TACHGISS JAMPREECHA : FABRICATION, PERFORMANCE AND THERMOELECTRIC PROPERTIES OF MONOLITHIC β–Zn_4Sb_3/ZnO THERMOELECTIC GENERTOR MODULES. THESIS ADVISOR : PROF. SANTI MAENSIRI, D. Phil. 117 PP.

Keyword: THERMOELECTRIC, MOLOLITHIC, THERMOELECTRIC GENERATOR MODULE (TEGs), ZINC ANTIMONIDE

In this research, the processes synthesis and thermoelectric properties of thermoelectric materials of zinc antimony alloy beta phase (β–Zn_4Sb_3) powders were studied before the β–Zn_4Sb_3 powder before using these powders to fabricate monolithic β–Zn_4Sb_3/ZnO thermoelectric generator module (TEG). The performance of the monolithic β–Zn_4Sb_3/ZnO TEG modules were evaluated using self–made heating/cooling system with IV measurement capabilities. The characterization of processes, structural analysis, fabrication processes and performance evaluation were described in a detailed, step by step.

Initially, β–Zn_4Sb_3 powders were synthesized through solid state reaction process. Zn and Sb powder were combined in a stoichiometric ratio 4:3, with additional Zn added to compensate for evaporation during high temperature calcination. The optimal amount of added Zn was 12 at.% Zn. The precursor mixture of of Zn–Sb powders was calcined at 450 °C for 3 hours under Ar gas flow. The synthesized β–Zn_4Sb_3 powders were analyzed using X–ray diffraction (XRD) technique. The XRD pattern results showed dominant crystalline structure pure phase of β–Zn_4Sb_3 and correspondingly Mozharivskyj's model. However, slight diffraction pattern of secondary phase of ZnSb, Zn, and Sb, were also observed due to temperature stability limitations during calcination under Ar gas flow. Additionally, the synthesized β–Zn_4Sb_3 powders were also investigated ionization energy of exciting core electrons at Zn K–edge and Sb L–edges using normalized X–ray absorption near edge spectroscopy (XANES) and derivative of normalized XANES. The normalized XANES spectrum result of Zn K–edge revealed main absorption edge at 9,659 eV. The main absorption edge of Zn K–edge was confirmed by derivation of normalized XANES spectrum result. For Sb L3, L2 and L1–edges, the main absorption edges were observed at 4,132 eV, 4,380 eV and 4,698 eV, respectively, also confirmed by the derivative. The normalized XANES spectra and derivation of normalized XANES spectra results of Zn K–edge and Sb L–edges, indicate that the ionization energy of exciting core electrons corresponds to the oxidation state of Zn^0 and Sb^0. The synthesized β–Zn_4Sb_3 powders were pressed into ceramic pellets using circular compression mold. The powders were pressed at 700 MPa. Then the pressed β–Zn_4Sb_3 pellets were sintered under Ar gas flow at

500 °C, and held for 6 hours. Afterwards, thermoelectric properties of the ceramic pellets were investigated. The measurement of the ceramic β–Zn_4Sb_3 pellets revealed a notable Seebeck coefficient of approximately 255 µV/°C at 320 °C. Moreover, the electrical resistivity of the ceramic pellets remained consistently poor across the temperature range of 250–400 °C, with a value about $8x10^{-5}$ Ω.m. The high Seebeck coefficient and poor electrical resistivity suggest that the sintered β–Zn_4Sb_3 pellets have excellent thermoelectric properties, as indicated by the figure of merit (ZT). Additionally, the maximum power factor of the ceramic pellets about 0.56 mW/m°C^2 was observed at the optimal performance temperature range of 220–240 °C. Fortunately, the good thermoelectric properties of the synthesized β–Zn_4Sb_3 powders are preferable for fabrication of monolithic TEG modules.

The monolithic β–Zn_4Sb_3/ZO TEGs were fabricated using cyclical compression process. The synthesized β–Zn_4Sb_3 powders were first filled into a square compression mold size 1×1 cm, and softly pressed at 100 MPa for a while. Next, the commercial ZO powders also were filled into the same compression mold, and softly pressed. The soft compression was performed cyclically. Multi–stack of β–Zn_4Sb_3/ZnO pellets were firmly hard pressed at 700 MPa for 15 minutes. The pressed multi–stacks pellets were sintered under Ar gas flow at 500 °C for 6 hours. The β–Zn_4Sb_3 components of the multi–stacks pellet was connected in series with positive and negative terminal. The monolithic β–Zn_4Sb_3/ZnO TEGs were evaluated IV–curves and electrical output power curves using custom-built heating/cooling system with IV measurement capabilities. The measurement temperatures were conducted at operating temperature (T_h) of 100 °C, 200 °C and 300 °C, with gradient temperature (ΔT) of 50 °C and 100 °C. The results revealed an increase in open–circuit voltage (V_{oc}) with higher T_h and ΔT. The highest maximum electrical power output of 550 µW, and the highest V_{oc} of 73.1 mV were achieved at T_h=300 °C with ΔT=100 °C. However, the optimal operating conditions for the monolithic β–Zn_4Sb_3/ZnO TEG was found to be T_h=200 °C with ΔT=50 °C and ΔT=100 °C, as these conditions demonstrate a wide and prominent electrical power output curves, indicating good performance of the module.

School of Physics
Academic Year 2023

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