Abstract

Lu$^{3+}$/Yb$^{3+}$ and Lu$^{3+}$/Er$^{3+}$ co-doped Sb$_2$Se$_3$ nanomaterials were synthesized by co-reduction method in hydrothermal condition. Powder X-ray diffraction patterns indicate that the Ln$_x$Ln$_{0.00-0.04}$Sb$_{2-x}$Se$_3$ Ln: Lu$^{3+}$/Yb$^{3+}$ and Lu$^{3+}$/Er$^{3+}$ crystals are isostructural with Sb$_2$Se$_3$. The cell parameters were increased for compounds upon increasing the dopant content ($x$). Scanning electron microscopy and transmission electron microscopy images show that co-doping of Lu$^{3+}$/Yb$^{3+}$ ions in the lattice of Sb$_2$Se$_3$ produces nanorods, while that in Lu$^{3+}$/Er$^{3+}$ produces nanoparticles, respectively. The electrical conductivity of co-doped Sb$_2$Se$_3$ is higher than that of the pure Sb$_2$Se$_3$ and increases with temperature. By increasing the concentration of Ln$^{3+}$ ions, the absorption spectrum of Sb$_2$Se$_3$ shows red shifts and some intensity changes. In addition to the characteristic red emission peaks of Sb$_2$Se$_3$, emission spectra of co-doped materials show other emission bands originating from $f$-$f$ transitions of the Yb$^{3+}$ ions.

Keywords: Co-doped, Nanomaterial, Luminescent, Electrical conductivity, Hydrothermal

Background

Nanosized semiconductor materials have drawn much research attention because their physical and chemical properties, due to size quantization effect, dramatically change and, in most case, are improved as compared with their bulk counterparts [1-3]. Rare earth-substituted compounds with various compositions have become an increasingly important research topic in diverse areas, such as luminescent device, light-emitting displays, biological labeling, and imaging [4-6], due to the introduction of dopant levels within the bandgap and modification of the band structure. In addition, significant efforts have been devoted to enhance the activity of wide bandgap photocatalysts by doping for environmental remediation [7,8]. Semiconductor selenides find applications as laser materials, optical filters, sensors, and solar cells. Antimony selenide, an important member of these $V_2VI_3$ compounds, is a layer-structured semiconductor of orthorhombic crystal structure and exhibits good photovoltaic properties and high thermoelectric power, which allows possible applications for optical and thermoelectronic cooling devices [9-11]. The research of impurity effects or doping agents on the physical properties of Sb$_2$Se$_3$ is interesting both for basic and applied research. Doping of some transition metal and lanthanide to the lattice of metal chalcogenides has been investigated [12-20]. The incorporation of large electropositive ions such as lanthanides into metal chalcogenide frameworks is expected to affect the electronic properties of that framework. In this work, we report the preparation, structural, electrical, and optical properties of Lu$^{3+}$/Yb$^{3+}$ and Lu$^{3+}$/Er$^{3+}$ co-doped antimony selenide via co-reduction method at hydrothermal condition.

Methods

All chemicals were of analytical grade and were used without further purification. Gray selenium (1 mmol) and...
NaOH (5 mmol) were added to distilled water (60 mL) and stirred well for 10 min at room temperature. Afterwards, hydrazinium hydroxide (2 mL, 40 mmol), SbCl₃ (1.98, 1.96, 1.94, and 1.92 mmol) and Ln₂O₃ (0.00, 0.01, 0.02, and 0.04 mmol) (Ln: Lu³⁺, Yb³⁺, Er³⁺) based on the molecular formula LnₙLn₀°ₙSb₂⁻ₓSe₃ (0 ≤ x ≤ 0.04) were added, and the mixture was transferred to a 100-mL Teflon-lined autoclave. The autoclave was sealed, maintained at 180°C for 48 h, and then cooled to room temperature. The optimum conditions for this reaction are pH = 12, temperature = 180°C, and reaction time = 48 h. The black precipitate obtained was filtered and washed with ethanol and water. It was dried at room temperature. Yields for the products were 75% to 85%. Phase identification was performed by powder X-ray diffraction (XRD, D5000 Siemens AG, Munich, Germany) with Cu Kα radiation. Cell parameters were calculated using the Celref program (CCP14, London, UK) from powder XRD patterns, and reflections have been determined and fitted using a profile fitting procedure with the WinXPOW program (STOE & CIE GmbH, Darmstadt, Germany). The reflections observed in 2θ = 4° to 70° were used for the lattice parameter determination. The morphology of materials was examined by scanning electron microscopy (SEM, Hitachi S-4200, Hitachi High-Tech, Minato-ku, Tokyo, Japan). A linked ISIS-300 Oxford EDS detector (Oxford Instruments plc, Oxfordshire, UK) was used for elemental analyses. The high-resolution transmission electron microscopy (HRTEM) image and selected area electron diffraction (SAED) pattern were recorded by a Cs-corrected HRTEM (JEM-2200FS, JEOL Ltd., Akishima, Tokyo, Japan) operated at 200 kV. Photoluminescence measurements were carried out using a Spex FluoroMax3 spectrometer (HORIBA Jobin Yvon Inc., Edison, NJ, USA) after dispersing a trace amount of sample via ultrasound in distilled water. Four-point probe method was used for the measurement of electrical and thermoelectrical resistivity of samples. A small oven was needed for the variation of temperature of the samples from the room temperature to about 200°C (maximum). A small chip with 1-mm thickness and 7-mm length was used for this analysis.

