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STRUCTURAL, MICROSTRUCTURAL AND OPTICAL PROPERTIES OF MULTIPHASE Ge—Co—Te SYSTEM

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Abstract. Structural and optical properties of $Ge_{35}Co_xTe_{65}$ alloys where $x = 10$, 15 and 25 at % in the bulk state investigated using XRD, SEM and FIR spectroscopy. Replacement of Te by Co leads to appearance of cubic $Co_2Ge_3Te_3$ phase at higher Co values. All obtained samples have multiphase structure. The final composition of the prepared material was significantly influenced by the preparation method. SEM shows that all samples have different types of grains corresponding to the multiphase structure, their size in the range 5—10 μm. IR spectra of the Ge-Co-Te alloy shows that have a phonon absorption in the spectral range 1000—800 cm^{-1}.

Keyword: GeTe doped with transition metal “cobalt”, structural investigation, IR absorption, surface morphology.

INTRODUCTION

Compounds with the skutterudite structure ($CoAs_3$) have attracted the attention of thermoelectric research for new generation of thermoelectric materials. N-type $CoGe_{1.5}Te_{1.5}$ compound for the first time was studied as a potential thermoelectric material [1]. Due to the specific way of preparation, the samples of $CoGe_{1.7}Te_{1.47}$ composition have high overstoichiometry of Ge and some substoichiometry of Te. Compound has cubic structure, but some of lower symmetry (space groups No. 195 — $P23$, No. 200 — $P2/m3$ or No. 201— $P2/n\bar{3}$) unlike the most of other skutterudite compounds (space group $Im3$).

$CoGe_{1.5}Te_{1.5}$ is an n-type semiconductor as like as $CoGe_{1.5}Se_{1.5}$ except that, the temperature at which the Seebeck coefficient reaches a minimum value is 115 K for $CoGe_{1.5}Te_{1.5}$ and 150 K for $CoGe_{1.5}Se_{1.5}$ [2, 3]. CoGeTe alloys are very perspective compounds for thermoelectric applications. Thermoelectric devices can be used for cooling applications or for power generation from a heat source. $CoGe_3Te_3$ adopts orthorhombic symmetry, space group *Pbca* with unit cell parameters $a = 6.1892(4)$ Å, $b = 6.2285(4)$ Å, $c = 11.1240(6)$ Å, $V = 428.8(1)$ Å^3 and $Z = 8$. CoGeTe represents as a ternary ordered variant of $NiAs_2$ type structure. CoGeTe has short Co–Co distance across the shared edge of $[CoGe_3Te_3]$ octahedra. CoGeTe melts incongruently at about 725 °C; decomposes into GeTe, CoGe and $CoTe_2$ [4]. Magnetic properties of GeTe based diluted magnetic semiconductors with transition metals from Ti to Ni shows paramagnetic order for GeTe doped films with Co [5].

Investigation of triangular ternary system revealed the ternary compound $Co_2Ge_3Te_3$ has $\rho = 60\ \Omega \cdot cm$ and TEP –590 μV/° C. GeTe is in equilibrium with $CoTe_2$, $CoGe_2$ and Co_5Ge_7. GeTe-Co_2Te cross-section and has a complex structure crossing at the two-phase region; Co_2Ge is not in equilibrium with GeTe [6—10].

SAMPLE PREPARATION AND EXPERIMENTAL METHODS

In our work $Ge_{35}Co_xTe_{65}$ where $x = 10$, 15 and 25 were prepared from a single crystal Ge, weakly doped at the level 10^{-17} at.%, Te of 99.997 % and Co of 98.799% purity. Starting Ge, Te and Co were mixed together with their direct reaction at 950 ± 30° C for 24 hr in evacuated quartz ampoules. The obtained ingots were ground manually in agate mortar in the presence of acetone of purity 95% to prevent oxidation. The obtained powder was loaded in a steel press mold and pressed 30 min at pressure 150 kF/cm^2 into cylindrical pellets with diameter 13 mm. Pellets were stacked in columns in the ampoules and then sealed into evacuated quartz ampoules. The ampoules were placed in vertical furnace to reduce the temperature gradient and heat treated at 600 ± 20° C for 3 days. The resulted material was once more grounded under acetone and the above mentioned process was repeated.

