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Structural and optical characterization of hemimorphite with flower-like morphology synthesized by a novel low-temperature method

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ABSTRACT

We report on novel, low temperature synthesis of well crystallized hemimorphite zinc silicate $Zn_4Si_2O_7(OH)_2(H_2O)$ (ZSO) with flower-like morphology, via one-pot method that includes the assistance of a non-ionic block copolymer. The morphology of the synthesized ZSO powder was observed by SEM and FESEM. The structure of the ZSO sample was refined down to the *R*-factor of 8.6%. The refinement revealed the ZSO powder that belongs to the orthorhombic system with space group Imm2, and ZnO nanoparticles as a minor phase in the synthesized powder. The photoluminescence (PL) and diffuse reflectance spectroscopy (DRS) measurements demonstrated optical properties of the minor ZnO phase.

1. Introduction

Zinc silicate (ZSO), a representative member of the family of silicate compounds, has attractive features and thus is suitable for various applications in coating [1], in protecting steel from corrosion [2], in cathode ray tubes [3], as a host for up conversion of luminescent materials [4], as catalyst [5], etc. Hemimorphite (ZSO), one of the three crystalline phases formed by zinc silicates, belongs to the orthorhombic system with space group Imm2 [6,7]. A unique synthetic route that can provide high quality materials regarding their morphology and crystallinity, with enhanced properties (photoluminescent and catalytic) for improved performance in some fields, has not yet been developed and remains a challenge.

In this paper, we have described a novel low temperature synthetic method for the production of well crystallized ZSO powders, with minor ZnO content. The properties of the ZSO powder were studied in detail using scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) with energy dispersive spectroscopy (EDS), X-ray powder diffraction (XRPD), photoluminescence (PL) and UV–vis diffuse reflectance spectroscopy (DRS).

2. Experimental procedure

All chemicals ($Na_2WO_4 \cdot 2H_2O$ (Riedel-de Haën 99%), $ZnCl_2$ (Merck 99%), non-ionic surfactant Pluronic F68 (polyoxyethylene–polyoxypropylene block copolymer, $M_n \sim 8400$ (Aldrich)) and NaOH (Fluka 98%)) were of the highest purity available.

Typically, 50 ml of 0.1 M $ZnCl_2$ solution was mixed with 100 ml of copolymer solution (10 g/l). The pH was adjusted to 12 with 0.1 M NaOH solution [8]. As a source of Si small glass balls were added into the flask. Then, under vigorous stirring, 50 ml of 0.1 M $Na_2WO_4 \cdot 2H_2O$ was added dropwise. After that, the mixture was refluxed at 95 °C for 120 h. During the reflux, precipitation of ZSO took place. The precipitated ZSO powder was separated from the solvent containing copolymer immediately after synthesis by ultracentrifugation. The precipitate was centrifugally washed with ethanol and distilled water and then annealed at 95 °C for 18 h. It should be emphasized here that Na_2WO_4 allowed at relatively high pH and heating time the release of Si from small glass balls without participating in the reaction and the precipitation of ZSO (see text below). In the absence of Na_2WO_4, however, even if the small glass balls are present, ZSO cannot be obtained. To confirm that the heating time is not responsible for the crystallinity of the synthesized sample or the remained ZnO phase in it, the heating was prolonged (120 h).

The scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6460LV instrument. The field emission scanning electron microscopy (FESEM) ones by a TESCAN Mira3 XMU at 20 kV.

The chemical composition of the sample was analyzed using an Isis 3.2 energy dispersive spectrometer (EDS), with a SiLi X-ray detector connected to an SEM JEOL JSM-5800 and a computer multi-channel analyzer.

Diffuse reflectance spectra (DRS) of the ZSO pellet were obtained using a Thermo Scientific Evolution 600 UV–vis spectrophotometer.

Photoluminescence (*PL*) spectra of the ZSO pellet were recorded on a Fluorolog-3 Model FL3-221 spectrofluorometer system (Horiba Jobin-Yvon), using a 450-W xenon lamp as the

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excitation source and a R928 photomultiplier tube as the detector.

The X-ray powder diffraction (XRPD) pattern was obtained on an automated Philips PW-1050 X-ray diffractometer using CuK_α radiation (operated at 40 kV and 30 mA). Diffraction data for structural analysis were collected in the 2Θ range of 10–110°, count time for 12 s/step and step size of 0.02°. Structure analysis was done by the use of the KOALARIE computing program [9] based on the Rietveld full profile refinement method [10]. The sample for XRPD measurement was prepared following the standard protocol [11].

3. Results and discussion

The morphology and microstructure of the ZSO powder were studied by SEM and FESEM. Low magnification images (Fig.1A and B) reveal the ZSO structure composed of nanorod and nanoleaf bundles with bush-like forms between them, and all assembled in floral arrangements. Similar morphologies for ZSO have already been observed [12,13]. High magnification SEM and FESEM images (not given here) show local population of small nanoparticles of undefined shapes. This is in accordance with the structural analysis, which revealed the presence of ZnO as the minor phase with nanocrystallites in the ZSO synthesized powder (see text below).

