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Microwave-Assisted Solvothermal Synthesis of $Sr_3V_2O_8$ Nanoparticles and Their Spectroscopic Properties†

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The $Sr_3V_2O_8$ nanoparticles have been synthesized successfully *via* microwave-assisted solvothermal route followed by heat-treatment. Well-crystallized $Sr_3V_2O_8$ nanoparticles with a fine and homogeneous morphology and the particle size of 100-150 nm have been formed after annealing at 600 ºC for 3 h. The $Sr_3V_2O_8$ nanoparticles have been characterized by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy and transmission electron microscopy. The optical properties have been investigated by photoluminescence emission and Raman spectroscopy.

Keywords: $Sr_3V_2O_8$, Microwave-assisted solvothermal, Nanoparticles, Luminescence, Raman spectroscopy.

INTRODUCTION

Metal orthovanadates have attracted considerable attention for potential applications in nanophotonics, IR-laser systems, light-emitting diodes, photocatalysis, ferroelectric and microwave devices[1-3]. Several processes have been developed over the past decade to enhance the applications of $Sr_3V_2O_8$ prepared by a range of processes, such as a solid-state reaction[4,5], the solution phase metathetic method[6], the sol gel method[7], the solid-state metathesis approach[8], the mechano-chemical method[9] and the floating zone technique[10]. Among different methods, solution-based chemical synthetic methods play the key role in the design and production of fine oxide powders and are successful in overcoming many limitations of traditional solid-state high temperature methods[11-16]. As compared to common methods, the microwave synthesis technique provides such advantages as a very short reaction time, small particle size, narrow particle size distribution and it is the high purity method suitable for the preparation of polycrystalline products. The microwave heating is delivered to the surface of the material by radiant and/or convection heating, which is transferred to the bulk of the material *via* conduction. So, the microwave energy is delivered directly to the material through the molecular interactions with electromagnetic field. Heat can be generated through volumetric heating because microwaves can penetrate the material and supply energy[17].

Hydrothermal synthesis is an efficient low-temperature method which allows one to form the nano- or microparticles with a high degree of crystallinity and easy dispersion in an aqueous medium. The use of microwave energy in a hydrothermal system promotes the development of a rapid heating to the temperature required for the complex oxide crystallization[18,19]. Bi *et al.*[20] and Thongtem *et al.*[21] have reported the method applicable for the preparation of nanocrystalline metal tungstate particles with enhanced properties by an MAS (microwave-assisted solvothermal) process. The solvothermal technique is one of the most powerful method employed for the crystallization of various unique nanoparticles[22-24]. The solvothermal process is the reaction of a hot solution within or on the surface of a substance. Ethylene glycol, as a polar solvent with a relatively high boiling point of 197 ºC, is a good candidate for the MAS process. When ethylene glycol is used as a solvent, the reactions are produced in a sealed pressure autoclave at the temperatures near the boiling point of ethylene glycol. The microwave radiation is supplied to the ethylene glycol so that the components dissolving in the ethylene glycol are capable of coupling with the radiation. When a large amount of microwave radiation is applied into the ethylene glycol under a high sealed pressure, the charged particles are vibrated in the electric field interdependently. Therefore, it is possible to achieve rapid and uniform heating

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of microwave dielectric materials. An MAS process using ethylene glycol as a solvent is a convenient process that provides a high-qualified yield with a cost-effective balance and for short time periods.

However, the MAS process of $Sr_3V_2O_8$ nanoparticles was not being evaluated previously. Therefore, the precise observation of the optical properties and the MAS process of $Sr_3V_2O_8$ nanoparticles are required for a wide range of possible applications. In the present study, the $Sr_3V_2O_8$ nanoparticles were synthesized using an MAS reaction in ethylene glycol under the high sealed pressure. The characteristics of the synthesized $Sr_3V_2O_8$ nanoparticles are discussed in detail. The final $Sr_3V_2O_8$ nanoparticles product was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM). The optical properties of the oxide were examined by photoluminescence (PL) emission and Raman spectroscopy.

EXPERIMENTAL

$SrCl_2·6H_2O$, Na_3VO_4 and ethylene glycol of the analytical reagent grade (Aldrich) were used as starting reagents in the preparation of the $Sr_3V_2O_8$ compound. A mixture of 0.012 mol $SrCl_2·6H_2O$ and 0.008 mol Na_3VO_4 was dissolved in 30 mL ethylene glycol. The solution was prepared and adjusted to a pH 9.5 using NaOH. Then, the solution was stirred in an ultrasonic bath at room temperature. After this, the mixture was transferred into a Teflon-lined digestion vessel of 120 mL capacity. The Teflon vessel was placed into a MAS oven (2.45 GHz, maximum power 800 W). The MAS conditions were being kept at 200 ºC for 23 min. After the MAS process, the oven was cooled to room temperature. The resulting solution was treated with ultrasonic radiation and washed many times with distilled hot water. The white precipitate was collected and dried at 100 ºC in an oven. Finally, the powder product was being heated at 600 ºC for 3 h.

