

# EFFECT OF DOPING GE-TE ALLOYS WITH CO ON THE STRUCTURAL AND OPTICAL PROPERTIES

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Поступила в редакцию 30.09.2008 г.

**Аннотация.** Структурные и оптические свойства GeTe и  $\text{Ge}_{50-x}\text{Co}_x\text{Te}_{50}$  твердых растворов с  $x = 5, 10$  and  $15\%$  были изучены методами рентгеновской дифракции и ИК-спектроскопии. В результате исследований было показано, что полученные образцы имеют кристаллическую форму, а кристалл GeTe обладает ромбоэдрической структурой, в то время как при частичном замещении Ge на Co в твердом растворе меняется сингония кристалла GeTe с ромбоэдрической на орторомбическую с образованием двух дополнительных фаз  $\text{CoTe}_2$  и CoGe. ИК-спектры поглощения, полученные по методике нарушенного полного внутреннего отражения показали, что исследованные кристаллы GeTe и GeCoTe имеют полосы фононного поглощения в диапазоне  $1000\text{--}800\text{ см}^{-1}$ .

**Ключевые слова:** халькогенид GeTe, кобальт, легирование, рентгеновская дифрактометрия, ИК-спектроскопия.

**Abstract.** Structural and optical properties of GeTe and  $\text{Ge}_{50-x}\text{Co}_x\text{Te}_{50}$  alloys where  $x = 5, 10$  and  $15\%$  in the bulk state were studied. The X-ray diffraction measurements show that, the prepared samples are in crystalline form, GeTe has rhombohedral structure, otherwise the partial replacement of Ge by Co in the ternary alloys change the GeTe structure from rhombohedral to orthorhombic with additional two phases; orthorhombic  $\text{CoTe}_2$  and monoclinic CoGe phase. The IR absorption measurements shows that, the investigated GeTe and GeCoTe samples have a phonon absorption in the spectral range  $1000\text{--}800\text{ cm}^{-1}$ .

**Keys word:** chalcogenide GeTe, transition metal “Co”, doping, structure measurements, IR Absorption.

## 1. INTRODUCTION

Compounds with the skutterudite structure ( $\text{CoAs}_3$ ) have attracted the attention of thermoelectric research since the early 1990s in its pursuit for new generation of thermoelectric materials. Due to their structure, containing two large voids in the unit cell, which could be “filled” with a foreign ions acting here as effective phonon-scattering centres, skutterudites serve as a very typical example of an ideal thermoelectric material. N-type  $\text{CoGe}_{1.5}\text{Te}_{1.5}$  compound was for the first time studied as a potential thermoelectric material [1]. Due to the specific way of preparation, the samples of  $\text{CoGe}_{1.7}\text{Te}_{1.47}$  composition with high overstoichiometry of Ge and some substoichiometry of Te were studied. From x-ray diffraction studies revealed that, the compound is of 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  $Im\bar{3}$ ). Tellurium vacancies or ionized surplus Ge atoms are pro-

posed to be responsible for observed n-type conductivity. Two regions corresponding to extrinsic and intrinsic conductivity were identified on the temperature dependence of electrical conductivity. The potential possibility to change quantity of the incorporated Ge and Te in wide range around stoichiometric composition ( $\text{CoGe}_{1.5}\text{Te}_{1.5}$ ) together with possibility to influence its thermoelectric properties by proper doping and void filling is therefore of interest of further thermoelectric research.

Analysis of the high-resolution powder neutron diffraction data indicates that the structure of  $\text{CoGe}_{1.5}\text{Te}_{1.5}$  retains the  $a^+a^+$  tilt system of the ideal skutterudite structure, while the anions are ordered in layers perpendicular to the (1 1 1) direction of the skutterudite unit cell. This anion ordering results in a lowering of the symmetry from cubic to rhombohedral (space group  $R\bar{3}$ ,  $a = 12.3270(5)$  and  $c = 5.102(1)$  Å at 293 K). The temperature dependence of the electrical resistivity and the magnitude of the Seebeck coefficient indicate that  $\text{CoGe}_{1.5}\text{Te}_{1.5}$  is an n-type semiconductor as like as  $\text{CoGe}_{1.5}\text{Se}_{1.5}$  except that, the temperature at which the Seebeck coefficient reaches

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a minimum value is 115 for  $\text{CoGe}_{1.5}\text{Te}_{1.5}$  and 150 K for  $\text{CoGe}_{1.5}\text{Se}_{1.5}$  [2, 3].

