Phase Formation and Microstructural Analysis of ZnFeSnO Oxide System

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Abstract

ZnO is a promising n-type thermoelectric material due to its relatively high-temperature stability and high figure of merit. However, its performance is limited by low electrical conductivity and high thermal conductivity. To address these limitations, this study has systematically investigated the dopant effects and found a possible combination of doping elements which may enhance thermoelectric performance of ZnO. Therefore, this project intends to focus on investigating the co-doped system of $Zn_{1-x-y}Fe_xSn_yO$ (ZFSO) composition. ZFSO powders and ceramics were synthesized by solid reaction, where x = 0, 0.001, 0.002, 0.003, 0.004, 0.005 mol fractions, and y = 0.00, 0.01 mol fractions. After being calcined at 800 °C for 6 h and sintered at 900 °C for 8 h in a normal atmosphere, all samples were characterized for phase and crystal structure using X-ray diffractometry (XRD). The microstructure and chemical composition were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The results were compared to those reported in literature and the quality was analyzed for further thermoelectric property determination.

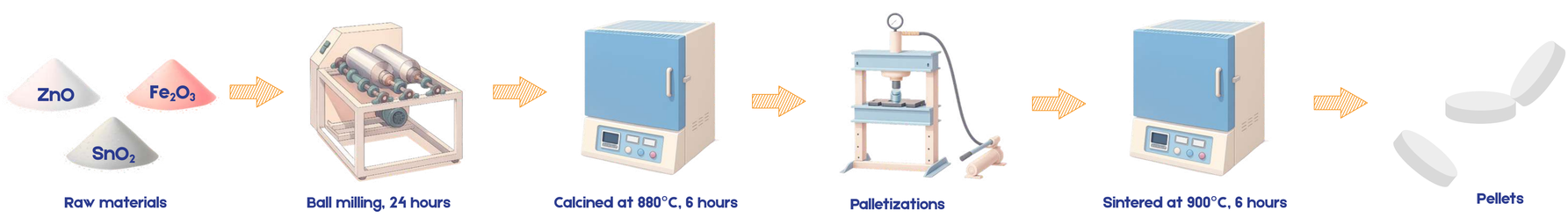
Introduction

Thermoelectric power generation has attracted widespread attention as a green and clean energy technology. The performance of thermoelectric materials is generally evaluated by the thermoelectric figure of merit (ZT), which is consisted of electrical conductivity, Seebeck coefficient and thermal conductivity. Improving the ZT value requires high electrical conductivity, high Seebeck coefficient, and low thermal conductivity. But this is very challenging due to the complex interdependence between these parameters and the carrier concentration. ZnO is a promising n-type thermoelectric material due to its relatively high-temperature stability and high figure of merit. However, its performance is limited by low electrical conductivity and high thermal conductivity. To address these limitations, this study has systematically investigated the dopant effects and found a possible combination of doping elements which may enhance thermoelectric performance of ZnO. Therefore, this project intends to focus on investigating the co-doped system of $Zn_{1-x-y}Fe_xSn_yO$ (ZFSO) composition.

Methodology

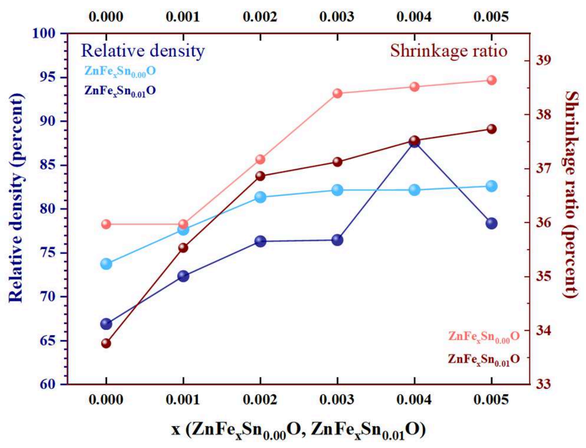
Solid state reaction method

ZFSO powders and ceramics were synthesized by solid reaction, where x = 0, 0.001, 0.002, 0.003, 0.004, 0.005 mol fractions, and y = 0.00, 0.01 mol fractions. After being calcined at 800 °C for 6 h and sintered at 900 °C for 8 h in a normal atmosphere, all samples were characterized for phase and crystal structure using X-ray diffractometry (XRD). The microstructure and chemical composition were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).



