Bi_2O_2Se – A PROSPECTIVE THERMOELECTRIC MATERIAL?

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Abstract

Bi_2O_2Se was synthesized from Bi_2Se_3 and Bi_2O_3 by solid state reaction in an evacuated quartz ampoule. The product of the reaction was characterized by X-ray diffraction analysis. In accordance with the literature, it was observed that the prepared samples crystallize in tetragonal type lattice (space group I4mmm - D_{4h}^{17}) with the lattice parameters a = 0.38859 nm, and c = 1.22055 nm. Diffractogramm of the sample exhibits lines of the Bi_2O_2Se structure only. Polycrystalline samples (dimensions $15\times3\times3$ mm^3) for measurements of thermoelectric properties were prepared using hot uniaxial pressing of the powders in rectangular graphite dies. The samples were characterized by the measurements of Seebeck coefficient, electrical conductivity and thermal conductivity as a function of temperature. From the experimental data we calculate the thermoelectric figure of merit Z and we discuss its temperature dependence.

1. Introduction

Bismuth selenide Bi_2Se_3 is a component of materials applied in thermoelectric devices as solid state coolers or generators with the best figure of merit in the range around room temperature [1].

Substituting O atoms for Se atoms in Bi_2Se_3 one can formally derive a ternary compound of composition Bi_2O_2Se. The identification of the compound was reported in papers of H. Boller and H. Oppermann et al. [2-9]. According to the work by Boller [2] Bi_2O_2Se has a $(Na_{0.25}Bi_{0.75})_2O_2Cl$-type structure (space group I4 mmm - D_{4h}^{17}) with lattice parameters a = 0.3891 nm a c= 1.221_3 nm. The structure consists of tetragonal $(BiO)_n$ layers; Se occupies interlayer positions. The papers by H. Oppermann et al. [3-9] are focused on the study of phase equilibrium with the aim to prepare compounds that may exist in the system using the chemical transport reaction. The papers describe the enthalpy of formation and entropy of compounds. We note that no literature data exist on transport or optical properties of Bi_2O_2Se.

In this communication we report on preparation of Bi_2O_2Se in a polycrystalline form and we present some transport properties measured on a hot pressed (HP) sample. The sample was characterized by the measurement of electrical resistivity, thermal conductivity and Seebeck coefficient as function of temperature in the range of temperature 5 – 300 K, with the aim to reveal potentially useful thermoelectric properties in terms of the thermoelectric figure of merit Z = f(T).

2. Experimental

The material was synthesized from Bi_2O_3 and Bi_2Se_3 powders. The stoichiometric mixture of powders was thoroughly homogenized and then heat treated at 500 °C for 300 hours in an evacuated quartz ampoule. We have used three different routes of synthesis.

a) The mixture of powders was hot pressed (500°C/50MPa) and then was heat treated.

b) The mixture of powders was cold pressed (20°C/1000MPa) and then heat treated
c) The mixture of powders was heat treated without any pressing.

The products of all three routes were identified by means of X-ray diffraction (see Fig.1 a, b, c). While first two routes produce a mixture of Bi_2O_2Se and other related phases (Bi_2O_3, Bi_2Se_3, $Bi_{18}SeO_{29}$), the third route produces pure Bi_2O_2Se down to the detection limit of our facility. Even prolonged heat treatment at various

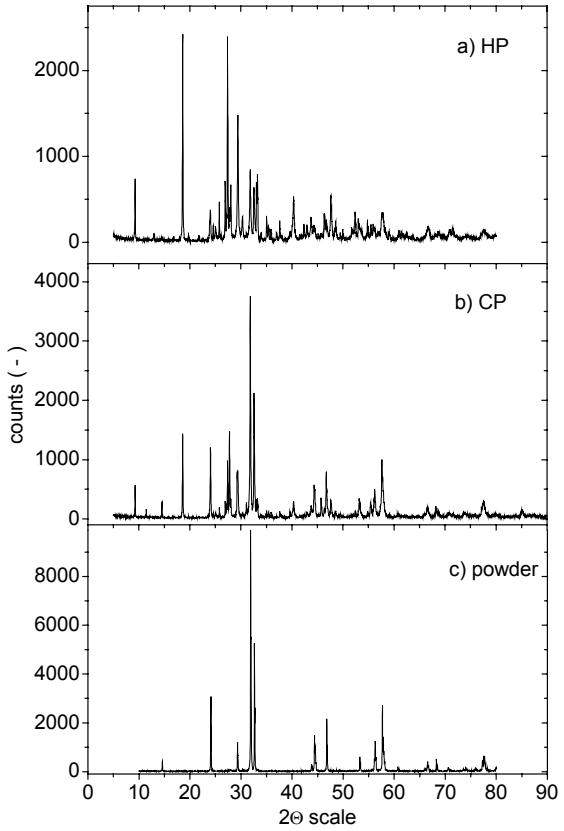

Fig.1. X-ray diffractogramms of Bi_2O_2Se a) hot pressed, b) cold pressed and c) powder mixture of Bi_2O_3 and Bi_2Se_3 after annealing at 500 °C for 300h.