The phase composition of the $Sr_3V_2O_8$ particles after the MAS process was identified by powder XRD (CuK_α radiation, Rigaku D/MAX 2200, Japan). The microstructure, particle morphology and qualitative chemical composition of the $Sr_3V_2O_8$ particles were observed by SEM (JSM-5600, JEOL, Japan), EDS and TEM (JEM 2000-FX, 250 kV, Japan). The photoluminescence spectra were recorded using a spectrophotometer (Perkin Elmer LS55, UK) at room temperature. Raman spectroscopy measurements were performed using LabRam HR (Jobin-Yvon, France). The 514.5 nm line of an Ar-ion laser was used as the excitation source and the power was kept at 0.5 mW on the samples.

RESULTS AND DISCUSSION

The XRD pattern of the synthesized $Sr_3V_2O_8$ nanoparticles is shown in Fig. 1. All the observed diffraction peaks can be assigned to the trigonal phase (space group R-3m), which is in good agreement with the crystallographic data of $Sr_3V_2O_8$ (JCPDS: 81-1844)[8]. This indicates that the trigonal phase of $Sr_3V_2O_8$ can be successfully prepared using the MAS route. So, the MAS synthesis is suitable for the growth of $Sr_3V_2O_8$ crystallites and the development of the strongest intensity peaks

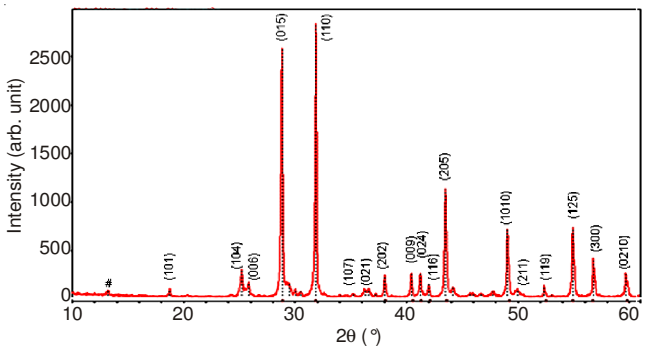

Fig. 1. XRD pattern of the synthesized $Sr_3V_2O_8$ nanoparticles

from the (015), (110) and (205) planes, which are the major peaks of trigonal $Sr_3V_2O_8$, with some preferred orientation. A small component of NaCl was observed at 13.2º and marked with #. The MAS process occurs in accordance with the reaction: $3SrCl_2·6H_2O + 2Na_3VO_4 \rightarrow Sr_3V_2O_8 + 6NaCl + 18H_2O$. Respectively, the residual NaCl can be captured from the solution during $Sr_3V_2O_8$ precipitation.

The SEM and TEM patterns recorded from the $Sr_3V_2O_8$ nanoparticles are shown in Fig. 2. The SEM image displays the well-defined and homogeneous micromorphology of $Sr_3V_2O_8$ nanocrystals, while the TEM measurements indicate the particle size in the range of 100-150 nm. The MAS synthesis proceeds the reaction of $3SrCl_2·6H_2O$ and Na_3VO_4 species in a hot ethylene glycol solution taken as a polar solvent with the boiling point of 197 ºC. When the microwave radiation is supplied to ethylene glycol under a sealed pressure and at the boiling point, the components dissolving in the ethylene glycol are charged and vibrated in the electric field interdependently. The MAS process is adjusted to heat the metal orthovanadates uniformly and that results in the formation of fine particles with controlled morphology. This permits to fabricate the powder product in a green manner and without drastic generation of the solvent waste.

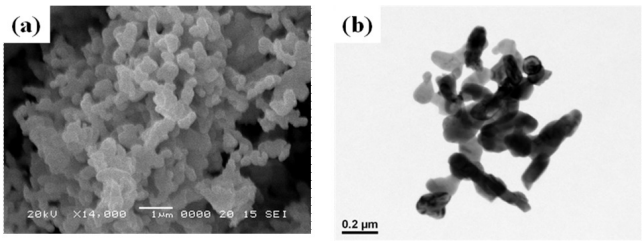

Fig. 2. (a) SEM image and (b) TEM image of the synthesized $Sr_3V_2O_8$ nanoparticles

The MAS reaction involves the exchange of atomic/ionic species, where the driving force is the exothermic reaction in ethylene glycol accompanying the formation of NaCl with a high lattice energy. The MAS reaction occurs so rapidly that the temperature and the pressure of ethylene glycol increases so quickly that the reaction products are essentially heated up. So, the MAS reactions provide a convenient route for the synthesis of $Sr_3V_2O_8$ nanoparticles at considerably lower temperatures and at a higher pressure in comparison with the conditions usually employed for the synthesis. The well-defined $Sr_3V_2O_8$ nanoparticle parameters, when the oxide is

synthesized by the MAS process, are a valuable feature of this method that can be used in technological applications.