Results and discussion

The powder XRD patterns (Figure 1) of LuₓYbₓSb₂₋ₓSe₃ samples indicate that the Lu³⁺/Yb³⁺ co-doped antimony selenide has the same orthorhombic structure as Sb₂Se₃ and that single-phase Sb₂Se₃ is retained at lower doping concentrations of Lu³⁺/Yb³⁺. All the peaks in Figure 1 can be attributed to the orthorhombic phase of Sb₂Se₃.
with Pbnm space group and lattice parameters $a = 11.62 \, \text{Å}$, $b = 11.76 \, \text{Å}$, and $c = 3.95 \, \text{Å}$ (JCPDS card file 72–1184). For doping levels higher than $x = 0.04$ for Lu$^{3+}$ and Yb$^{3+}$, additional unknown phases were observed (curve c of Figure 1). In the case of Lu$^{3+}$/Er$^{3+}$ co-doped compounds, the intensity of some peaks has been changed, and for doping levels higher than $x = 0.04$ for Lu$^{3+}$ and Er$^{3+}$, additional unknown phases were also observed (see Additional file 1).

In addition, a little shift toward the low angle was seen in the diffraction peaks of the co-doped Sb$_2$Se$_3$ compared with those of the undoped Sb$_2$Se$_3$ nanocrystals. This suggests that the larger lanthanide ions substitute the antimony ions, resulting in increased lattice constants. As expected, the EDX and ICP analyses of the product confirm the ratio of Sb/Se/Ln/Ln$^{0}$ (see Figure 2).

The cell parameters of the synthesized materials were calculated from the XRD patterns. With increasing dopant content ($x$), the lattice parameters were increased for these materials, as shown in Figure 3. This trend is similar to the previous reported Ln-doped Sb$_2$Se$_3$ compounds [16-20].

Figure 4a shows SEM images of Lu$_{0.04}$Yb$_{0.04}$Sb$_{1.92}$Se$_3$ nanorods with 3-μm lengths and thicknesses of 70 to 200 nm. Co-doping of Lu$^{3+}$ and Yb$^{3+}$ into the structure of Sb$_2$Se$_3$ does not change the morphology of the Sb$_2$Se$_3$ nanorods, but doping of Lu$^{3+}$ and Er$^{3+}$ into the structure of Sb$_2$Se$_3$ changes the morphology from rods to particles. The diameter of Lu$_{0.04}$Er$_{0.04}$Sb$_{1.92}$Se$_3$ particles is around 25 nm (Figure 4b).

Figure 5a shows TEM image of as-prepared Lu$_{0.04}$-Yb$_{0.04}$Sb$_{1.92}$Se$_3$ nanorods. The SAED pattern and typical HRTEM image recorded from the same nanorods of Lu$_{0.04}$Yb$_{0.04}$Sb$_{1.92}$Se$_3$ is shown in Figure 5b,c. The crystal lattice fringes are clearly observed, and the average distance between the neighboring fringes is 0.82 nm, corresponding to the [1-10] plane lattice distance of the orthorhombic-structured Sb$_2$Se$_3$, which suggests that

Figure 2 EDX patterns of Ln$_x$Ln$^{0}_x$Sb$_{2-x}$Se$_3$ compounds.
Lu_{0.04}Yb_{0.04}Sb_{1.92}Se_{3} nanorods grow along the [1] direction. The HRTEM image and SAED pattern are the same for Sb_{2}Se_{3} and show similar growth direction (see the Additional file 1).

Figure 6a,b shows the TEM image and SAED patterns of Lu_{0.04}Er_{0.04}Sb_{1.92}Se_{3} nanoparticles obtained in ethanol/water media that confirms the result through SEM images and shows high crystallinity of the sample.

