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# Thermoelectric properties of $YbCd_2Sb_2$ doped by Mg

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ABSTRACT

p-type $YbCd_{2-x}Mg_xSb_2$ (x = 0.1, 0.2, 0.4, 0.6, 0.8) Zintl phases have been synthesized via melting reaction followed by suitable cooling, annealing, grinding, and spark plasma sintering (SPS) densification processes. The effects of isoelectronic substitution of Mg for Cd on thermoelectric properties have been investigated. Electrical conductivity, Seebeck coefficient, and thermal conductivity measurements have been performed as a function of temperature from 300 to 650 K. The XRD patterns show that the solubility limit x of Mg in the $YbCd_{2-x}Mg_xSb_2$ is less than 0.8. With increasing Mg content x, the cell parameters a and c of the $YbCd_{2-x}Mg_xSb_2$ compounds decrease. The isoelectronic substitution of Mg for Cd leads to a remarkable decrease in total thermal conductivity and an increase in Seebeck coefficient, though a slightly decease in electrical conductivity. As a result, the maximum dimensionless figure of merit ZT of 1.08 is obtained at 650 K for $YbCd_{1.9}Mg_{0.1}Sb_2$. Compared with the ZT of 0.78 at 650 K in the unsubstituted $YbCd_2Sb_2$, it is improved greatly by 38%.



## 1. Introduction

Through the use of thermoelectric materials, electricity from waste heat sources is another potential source of power [1]. The heat can come from the combustion of fossil fuels, from sunlight, or as a byproduct of various processes (e.g. combustion, chemical reactions and nuclear decay) [2]. Therefore, thermoelectric materials can play an important role in both primary power generation and energy conservation. Thermoelectric modules are solid-state devices that directly convert thermal energy into electrical energy. The efficiency of a thermoelectric (TE) material performance is quantified by a dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the absolute temperature [3]. Accordingly, a good TE material with high ZT value requires the combination of high electrical conductivity σ, low thermal conductivity κ, and high thermopower or Seebeck coefficient S. Materials that meet these requirements are found for typically heavily doped, small band-gap semiconductors or semimetals [4,5]. Such materials provide a balance between the high Seebeck coefficient of semiconductors and the high electrical conductivity of metals. In addition, good TE materials have complex crystal structures that scatter phonons, resulting in a low thermal conductivity [6]. Recently, it is shown that several CdSb-based compounds [7,8], which are representatives of the $CaAl_2Si_2$ type of crystal structure [9] partly meet the above mentioned requirements and show a high thermoelectric figure of merit ZT. In particular, $YbCd_2Sb_2$ gives a peak ZT value of 0.98 at 700 K [7]. The good thermoelectric properties were attributed to the high atomic mass of Sb causing a low lattice thermal conductivity [10] or to special features in atomic interactions [11]. A further reduction of the thermal conductivity can be expected by the partial substitution of the constituting elements. It has already been shown that the thermoelectric properties of the respective ternary compounds are improved within the quaternary solid solutions $Ca_{1-x}Yb_xZn_2Sb_2$ [6] and $YbZn_xCd_{2-x}Sb_2$ [7]. Note that $YbMg_2Sb_2$ [12] is isostructural to $YbCd_2Sb_2$, it therefore inspired our present study of the Mg substitution on the Cd site. In this work, we investigate thermoelectric properties in the system $YbCd_{2-x}Mg_xSb_2$ for the compositions with x = 0.0, 0.1, 0.2, 0.4, 0.6 and 0.8. One would expect to observe that the Mg substitution would improve or finely tune the transport properties of $YbCd_2Sb_2$.

## 2. Experimental procedures

The Zintl phases $YbCd_{2-x}Mg_xSb_2$ (x = 0.2, 0.4, 0.5, 0.6 and 0.8)

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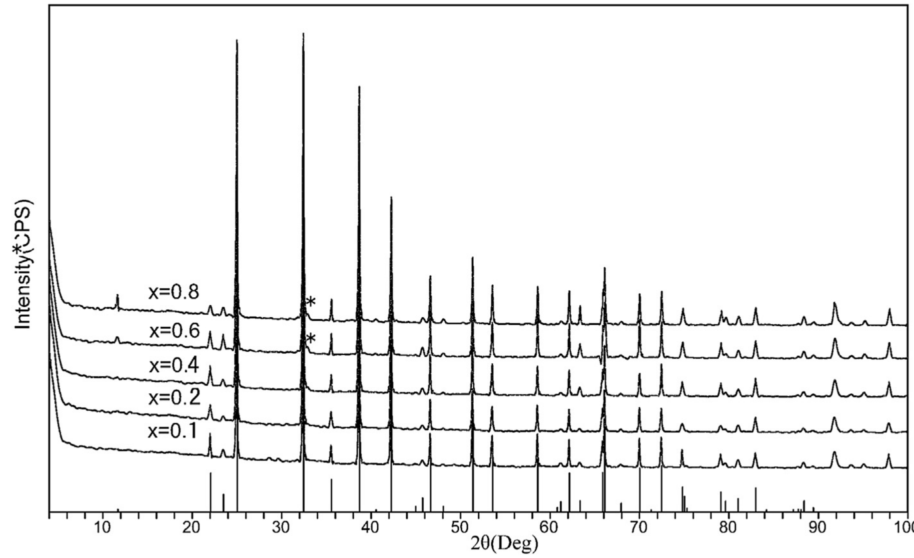