The photoluminescence emission spectrum of the $Sr_3V_2O_8$ nanoparticles excited at 250 nm at room temperature is shown in Fig. 3. The emission spectra of metal orthovanadates are due mainly to charge-transfer transitions within the $[VO_4]^{3-}$ complex. Under the excitation at 250 nm, the $Sr_3V_2O_8$ nanoparticles exhibit major photoluminescence emissions in the blue wavelength range of 420-430 nm. The spectrum shows a broad band with several fine structures.

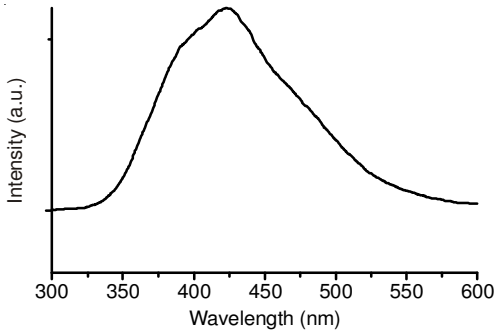

Fig. 3. Photoluminescence emission spectrum of the synthesized $Sr_3V_2O_8$ nanoparticles excited at 250 nm at room temperature

Raman spectrum of the $Sr_3V_2O_8$ nanoparticles is shown in Fig. 4. The peaks are narrow and verifies high crystallinity of the final powder product. The vibration modes in the Raman spectra of $Sr_3V_2O_8$ nanoparticles can be divided into two groups-internal and external. The internal vibrations are related to the $[VO_4]^{3-}$ molecular groups with a stationary mass center[25,26]. The external vibrations or lattice phonons are associated with the motion of the Sr^{2+} cations and rigid molecular units. The Raman modes for the $Sr_3V_2O_8$ nanoparticles were classified as $\nu_1(A_g)$, $\nu_3(B_g)$, $\nu_3(E_g)$, $\nu_4(E_g)$, $\nu_4(B_g)$ and $\nu_2(B_g)$ vibrations at 860, 855, 785, 396 and 329 cm^{-1}, respectively. The free rotation mode was detected at 180 cm^{-1} and the external modes were localized at 146 and 127 cm^{-1}.

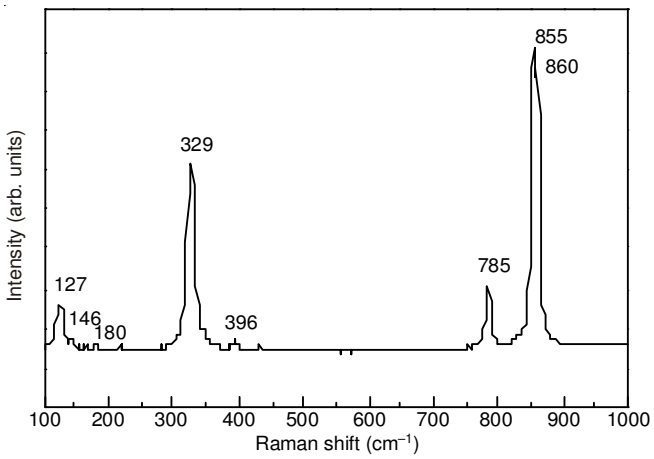

Fig. 4. Raman spectrum of the synthesized $Sr_3V_2O_8$ nanoparticles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the samples

Conclusion

The $Sr_3V_2O_8$ nanoparticles were synthesized successfully using an MAS route in a hot ethylene glycol solution as a polar solvent. Well-crystallized $Sr_3V_2O_8$ nanoparticles were formed after heating at 600 ºC for 3 h. The final powder product showed a fine and homogeneous micromorphology with the particle size of 100-150 nm. With excitation at 250 nm, $Sr_3V_2O_8$ exhibits the major photoluminescence emissions over the blue wavelength range of 420-430 nm. Raman modes of the $Sr_3V_2O_8$ nanoparticles were detected at 860, 855, 785, 396 and 329 cm^{-1}, the free rotation mode was detected at 180 cm^{-1}, and the external modes were localized at 146 and 127 cm^{-1}. The well-resolved sharp peaks for the $Sr_3V_2O_8$ nanoparticles indicate that the synthesized particles are highly crystallized. Generally, it can be concluded that the MAS synthesis in the ethylene glycol solution can be developed for the preparation of the complex $Sr_3V_2O_8$-based oxide compositions and rare-earth-activated orthovanadates.

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