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Optical and phonon properties of nanocrystalline $Al_2(WO_4)_3$ doped with chromium(III) prepared by co-precipitation method

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ABSTRACT

Pure and chromium(III) doped nanosized $Al_2(WO_4)_3$ was prepared by co-precipitation method. X-ray, transmission electron microscopy, vibrational, absorption and luminescence studies of the obtained nanoparticles are reported. The particle size of the obtained samples ranged from about 20 nm to a few hundreds of nm. Raman and IR studies showed that vibrational properties have been modified in comparison with the bulk material, indicating that with decreasing particle size some weak structural changes are induced in $Al_2(WO_4)_3$. The luminescence revealed that the prepared materials have similar properties as the bulk material and chromium(III) ions occupy sites of intermediate crystal field strength. Nevertheless, the obtained results indicate that the electron–phonon coupling slightly decreases with decreasing particle size.

1. Introduction

$B_2(XO_4)_3$ molybdates and tungstates, where B = Y, In, Sc, Al, Ga and X = Mo, W, have received considerable attention due to their negative thermal expansion (NTE) properties [1,2]. NTE properties are especially interesting for commercial application since they make these molybdates and tungstates promising materials for use in composites with tailored thermal expansion characteristics. In particular, materials with zero thermal expansion between −50 °C till about 100 °C are highly desired for optical devices [2]. These compounds have also been extensively studied due to interesting physical phenomena such as temperature- and pressure-induced phase transition into a ferroelastic phase and pressure-induced amorphization [3–6]. $Al_2(WO_4)_3$ doped with Cr(III) or rare earth ions has also been shown to exhibit attractive optical properties [7–9]. $Al_2(WO_4)_3$ can also be used for fabrication of an ion-selective electrode for Fe(III) determination in rocks, pharmaceuticals and water [10].

$Al_2(WO_4)_3$ crystallizes in the Pbcn structure [7,11] and this compound exhibits a ferroelastic phase transition below room temperature. The phase transition temperature was reported to be −6 °C [3], −63 °C [7] or −22 °C [11]. Symmetry of the ferroelastic phase was suggested to be $P2_1/a$ [3] or $P2_1/n$ [7]. Recent X-ray diffraction studies confirmed the $P2_1/n$ symmetry [11].

In the present paper synthesis and characterization of $Al_2(WO_4)_3$ doped with 1%, 2% and 3% of chromium(III) are reported. Bulk $Al_2(WO_4)_3$ doped with chromium(III) was previously studied by us [7]. These studies allowed to propose detailed assignment of vibrational modes and characterize properties of chromium(III) doped in this matrix. Since properties of materials can be strongly modified by size of crystallites, we have attempted to obtain nanocrystalline $Al_2(WO_4)_3$ doped with chromium(III) in order to investigate the influence of the grain size on luminescence, structural and phonon properties. Recently, co-precipitation method was successfully applied for synthesis of undoped $Al_2(WO_4)_3$ [12,13]. We will show in the present paper that this method can also be used for preparation of nanocrystalline aluminum tungstate doped with chromium(III).

2. Experimental

$Al_2(WO_4)_3$ doped with chromium(III) was prepared by mixing aqueous solutions of $Al(NO_3)_3{\cdot}9H_2O$ (p.a), $Cr(NO_3)_3{\cdot}9H_2O$ (p.a) and $Na_2WO_4{\cdot}2H_2O$ (p.a) (0.1 M). After stirring at room temperature for 10 h, the precipitate was collected, washed with distilled water and dried at 80 °C for 5 h. The obtained in this way precursors were heat-treated for 5 h at different temperatures ranging from 430 to 830 °C to obtain nanocrystalline $Al_2(WO_4)_3$ doped with chromium (III).

XRD patterns were recorded at room temperature by using X'Pert PRO powder diffractometer (PANalytical, The Netherlands)

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working in the reflection geometry, equipped with a linear PIXcel detector and using Cu $K\alpha_1$ radiation ($\lambda = 1.54056$ Å) in the 2Θ range from 5° to 90° with a step of 0.026°.

The particle size and morphology of prepared materials were observed using a 90 kV Tesla BS-500 transmission electron microscope (TEM). Specimens for TEM were prepared by grinding the samples in mortar and dispersing in methanol with ultrasonic agitation. A droplet of suspension was deposited on a microscope grid covered with carbon film.

Infrared spectra were measured with a Biorad 575C FT-IR spectrometer in KBr pellet for the 1200–400 cm^{-1} region and in Nujol suspension for the 500–50 cm^{-1} region. FT-Raman spectra were measured using BRUKER 110/S spectrometer with the YAG:Nd^{3+} excitation. Both IR and Raman spectra were recorded with a spectral resolution of 2 cm^{-1}.

The absorption spectra were registered on Jasco UV–VIS–NIR spectrophotometer.

The emission and excitation spectra were recorded on a SSF-01 spectrofluorimeter. The excitation source was a 150 W xenon lamp. The system response was calibrated with a standard tungsten–halogen lamp to correct the emission spectra. The experimental measurements were done with temperature variation between 10 and 300 K with aid of Oxford cryostat with continuous liquid helium flow.