Table 1. EDX Results of the obtained ingot

Weighted composition	$Ge_{35}Co_{10}Te_{55}$	$Ge_{35}Co_{15}Te_{50}$	$Ge_{35}Co_{25}Te_{40}$
Obtained composition	$Ge_{38.17}Co_{8.17}Te_{53.66}$	$Ge_{36.82}Co_{14.02}Te_{49.16}$	$Ge_{37.77}Co_{26.74}Te_{35.49}$

Crystalline nature and structural properties investigated using X-ray diffractometer DRON 4-07 with $Co_{K\alpha}$-radiation in the angular range from 20° to 90° (2θ) after every preparation step, all measurements carried out at room temperature.

Surface morphology and contents of cobalt, germanium and tellurium were determined by an electron scanning microscope JEOL JSM-6380LV and energy-dispersive X-ray microanalyzer Oxford Instruments. The accelerating voltage of the primary electron beam was 20 kV.

Infrared absorption for fine powder was carried out using FIT-spectrometer Vertex 70 (Bruker) at room temperature in the spectral range from 4000 to 500 cm^{-1}.

RESULTS AND DISCUSSION

The final composition of the prepared material was significantly influenced by the preparation method as shown in Table 1. As mentioned in the experimental part we have used cold-pressed pellets which were loaded into evacuated quartz ampoules ($p \sim 10^{-4}$ Pa). We would like to remark that all the samples were multi-phased, as we will discuss below. Figure 1 shows SEM for the obtained ingots, in every picture appeared a different grain size. Grain size ranged between 5—10 μm in accordance with multiphase structure of the samples. The difference appeared not only in grain size but also in their type. That change in grain type corresponding to the difference in the crystal structure for each phase involved in each sample.

XRD patterns of $Ge_{38.17}Co_{8.17}Te_{53.66}$, $Ge_{36.82}Co_{14.02}Te_{49.16}$ and $Ge_{37.77}Co_{26.74}Te_{35.49}$ are shown in Figure 2. Comparison between the calculated interplanar spacing $d_{(hkl)}$ for each sample and those of standards JCPDS cards shows, that the main phase in $Ge_{38.17}Co_{8.17}Te_{53.66}$ alloy is GeTe and the most of other diffraction peaks related to $CoTe_2$ and Te with unknown peaks as shown in Figure (2*a*). As shown in Figure (2*b*), Te disappeared with increasing Co content in $Ge_{36.82}Co_{14.02}Te_{49.16}$ sample. The main phase is GeTe in addition to $CoTe_2$ and some unknown diffraction peaks. But with another ternary system $Co_2Ge_3Te_3$ which appeared corresponding to increasing Co content. Figure (2*c*) shows that main phase in $Ge_{37.77}Co_{26.74}Te_{35.49}$ sample became $Co_2Ge_3Te_3$ in addition to GeTe, $CoTe_2$ and few numbers of unknown beaks. From the above description of the XRD pattern

