MATEC Web of Conferences **43**, 04001 (2016)
DOI: 10.1051/matecconf/20164304001

Some Physicochemical Properties of $Yb_{14}MnSb_{11}$ and Its Solid Solutions with Gadolinium $Yb_{14-x}Gd_xMnSb_{11}$ Type

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Abstract. Data on structure, melting temperatures, density, thermal dilatation, kinetic of oxidation of $Yb_{14}MnSb_{11}$ and its solid solutions with gadolinium are presented in this article.All solid solutions are isostructural with Zintlcompound $Ca_{14}AlSb_{11}$ and crystallizes in tetragonal structure. Investigations melting temperatures, thermal dilatation, oxidation have shown that GdincorporatenearGd≈ 0.5 and increased melting point and thermal dilatation.

1 Introduction

Zintl phases form a large family of compounds whose electronic conform to 8-N or Zintl – Klemm concept. This class of materials has been identified as promising for thermoelectric(TE) applications.A new direction of thermoelectric materials began when Slack theorized the so-called "electron crystals-phonon glass"[1]. Slack considered that a good TE material should have the electronic structure of a heavily doped narrow-band-gap semiconductor and thermal conductivity like a glass. One of new class materials for utilization as high-temperature thermoelectric materials are Zintl phases that employ the pnictides of rare earth elements and have the $Ca_{14}AlSb_{11}$ structure type.For the first time Zintl phase of $Yb_{14}MnSb_{11}$ was obtained in 1998[2]. $Yb_{14}MnSb_{11}$is high-temperature thermoelectricalmaterial [2-5].

Effectiveness of the material which is often used to convert thermal energy into electrical is characterized by coefficient zT ($zT=S^2T/\rho k$)**,** where **S-**Zeebeck coefficient, **ρ-**electrical resistance, **k-**thermal conductivity). All these three parameters are interlinked and one is optimized at the expense of others.Solidsolutions with lanthanum, cerium, thulium, lutetium (partial replacement of ytterbium) [6-11], with aluminum (replacement of manganese) [12], germanium, tellurium (partial replacement of antimony) [13,14] have been investigated with an aim towards increasing zT.

In spite of numerous publications, there are no works on thermal properties, there are no works on chemical properties. From the position of thermoelectrical materials thermal stability of these materials is also functional property since the exploitation of the material is carried out under high temperatures, where diffusion, volatility, oxidation processes easily occur.

Due to this the results of melting temperature and thermal dilatation, kinetic of oxidation of $Yb_{14}MnSb_{11}$ and its solid solutions with gadolinium are presented in the present work.

2 Experimental details

2.1 Synthesis

Crystals with the expected stoichiometry of $Yb_{14-x}Gd_xMnSb_{11}$ were grown from a molten Sn flux ($Yb_{14-x}Gd_xMn_6Sb_{11}Sn_{86}$) in a glassy carbon crucible. The elements were divided into layers: antimony- manganese-Gd- ytterbium-tin and quartz cotton that plays the role of filter at centrifugation was placed above. The crucible was placed in quartz ampoule pump out and seal. Pumped out quartz ampoule is placed in to the furnace and heat up to 1000°C with the delay at this temperature for 6 hours. Cooling up to 700°C was made at rate 2°/hour. At700°C ampoule was taken out from the furnace and centrifuged for 5 minutes. Crystals are separated into dry box [2].

2.2Electron microprobe analysis

The samples analyzed using a Camera JXA-8100 (JEOL, Japan) Electron Probe Micro-analyzer equipped with a wavelength-dispersive spectrometer with 20 keV accelerating potential and 30nA beam current.Net elemental intensities were determined with respect to calibration standards of $YbPO_4$, $GdPO_4$, SnO_2, Sb (high concentration relation to that in "14-1-11"), and Al-garnet-Arizona ruby O-145 (here content of MnO was 9.9 mass.%). The composition of the major phase in each sample was determined by calculating averages and standard deviations from 15-30 random data points. The

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Article available at http://www.matec-conferences.org or http://dx.doi.org/10.1051/matecconf/20164304001

composition of the minor phases was determined from 5-7 data points depending on the area of the phases and it was not sufficient for standard deviation (Table 1).