In doped semiconductors, two types of emissions are responsible for dopant (impurity) luminescence. One can be observed only upon direct excitation of the dopant. The other type is obtained if energy transfer from

**Figure 3** The lattice constants of co-doped Sb_{2}Se_{3} dependent upon Ln^{3+} doping on Sb^{3+} sites.

**Figure 4** SEM images of co-doped antimony selenide. (a) Lu_{0.04}Yb_{0.04}Sb_{1.92}Se_{3} nanorods (b) Lu_{0.04}Er_{0.04}Sb_{1.92}Se_{3} nanoparticles.
host to dopant occurs. Binary compounds such as Sb$_2$Se$_3$ and its alloys are thermoelectric materials with layered crystalline structures. These materials have been investigated for the direct conversion of thermal energy to electric energy, and they are specially used for electronic refrigeration [9]. The four-point probe method was used for the measurement of electrical and thermoelectrical resistivity of samples (Figure 7).

At room temperature, the electrical resistivity of pure Sb$_2$Se$_3$ was of the order of 0.2 $\Omega\cdot$m; in the case of Lu$_{0.04}$Yb$_{0.04}$Sb$_{1.92}$Se$_3$, the minimum value of electrical resistivity is 0.009 $\Omega\cdot$m, and for Lu$_{0.04}$Er$_{0.04}$Sb$_{1.92}$Se$_3$, it is 0.032 $\Omega\cdot$m. With the increase in lanthanide concentration, the electrical resistivity of synthesized nanomaterials decreased obviously (Figure 8a).

The temperature dependence of the electrical resistivity for co-doped Sb$_2$Se$_3$ nanomaterials between 290 and 350 K is shown in Figure 8b. Electrical resistivity decreases linearly with temperature, and the minimum value for Lu$_{0.04}$Yb$_{0.04}$Sb$_{1.92}$Se$_3$ was measured as 0.0006 $\Omega\cdot$m and for Lu$_{0.04}$Er$_{0.04}$Sb$_{1.92}$Se$_3$ as 0.005 $\Omega\cdot$m. Two factors that include the overlapping of wave functions of electrons in doped Sb$_2$Se$_3$ and that acting as a charge carrier due to lanthanide atomic structure (having empty f orbitals) are important reasons for decreasing electrical
resistivity. The obtained data shows higher electrical resistivity for co-doped samples in comparison with doped samples in the case of Lu\(^{3+}\), Yb\(^{3+}\) and Er\(^{3+}\) doped Sb\(_2\)Se\(_3\) [16,17]. The measurements indicate that the co-doping materials have higher electrical and thermoelectrical conductivity than the doped compounds in spite of lower lanthanide content [16-20]. Comparing both doped and co-doped data, the combining energy levels of the two lanthanides and the overlapping of wave functions of electrons in two different lanthanides are responsible for the difference between the obtained results. Among the co-doped compounds, Lu\(^{3+}\)/Yb\(^{3+}\)-doped Sb\(_2\)Se\(_3\) has the higher electrical conductivity.

UV–vis spectra of Lu\(_{0.04}\)Yb\(_{0.04}\)Sb\(_{1.92}\)Se\(_3\) are shown in Figure 9a. The absorption spectra reveal the existence of Sb\(_2\)Se\(_3\) and Lu\(^{3+}\) ions (in the visible domain) and Yb\(^{3+}\) ions in the near-IR domain. By increasing the concentration of Ln\(^{3+}\) ions, the absorption spectrum of Sb\(_2\)Se\(_3\) shows red shifts and some intensity changes (see Figure 9).

Figure 8 Electrical (a) and thermoelectrical (b) resistivity of co-doped Sb\(_2\)Se\(_3\) compounds.

Figure 9 Absorption spectra of co-doped antimony selenide at room temperature. (a) Lu\(_{0.04}\)Yb\(_{0.04}\)Sb\(_{1.92}\)Se\(_3\) (b) Lu\(_{0.04}\)Er\(_{0.04}\)Sb\(_{1.92}\)Se\(_3\).

Figure 10 Emission spectra for co-doped antimony selenide at room temperature (\(\lambda_{exc}=470\) nm). (a) Lu\(_{0.04}\)Yb\(_{0.04}\)Sb\(_{1.92}\)Se\(_3\) (b) Lu\(_{0.04}\)Er\(_{0.04}\)Sb\(_{1.92}\)Se\(_3\).
Additional file 1). The Lu$^{3+}$ ion has no excited 4f levels; therefore, the peaks between 500 and 600 nm can be assigned to the ionization of Lu 5d orbitals and lattice of Sb$_2$Se$_3$[21,22], and the peak at 830 nm can be assigned to the $2F_{7/2} \rightarrow 2F_{5/2}$ transition (f-f transitions) of the Yb$^{3+}$ ions [23].