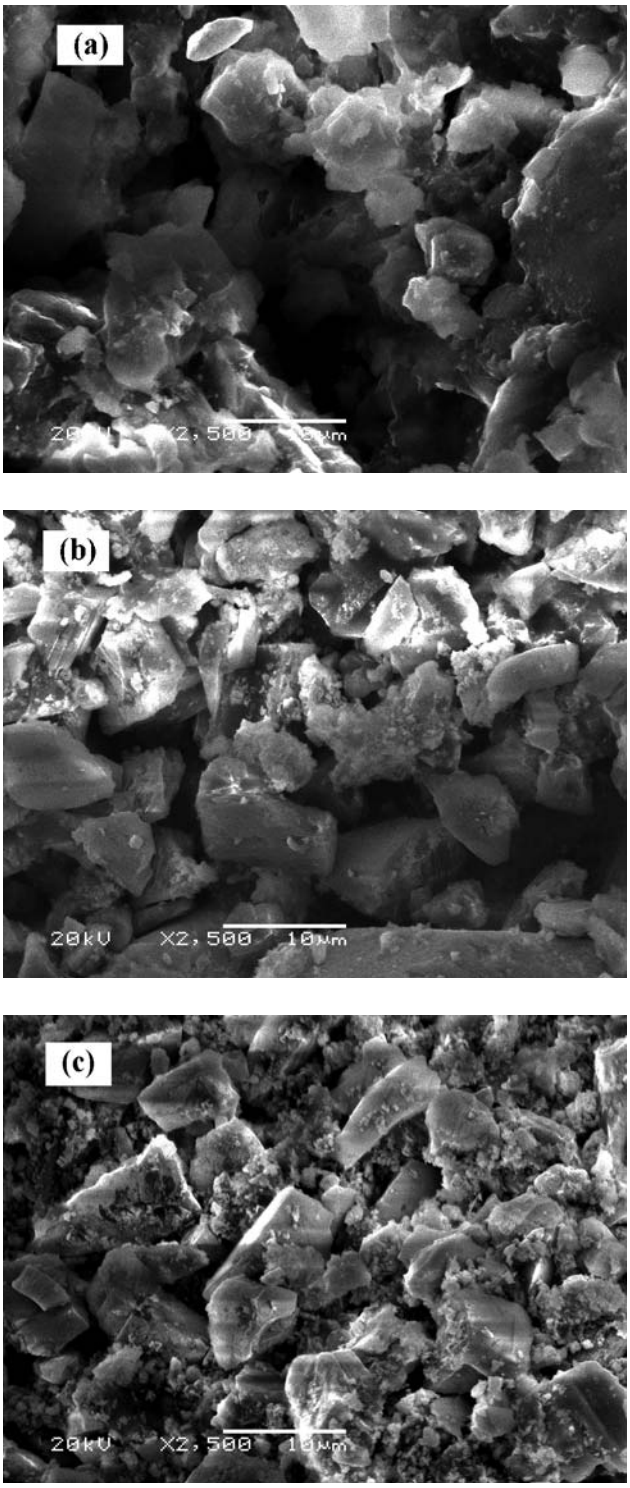

Fig. 1. SEM image for: $Ge_{38.17}Co_{8.17}Te_{53.66}$ (*a*), $Ge_{36.82}Co_{14.02}Te_{49.16}$ (*b*), $Ge_{37.77}Co_{26.74}Te_{35.49}$ (*c*).