GeCoTe alloys are very perspective compounds for thermoelectric applications. Thermoelectric devices can be used for cooling applications or for power generation from a heat source. The crystal structure of cobalt germanium telluride CoGeTe has been studied. CoGeTe adopts orthorhombic symmetry, space group  $Pbca$  with unit cell parameters  $a = 6.1892(4) \text{ \AA}$ ,  $b = 6.2285(4) \text{ \AA}$ ,  $c = 11.1240(6) \text{ \AA}$ ,  $V = 428.8(1) \text{ \AA}^3$  and  $Z = 8$ . Its crystal structure is formed by  $[\text{CoGe}_3\text{Te}_3]$  octahedra sharing both edges and corners. CoGeTe represents a ternary ordered variant of -NiAs2 type structure. An important feature present in CoGeTe is an occurrence of short Co—Co distance across the shared edge of  $[\text{CoGe}_3\text{Te}_3]$  octahedra. Differential thermal analysis has revealed that CoGeTe melts incongruently at about 725 °C; CoGeTe decomposes into GeTe, CoGe and  $\text{CoTe}_2$ . Temperature dependence of the electrical conductivity and Seebeck coefficient at 300K revealed that, CoGeTe sample has a very weak temperature dependence of the electrical conductivity and quit high value of the Seebeck coefficient at 300 K [4].

Diluted magnetic semiconductors (DMSs) have provided a wealth of scientific information, and potential technological applications such as high efficient spin injectors into a semiconductor and tunable ferromagnetic devices using carrier-induced ferromagnetism. Magnetic properties of IV—VI compounds GeTe based diluted magnetic semiconductors with transition metals from Ti to Ni have been investigated, ferromagnetic order was observed for the Cr, Mn and Fe doped GeTe films, whereas the Ti, V, Co and Ni doped films were paramagnetic [5].

The phase diagram of  $\text{CoTe}_2$ - $\text{Ge}_{0.98}\text{Te}$  was constructed from the differential thermal analysis, microstructure and XRD analysis [6].

Microstructure, differential thermal analysis and structural analysis of the CoGeTe system were investigated and revealed that, the ternary Co-Ge-Te system has a polythermal cross-section and isothermal cross-section in all range of concentrations at temperature less than solidus surface. Investigation of triangular ternary system revealed the ternary compound  $\text{Co}_2\text{Ge}_3\text{Te}_3$ . GeTe is in equilibrium with  $\text{CoTe}_2$ ,  $\text{CoGe}_2$  and  $\text{Co}_3\text{Ge}_7$ . GeTe- $\text{Co}_2\text{Te}$  cross-section has a complex structure crossing at the two-phase region,  $\text{Co}_2\text{Ge}$  is not in equilibrium with GeTe [7].

Thermal analysis and phase diagram of Co-Ge-Te system was studied [8, 9]. microstructural, XRD analysis and micro-hardness of the ternary CoGeTe system revealed, that the  $\text{Co}_2\text{Ge}_3\text{Te}_3$  has a specific resistance  $60 \text{ \Omega}\cdot\text{cm}$  and thermoelectric power —  $590 \text{ \mu V}/^\circ\text{C}$  [10]

## 2. SAMPLE PREPARATION AND MEASUREMENT METHODS

GeTe compound was prepared from a single crystall Ge, weakly doped at the level  $10^{-17}$  at. % and Te of 99.997 %; purity. with there direct reaction at  $950 \pm 30 \text{ }^\circ\text{C}$  for 24 hr in evacuated quartz ampoules.  $\text{Ge}_{5-x}\text{Co}_x\text{Te}_{50}$  where  $x = 5, 10$  and 15 were prepared from the same Ge and Te used above and Co of 99.99 % purity, Starting Ge, Te and Co were mixed together with there direct reaction at  $950 \pm 30 \text{ }^\circ\text{C}$  for 24 hr in evacuated quartz ampoules. The obtained ingot 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 die and cold pressed into cylindrical pellets at pressure  $150 \text{ k/cm}^2$ . The pellets were then sealed into evacuated quartz ampoules. The ampoules were then heated at  $600 \pm 20 \text{ }^\circ\text{C}$  for 3 days. The resulted material was once more grounded under acetone and the above mentioned process was repeated.