temperatures brings no improvement for the first two routes of synthesis. Thus, it is evident that the reaction runs through vapor phase quite quickly, while the kinetics of diffusion reaction needs higher temperatures where the thermodynamic stability of the compound is questionable. The sample with dimensions of 15x3.5x3.5 mm^3 was prepared using high pressure (HP) (500°C/50MPa) technique in a graphite die from the powder synthesized by the route c.

The polycrystalline sample was defined by measurements of lattice parameters and characterized by the temperature dependence of electrical resistivity ρ, Seebeck coefficient S and thermal conductivity κ in the temperature range of 5-300 K. Experimental techniques are described elsewhere [10].

3. Results and discussion

Because at T = 500°C graphite can work as a reducing agent we have checked the identity of the sample using X-ray diffraction. The hot pressed sample has shown the same purity as the starting powder. The lattice parameters of this material differ slightly from the literature values (see Table 1).
The difference in the lattice parameters is likely due to different preparation routes and possibly also due to different lattice

Table 1 Lattice parameters of Bi_2O_2Se

	a (nm)	c (nm)
Boller [2]	0.38910	1.221_3
Synthesized powder	0.38859	1.22055
Sample after HP	0.38860	1.22023

defect concentrations. The synthesis in Ref. 2 was carried out at 800-850 °C while the present material was synthesized at 500 °C (to prevent Bi_2O_3 reacting with the quartz ampoule).

The results of the measurements of temperature dependence of electrical resistivity ρ, Seebeck coefficient S and thermal conductivity κ are presented in Figs. 2-5. The results suggest Bi_2O_2Se is a degenerate semiconductor like Bi_2Se_3. The electrical resistivity increases with temperature (Fig2). In the temperature

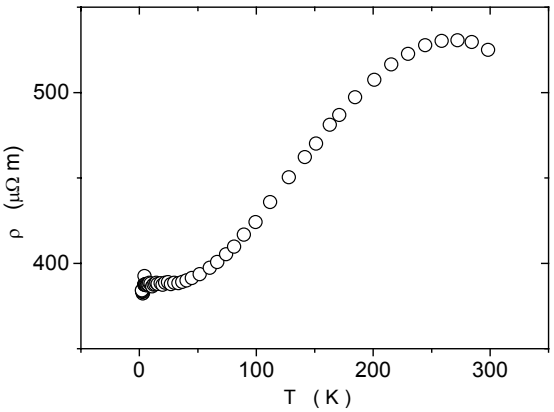

Fig.2. Electrical resistivity of Bi_2O_2Se as a function of temperature.

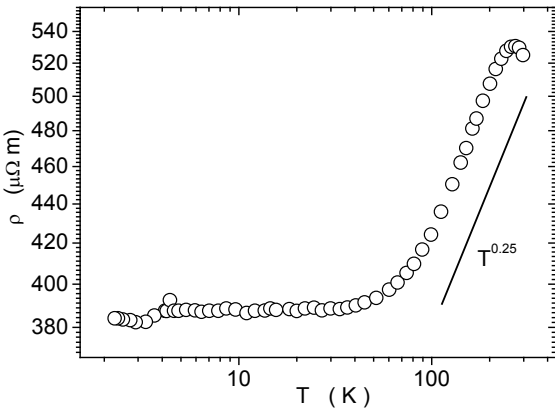

Fig.3. Electrical resistivity of Bi_2O_2Se as a function of temperature on log-scale.

