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Enhancing the thermoelectric performance of filled skutterudite nanocomposites in a wide temperature range via electroless silver plating

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ABSTRACT

So far high thermoelectric performance of filled skutterudite can only be obtained at relatively high temperature, which severely limits its application. Here, Yb-filled skutterudite ($Yb_{0.35}Co_4Sb_{12}$) composites incorporated with silver nanoparticles are fabricated via electroless plating for achieving enhanced thermoelectric performance. The content and homogeneity of Ag nanoparticle can be well controlled to optimize the thermoelectric properties of bulk composite. As a result, the $Yb_{0.35}Co_4Sb_{12}$ composite with optimum Ag content shows remarkably improved Seebeck coefficient and power factor, which leads to high ZT values above 0.8 from 450 to 800 K and a peak value of 1.0 at 603 K.

As a green technology for obtaining sustainable energy, thermoelectric (TE) devices based on TE materials that can directly convert energy between heat and electricity have attracted great attention due to the advantages such as long operating time, no moving parts and high reliability [1,2], although they also suffer from the generally low conversion efficiency which is governed by the dimensionless figure of merit $ZT = \alpha^2\sigma T/\kappa$, where α, σ, κ, T are the Seebeck coefficient, electrical conductivity, thermal conductivity and the absolute temperature [3].

Among the promising TE materials, skutterudite structural compound $CoSb_3$ has been intensively investigated [4,5],owing to its reasonable band gap, high carrier mobility, and inexpensive environment-friendly elements [6]. However, the thermal conductivity of the pure binary $CoSb_3$ is too high, which results in low ZT values. Filling various foreign atoms, such as rare earth [7–10], alkaline earth [11,12], alkali metals [13,14], and other ions[15,16]into the voids can act as centers effectively scattering phonons that have similar vibration frequencies and thus reducing the lattice thermal conductivity dramatically [17]. In light of this, single-filled [8–16], double-filled [18,19] or even multiple-filled [20–23] skutterudites have been studied in order to boost the phonon scattering effect and optimize thermoelectric properties. However, most of these materials reach their best TE performance at relatively high temperature (800–900 K) [18–22], which can significantly deteriorate the efficiency of TE devices. More importantly, various problems such as instability could occur by multiple filling [7–22], which is also not suitable for realistic application [24,25]. Although other methods such as nanostructuring have been proved to be very effective in some cases [26,27], preparing composite of single-filled skutterudite by employing nanoparticles as second phase is a more practical way for enhancing the TE performance of skutterudite in a wide temperature range.

As a typical second phase in composite, nano-sized Ag has been shown to have great potential for improving TE properties [28–30]. However, Ag nanoparticles tend to agglomerate when introduced to matrix by traditional methods, which could lead to declined performance and low repeatability. In this study, Ag nanoparticles were incorporated into skutterudite matrix by electroless silver plating for the first time, and the TE properties of obtained composites were investigated.

$Yb_{0.35}Co_4Sb_{12}$ ingot was synthesized by melting and long-term annealing at high temperature [8,9].The ingot was ground by hand into fine powders and coated with Ag nanoparticles by electroless silver plating. Specifically, the pre-cleaning was conducted by immersing the powders in 30 mL/L HCl aqueous solution at room temperature for 10 min under stirring. After that, the powders were cleaned by alcohol and dried in the vacuum oven. Sensitization was carried out by immersing of the powder in an aqueous solution containing 30 mL/L HCl and 10 g/L $SnCl_2$ at 50 °C for 30 min under stirring, then rinsed the samples with alcohol. The resulting samples were then immersed in an aqueous

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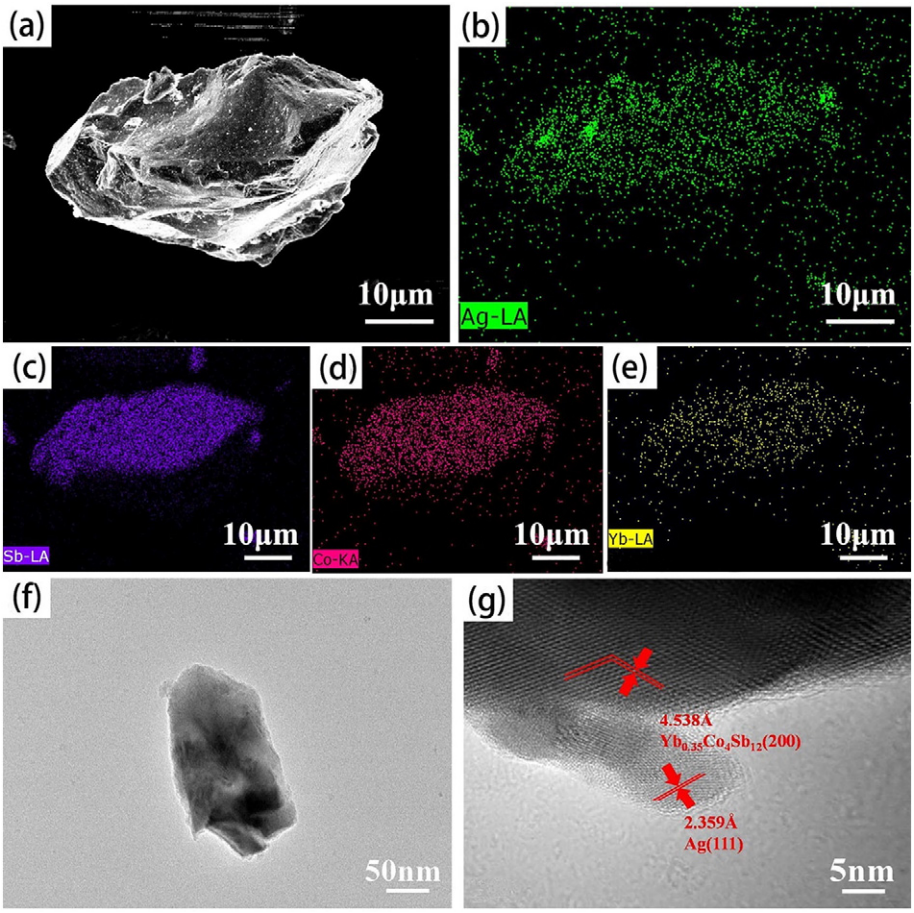

