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New composites of $ZnO–P_2O_5$/Ni having PTC transition and high Seebeck coefficient

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ABSTRACT

In this article, we report the electrical conductivity (σ) and Seebeck coefficient (S) of $ZnO–P_2O_5$ matrix filled with conductive powder of nickel (Ni). The variation of σ versus volume fraction of Ni showed a non-conducting to conducting phase transition at percolation threshold (28 vol. %). The change of S from high positive to negative values exhibits that this transition is accompanied by the passing of carrier charge from p to n type. On the other hand, the measurements of σ and S as function of temperature, above the percolation threshold, showed a positive temperature coefficient (PTC) phase transition at $T_c \geq 400$ K, linked with a high $S = -5000$ μV/K, giving highest power factor $PF = \sigma.S^2 \approx 2.10^{-4}$ W m^{-1} K^{-2}. The temperature dependence of the volume expansion enabled to confirm that this transition is associated to the thermal volume variation in matrix. However, the temperature dependence of σ below the percolation threshold showed two different mechanisms: thermally activated hopping behavior at high temperatures and Mott's variable range hopping (VRH) at low temperatures.

1. Introduction

The research of new materials with original properties for different applications is one of the aims in the activity of scientists. The study of material thermoelectric properties is among these objectives. The direct conversion between thermal energy and electric energy was discovered by Seebeck in 1882. Many applications were found to valorize this effect in thermoelectric power generation, microdevices, refrigeration …etc [1–4]. The performance of the thermoelectric material is measured with the figure of merit $ZT = S^2\sigma T/\kappa$ where T is absolute temperature, S is Seebeck coefficient, σ is electrical conductivity and κ is thermal conductivity; the applications require ZT higher than 1. Thus, the challenge of researchers is to find a material showing a high Seebeck coefficient, a large electrical conductivity and a weak thermal conductivity to maximize ZT [2,4].

Moreover, another important thermoelectric phenomenon is the positive temperature coefficient (PTC), showed by the abrupt decrease of the electrical conductivity at critical temperature, indicating a conductor – non conductor phase transition. The PTC effect has been obtained on ceramics derived from oxides combined with titanate of barium or polycrystalline titanate of barium doped with higher valence cations [5,6], in several types of materials based on vanadium oxides [7], ceramic materials or their composites [8] and polymer matrix composites [9,10].

This effect can be used in various fields of industrial applications: electronic devices and engineering such as auto-regulating heaters, thermal detectors, current limiters in circuit protection, and others [11,12].

According to this objective, the aim of this work is to study the thermoelectric properties of a new material as zinc phosphate glass 45 mol. % ZnO–55 mol. % P_2O_5 (ZP)/metal composites, by measuring their electrical conductivity and Seebeck coefficient as function of temperature. Indeed, the matrix-glasses of xZnO–$(100-x)$ P_2O_5, where x is mol. % and $30<x<60$ were prepared and structurally characterized. The ZP/metal (Ni, Co) composites were elaborated and electrically studied at room temperature by our team [13]. The results showed a high electrical conductivity above a critical volume fraction of the filler. This behavior was fairly interpreted in the percolation statistical frame [14].

Besides, zinc oxide is well-known for its use in different applications [15] and P_2O_5 oxide is characterized by a low glass transition temperature, optimizing coefficient of thermal expansion (CTE) based on the change of composition and high ultra-violet transmission [16]. Thus, the combination of these oxides to form a matrix filled with conductive particles may give interesting physical properties by changing temperature.

2. Experimental procedure

2.1. Preparation of composites

The method used to obtain composites has already been described elsewhere [13]. The matrix xZnO$(100-x)$$P_2O_5$, with x is mol. % and $30<x<60$, was prepared using the classical quenching technique. Powders of ammonium di-hydrogen phosphate ($(NH_4)H_2PO_4$ from

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Panreac type, 98%) and of zinc oxide (ZnO from Panreac type, 99%) are mixed in adequate molar proportion. X-ray diffraction has shown that amorphous phases were obtained when $30<x<60$. Then, thin particles of nickel (from Sigma-Aldrich with an average particle size of 149 μm, and a purity of 99.9 %) are mixed with a zinc phosphate glass matrix powder of 45 mol. % ZnO–55 mol. % P_2O_5 (ZP) in adequate proportions. The mixture of powder microcomposites was transferred into cylindrical mould and pressed into compact disk of 13 mm of diameter and 2–3 mm of thickness at a pressure of 7 ton/cm^2. Then, the disks were sintered at 300 °C for 2 hours in order to increase the cohesion of obtained composites. A series of composites was prepared with filler contents ranging from 1 to 40 vol. % into the matrix. The morphology and structure of the prepared composites were checked with SEM and X-ray diffraction. This study showed that the ZP-matrix is amorphous and the glass transition temperature is $T_g=430$ °C [13].

2.2. Electrical conductivity and thermoelectric power measurements

To characterize transport phenomena in composite materials, the direct conductivity (σ_{dc}) and the thermo-electric power ($S=-\Delta V/\Delta T$) were measured versus temperature between 150 K and 450 K. For the temperature study, the samples are put inside a vacuum chamber (10^{-2} mbar). σ_{dc} is measured by the four-point probe technique of Valdes [17]: current is injected by a Keithley 200 current source and voltage is measured with a Keithley 617 electrometer. S is determined using two point contacts: when a temperature gradient ($\Delta T=9$ K) was applied, the majority carriers can diffuse from the hot point to the cold one and thus an electrical potential (ΔV) is obtained. The detail of experimental protocol is described elsewhere [18,19].