2.3 Powder X-ray diffraction

X-ray structural study of single samples was conducted on the apparatus DRON-UM (R=192mm, CuKα-radiation, Ni-filter, scintillation detector with amplitude discrimination, step 0.02° 2θ, impulse storage time in each point 3 s, room temperature) in the region of angles from 5 to 80° 2θ. Total shooting time was 9 hours. After crystal pounding in the mortar with heptanes and suspension drying on the polished side of the standard quartz cavity, the sample was flat and thin (~ 100 μm) layer. All studied samples have tetragonal structure and obtained lattice parameters are given in the Table 2.

2.4 Thermal stability

Thermal analysis with 2-3 mg was repeated 3-5 times with each sample. Two procedures were developed to study thermal stability of the tested samples. First was heating with the rate of 3000°C/min up to 1900°C in apparatus with the He pressure equal to 7 atm. During heating, all variations with the sample were fixed and related to appropriating peaks on the heating curve. Second procedure was step-by-step heating with examination what happens with the sample being heated to a given temperature. Three temperatures were taken: up to 1500°C, then 1750°C and at last 1900°C to fix stability without any vaporization, melting, and incongruent evaporation of melt. The apparatus was calibrated by melting point of Pd (1554°C) used as standard and this action was performed before and after measurements of the sets of the samples.

2.5 Thermal expansion

Thermal expansionwasmeasured in cylindrical samples about 4 mm in diameter, 10-13mm long the temperature range 25-750°C using a high-temperature dilatometer which construction is described in [15].

2.6 Kinetica

Oxidation kinetics was studied using thermogravimetric method based on the continuous sample weighing at temperatures 773, 873 и 973°C. Oxidation was carried out in air atmosphere in alumina crucibles.

3 Results and discussion

The experimental data were treated mathematically and the compositions of the major and minor phases and their calculated errors are given in Table 1.

The powder X-ray diffraction patterns for some samples are shown in Figure1.

Table 1. Composition of the major and minor phases observed.

$Yb_{13.9}Gd_{0.1}MnSb_{11}$	$Yb_{13.88}Gd_{0.17}Mn_{1.13}Sb_{11}$ $Yb_{13.90}Gd_{0.17}Mn_{1.13}Sb_{11}$	Sn Sn
$Yb_{13.7}Gd_{0.3}MnSb_{11}$	$Yb_{13.61}Gd_{0.40}Mn_{1.11}Sb_{11}$ $Yb_{13.57}Gd_{0.40}Mn_{1.11}Sb_{11}$	$Yb_1Mn_{2.1}Sb_2Sn$ $Yb_1Mn_{2.1}Sb_2Sn$
$Yb_{13.5}Gd_{0.5}MnSb_{11}$	$Yb_{13.50}Gd_{0.49}Mn_{1.11}Sb_{11}$ $Yb_{13.47}Gd_{0.49}Mn_{1.10}Sb_{11}$	$Yb_1Mn_{2.1}Sb_2Sn$
$Yb_{13.3}Gd_{0.7}MnSb_{11}$	$Yb_{13.50}Gd_{0.48}Mn_{1.09}Sb_{11}$	$Yb_1Mn_{2.1}Sb_2$
$Yb_{13.1}Gd_{0.9}MnSb_{11}$	$Yb_{13.67}Gd_{0.48}Mn_{1.14}Sb_{11}$ $Yb_{13.60}Gd_{0.47}Mn_{1.14}Sb_{11}$	$Yb_1Mn_{2.1}Sb_2$ $(Yb_2Gd_3)Sb_5$

