

OPTICAL ENERGY BANDGAP TUNING OF SPINEL ZINC STANNATE BY ERBIUM/YTTERBIUM DOPING

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Abstract

This work shows the results of an optical energy bandgap (E_g) investigation supported by scanning electron microscopy (SEM) of spinel-type zinc stannate (Zn_2SnO_4) upon doping with rear earth (RE^{3+}) ions (Er^{3+} , Yb^{3+}). The powder samples are synthesized by a mechanochemical solid-state method with the final annealing step at 1200 °C. The reference Zn_2SnO_4 powder sample bandgap (3.87 eV) turning lower upon doping, precisely to 3.5 eV, and 3.37 eV bandgap values found for Er-doped Zn_2SnO_4 and Er, Yb-codoped Zn_2SnO_4 powder samples, respectively is a confirmation of the successful incorporation of the RE^{3+} ions into the Zn_2SnO_4 host structure. Morphology of the obtained powders shows, in general, the non-uniformly shaped agglomerates, while their particle sizes follow up the bandgap decreasing trend with doping.

Introduction

The ternary zinc tin oxide (ZTO) compound called zinc stannate with inverse spinel structure (Zn_2SnO_4) shows exceptional physicochemical properties that still cause attention in materials science. Its inverse cubic structure belongs to the space group $Fd\bar{3}m$ (No. 227) where the lattice parameter is ~ 8.65 Å, the Zn^{2+} cations occupy all tetrahedral sites, and the octahedral sites shared by Zn^{2+} and Sn^{4+} cations (Fig. 1). However, ZTO usually exhibits cation disorder when a portion of Sn^{4+} cations, even so, moves to tetrahedral sites.

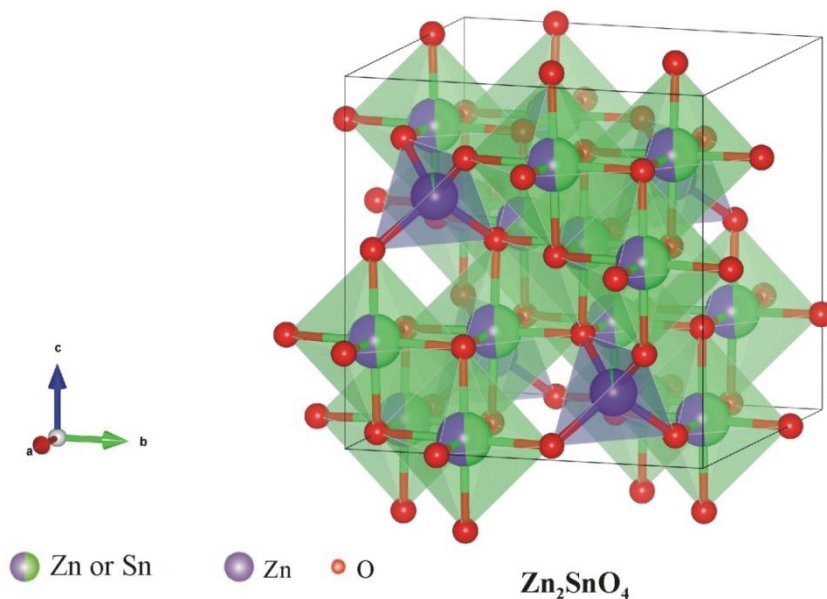


Figure 1. Crystal structure of Zn_2SnO_4 .

Zn_2SnO_4 is a transparent n-type semiconductor with high electron conductivity and chemical stability that finds applications in solar cells, sensing, lithium batteries, nanodevices, catalysis [1]. Therefore, the most investigated are its electrical and optical properties dependent upon the type of synthesis method used and the resulting ZTO microstructure.

ZTO was so far successfully synthesized by various methods like high-temperature calcination, mechanical grinding, sol-gel synthesis, hydrothermal/solvothermal, thermal evaporation, with different morphologies obtained, shapes like hollow -cages, -boxes, -tubes and -bowls; and nano -urchins, -flowers, -beads [2].

Reportedly its optical bandgap varies from 3.18 eV to 4.1 eV [3-5] depending on the synthesis method, conditions applied, due to variations in stoichiometry, while 3.6-3.7 eV is its proposed fundamental E_g [6].

