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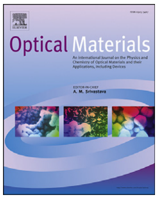

$ZnMoO_4:Er^{3+},Yb^{3+}$ phosphor with controlled morphology and enhanced upconversion through alkali ions doping

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ABSTRACT

A facile hydrothermal method was used to synthesize $ZnMoO_4:Er^{3+},Yb^{3+}$ nanoparticles. The shapes and sizes of the nanoparticles were well tuned by simply monitoring the pH of the starting solution. Microballs consisting of agglomerated nanograins were observed at strong acidic condition. At mild pH, plates and rectangular particles were realized, while strong basic pH stabilized rods. Further increasing pH to extremely basic conditions ($pH > 13$), rods changed to fragile hairy structures. The nucleation and growth mechanism of nanograins to form different morphology nanoparticles were studied and illustrated. XRD patterns confirmed well crystalline, triclinic structure despite small amount of aliovalent metal ions doping. Under 980 nm excitation, the $ZnMoO_4:Er^{3+},Yb^{3+}$ nanophosphor exhibited strong green (centered at 530 and 560 nm) and weak red (centered at 660 nm) upconversion (UC) emissions. Substitution of part of the Zn^{2+} ions by monovalent alkali ions intensified the UC emission intensities drastically. The order of intensification was $K^+ > Na^+ > Li^+ > Rb^+ >$ no alkali ion. When Zn^{2+} ions were substituted with 10 at% K^+ ions, the green and red UC emissions intensities increased by more than 50 and 15 folds, respectively. Time dependent measurements confirmed efficient Yb to Er energy transfer in the $ZnMoO_4:Er^{3+},Yb^{3+},K^+$ nanophosphor. The optimized $ZnMoO_4:Er^{3+},Yb^{3+},K^+$ phosphor exhibited intense UC emissions with 0.31% quantum yield. The upconverted light is visible to naked eye while pumping by laser of less than 1 mW power and opens door for variety of novel applications.

1. Introduction

Photon upconversion (UC) involves absorption of two or more low energy photons to generate a single high energy photon by an anti-Stokes process and possesses great promise for a broad range of applications [1,2]. Since its discovery in the 1960s, tremendous researches were carried out in this field due to their several potential applications, some of them are in solar cells [3], novel display technologies [4,5], inks for secure printing [6], optical communications and amplifiers [7], high density optical storage [8], infrared detection and sensors [9], and more recently bio-medical diagnosis and therapies [10].

One of the promising applications of the upconverting nanomaterials is their use in the solar cell industries to improve the conversion efficiency of the present solar cells [3,11–13]. Solar radiations with energies below the band gap of a semiconductor are not absorbed thus large fraction of sunlight is being wasted by present solar cell devices. Thus, efficiency of the present solar cells can be expected to increase remarkably if such unused solar radiations are utilizing properly. Upconverting nanomaterials, which can utilize low energy photons below the bandgap of such semiconductors and emit at the optimal spectral response range of solar cells, are promising candidates to increase the solar cell efficiencies. Further, optimization of upconverters and solar cells can be done simultaneously and just making a layer of upconverters at the rare face of the solar cells, improved device performance is possible. Fisher et al. demonstrated nearly 0.55% improved conversion efficiency of the crystalline silicon (c-Si) solar cell by applying $BaY_2F_8:Er^{3+}$ upconverter layer at the rare face. Efforts have also been made for the efficiency improvement of the GaAs- and Dye sensitized solar cells and remarkable increments were demonstrated [14,15]. Above literature suggest that use of upconverters is

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a promising way to increase the efficiency of various types of solar cells. However, improvements on the solar cell efficiencies are directly dependent on the UC emission efficiencies of the nanophosphors. Further, particles morphology and size distributions of the nanophosphors greatly affect the device assembly and their performances. Thus, development of highly efficient, environmentally resistant nanophosphors having narrow particles size distribution and low excitation threshold is desirable. Although there are lots of reports on the fluoride based upconverters, limited efforts have been made on oxide based upconverters due to their low upconversion efficiencies. Oxide hosts are usually chemically, mechanically and thermally stable and could therefore be promising host for the light UC if their efficiencies are addressed properly.

Another promising application of upconverting nanomaterials is their use in novel display devices and sensors [16]. With the advent of cheap laser diodes, the UC of infrared radiation by combinations of suitable Ln^{3+} ions is of current interest. For smart display applications, high brightness with continuous emissions in the full visible spectrum is desired. In addition, they should be resistant to photo-bleaching and harsh environment. However, present upconverting nanomaterials severely suffered from their low emission efficiencies needing high power lasers to be visualized to the human eye which is not permitted from the safety point of view. To increase the emission efficiency, several attempts have been made such as, codoping with sensitizer ions [17,18], crystal surface coating [19,20], core/shell synthesis [21,22], metal plasmon resonance [23,24], codoping with different metal ions [2,25–28], and many more. However, none of these efforts have achieved the desired level of UC efficiency enhancement. Ideally, upconverted emission should be well visualized while pumped by as low as 1 mW laser power to maintain the safety concern. Hence, the UC luminescence intensity enhancement of nanomaterials is still challenging topic.