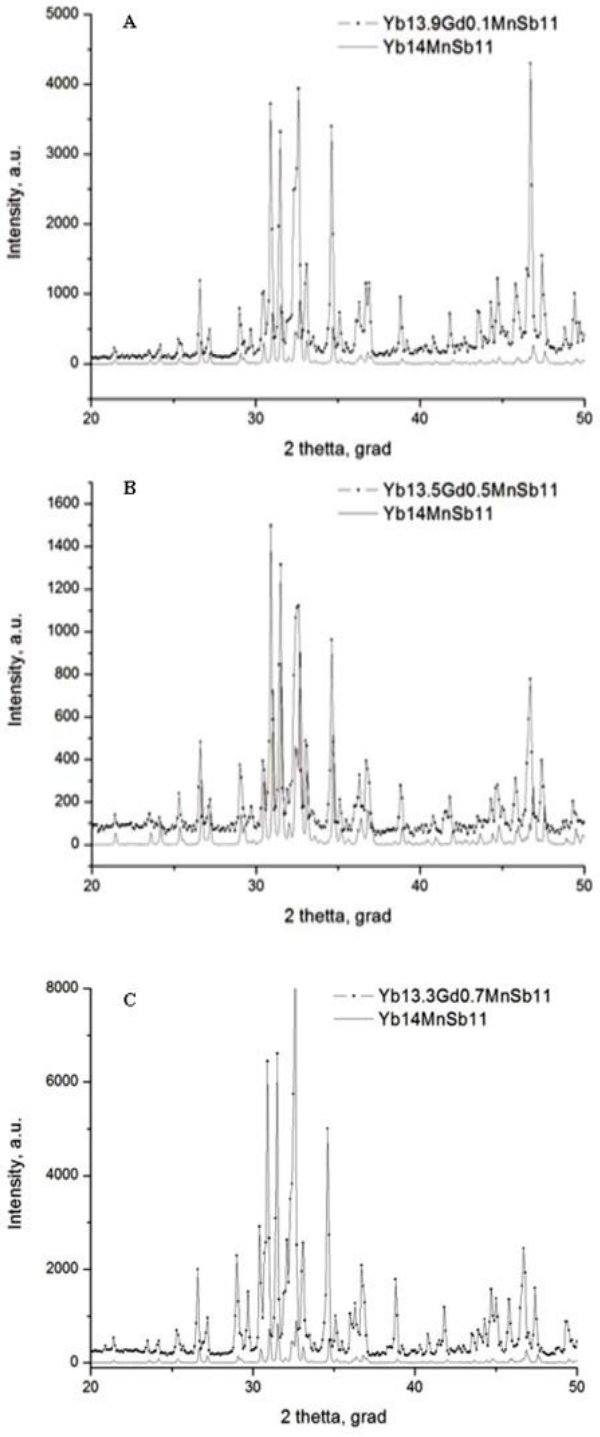

Figure 1. Power X-ray diffraction data for $Yb_{13.9}Gd_{0.1}MnSb_{11}$(A), $Yb_{13.5}Gd_{0.5}MnSb_{11}$(B) and $Yb_{13.3}Gd_{0.7}MnSb_{11}$(C).

All crystals have tetragonal structure and these lattice parameters are given Table2.

Table 2. Structural data of the samples $Yb_{14-x}Gd_xMnSb_{11}$.

Content Gd, x	a, Å	c, Å	V, Å ^{3}
0,1		22.000(11)	6075.47
0,3	16.624(8)	22.028(11)	6087.60
0,5	16.638(8)	22.055(11)	6105.33
0,7	16.639(8)	22.056(11)	6106.34
0,9*	16.636(8)	22.030(11)	6096.95

Thermo analysis found that compound $Yb_{14}MnSb_{11}$ and their solid solutions is melt at high temperature. Obtained temperatures of meltingare presented in the Table3.

Table 3. Some thermal properties of$Yb_{14-x}Gd_xMnSb_{11}$.

Compounds	Tmelt, ^{0}C	$\alpha\cdot10^{-6}$,K^{-1}	θ_D,K
$Yb_{14}MnSb_{11}$	1745	13.0	167
$Yb_{13.9}Gd_{0.1}MnSb_{11}$	1780	21.8	129
$Yb_{13.7}Gd_{0.3}MnSb_{11}$	1790	17.4	144
$Yb_{13.5}Gd_{0.5}MnSb_{11}$	1757	16.0	150
$Yb_{13.3}Gd_{0.7}MnSb_{11}$	1796	20.0	135
$Yb_{13.1}Gd_{0.9}MnSb_{11}$	1800	22.0	128

Investigation of thermal expansion determined that function $\Delta L/L_0$- f(T) is linear for all materials that indicate the constant coefficient of thermal dilatation α in this region of temperatures.

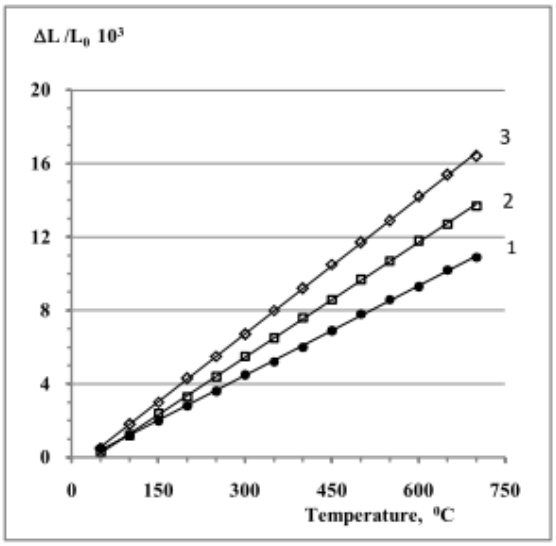

Figure 2. Determination $\Delta L/L_0$: 1 – $Yb_{13.9}Gd_{0.1}MnSb_{11}$; 2 - $Yb_{13.7}Gd_{0.3}MnSb_{11}$; 3 - $Yb_{13.5}Gd_{0.5}MnSb_{11}$.

