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Novel method for metal-oxide glass composite fabrication for use in thermoelectric devices

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ABSTRACT

A novel method for thermoelectric materials fabrication using a reduction of oxide precursors in hydrogen was reported. On the example of Bi–Sb, Bi–Sb–Te and Te–Ag–Ge–Sb compounds it was shown that this simple and easy method is suitable for fabrication of two-, three- and even multicomponent thermoelectric materials. It allows controlling a composition, microstructure and even type a of electrical charge carriers. As a result of reduction of oxide precursors a layered structure with an average thickness of layers equal tens of nanometers was formed. At the near-room temperature the best material with a figure of merit (ZT) close to 0.4 was $Bi_{0.8}Sb_{1.2}Te_3O_x$ reduced at 340 °C for 10 h. At 350 °C a value of $ZT = 0.8$ was reached by the $(GeTe)_{0.85}(AgSbTe_2)_{0.15}$ (TAGS85) sample reduced twice at 400 °C for 10 h.

1. Introduction

In a continuously growing world's demand for energy there is a necessity to either increase the efficiency of existing power generators or to find a way to utilize a waste heat. Thermoelectric generators are devices which can directly convert thermal energy into electrical energy and thus, using a waste heat for electricity generation, they are a part of the energy-saving trend. The usability of potential thermoelectric materials for both heat generation and cooling is determined by various parameters: Seebeck coefficient (α), electrical conductivity (σ) and thermal conductivity (κ). All of them are combined in a dimensionless figure of merit: $ZT = \alpha^2 T\sigma/\kappa$ [1], which is defined at a particular temperature (T). The higher are the Seebeck coefficient and the electrical conductivity of a material and the lower is the thermal conductivity, the better is the material from the thermoelectric applications point of view. However, thermal conductivity is a sum of electronic and lattice components:

$$\kappa = \kappa_e + \kappa_l$$

First indicates to electrons/holes transporting heat (κ_e) and second one to phonons travelling through the lattice (κ_l). Electronic thermal conductivity is directly proportional to the electrical conductivity. Thus if σ is high, then κ_e is also high and it finally results in a lower figure of merit. Therefore, we are able to manipulate only with a lattice component of thermal conductivity (κ_l). It is mainly determined by a mean free path of phonons and it can be controlled by chemical substitutions or by a material structure. According to the concept of Slack [2–4] the best thermoelectric material should be a kind of 'phonon-glass electron-crystal'. It means that an optimal material should have thermal properties of an amorphous or glass-like material to effectively scatter phonons and the electrical properties of a crystalline material.

Among the most commonly known thermoelectric materials one can find Bi_2Te_3 [5,6], Sb_2Te_3 [2], $(Bi,Sb)_2(Te,Se)_3$ [7], $(Sb_{0.8}Bi_{0.2})_2Te_3$[8], $Bi_2(Te_{0.8}Se_{0.2})_3$ [2] and $(GeTe)_{1-x}(AgSbTe_2)_x$ (TAGS) [9,10–14]. These materials are known from good thermoelectric performance ($ZT > 1$), but in particular temperature ranges. They can be synthesized via many techniques. One of the most commonly known is mechanical milling of metallic substrates [15]. The other are melting/solidification technique [16], vapor condensation [17], wet-precipitation process [18], arc discharge process [17], co-sputtering [19], pulsed laser deposition [20], electrochemical deposition [21] or mechanical alloying combined with microwave activated hot pressing (MAHP) [22]. Also a method starting from oxide reagents with further reduction in hydrogen and spark plasma sintering was reported in the literature [8].

Current striving to improve thermoelectric performance takes place at two levels. One is searching for novel materials with a high ZT. The second is finding a way for suitable structural modifications, such as nanostructuring, preparing composites of different grain sizes, forming thin films or multilayer systems. This kind of modifications may lead to the reduction of lattice component of

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thermal conductivity. However, it can also undesirably result in a decrease of carrier mobility.

In this paper we want to report a novel method for thermoelectric materials fabrication using a reduction of oxide precursors in hydrogen. It bases on our previous experience in reduction of oxide glasses. These materials are known for very low thermal conductivity, but their electrical conductivity is also very low. After reduction at high temperature in hydrogen metal ions are reduced to neutral atoms and then metal grains are formed in an amorphous glass matrix and on a glass surface [23–25]. Further reduction leads to the connecting of metal grains and to the formation of continuous, metallic layer on a surface of the glass. In our method we suggest to melt oxide reagents and then quench them in order to obtain an oxide bulk product (amorphous or partially crystalline – depending on the composition). If this bulk sample is ground to obtain a powder and then this powder is reduced, it is possible to fabricate a metal-oxide glass composite. This kind of material may have good thermoelectric properties, because of high phonon scattering on grain boundaries and, as a result, lower thermal conductivity.

The aim of this paper is to present a novel method of fabrication of thermoelectric materials. We want to show only the most representative results in order to prove that this simple and cheap method is suitable for fabrication of two-, three- and even multicomponent thermoelectric materials. Thus Bi–Sb, Bi–Sb–Te and Te–Ag–Ge–Sb systems have been taken for presentation. Deeper analysis of properties of these compounds can be found elsewhere [26,27].