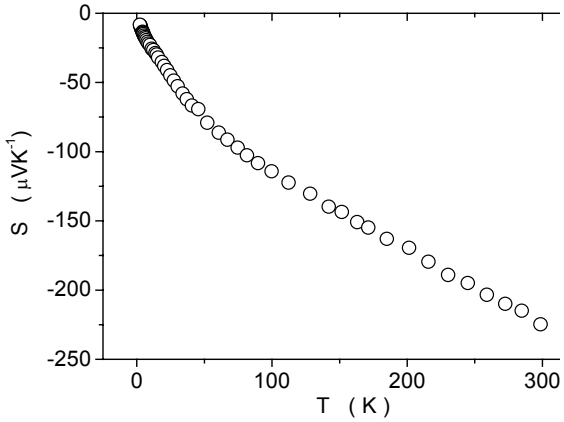

Fig.4. Seebeck coeficient of Bi_2O_2Se as a function of temperature.

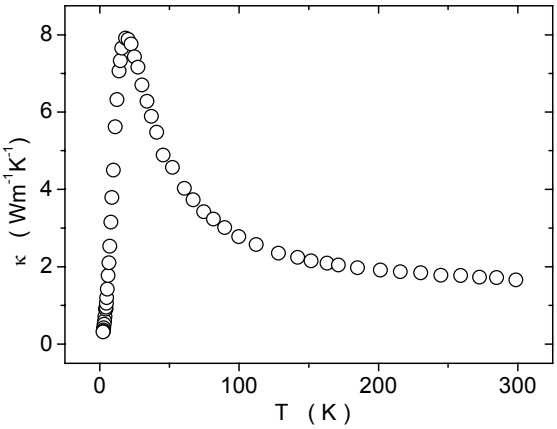

Fig.5. Thermal conductivity of Bi_2O_2Se as a function of temperature.

range 80 -300K, the ρ-T curves obey a power law of the form $\rho \sim T^m$ with $m \approx 0.25$. A deviation from $m = 1.5$ (acoustic phonons) is probably due to additional scattering on impurities as indicated by a rather high residual resistivity (Fig3). This supports our assumption of a degenerate semiconductor with negligible dependence of carrier concentration on temperature. The temperature dependence of the Seebeck coefficient (Fig. 4) shows quite large values of S, at T = 300 K $S_{300} \approx -225\ \mu VK^{-1}$. The negative values of S mean n-type conduction. The temperature dependence of the thermal conductivity (Fig. 5) has a typical shape with the maximum at $T \approx 20K$. Room temperature value of thermal conductivity is low ($\kappa_{300} \approx 1.7\ Wm^{-1}K^{-1}$) compared to Bi_2Se_3 ($\kappa_{300} \approx 3.1\ Wm^{-1}K^{-1}$) [11]. Regarding the magnitude of the Seebeck coefficient and thermal conductivity, Bi_2O_2Se seems to be a prospective thermoelectric material.

Dimensionless figure of merit $ZT = S^2T/\rho\kappa$ is the measure of usefulness of a thermoelectric material. In Fig. 6 we show the temperature dependence of the figure of merit of Bi_2O_2Se which in comparison to industrially employed materials ($ZT \approx 1.0$) [1] is by two orders of magnitude lower. However, Bi_2O_2Se seems to have the maximum in ZT value situated at higher temperatures than Bi_2Se_3/Bi_2Te_3 materials. In Fig. 6 we observe a steep increase in ZT above T = 200K, which promises higher values of ZT at elevated temperatures. Therefore, high temperature properties of Bi_2O_2Se will be a subject of our future investigation.

4. Conclusions

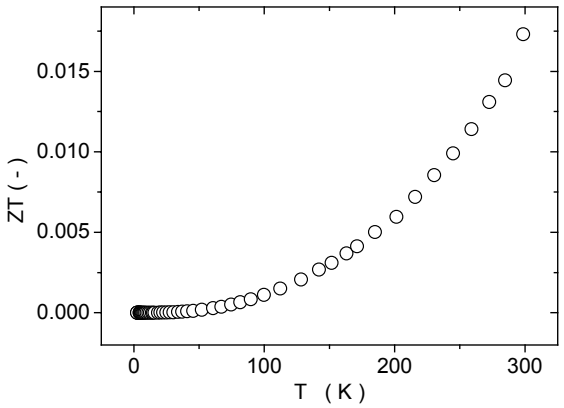

Fig.6. Dimensionless figure of merit of Bi_2O_2Se as a function of temperature.

In this paper we present original results of investigation of physical properties of Bi_2O_2Se. Measurements of Seebeck coefficient, electrical resistivity and thermal conductivity carried out in the temperature region 5-300 K allow the following conclusions:

a) A compound Bi_2O_2Se is an n-type degenerate semiconductor.

b) The steep increase in the thermoelectric figure of merit indicates that Bi_2O_2Se might be a promising thermoelectric material for the temperature range above 300 K.

Acknowledgement

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