The nature and structure of the prepared alloys were examined using X-ray diffractometer DRON 4-07 with  $\text{CuK}_\alpha$ -radiation in the angular range from  $20^\circ$  to  $80^\circ$  after every preparation step. Measurements were carried out at room temperature. The measured  $2\theta$  angles were converted into  $d_{(hkl)}$  values using Bragg's law, ( $\lambda = 2d_{(hkl)} \sin(\theta)$ ), where  $d_{(hkl)}$  is the interplaner spacing,  $\lambda$  is the wavelength of the used X-Ray,  $\lambda = 1.540562 \text{ \AA}$ ,  $\theta$  is the Bragg's angle.

## 3. EXPERIMENTAL RESULTS

### 3.1. XRD RESULTS

The XRD patterns of GeTe and ternary alloys with Co content of 5, 10 and 15 at. % are shown in Figures 1, 2, 3 and 4. Comparison between the calculated interplanar spacing  $d_{(hkl)}$  for GeTe spectrum shown in Fig. 1 using Bragg's law ( $n\lambda = 2d_{(hkl)} \sin(\theta)$ ) and those of standards JCPDS cards shows that the GeTe has a rhombohedral  $\alpha$ - GeTe structure. The partial replacement of Ge with Co, in the ternary alloys shows, that the GeTe rhombohedral structure changed to orthorhombic structure with additional two phases,

orthorhombic  $\text{CoTe}_2$  and monoclinic  $\text{CoGe}$  phase as shown in Table 1.

### 3.2. IR RESULTS

The Infrared absorption was measured for powder in the spectral range  $500$  to  $4000 \text{ cm}^{-1}$ . Figure 5 shows, that the  $\text{GeTe}$  and  $\text{GeCoTe}$  have a phonon absorption [11] in the spectral range ( $1000$ — $800 \text{ cm}^{-1}$ ),  $\text{GeTe}$  has phonon absorption at  $\omega = 966.285 \text{ cm}^{-1}$  "Band 1". However; in the doped alloys that band has split into two phonon absorption, and additional absorption band appears at spectral range  $841$ — $855 \text{ cm}^{-1}$  in the samples containing 5 and 15 at.% cobalt; "Band 2" as shown in Table 2. The splitting in "band 1" very weak in alloy containing 10 at.% cobalt, and very high in alloy containing 15 at.% cobalt.

### CONCLUSION

Structural studies of  $\text{GeTe}$  and  $\text{Ge}_{50-x}\text{Co}_x\text{Te}_{50}$  alloys where  $x = 5, 10$  and 15 at % in the bulk state

Table 1

Phases appeared in the  $\text{Co}_{50-x}\text{Ge}_x\text{Te}_{50}$ ;  $x = 0, 5, 10$  and 15 at %

Sample	Phases		
$\text{GeTe}$	GeTe Rhombohedral		
$\text{Ge}_{45}\text{Co}_5\text{Te}_{50}$	GeTe Ortho.	$\text{CoTe}_2$ Ortho.	CoGe Monocl.
$\text{Ge}_{40}\text{Co}_{10}\text{Te}_{50}$			
$\text{Ge}_{35}\text{Co}_{15}\text{Te}_{50}$			

shows that, the  $\text{GeTe}$  phase appeared in the ternary alloys changes from the rhombohedral structure in  $\text{GeTe}$  sample to orthorhombic structure when 5, 10 and 15 at. % of Ge replaced by cobalt with additional two phases: orthorhombic  $\text{CoTe}_2$  and monoclinic  $\text{CoGe}$ . The phases appeared in the three ternary alloys do not change with changing the Co percent in the alloy. The IR absorption measurements show, that the investigated  $\text{GeTe}$  and  $\text{GeCoTe}$  samples have a phonon absorption in the spectral range  $1000$ — $800 \text{ cm}^{-1}$ .