3. Results

3.1. X-ray diffraction and TEM

Fig. 1 shows representative XRD patterns of the products after co-precipitation and subsequent thermal treatment at various temperatures ranging from 80 to 830 °C. As seen in this figure, the product at 80 °C is amorphous. The XRD patterns of the samples heat-treated at 430, 630 and 830 °C show presence of diffraction peaks characteristic for crystalline $Al_2(WO_4)_3$ (JCPDS Card No 24-1101). Significant broadening of all diffraction lines for the samples heat-treated at 430 and 630 °C clearly shows that the nanocrystalline phase of $Al_2(WO_4)_3$ is formed. Fig. 1 shows that the peaks become sharper with increase of synthesis temperature that implies that the particle size increases. When annealing temperature increases to 830 °C, broadening of XRD peaks become negligible, indicating fast growth of the crystallites at this temperature.

The particle size can be estimated from Scherrer's formula $D = K\lambda/\beta\cos\Theta$, where D is the mean crystallite size along the [hkl] direction, λ is the X-ray wavelength (in our study $\lambda = 1.54056$ Å), β is the FWHM of the diffraction line (in radians), Θ is the angle of diffraction, and the Scherrer constant K is conventionally set to 1.0 [14,15]. The calculated average size of the undoped $Al_2(WO_4)_3$ crystallites calculated from broadening of the 102 diffraction peak is about 29.2 and 68.1 nm for the samples synthesized at 430 and 630 °C, respectively. The sample doped with 3% of chromium(III) and annealed at 430 °C has similar size of crystallites (28.7 nm). However, the sample doped with 3% of chromium(III) and annealed at 630 °C is composed of significantly smaller crystallites (about 36.3 nm) than the corresponding undoped sample (68.1 nm).

TEM micrographs of the $Al_2(WO_4)_3$ sample synthesized at 430 °C show that the synthesized powder is composed of irregular particles with size of about 20–100 nm (see Fig. 2a). The distribution of the crystallite sizes is inhomogeneous. When synthesis is performed at 630 °C, size of the crystallites increases up to 40–300 nm (see Fig. 2b).

3.2. Raman and IR

The factor group analysis predicts that there should be 201 optical modes for the Pbcn room temperature structure of $Al_2(WO_4)_3$ distributed among $25A_g + 26B_{1g} + 25B_{2g} + 26B_{3g} + 25A_u + 25B_{1u} + 24B_{2u} + 25B_{3u}$ irreducible representations of the factor group D_{2h} [7]. Selection rules state that all "g" modes are Raman-active, B_{1u}, B_{2u} and B_{3u} modes are IR-active and A_u modes are silent. Our previous studies of large crystals prepared by solid state reaction of respective oxides showed that the number of observed modes is much smaller than expected for the Pbcn structure because the factor group splitting is very small for majority of modes [7]. Our results showed also that the Raman and IR bands in the 830–1050 cm^{-1} range can be assigned to stretching modes of the WO_4 tetrahedra [5,7]. Bands in the 270–470 cm^{-1} range correspond to bending modes of the WO_4 tetrahedra coupled with translational motions of Al(III) and the bands below 270 cm^{-1} can be assigned to translational and librational motions of the WO_4 tetrahedra [5,7].

The evolution of Raman and IR spectra of pure and chromium(III) doped $Al_2(WO_4)_3$ with the annealing temperature (crystallite size) is presented in Figs. 3–5. For the comparison, the

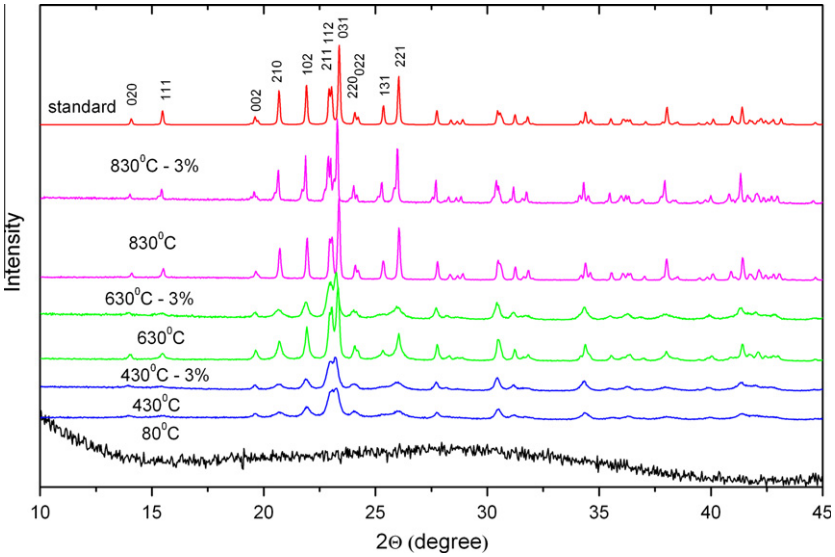

Fig. 1. X-ray powder diffraction patterns of precursor (80 °C) and nanocrystalline $Al_2(WO_4)_3$ samples. The standard pattern of $Al_2(WO_4)_3$ is presented at the top.