The UC intensity is mainly governed by following three factors: (1) phonon energies of the host lattices, higher the phonon energies more pronounced is the nonradiative loss by coupling with the transient energies of the active ions and hence lower the emission efficiencies (2) the energy transfer rate from sensitizers (*e.g.,* Yb^{3+}), to emission centers (*e.g.,* Er^{3+}), which intern depends on the extent of overlap between the transition dipoles of these two ions [29,30], and (3) the local environment of RE^{3+} ions in the host lattice which directly affects the absorption and emission probabilities. The $4f$–$4f$ transitions of RE^{3+} ions are partially forbidden [31]. The crystal field, which is responsible for breaking the selection rule of the forbidden f–f transitions, originates from the atoms surrounding the RE^{3+} ions. According to the Judd-Ofelt theory, the transition probabilities within the $4f$ electronic states can be enhanced by tuning the crystal filed asymmetry around the central metal ions [32]. For instance, Huang et al. improved the UC emission intensity of the $NaYF_4$:Er, Yb phosphor by small amount of Sc^{3+} ions doping [33]. The smaller Sc^{3+} ions occupies the bigger Y^{3+} site in the $NaYF_4$ lattice and lowers the local symmetry around the Er^{3+} emission center resulting a higher UC intensity. Recently, Singh et al. summarized the PL emission enhancement of the rare earth doped phosphors by various aliovalent ions codoping and explained the outlining phenomena [34]. We have also made efforts to intensify the emission intensities of various phosphors by alkali ions codoping [2,18,26–28,35–37]. We have realized more than 50 fold increased UC emission intensity in the Er^{3+} and Tm^{3+} doped $CaMoO_4$, $ZnMoO_4$ and $CaTiO_3$ phosphors by codoping with alkali ions.

In the past few years, lots of efforts have been made to control the particles morphology and dimensions without altering the luminescence efficiencies. However, when the particles dimensions reduced to nanometres scales, the luminescence intensity dramatically decreases due to presence of large numbers of surface defects in the nanomaterials [38]. Thus, synthesis of efficient upconverting nanophosphors is utmost essential for the practical applications. Herein, we report well tuning of particles morphology using a very simple hydrothermal method and more than 50 fold increased UC emission intensity by engineering the crystal symmetry around the central ions to improve the f-f transitions probabilities. Detail synthetic procedures, controlled morphologies, mechanism of different particles shape and sizes formation and UC emission enhancement according to the particles morphologies and aliovalent ions codoping will be discussed in detail.

2. Experiments

2.1. Synthesis of samples

The $ZnMoO_4$:RE^{3+},Yb^{3+} nanophosphors were prepared by simple hydrothermal process. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), Erbium nitrate pentahydrate ($Er(NO_3)_3.5H_2O$), Ytterbium nitrate pentahydrate ($Yb(NO_3)_3.5H_2O$), Alkali hydroxides, Ammonium molybdate ($(NH_4)_2MoO_4$), and Cetrimonium bromide (CTAB) were purchased from Sigma-Aldrich Japan. All the chemical are of reagent grade and used without further purification. In a typical hydrothermal reaction, 10 mM mixture of (Zn/Yb/Er) was prepared in 0.1 M CTAB solution with constant stirring. In a separate beaker, 10 mM solution of $(NH_4)_2MoO_4$ was prepared in distilled water. Then, 15 ml 10 mM molybdenum solution was slowly added to the 15 ml of metal-CTAB complex prepared above with constant stirring. After complete mixing, 40 mM urea (2.4 g) was added as precipitating agent. Final pH of the resulting solution was adjusted to desired value by adding ammonia and/or nitric acid. Five sets of samples were prepared changing the pH; namely, at strong acidic pH ~1, slightly acidic pH ~6, moderate basic pH ~9, strong basic pH ~12 and extreme basic $pH > 13$. For each set of experiments, 30 ml of the mixture was poured into a 50 ml Teflon lined stainless steel autoclave and kept at 180 °C for 24 h. The white solid obtained was centrifuged, washed multiple times with distilled water until the pH reached nearly neutral followed by washing with ethanol and freeze dried. Since as prepared hydrothermal products, especially oxides, contain surface hydroxyl groups that reduce the luminescence properties by creating the quenching pathways, each samples were further calcined at 500 °C for 3 h to get the final crystalline $ZnMoO_4$:Er^{3+},Yb^{3+} phosphors. Alkali ions substituted $ZnMoO_4$:Er^{3+},Yb^{3+} samples were prepared as above by substituting equivalent amounts of Zn sites with the alkali ions.

2.2. Characterizations

Phase identification was carried out using a Shimadzu XRD-6300 instrument with a Cu-Kα radiation. The morphology of the phosphor particles were observed using Hitachi-S3000 N scanning electron microscope (SEM). Elemental analysis was carried out using EDX coupled with SEM. Before SEM measurements, each sample was coated roughly 5 nm in thickness with platinum-palladium using Hitachi E−1030 ion sputter. UC emission spectra pumped by a 980 nm cw laser (0–200 mW) were recorded using USB 4000 UV-VIS-NIR miniature fiber optic spectrometer (Ocean optics). CIE 1931 color chromaticity values were obtained using BW TEK spectrometer and $BaSO_4$ as a white standard. Absorption spectra were measured using an integrating sphere. The quantum yield (QY) of nanophosphor in powder form was measured using an Otsuka Photal QE-2100 instrument consisting of an integrating sphere (MCPD-9800; 3095C) and a power tunable 980 nm laser. An