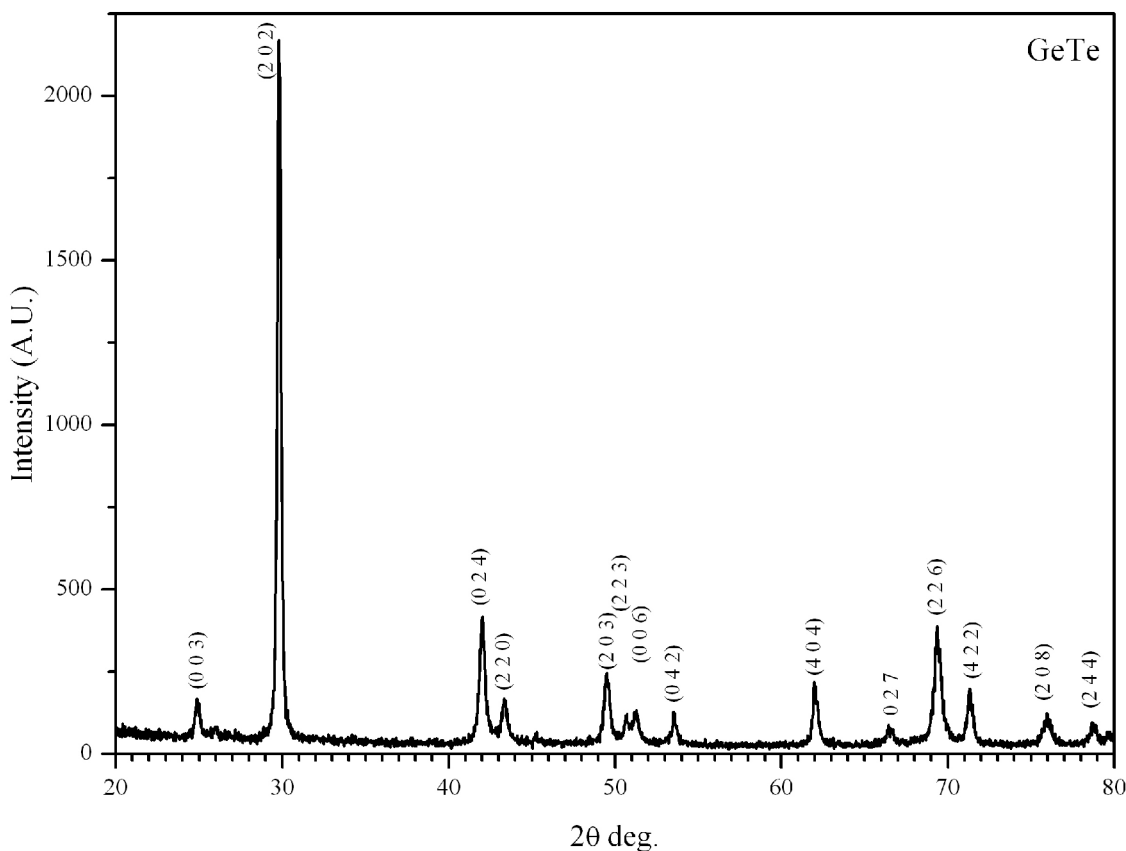


Fig. 1. Representation of XRD pattern for  $\text{GeTe}$ .