Results

Relative density & Shrinkage ratio



XRD

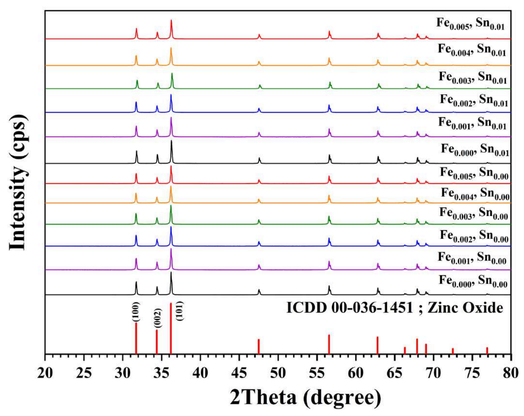


Fig 1. The relative density and shrinkage ratio of ZFSO ceramic (left). , The XRD pattern of ZFSO ceramic (right).

Co-doping with tin (Sn = 0.01) significantly improves the physical properties of the ZFSO system compared to the Sn-free samples. The relative density and shrinkage ratio consistently increase with higher iron (Fe) content, peaking at 87.66% (x = 0.004) and 37.74% (x = 0.005), respectively. This demonstrates that Fe and Sn co-doping effectively enhances material densification. Structural analysis via XRD confirms that all samples maintain a high-purity ZnO phase (ICDD 00-036-1451). No secondary or impurity phases from Fe or Sn were detected, indicating that the dopants are successfully and uniformly integrated into the ZnO host lattice without causing structural distortion.

EDS

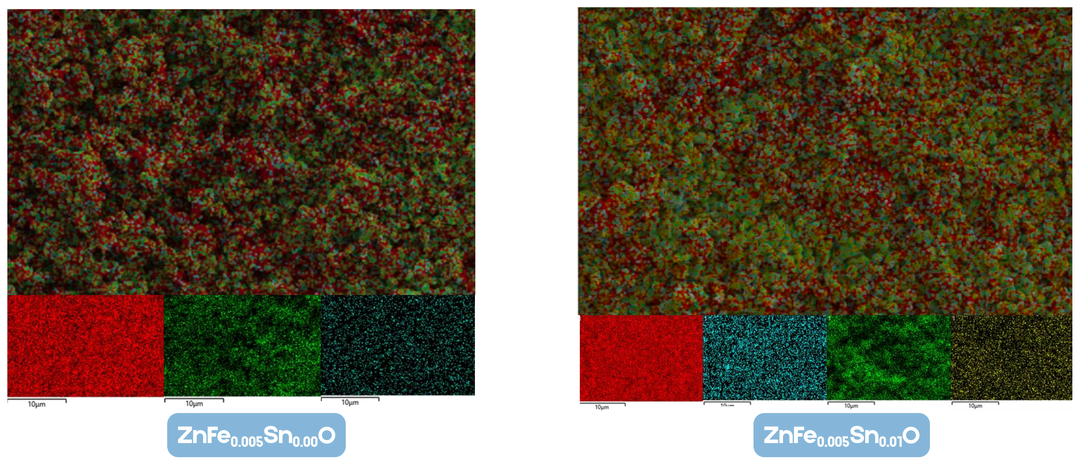


Fig 2. The EDS analysis of ZFSO ceramic at 15 000x.

The EDS analysis at 15,000x magnification confirms the successful doping of the ceramic system. Quantitative results show that the detected iron (Fe) content increases in correlation with the doping level (x), rising from 0wt% to a maximum of 0.37 wt% at x = 0.005. Although a slight fluctuation was observed at x = 0.004 0.27wt%, the overall trend remains consistent. Furthermore, EDS mapping of Fe, Sn, Zn, and O reveals a highly homogeneous distribution across the surface, with no evidence of elemental clustering or phase segregation. This confirms that the Fe and Sn dopants are uniformly integrated into the ZnO host lattice.

