aqueous citric acid solution was added to the nitrate solution and another half was added to the tungstate solution. After complete homogenisation, both solutions were mixed together. The formation of complex ring-shaped compounds around the metal cations takes place in the solution. Metals ions are chelated by the carboxyl groups of the citric acid and remain homogeneously distributed in the solution. To create a rigid polyester net, the appropriate amount of ethylene glycol was added (the molar ratio of the glycol to citric acid was 1:1). The mixture was dried at 80 °C for 20 h with stirring and then heated at 110 °C in air for 5 days. During this time, the solution turned into yellowish gel which expanded several times of its original volume and, in the end, a brown resin was obtained as a result of the whole procedure. The resin was hard and transparent both for the double potassium–europium tungstate and for the double potassium–gadolinium tungstate.

In the next step, the decomposition of the obtained resin was performed. Pieces of the crushed resin were annealed in the air atmosphere at selected temperatures between 500 and 1000 °C for 1 h to obtain the white nanopowder tungstate. The time and temperature of the annealing procedure determines the size of the grains of desired nanomaterial. Single phases of potassium–europium double tungstate and potassium–gadolinium double tungstate with different crystallite sizes were the only final products for the temperatures exceeded about 550 °C. When the annealing temperature is lower, the polymeric decomposition is not complete and residual organic molecules are still present.

2.2. Experimental techniques

X-ray powder diffraction patterns were recorded at room temperature by using STADI-P powder diffractometer (STOE, Germany) working in the transmission geometry and equipped with a linear 140°-PSD detector. Cu$K\alpha_1$ radiation in the 2Θ range from 3.0° to 90.0° with a step of 0.03° was used.

The crystal structure analyses were made by the Rietveld method with the FullProf program using the profile function of pseudo-Voigt with axial divergence asymmetry [12,13]. The effective 2Θ-range was limited to 10–70°.

The average grain size was evaluated from the full width at half maximum (FWHM) of the diffraction peak using the Scherrer equation, which assumes the small crystallite size to be the only cause of X-ray line broadening [14–16]:

$$D = \frac{K\lambda}{\beta \cos \Theta}, \quad (1)$$

where D is the diameter of the crystallite (in the approximation of a spherical shape), λ is the X-ray wavelength (1.54056 Å), β is the FWHM of the diffraction line (in radians), Θ is the Bragg angle of diffraction peak, and the Scherrer constant K is conventionally set to 1.0 [17–21]. The contribution from instrumental broadening was removed by subtracting the FWHM of the corresponding line of well-annealed, bulk crystal using the Halder–Wagner parabolic approximate relation:

$$\beta = \frac{B - b^2}{B}, \quad (2)$$

where β is the FWHM of the true diffraction profile, B and b are the measured FWHM of the equivalent diffraction lines in the specimen and the reference (bulk) sample, respectively [17,20,22–24].

Vibrational spectra of the europium and gadolinium double tungstates were measured at room temperature as a function of the annealing temperature. Infrared spectra were measured with a Biorad 575C FT-IR spectrometer in KBr pellet for the 4000–400 cm^{-1} region and in Nujol suspension for the 500–50 cm^{-1} region. FT-Raman spectra were measured using Bruker RFS 100/S Raman spectrometer with the back scattering arrangement. The 1064 nm line of Nd:YAG laser was used as an excitation source. Signal detection was performed with an InGaAs detector. Both IR and Raman spectra were recorded with a spectral resolution of 2 cm^{-1}.

Optical spectra were recorded at ambient temperature. Reflection spectra were measured using a Cary 5E spectrophotometer with the Praying Mantis diffuse reflectance accessory. The resolution was 0.5 nm. Both the excitation and emission spectra were recorded using a Dongwoo Optron Model DM 711 spectrofluorymeter (South Korea), the spectral resolution of this apparatus was approximately of 0.5 nm. Scanning system consisted of 10 W xenon lamp as the excitation source and coupled with an excitation monochromator with 150 mm focal length and emission monochromator having 750 mm focal length was equipped with a photomultiplier and an InGaAs detector. The emission signal collected was very strong and measurements were not required any correction for the diffraction grating of the monochromator. Excitation spectra in the UV and visible region were corrected with emission spectra of the ozone-free Xe lamp.

3. Results and discussion

3.1. X-ray diffraction studies

The X-ray diffraction patterns for some annealing temperatures of the precursor are shown in Fig. 1. When the temperature was below 540 °C (not showing in Figure), only a mixture of oxide compounds was obtained. At 540 °C, the crystallisation of single phase KEW or KGEW begins because most of the diffraction patterns are sharp and intense. However, the residual organic molecules are still present. The annealing at higher temperature gives rise to crystals of pure phase tungstates with desired composition.

All powder diagrams show the diffraction lines corresponding to the reference crystal structure of $KGd(WO_4)_2$ [25,26]. Therefore, as the crystal structure of $KEu(WO_4)_2$ is not studied yet, we decided to solve them using the powder sample prepared from single crystal. The structure was successfully refined using the atomic parameters from $KGd(WO_4)_2$ crystal as the starting data [25,26]. Both crystals are fully isostructural. In the refinement, we used a non-standard setting $I2/c$ of the recommended $C2/c$ space group [27]. The atomic coordinates are given in Table 1 and selected interatomic distances in Table 2. Fig. 2 shows the final Rietveld plot with a good agreement between the observed and the calculated patterns. Similar structure refinements were made

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