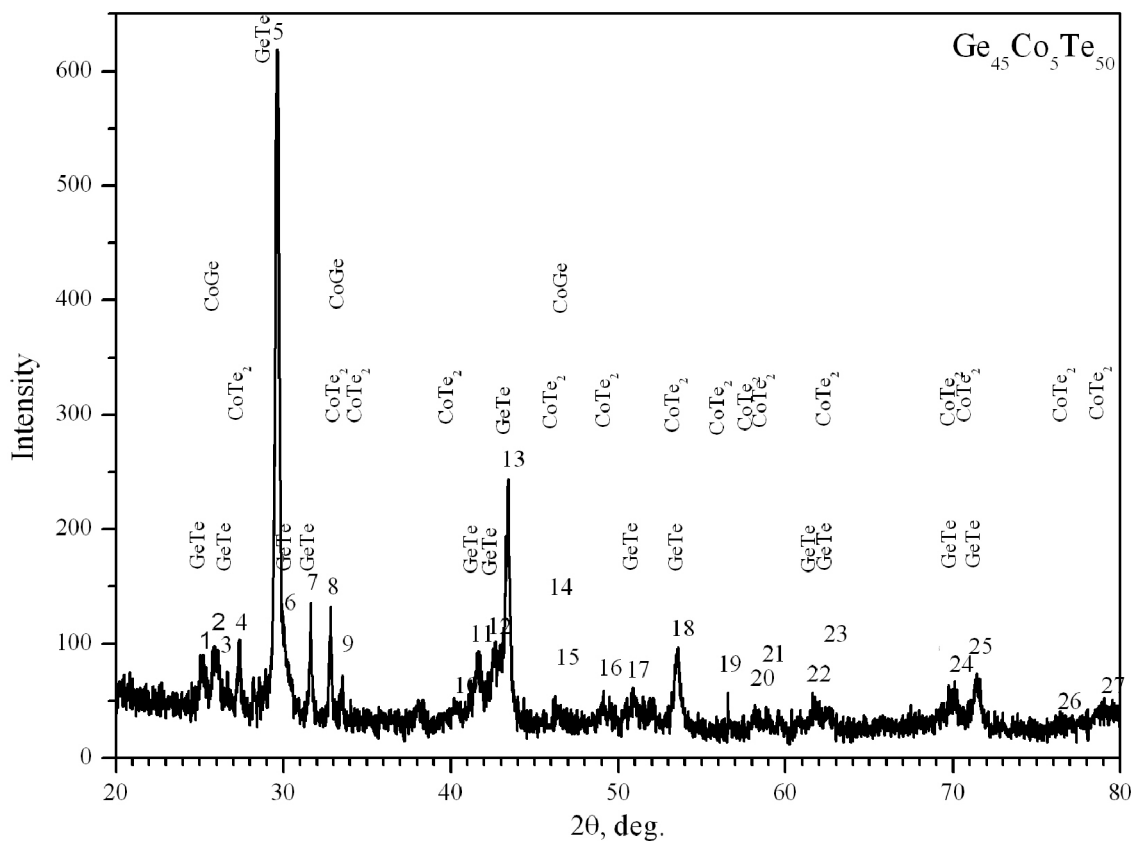


Fig. 2. Representation of XRD pattern for  $\text{Ge}_{45}\text{Co}_5\text{Te}_{50}$ .