For Lu$_{0.00}$Er$_{0.00}$Sb$_{1.90}$Se$_3$, the transition of the Er$^{3+}$ ion is not observed because of instrument limitation. The peaks between 500 and 600 nm can then be assigned to the lattice of Sb$_2$Se$_3$ (Figure 9b). The difference between absorption patterns of compounds is related to various defects created in the lattice. There is a red shift in the doped materials in comparison with pure Sb$_2$Se$_3$ because of the smaller nanoparticles of Sb$_2$Se$_3$, in which the bandgap is higher than the doped nanomaterials [24,25]. It is well known that the fundamental absorption can be used to determine the nature and value of the optical bandgap of the nanoparticles. The bandgap energies of the smaller nanoparticles of Sb$_2$Se$_3$, in which the bandgap is higher than the doped nanomaterials [24,25].

The Lu$^{3+}$ 5d-4f luminescence is almost completely quenched at temperatures $T > 200$ K. The Lu$^{3+}$ ion has no excited 4f levels, and therefore, thermal quenching of Lu$^{3+}$ 5d-4f luminescence cannot have been caused by nonradiative transitions to 4f levels and should be attributed to the thermally activated ionization of 5d electrons to the conduction band [21,22]. The peaks at 500 to 700 nm can then be assigned to the crystal structure of Sb$_2$Se$_3$, and its defects and the band at 880 nm is related to $2F_{5/2} \rightarrow 2F_{7/2}$ transition of Yb$^{3+}$ ions.

In case the of Lu$_{0.00}$Er$_{0.00}$Sb$_{1.90}$Se$_3$, intra-4f Er$^{3+}$ transitions of the $^1I_{15/2}$ and $^1I_{13/2}$ levels to the ground state ($^4I_{15/2}$) are expected around 1.54 μm. These could, however, not be determined due to equipment limitations [24]. Therefore, emission bands at 550 to 700 nm are related to the crystal structure of Sb$_2$Se$_3$ (Figure 10b). The optical properties of co-doped compounds considering absorbance and photoluminescence spectra show similar f-f transitions in the case of Yb-doped materials and similar results for Lu- and Er-doped materials as obtained for Ln-doped Sb$_2$Se$_3$. We expect that these materials can be good candidates as novel photocatalysts due to their modified bandgaps by doping with lanthanides. Indeed, doping is the best way for the modification of semiconductors for special uses such as photocatalysts in order for the degradation of azo dye and organic pollutant to take place.

Conclusions

New thermoelectric Ln$_2$Sb$_{2-x}$Se$_x$ (Ln: Lu$^{3+}$/Yb$^{3+}$ and Lu$^{3+}$/Er$^{3+}$)-based nanomaterials were synthesized by a simple hydrothermal method. The cell parameters were increased for compounds upon increasing the dopant content (x). According to the SEM and TEM images, different morphologies were seen in co-doped Sb$_2$Se$_3$. The HRTEM image and SAED pattern show similar growth [1] directions for Lu$^{3+}$/Yb$^{3+}$ co-doped like Sb$_2$Se$_3$ nanorods. Lanthanide doping promotes the electrical conductivity of Sb$_2$Se$_3$ as well as thermoelectrical conductivity. UV-vis absorption and emission spectroscopy reveals mainly the electronic transitions of the Ln$^{3+}$ ions in the case of Yb$^{3+}$-doped nanomaterials.

Competing interests

The authors declare that they have no competing interests.

Authors’ contributions

YH carried out the experiments and drafted the manuscript. SW directed the study and provided the analyses. BM carried out the experimental analysis. All authors read and approved the final manuscript.

Acknowledgments

This work is funded by the World Class University grant R32-2008-000-20082-0 of the National Research Foundation of Korea.

Referencess

1. Calvert P. Rough guide to the nanoworld. Nature 1996, 383:300–301.
2. Weller H. Quantized semiconductor particles: a novel state of matter for materials science. Adv Mater 1993, 5:88-95.
3. Alivisatos AP. Semiconductor clusters, nanocrystals, and quantum dots. Science 1996, 271:933–937.
4. Wang F, Han Y, Lim CS, Lu YH, Wang J, Xu J, Chen HY: Simultaneous phase and size control of upconversion nanocrystals through lanthanide doping. Nature 2010, 463:1061–1065.
5. Tadchikara T, Ishigaki T, U J, Fujutsu M Defect mediated photoluminescence dynamics of Eu$^{3+}$-doped TiO$_2$ nanocrystals revealed at the single particle or single aggregate level. Angew Chem Int Ed 2008, 47:5348–5352.
6. Sun Y, Chen Y, Tian L, Yu Y, Kong XG: Morphology-dependent upconversion luminescence of ZnO:Er$^{3+}$ nanocrystals. J Lumin 2008, 128:15–21.
7. Batzill M, Morales EH, Diebold U: Influence of nitrogen doping on the defect formation and surface properties of TiO2 rutile and anatase. Phys Rev Lett 2006, 96:026103-4.

8. Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y: Visible-light photocatalysis in nitrogen-doped titanium oxides. Science 2001, 293:269-273.

9. Chm T, Chun B: Microstructure and thermoelectric properties of n- and p-type Bi2Te3 alloys by rapid solidification processes. J Alloys Compd 2007, 437:225-230.

10. Qiu X, Burda C, Fu R, Pu L, Chen H, Zhu J: Co-reduction synthesis, spectroscopic and structural studies of novel Ln3+-doped Sb2Se3 nanorods and investigation of their physical properties. J Nanophotonics 2011, 5:050503.

11. Mastrovito C, Lekse JW, Aitken JA: Rapid solid-state synthesis of binary group 15 chalcogenides using microwave irradiation. J Solid State Chem 2007, 180:3262-3270.

12. Larson P, Lambrecht RL: Electronic structure and magnetism in Bi2Te3, Bi2Se3, and Sb2Te3 doped with transition metals (Ti–Zn). Phys Rev B 2008, 78:195–207.

13. Janíček P, Drasar C, Losták P, Vejpravová J: Transport, magnetic, optical and thermodynamic properties of Bi2−xMnxSe3 single crystals. Physica B 2008, 403:3553-3558.

14. Lostak P, Drasar C, Klichova I, Cernohorsky T: Properties of Bi2Se3 single crystals doped with Fe atom. Phys Status Solidi B 1997, 200:289-296.

15. Alemi A, Klein A, Meyer G, Dolatyari M, Babalou A: Synthesis of new LnBi2−xS3 Ln (Ln: Sm3+, Eu3+, Gd3+, Tb3+) nanomaterials and investigation of their optical properties. Z Anorg Allg Chem 2011, 637:87-93.

16. Alemi A, Hanifehpour Y, Joo SW, Min B: Synthesis of novel Ln3+,Sb2−xSe3 (Ln: Lu3+, Ho3+, Nd3+) nanomaterials via co-reduction method and investigation of their physical properties. Colloids and Surfaces A: Physicochem. Eng. Aspects 2011, 390:142-148.

17. Alemi A, Hanifehpour Y, Joo SW, Khandar A, Monsali A, Min B: Co-reduction synthesis of new Ln,Sb2−xSe3 (Ln: Nd3+,Lu3+,Ho3+) nanomaterials and investigation of their physical properties. Physica B 2011, 406:2801-2806.

18. Alemi A, Hanifehpour Y, Joo SW, Khandar A, Monsali A, Min B: Synthesis and characterization of new Ln3+,Sb2−xSe3 (Ln: Yb3+, Er3+) nanoflowers and their physical properties. Physica B 2012, 407:38-43.

19. Alemi A, Hanifehpour Y, Joo SW, Min B: Structural studies and physical properties of novel Sm3+−doped Sb2Se3 nanorods. Physica B 2011, 406:3831–3835.

20. Alemi A, Hanifehpour Y, Joo SW, Min B: Co-reduction synthesis, spectroscopic and structural studies of novel Gd3+−doped Sb2Se3 nanorods. J Nanomater 2012, doi:10.1155/2012/983150.

21. Makhov VN, Batygov SK, Dmitruk LN, Kirm M, Weihauer S: VUV 5d–4f luminescence of Gd4f and Lu4f ions in the CaF2 host. Phys Solid State 2008, 50:1625–1630.

22. Zych E, Hreniak D, Strek W: Spectroscopic properties of Lu2O3:Eu3+ nano-crystalline powders and sintered ceramics. J Phys Chem B 2002, 106:3805–3812.

23. Loh E: 4f−4f 5d Spectra of rare-earth ions in crystals. Phys Rev 1968, 175:533–536.

24. Strohheeder C, Polman A: Absorption and emission spectroscopy in Er3+-Yb3+ doped aluminum oxide waveguides. Opt Mater 2003, 21:705–712.

25. Hoven GN, Elsken JA, Polman A, Dam C, Uffelen K, Smit MK: Absorption and emission cross sections of Er3+ in Al2O3 waveguides. Appl Opt 1997, 36:3338–3341.