**Fig. 1.** XRD patterns of $YbCd_{2-x}Mg_xSb_2$ compounds. Unknown phase marked with *.

were prepared by the melting and spark plasma sintering method. In this method, the reaction among all the elements was allowed to take place gradually in the carbon crucible. All materials were handled in a nitrogen-filled glove box with $H_2O/O_2$ levels below 1.0 ppm. The mixtures of Yb (99.99%), Cd (99.999%) Mg (99.9%) and Sb (99.999%) in a molar ratio 1:2-x:x:2 were placed in carbon crucible with 10 mm diameter and 30 mm hight and sealed into evacuated quartz tubes. These assemblies were then heated slowly to 1000 °C at a rate of 1 °C/min, kept for 72 h, subsequently cooled to room temperature at a rate of 2 °C/min. The products were finely powdered, pressed into pellets and annealed at 600 °C for 7 days. The so-obtained products were ground in an agate mortar to fine powders. In order to obtain bulk substituted compounds $YbCd_{2-x}Mg_xSb_2$ samples successfully, spark plasma sintering (SPS 2040) was carried out at around 480 °C for 10 min under a uniaxial pressure of 60 MPa in vacuum. The sample showed metallic luster and stability to air. The densities of ceramic pellets were measured by the Archimedes method. The relative densities were above 93% of the theoretical densities. To measure thermoelectric properties, bar-shaped specimens of average size 10mm × (~) 3.0mm × (~) 2.0 mm were cut from the bulk samples.

The phase purity of final samples was checked by X-ray powder diffraction (XRD) on a Huber G670 Image Plate Camera (Cu K$\alpha_1$ radiation, $\lambda = 1.5406$ Å). Chemical composition of the phases was determined by using electron probe microanalysis (EPMA, 8705QH2). The heat capacity and Hall effect were measured with a physical property measurement system (PPMS, Quantum Design, Inc.) from 2 to 300 K with a magnetic flux density up to ±5 T. The carrier concentration n was calculated according to $n = 1/qR_H$, where q is electric charge, $R_H$ is the Hall coefficient. And the charge mobility μ was determined by $\mu = \sigma R_H$.

The thermal conductivity of the pellets can be derived from the relationship $\kappa = dC_p\lambda$, where d is the experimental density, λ is the experimental thermal diffusivity, and $C_p$ is the room temperature heat capacity. The thermal diffusivity of several specimens was determined by using a NETZSCH LFA 427 Micro Flash instrument. The electrical conductivity and Seebeck coefficient are measured simultaneously under a helium atmosphere from 300 K to about 650 K using an ULVAC-RIKO ZEM-3 instrument system. According to the DTA data, $YbCd_{1.9}Mg_{0.1}Sb_2$ starts to decompose at 700 K, which gives the temperature limit of 650 K for properties measurements.

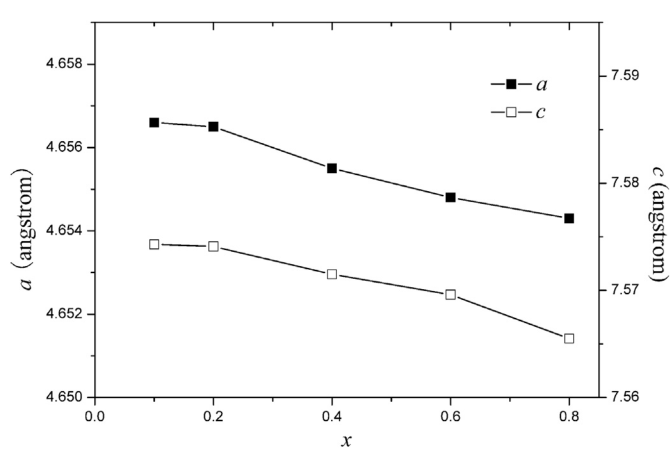


**Fig. 2.** Cell parameters a and c dependence on Mg contents x.

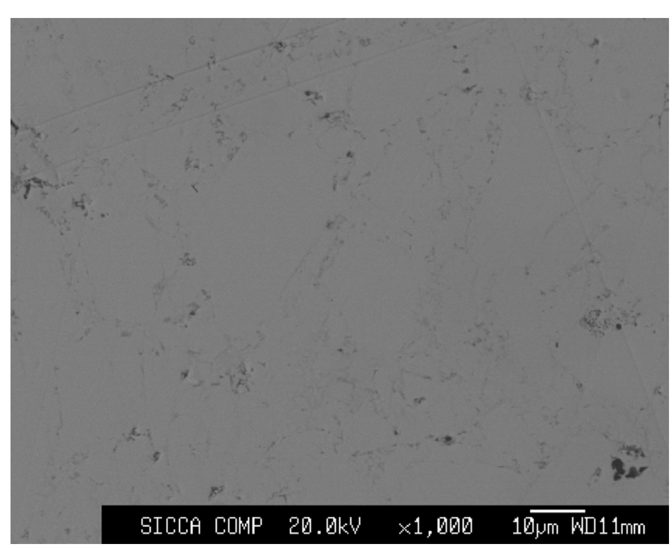


**Fig. 3.** Back-scattered electron image (BSEI) for the selected sample $YbCd_{0.2}Mg_{0.8}Sb_2$.