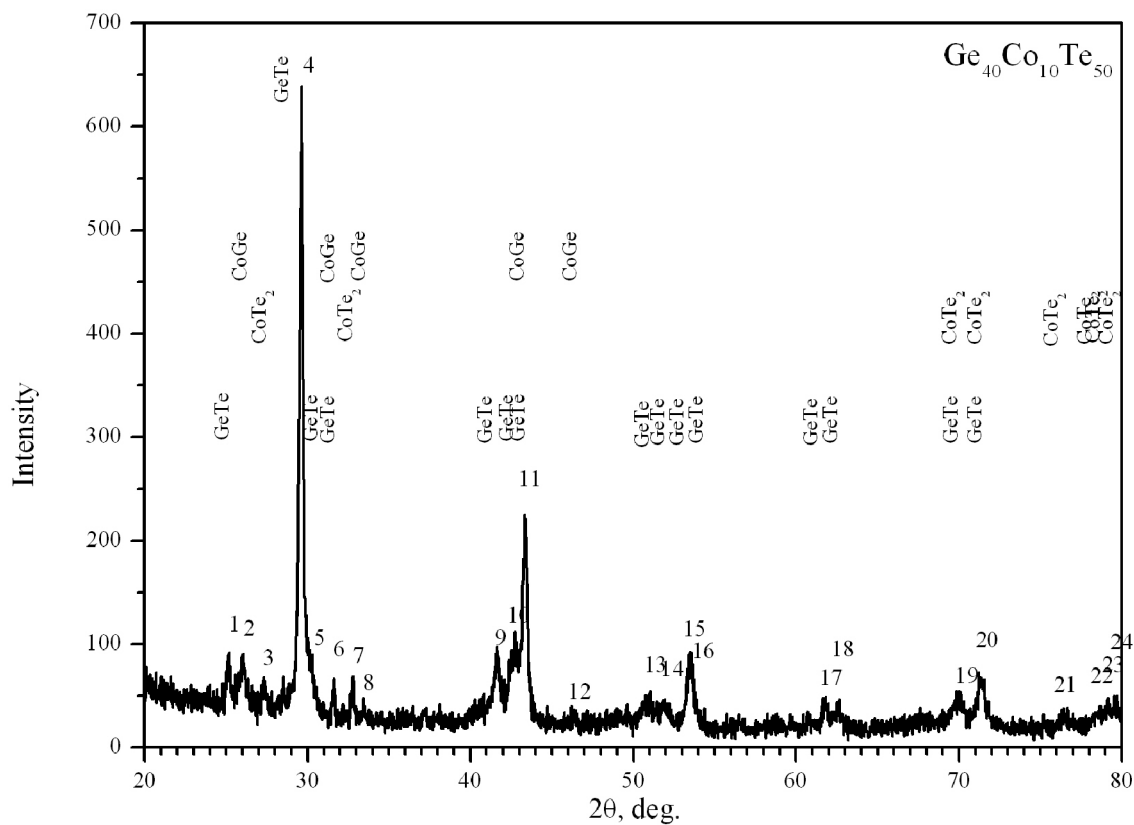


Fig. 3. Representation of XRD pattern for  $\text{Ge}_{40}\text{Co}_{10}\text{Te}_{50}$ .

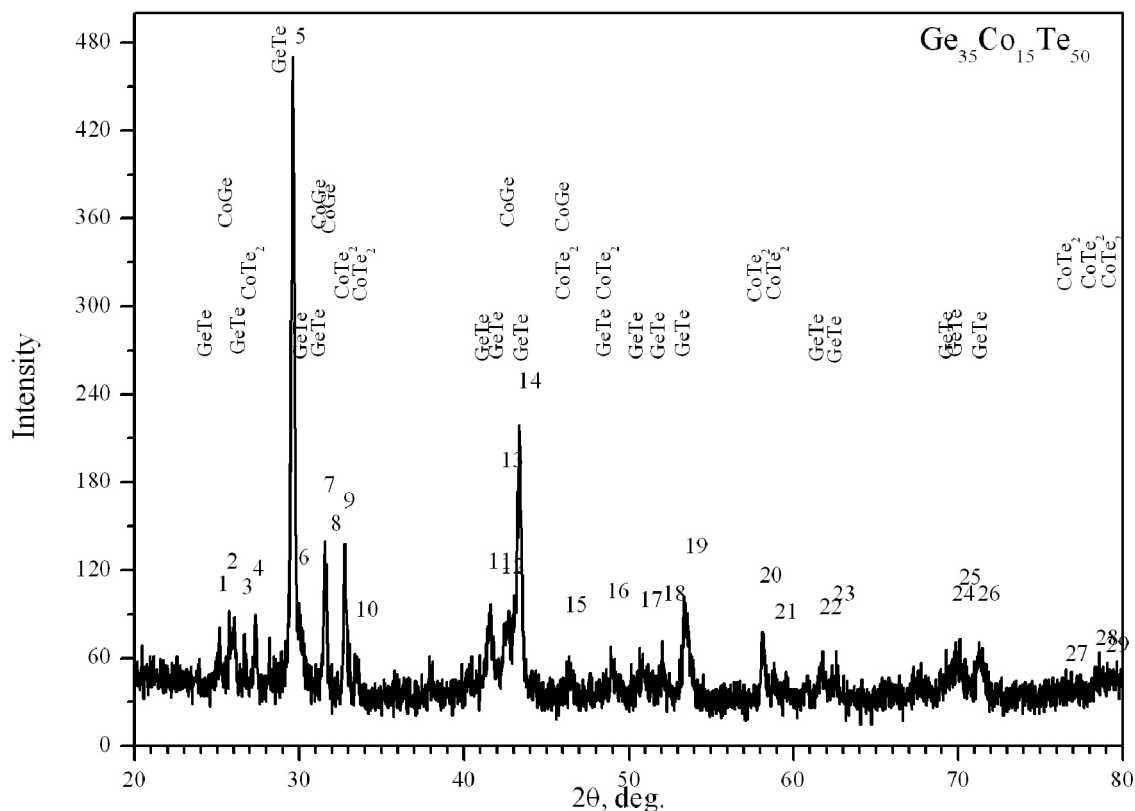


Fig. 4. Representation of XRD pattern for  $\text{Ge}_{35}\text{Co}_{15}\text{Te}_{50}$ .