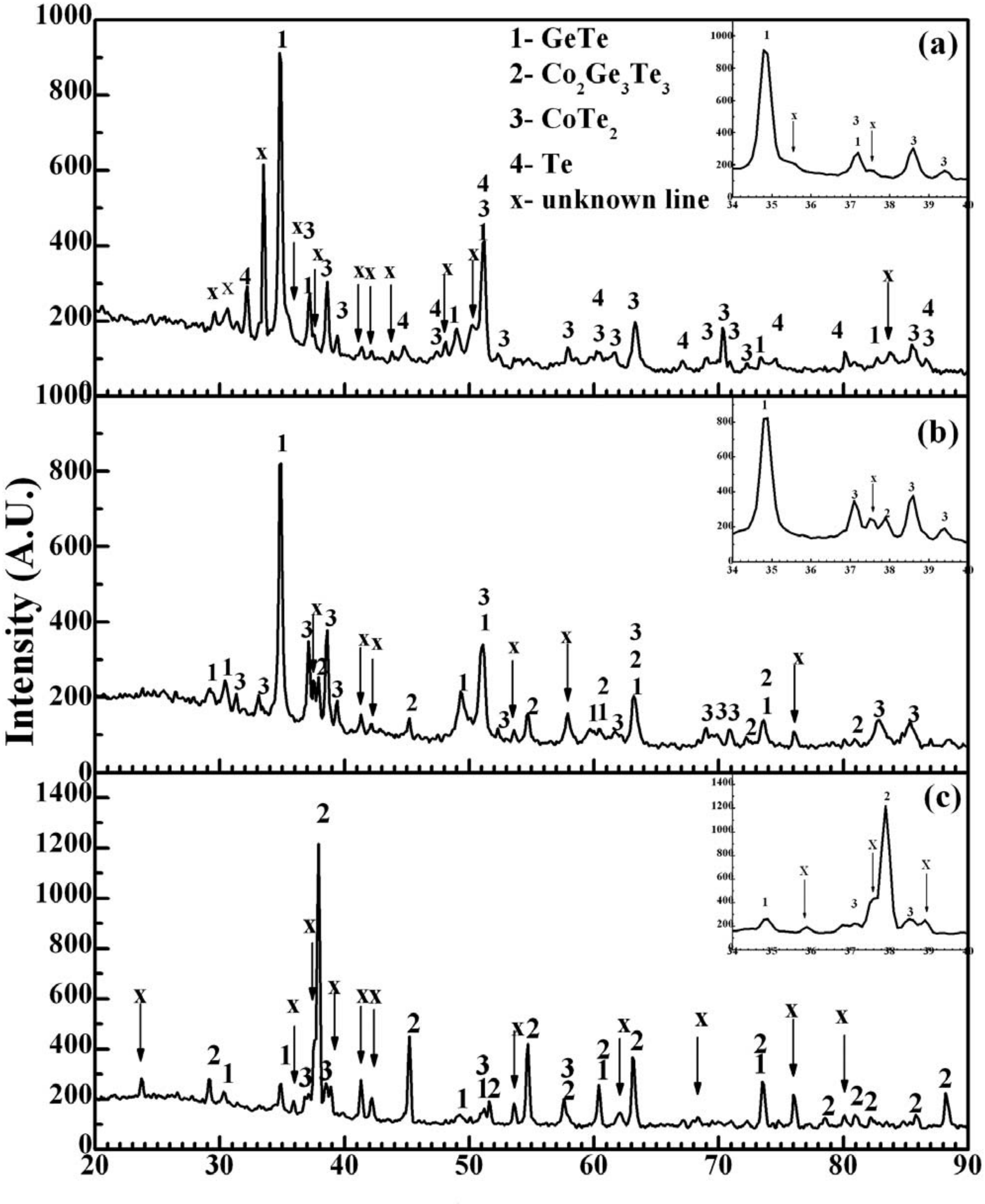

Fig. 2. X-Ray diffraction pattern of: Ge$_{38.17}$Co$_{8.17}$Te$_{53.66}$ (*a*), Ge$_{36.82}$Co$_{14.02}$Te$_{49.16}$ (*b*), Ge$_{37.77}$Co$_{26.74}$Te$_{35.49}$ (*c*).

of $Ge_{35}Co_xTe_{65-x}$ system where $x \leq 15$ at.% the main phase in the obtained alloy is GeTe a combined with $CoTe_2$ and another phases changed with changing the Co content as shown in Table 2.

Structural and microstructure results shows, that GeTe in equilibrium with $CoTe_2$ and ternary compound $Co_2Ge_3Te_3$. This result confirmed with the result mentioned before in [7], GeTe in equilibrium with $CoTe_2$, $CoGe_2$, Co_5Ge_7 and ternary system.

Infrared absorption investigated for a fine powder in the spectral range from 4000 to 500 cm^{-1} using Attenuation Total Reflection method (ATR). As shown in Figure 3, IR absorption spectrum for investigated

Table 2. Phases appeared in the Ge—Co—Te system

Sample	Phases
$Ge_{38.17}Co_{8.17}Te_{53.66}$	Rhombohedral GeTe + Orthorhombic $CoTe_2$ + Te + unknown peaks
$Ge_{36.82}Co_{14.02}Te_{49.16}$	Cubic $Co_2Ge_3Te_3$ + Rhombohedral GeTe + Orthorhombic $CoTe_2$ + unknown peaks
$Ge_{37.77}Co_{26.74}Te_{35.49}$	