2. Experimental

Oxide samples $20Bi_2O_3$-$80TeO_2$ (denoted as $Bi_2Te_4O_x$), $25Bi_2O_3$-$75TeO_2$ (denoted as $Bi_2Te_3O_x$), $5Bi_2O_3$-$20Sb_2O_3$-$75TeO_2$ (denoted as $Bi_{0.4}Sb_{1.6}Te_3O_x$), $10Bi_2O_3$-$15Sb_2O_3$-$75TeO_2$ (denoted as $Bi_{0.8}Sb_{1.2}Te_3O_x$) and $38.2GeO_2$-$51.7TeO_2$-$6.72AgNO_3$-$3.38Sb_2O_3$ (denoted as $(GeTe)_{0.85}(AgSbTe_2)_{0.15}$ or TAGS85) have been produced from appropriate reagent grade oxides: TeO_2,AgO, GeO_2 and Sb_2O_3. The procedure applied for first four compounds was reported elsewhere [26]. First, the reagents were pulverised in an agate mortar and melted in a ceramic crucible at 950–1000 °C in air for 2 h. Pouring them on a stainless steel plate quenched the melts. As a result, bulk samples have been obtained. In the next step the samples were ground in an agate mortar to obtain a powder. Then the powder was reduced at 340 or 400 °C in H_2 for 10 h. After that it was put to the cylindrical matrix and shortly pressed uniaxially in a hydraulic press (p = 40 MPa) under elevated temperature (180 °C) in a hydrogen atmosphere. In consequence, bulk cylindrical pellets ($h \approx 5$ mm; $Ø \approx 5$ mm) of a metallic colour have been obtained.

Table 1
Experimental densities and porosities of samples investigated in this paper. Accuracy: ±5%.

Composition	Conditions of reduction	Density ($g\,cm^{-3}$)	Porosity (%)
$Bi_2Te_4O_x$	400 °C, 10 h	6.70	12.0
$Bi_2Te_3O_x$	340 °C, 10 h	5.90	23.0
$Bi_{0.4}Sb_{1.6}Te_3O_x$	400 °C, 10 h	5.09	24.0
$Bi_{0.8}Sb_{1.2}Te_3O_x$	340 °C, 10 h	5.32	23.0
$(GeTe)_{0.85}(AgSbTe_2)_{0.15}$	400 °C, 2.5 h	4.91	5.4
$(GeTe)_{0.85}(AgSbTe_2)_{0.15}$	400 °C, 10 h	4.95	14.1
$(GeTe)_{0.85}(AgSbTe_2)_{0.15}$	400 °C, 10 h + 10 h	4.94	8.9

In the case of $(GeTe)_{0.85}(AgSbTe_2)_{0.15}$ (another notation is $Ge_{0.37}Te_{0.50}Ag_{0.065}Sb_{0.065}$) compound the procedure was modified. After reagents melting and quenching, the fabricated bulk sample was ground with the Fritsch planetary mill Pulverisette 6 for 12 h to obtain a powder. Then the powder was reduced at 400 °C in H_2 for 2.5 or 10 h. After that it was put to the cylindrical matrix and pressed uniaxially in a hydraulic press (p = 60 MPa) at 340 °C in an argon atmosphere. As previously, the bulk cylindrical pellets ($h \approx 5$ mm; $Ø \approx 5$ mm) of a metallic colour have been finally obtained. In order to investigate the influence of repeated reduction process on the properties of TAGS, a sample previously reduced for 10 h was reduced once again at 400 °C for 10 h in

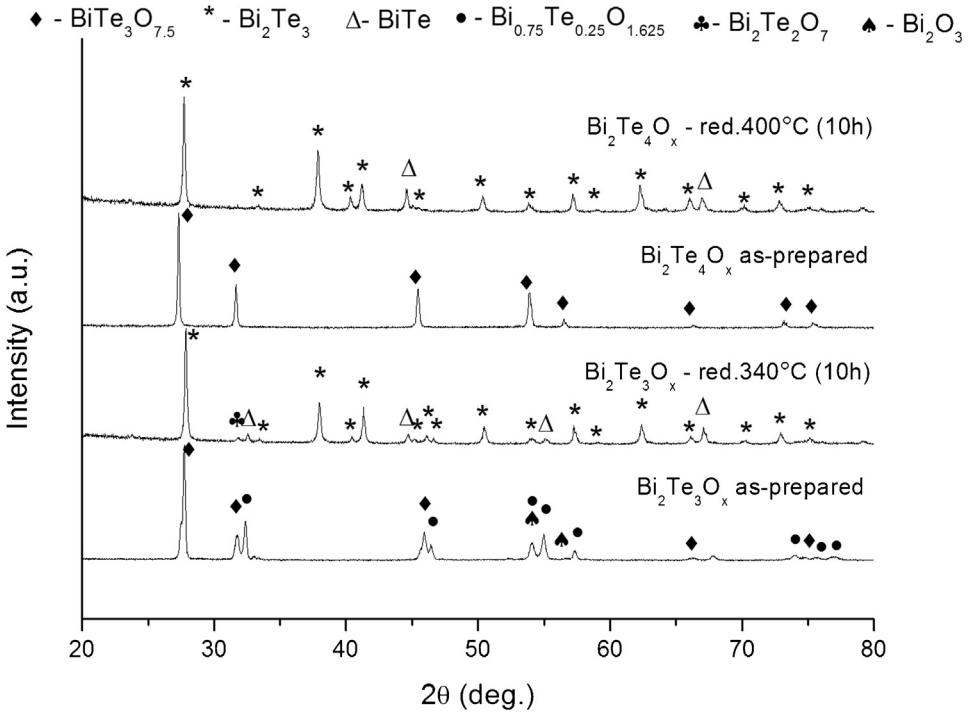

Fig. 1. XRD plots of as-prepared $Bi_2Te_4O_x$ and $Bi_2Te_3O_x$ samples, as well as after reduction in hydrogen at 400 °C or 340 °C for 10 h, respectively. Reproduced from Ref. [26].