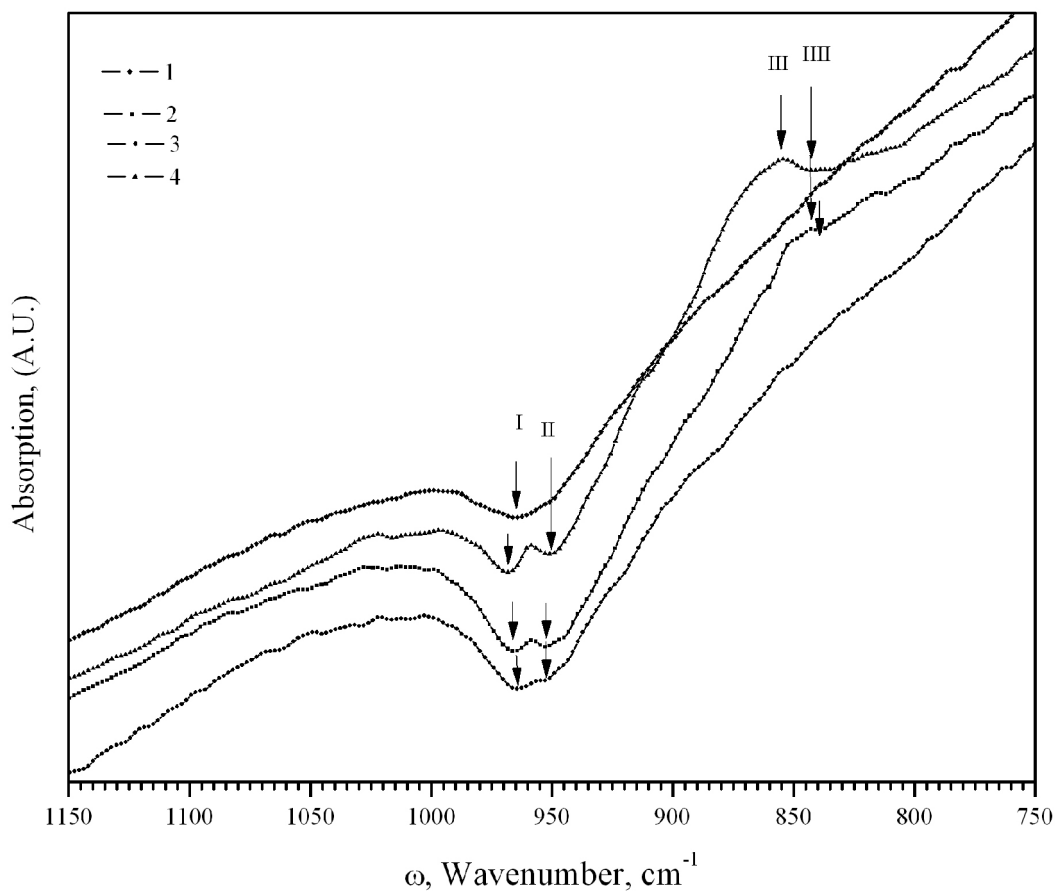


Fig. 5. Representation of IR absorption for: (1):  $\text{GeTe}$ , (2):  $\text{Ge}_{45}\text{Co}_5\text{Te}_{50}$ , (3):  $\text{Ge}_{40}\text{Co}_{10}\text{Te}_{50}$  and (4):  $\text{Ge}_{35}\text{Co}_{15}\text{Te}_{50}$ .

Table 2

IR Absorption for  $Co_{50-x}Ge_xTe_{50}$ ;  $x = 0, 5, 10$  and  $15$  at %

Sample	$\omega$ cm <sup>-1</sup>			
	Band 1		Band 2	
	I	II	III	IV
GeTe	966.28357			
Co-5	966.28357	952.7826	842.84615	838.98873
Co-10	964.3586	952.7826	—	—
Co-15	968.212	950.853	854.418	842.84615

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