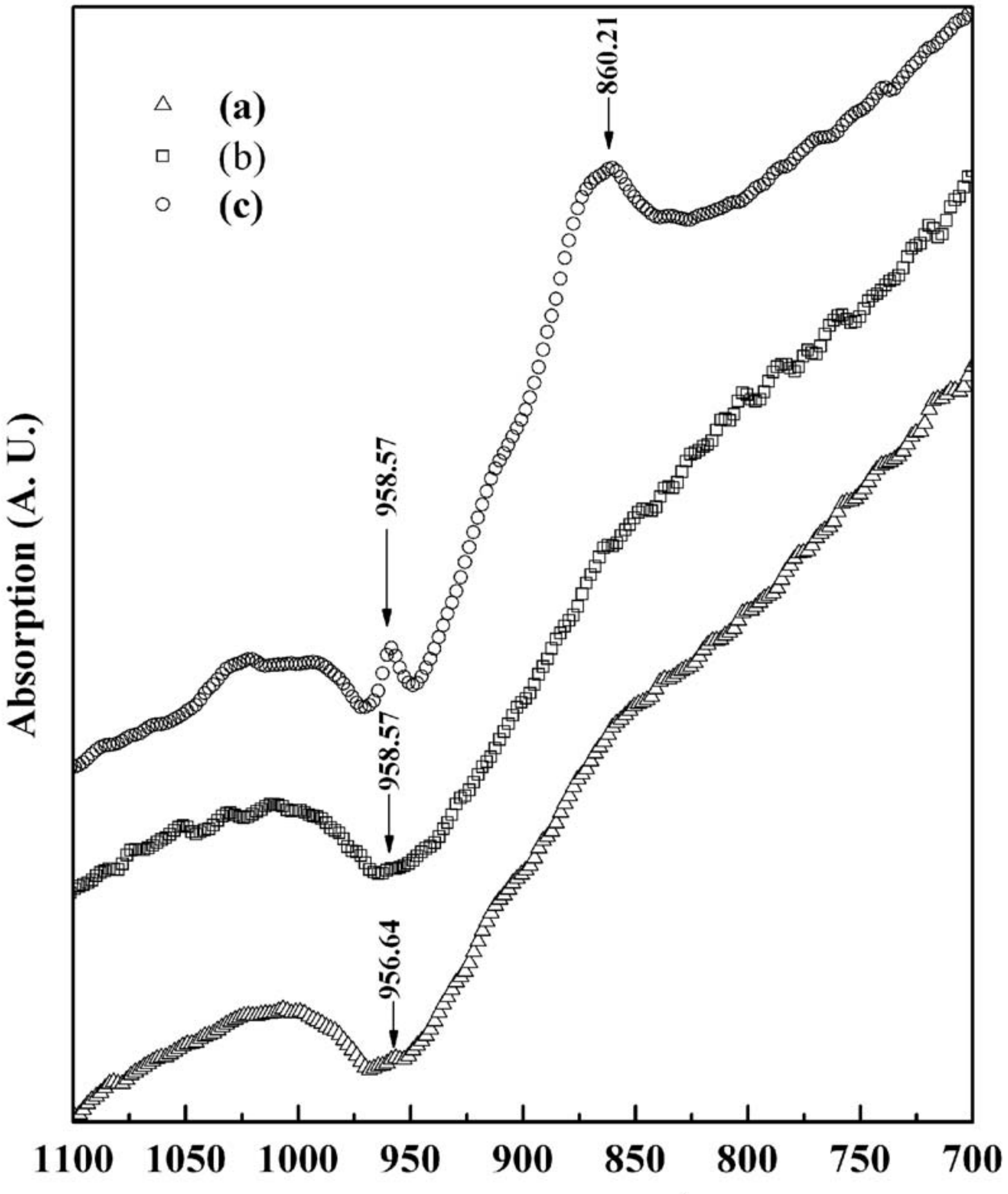

Fig. 3. Infrared absorption Spectra for: $Ge_{38.17}Co_{8.17}Te_{53.66}$ (*a*), $Ge_{36.82}Co_{14.02}Te_{49.16}$ (*b*), $Ge_{37.77}Co_{26.74}Te_{35.49}$ (*c*).

Table 3. IR Absorption for Ge—Co—Te alloys

Sample	Peak position (ω) cm^{-1}	
	Band 1	Band 2
$Ge_{38.17}Co_{8.17}Te_{53.66}$	956.57	—
$Ge_{36.82}Co_{14.02}Te_{49.16}$	956.57	—
$Ge_{37.77}Co_{26.74}Te_{35.49}$	958.57	860.21

Ge—Co—Te materials have characteristic for degenerate semiconductors at the spectral range 1000—800 cm^{-1}, Figure 3 shows the Ge—Co—Te has a two phonon absorption peaks appeared at 958.57 cm^{-1} and 860.21 cm^{-1} [11]. Absorption peaks appeared at higher values of cobalt content. Appearance of absorption peaks matches with the appearance of ternary compound which appeared at higher cobalt values.

CONCLUSION

Structural studies of $Ge_{35}Co_xTe_{65-x}$ alloys where $x = 10$, 15 and 25 at% shows, that the appearance of ternary phase at higher values of cobalt. Where $x \leq 15$ at.% the main phase in the obtained alloy is GeTe a combined with $CoTe_2$ and another phases changed with changing the Co content and appearance of unknown beaks that my be related to a new ternary phase. The SEM result confirms the multiphase structure according to the appearance of different types of grains.

The IR absorption measurements shows, the investigated GeCoTe samples have a phonon absorption in the spectral range 1000—800 cm^{-1} at higher values of cobalt content.

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