Experimental

Synthesis

The non-doped reference Zn_2SnO_4 , Er (1 at.%) -doped Zn_2SnO_4 and Er (1 at.%) / Yb (1 at.%) -co-doped Zn_2SnO_4 powder samples were synthesized by a following solid-state method. Starting precursors (ZnO and SnO_2 , Sigma-Aldrich, purity 99.9%) mixed in stoichiometric ratio with or without the addition of 1 at.% of Er (Er_2O_3 , Sigma-Aldrich, purity 99.9%), and 1 at.% of Er and 1 at.% of Yb (Yb_2O_3 , Sigma-Aldrich, purity 99.9%), are milled by Retsch GmbH PM100 at 320 rpm for 160 min and annealed at 1200 °C for 2 hours. For reference, we use the labels ZTO, ZTO:Er, and ZTO:Er,Yb further in the text for the easier marking of un-doped, erbium-doped, and erbium, ytterbium-co-doped Zn_2SnO_4 powder samples, respectively.

Characterization

UV-Vis reflectance was measured using the Ocean Optics QE65000 High-sensitivity Fiber Optic Spectrometer. The microstructure was investigated by scanning electron microscopy (JEOL JSM 7001F).

Results and discussion

Fig. 2 shows that the optical absorption threshold of ZTO redshifts from around 320 nm to ~354 nm and ~368 nm for ZTO:Er and ZTO:Er,Yb powder samples, respectively. The “knees” appearance in the reflectance spectra points to the presence of a secondary phase. Such behavior occurred upon doping in analogous systems [7]. The X-ray diffraction measurements (shown elsewhere [8]) confirmed the presence of the low weights shares of the secondary $\text{Er}_2\text{Sn}_2\text{O}_7$ phase in doped samples. The reflectance measurements (Fig. 2) were used to estimate the optical energy gap of ZTOs by extrapolation of the spectral “knees” using the plots of Kubelka-Munk transformed reflectance spectra for the allowed-direct transitions $[F(R) \cdot hv]^2$ vs. photon energy (hv) [4]. For E_g estimated values of reference Zn_2SnO_4 , Zn_2SnO_4 :Er, and Zn_2SnO_4 :Er,Yb samples are 3.87 eV, 3.5 eV, and 3.37 eV, respectively. The lowering of the optical energy bandgap suggests the successful incorporation of RE^{3+} ions into the Zn_2SnO_4 matrix compound structure. The successful RE^{3+} ions incorporation has been confirmed by our recent luminescence report [8], where the up-conversion luminescence of Zn_2SnO_4 : Er^{3+} , Yb^{3+} powder phosphors was described. The appearance of luminescence emissions shown in Ref. [8] is possible only when the matrix compound (here Zn_2SnO_4) hosts the luminescence activator ions (here $\text{RE}^{3+} = \text{Er}^{3+}$ and Yb^{3+}) in its crystal lattice.