2.3. Volume expansion measurements

The volume expansion of the composites was obtained with a SETARAM TMA 92 thermo-mechanical analyzer, using a programmed heating rate of 2 K/min in a temperature range varying from 300 to 500 K.

3. Results

3.1. Non-conducting/conducting phase transition by changing filler concentrations

Fig. 1 gives the electrical transport versus filler volume fraction ϕ at room temperature for 45 mol. % ZnO–55 mol. % P_2O_5 (ZP) loaded with Ni particles. The measurements of the electrical conductivity with the square four-point probe technique on the surface of the samples give almost the same behavior than those obtained with volume sandwich 2 points method [13]. A jump from 10^{-8} to ~1S/cm was observed, indicating a non-conducting to conducting phase transition at percolation threshold of $\phi_c=28$ vol. %, when an infinite conductive path of clusters is formed. On Fig. 1, the Seebeck coefficient data are also reported, the percolating behavior is confirmed. The conduction threshold is almost the same as the one obtained with conductivity. Moreover, the coefficient S changes its sign from positive to negative for low and high level filling, respectively. Indeed, below percolation threshold, high positive values over 3000 μV/K are obtained with a low conductivity ($\sigma=10^{-8}S$/cm). Then, above but close to the percolation threshold ($\phi=30$ vol. %), S becomes negative ($S=-100$ μV/K) corresponding to $\sigma=1S$/cm. For high amounts of Ni, S increases to typically metallic values (between −10 and −20 μV/K). This behavior indicates a passing from p to n semiconductor material type or insulator/conductor phase transition, in good agreement with conductivity results.

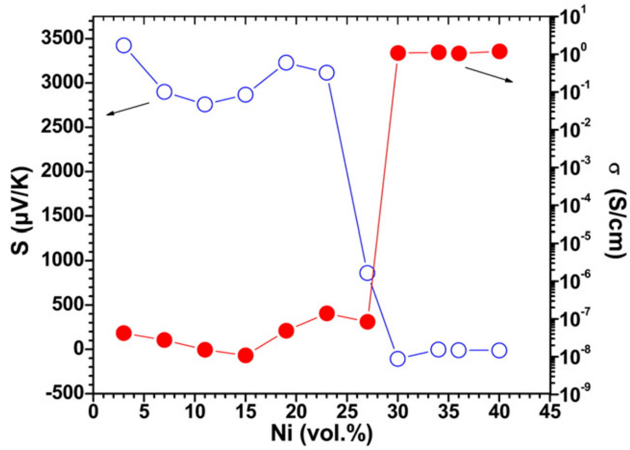

Fig. 1. Dependence of Seebeck coefficient (○) and electrical conductivity (●) of ZP/Ni composites versus nickel volume fraction percentage.

3.2. Positive temperature coefficient (PTC) phase transition

The temperature dependence of the conductivity for different filler contents (30, 36 and 40 vol. %) above the percolation threshold incorporated in ZP-matrix is given on Fig. 2. It can be seen that two regimes characterize the conductivity versus temperature:

- 220 K$<T<$400 K, conductivity decreases slightly when the temperature increases. Such a variation is characteristic of a metallic behavior.
- Around and $T\geq400$ K, abrupt and important decrease of the electrical conductivity of the composites ZP/Ni is observed, indicating the occurrence of conductor-semiconductor phase transition, called positive temperature coefficient (PTC) effect. This phenomenon is observed for high concentrations of metal (i.e. $\phi_{Ni}\geq\phi_c$) and below T_g. The temperature of transition T_{PTC} increases slightly with a metallic amount ($\phi\geq\phi_c$) incorporated in ZP-matrix. The PTC intensity can be given as:

$$I_{PTC}=log\left({}^{\sigma_{low}}/_{\sigma_{RT}}\right) \quad (1)$$

where σ_{RT} is the room temperature conductivity and σ_{low} is the lowest conductivity after PTC transition.

It may be noted that the PTC effect is even higher when the filler content in ZP is significant and greater than the percolation threshold:

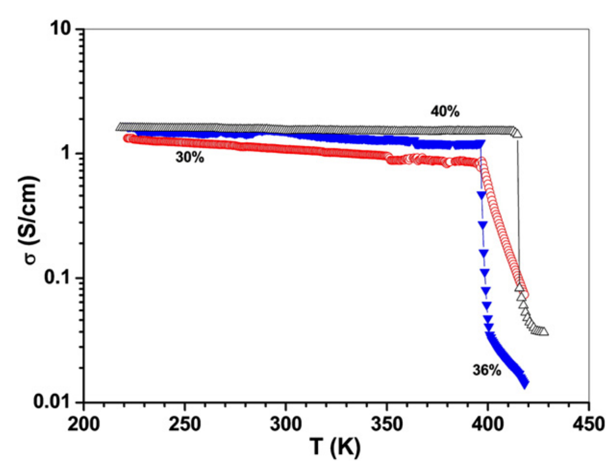

Fig. 2. Temperature dependence of electrical conductivity of ZP/Ni composites for high filling: (○) 30, (▼) 36 and (△) 40Ni vol. % .