SEM

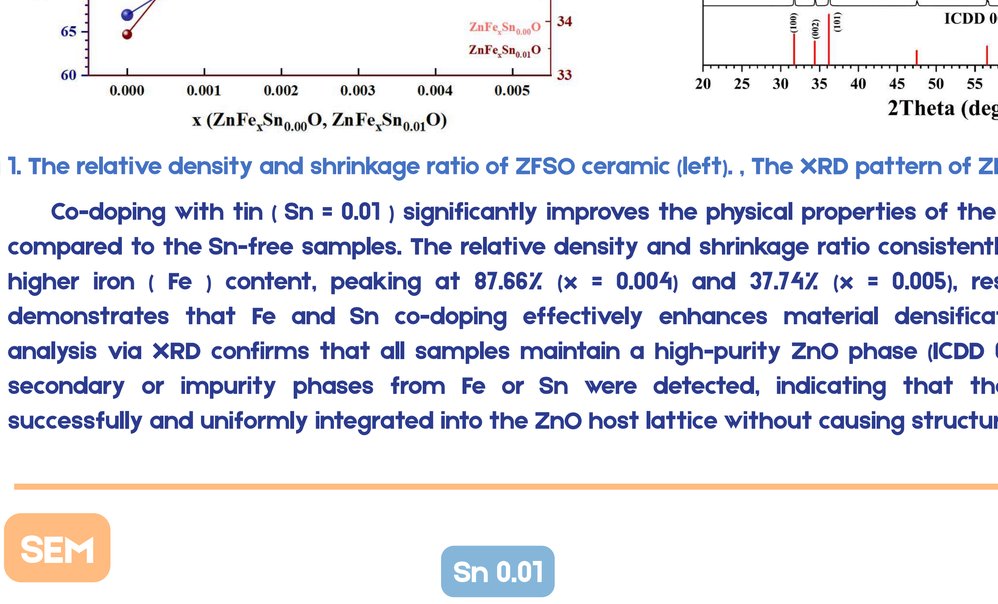


Fig 3 . The structure of ZFSO ceramic at 20 000x.

The SEM microstructure of the $ZnFe_{0.005}Sn_{0.00}O$ sample is shown in Fig. 3. This composition was selected as a representative sample because the microstructures of other compositions exhibited similar morphological features.The morphological and microstructural analysis of the ZFSO ceramic system, conducted via Scanning Electron Microscopy (SEM) at a magnification of 20,000x, reveals a highly uniform and dense grain arrangement across the surface. Measurement results indicate that the material maintains an average grain size ranging from approximately 300 nm to 900 nm, remaining consistently within the nanometer scale across all experimental proportions. The addition of tin (Sn) plays a significant role in grain refinement: samples containing Sn (y = 0.01) exhibit a reduction in average grain size compared to those without Sn (y = 0.00). The grains exhibit distinct clustering with a noticeable reduction in inter-granular porosity as the iron (Fe) dopant concentration increases.

Conclusions

The study of the $Zn_{(1-x-y)}Fe_xSn_yO$ (ZFSO) system (x = 0.000–0.005 and y = 0.00, 0.01) demonstrates that co-doping with Fe and Sn significantly enhances the densification and microstructural properties of ZnO ceramics. The addition of Sn (y = 0.01) shows a marked improvement in physical properties compared to Sn-free samples (y = 0.00), with the relative density and shrinkage ratio increasing as Fe content rises, peaking at 87.66% (x = 0.004) and 37.74% (x = 0.005) respectively. XRD analysis confirms a high-purity ZnO phase across all compositions, indicating successful dopant integration without impurity phases. EDS mapping further verifies a highly homogeneous elemental distribution, with detected iron reaching a maximum of 0.37 wt%. SEM results reveal a dense microstructure with an average grain size of 300–900 nm, where porosity decreases as the Fe dopant concentration increases. These findings suggest that the optimized ZnFeSnO system is a promising candidate for high-performance thermoelectric applications.

References

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