Fig. 1. The SEM image of a $Yb_{0.35}Co_4Sb_{12}$@Ag-10 min particle after electroless plating(a) and EDS mapping results for Ag (b), Sb(c), Co(d), and Yb(e) of the same particle; TEM (f) and HRTEM (g) images of a $Yb_{0.35}Co_4Sb_{12}$@Ag-10 min particle.

solution of 1 g/L $PdCl_2$–30 mL/L HCl for activation, before cleaned the samples by alcohol and dried in the vacuum oven. The activated samples were immersed in electroless plating bath (contained silver salts solution A and formaldehyde-based reducing solution B) at room temperature for X min (X = 8, 10, 12, and 14) under vigorous stirring, and are denoted as $Yb_{0.35}Co_4Sb_{12}$@Ag-X min accordingly. The reaction can be written as:

$$2\left[Ag(NH_3)_2\right]OH + HCHO = 2Ag + HCOOH + 4NH_3 + H_2O \quad (1)$$

After that, the resulting samples were cleaned again with alcohol using centrifugation, and dried in vacuum for 12 h. The dried powder was sintered by Spark Plasma Sintering (SPS) at 650 °C under a pressure of 70 MPa for 15 min.

The phase of the samples was characterized by X-ray diffraction (XRD) using a Rigaku D/Max-2550 PC diffractometer (Tokyo, Japan) equipped with CuKα radiation. The microstructures and chemical compositions were investigated by field-emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), energy dispersive spectroscopy (EDS) and inductively coupled plasma emission spectrometer (ICP). The resistivity and Seebeck coefficient were measured using an ULVAC-ZEM3 system. The thermal conductivity was calculated from the thermal diffusivity λ measured by a laser flash system(LFA457,Netzsch), density d obtained by the Archimedes method and the specific heat C_p was measured by differential scanning calorimetry (DSC) using a Netzsch equipment (204F1). The Hall coefficient (R_H) at room temperature was measured by the Van der Pauw's method using Hall measurement system (Lake Shore 8400 Series) at 1.7 T. Disc samples with the dimension of 1 mm×∅10 mm were used for this measurement.

The result of electroless silver plating was first characterized by EDS. From a typical particle of $Yb_{0.35}Co_4Sb_{12}$@Ag-10 min powder (Fig. 1(a)), it can be seen that the elements of Sb, Co, Yb are homogeneously distributed in the skutterudite particle without local enrichment. Similarly, the distribution of silver element is generally homogeneous over the surface

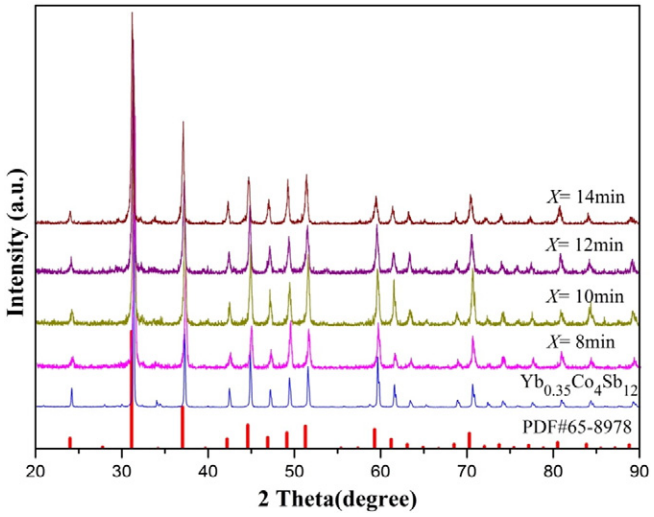

Fig. 2. XRD patterns of $Yb_{0.35}Co_4Sb_{12}$ bulk sample and the $Yb_{0.35}Co_4Sb_{12}$@Ag-Xmin bulk composites.