Fig. 2 shows the SEM microstructure and EDS analysis of the ZSO powder. The results confirmed, detecting only Zn, O and Si, the purity of our samples. The absence of tungsten proves that Na_2WO_4 present at relatively high pH and heating time allows the release of Si from small glass balls and that it does not take part in the precipitation of the ZSO powder.

Optical properties of the ZSO powder were studied using a combination of PL and DRS techniques. Fig. 3A shows the emission spectra of ZSO sample with the minor phase being ZnO, at different excitation energies (3.54 eV (a), 3.87 eV (b) and 4.13 eV (c)). The PL spectra show significant peak broadening and strong emission between 2.24 and 3.8 eV with maxima around ~3 eV. Broad emission bands were then fitted to the Gaussian peaks for a better understanding of the contribution from various kinds of defects or phases. The PL spectrum excited at 3.54 eV (a) was fitted to three Gaussian peaks centered at 3.14, 2.92 and 2.67 eV. The broad luminescence band excited at 3.87 eV (b) was fitted to four Gaussian bands peaked at 3.25, 3.15, 2.84 and 2.78 eV. The last PL spectrum excited at 4.13 eV (c) was fitted to four Gaussian bands peaked at 3.66, 3.25, 2.91 and 2.67 eV. Sun et al. [12] found that the PL spectra of ZSO consist of a strong emission peak located at 2.84 eV and several weak ones at 3.25, 2.97 and

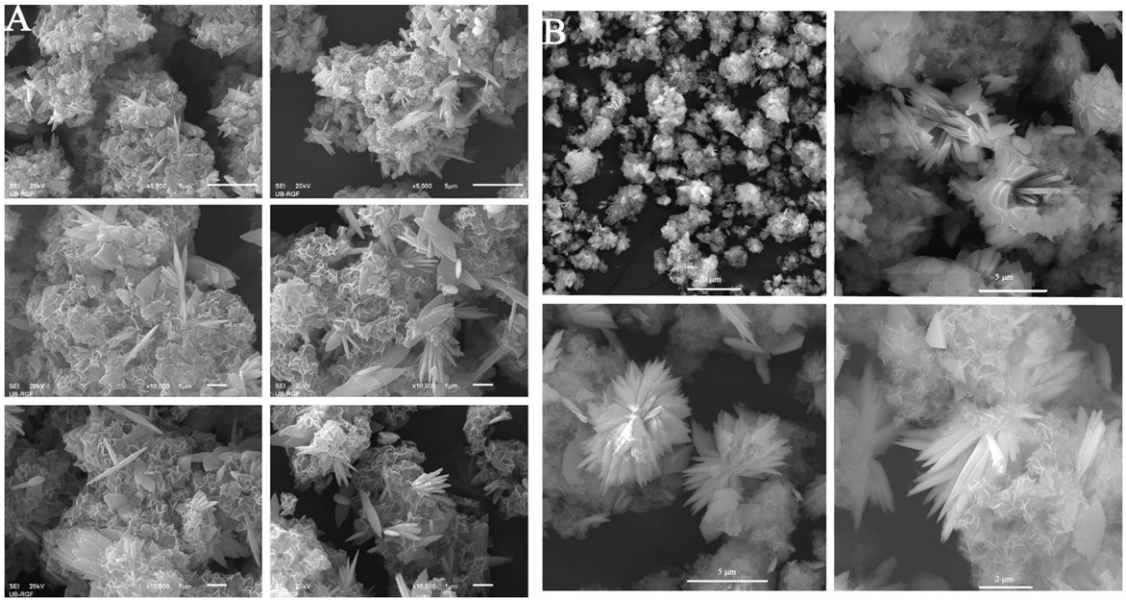

Fig. 1. SEM (A), bars: first row 5 μm the other two rows 1 μm; and FESEM (B), bars: up left 20 μm, up right and down left 5 μm, down right 2 μm; micrographs of the ZSO structure.

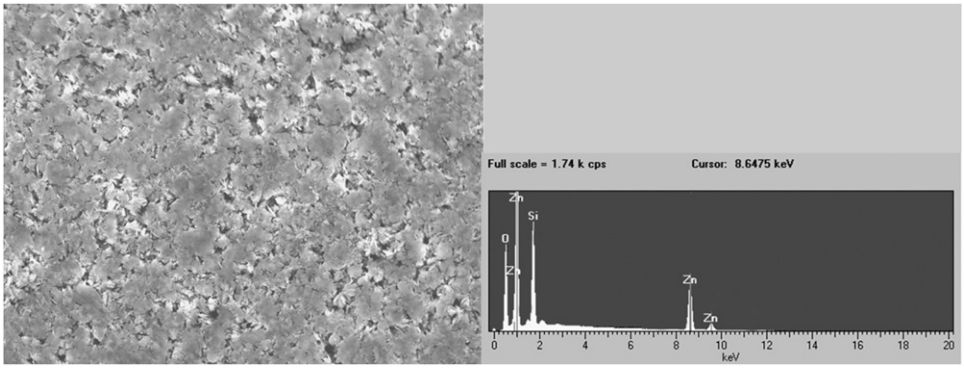

Fig. 2. SEM microstructure and EDS analysis of the ZSO powder.