Thermal expansion coefficients presented in the table are found by slopes of straight lines.

To obtain information on chemical link stability characteristic temperature Debye and mean-square substitution in crystal were calculated.

In [16], equation (1) which links thermal expansion coefficient with characteristic Debye temperature, was obtained by superposition of the Lindermann -Borelius and Grueneizen expressions:

$$\Theta_D = \frac{19.37}{\sqrt{\bar{A}\, v^{2/3}\alpha}} \qquad (1)$$

where Ā- mean-square atomic weight; V- molecular volume; α- coefficient of thermal expansion.

Both thermal expansion coefficients, melting temperatures and Debye temperatures evidences of changes after composition of gadolinium≈ 0.5 characteristics. Probably it can be explained by that fact that solubility limit of gadoliniumin this compound switches to this concentration.

The oxidation rate increases in all samples with the temperature increase. Oxidation curves have parabolic form with intensive oxidation rate in the initial period.InFigures3-6 oxidation kinetic curves of solid solutions are presented. According to the kinetic curves built basing on change in sample weight depending on time, the oxidation rate was calculated at each temperature. True oxidation rate of the compounds calculated according to tangent, drawn from the coordinate start to the curves and calculated by formula: K= g/s·Δt, is presented in Table4. According to the direct dependence lgK- 1/T, apparent activation energy was calculated(Table4).

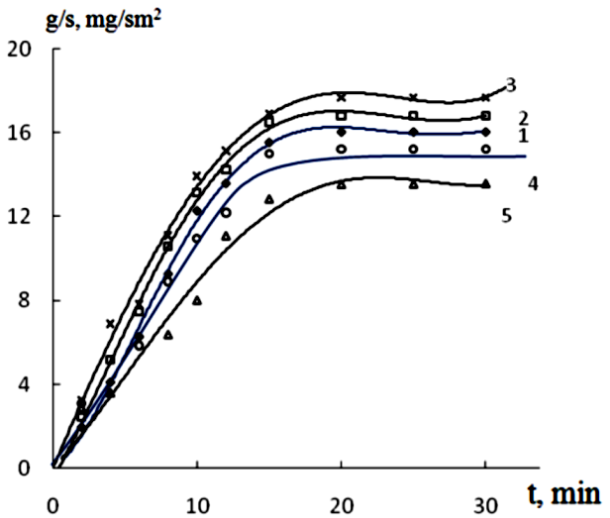

Figure 3. Kinetic curves oxidation $Yb_{14-x}Gd_xMnSb_{11}$ at 773K.

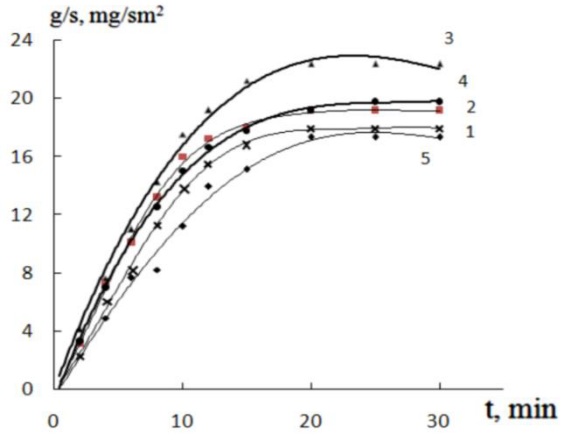

Figure 4. Kinetic curves oxidation $Yb_{14-x}Gd_x$ $MnSb_{11}$ at 873K.