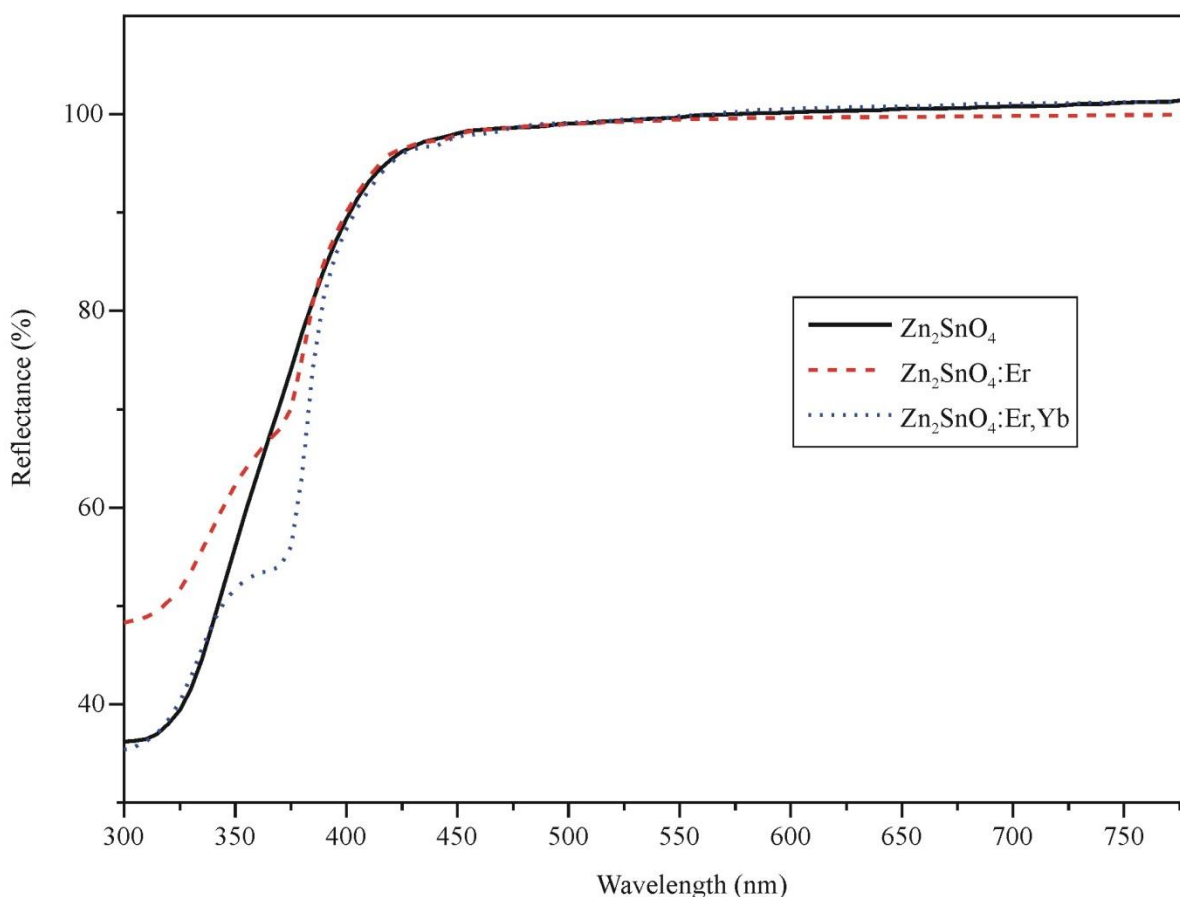


Figure 2. Reflectance spectra of reference ZTO, ZTO:Er and ZTO:Er,Yb powders.

Fig. 3 shows the SEM images of ZTO, ZTO:Er, and ZTO:Er,Yb powder samples. The morphologies consist of non-uniform in shape agglomerates of more or less pasted Zn_2SnO_4 particles with sizes in the range of one to five microns. Doping causes particle sizes to decrease [8].

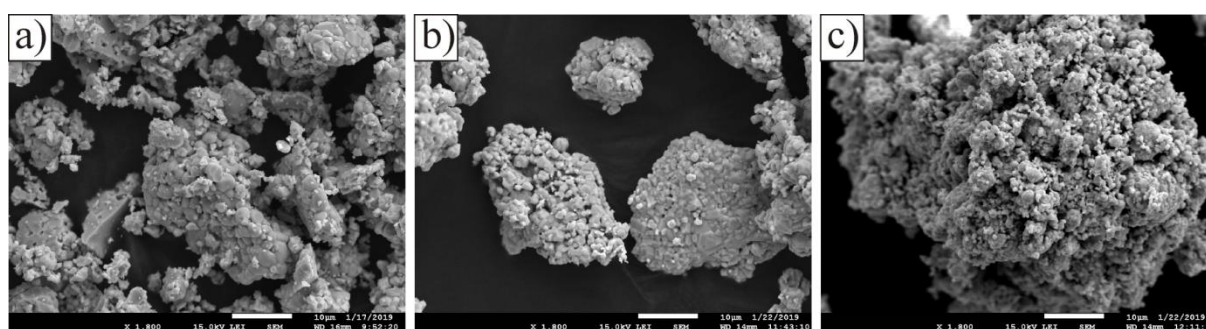


Figure 3. SEM images of a) reference ZTO, b) ZTO:Er, and c) ZTO:Er,Yb powders with $\times 1,800$ magnification.

Conclusion

In this work, we report the potential of band structure tuning of spinel zinc stannate powder by doping with rear earth ions (Er^{3+} , Yb^{3+}) when synthesized using the mechanochemically initiated solid-state reaction method followed by annealing. The optical bandgap characterization points to the successful incorporation of rear-earths into the spinel cubic crystal structure of zinc stannate. The scanning electron microscopy images of the obtained powder

samples showed non-uniformity in shapes of agglomerates with particle size decrease by doping. Our optical measurements report the Zn_2SnO_4 bandgap of 3.87 eV for a direct-allowed transition, and E_g tuning to lower values of 3.5 eV and 3.37 eV when doped with 1 at.% of Er^{3+} ion and co-doped with 1 at.% of Er^{3+} and 1 at.% Yb^{3+} ions, respectively.

Acknowledgements

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