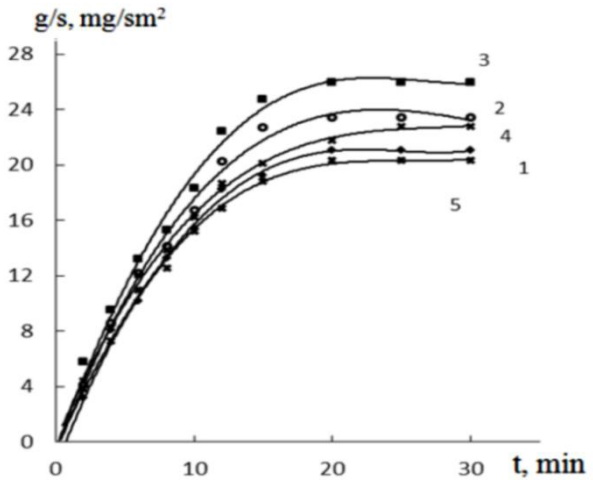

Figure 5. Kinetic curves oxidation $Yb_{14-x}Gd_x$ $MnSb_{11}$ at 973K.

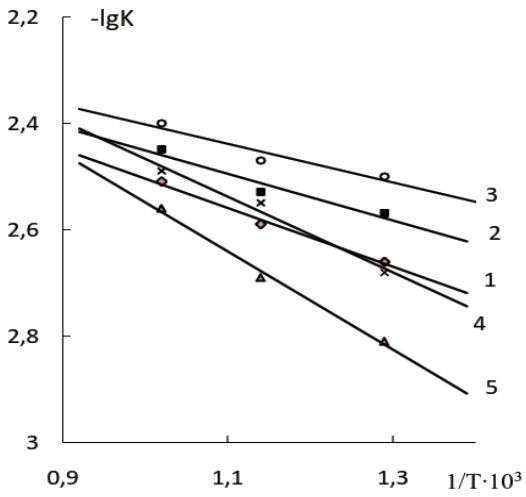

Figure 6. Dependence lgK on 1/T for $Yb_{14-x}Gd_xMnSb_{11}$ with composition: 1- $Yb_{13,9}Gd_{0,1}MnSb_{11}$; 2- $Yb_{13,7}Gd_{0,3}MnSb_{11}$; 3- $Yb_{13,5}Gd_{0,5}MnSb_{11}$; 4- $Yb_{13,3}Gd_{0,7}MnSb_{11}$; 5- $Yb_{13,1}Gd_{0,9}MnSb_{11}$.

Table 4. Kinetic and energetic parameters of oxidation alloys.

Solid solution compositions	Oxidation temperature,K	Oxidation rate, $K \cdot 10^{-4}$ $kg/m^2 \cdot s^{-1}$	Apparent activation energy, Kj/mol
$Yb_{13.9}Gd_{0.1}MnSb_{11}$	773 873 973	$0.22 \cdot 10^{-3}$ $0.25 \cdot 10^{-3}$ $0.31 \cdot 10^{-3}$	75.21
$Yb_{13.7}Gd_{0.3}MnSb_{11}$	773 873 973	$0.27 \cdot 10^{-3}$ $0.29 \cdot 10^{-3}$ $0.36 \cdot 10^{-3}$	62.7
$Yb_{13.5}Gd_{0.5}MnSb_{11}$	773 873 973	$0.31 \cdot 10^{-3}$ $0.33 \cdot 10^{-3}$ $0.39 \cdot 10^{-3}$	54.3
$Yb_{13.3}Gd_{0.7}MnSb_{11}$	773 873 973	$0.21 \cdot 10^{-3}$ $0.27 \cdot 10^{-3}$ $0.33 \cdot 10^{-3}$	91.96
$Yb_{13.1}Gd_{0.9}MnSb_{11}$	773 873 973	$0.15 \cdot 10^{-3}$ $0.20 \cdot 10^{-3}$ $0.28 \cdot 10^{-3}$	112.86

The maximum amount of each RE substituted for Yb was determined to be 0.7 for La, 0.6 for Ce, and 0.5 for Tm [5-8]. Microprobe analysis of the crystals of $Yb_{14-x}Gd_{0x}MnSb_{11}$ of which properties were measured provided the following compositions (Table 1) showing that the maximum amount of Gd that can substitute for Yb in $Yb_{14-x}Gd_xMnSb_{11}$ is x = 0.48.As data show (Tables 2-4) maximum introduction of does not exceed x=0.5, that proves obtainedvalues of melting,temperature, coefficient of thermal expansion andactivation energy.

Obtained physic-chemical characteristics along with another property allow us to assume the nature of this new class of inorganic materials.

Acknowledgements

This work was supported by International Science & Technology Center(ISTC), #Project T-2067.

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