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The new tetragonal phase of ternary compound CoGeTe with ferroelectric and magnetic responses.

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Abstract.
The aim of this work is to determine the atomic composition, crystal system and lattice parameters as well as the study of ferroelectric and magnetic responses in alloys $Co_xGe_{35}Te_{65-x}$ at 35 at.%,
prepared by direct fusion of the respective batches in an evacuated quartz ampoule followed by twice of grinding and annealing.
New tetragonal modification of ternary compound CoGeTe with atomic composition $Co_{34,5}Ge_{32,5}Te_{33}$ in the form of well-faceted microcrystals with sizes ranging from 4 to 11 microns was obtained.
The new tetragonal phase CoGeTe having parameters: a = 6.204 ± 0.01 Å and c = 11.273 ± 0.03 Å, is ferroelectric material and exhibits a magnetic response.
Keywords: ternary compound, the tetragonal phase, atomic composition, ferroelectric material, magnetic response.

1.**Introduction.**

Currently known materials in the ternary system Co-Ge-Te are magnetic and are very stable in the crystalline and the amorphous state at room temperature, which makes them promising materials in the production of memory elements microactuators, infrared sensors, switches operating in the thermal infrared range, and dynamic random access memory.
The magnetic properties of this ternary system due cobalt.
Triangulation of ternary Co-Ge-Te systems is determined by the semiconductor n-type compound $Co_2Ge_3Te_3$ [1], which is in equilibrium with the binary compounds $CoGe_2$, $CoTe_2$ and Co_5Ge_7 (Co_2Ge_3). $Co_2Ge_3Te_3$ crystal structure depending on the method of production may vary from cubic to hexagonal.
It is also known ternary orthorhombic compound CoGeTe [2,3] with space group P bca, and parameters a = 6.1892, b = 6.2285, c = 11.1240 Å and assumed behavior of a semiconductor.
Previously, we have synthesized and investigated in a ternary system Co-Ge-Te two groups of samples [4-6].The results showed that when the content of cobalt Co ≤ 10 at.% in the bulk samples the main phase rombohedral α-GeTe is in equilibrium with the binary cobalt phases: monoclinic CoGe and orthorhombic γ-CoTe2.
With increasing concentration of cobalt up to 15 at.% in a multiphase system appears cubic ternary compound $Co_2Ge_3Te_3$, which becomes the main phase in the samples with formula $Co_xGe_{35}Te_{65-x}$, until the cobalt content in the alloys 27 at.%.
The purpose of this work is to determine the atomic structure, symmetry and lattice parameters, as well as the study of ferroelectric and magnetic responses of the ternary alloys with formula $Co_xGe_{35}Te_{65-x}$ at x = 32 and 35 at.%.

2. Materials and Methods.

All samples of alloys $Co_xGe_{35}Te_{65-x}$ with x = 32 and 35 at.% were prepared from the single crystal of Ge 99,999% and Te 99,997% and Co purity 98.799% by direct fusion of a respective batches in evacuated quartz ampoules during 24 hours at a temperature of 950 ± 30 °C.
After cooling, the ampoule samples were ground to a fine powder in an agate mortar in the presence of 95% purity acetone to prevent oxidation during grinding.
The thus prepared powder was loaded into a steel mold and for 30 minutes under a pressure of 150 Kg/cm^2 was converted into cylindrical washer with a diameter of 13 mm, which were then placed in evacuated quartz ampoule in a vertical furnace for thermal annealing at 600±20 °C during 3 days. After annealing the ampoule cooled with speed 1,6 ° / min.
The thus obtained material is grinding again in the presence of acetone, then was compressed, and the above annealing process repeated.
Diffractograms of the samples were obtained on diffractometer DRON 4-07 using cobalt Kα radiation at voltage of 25 kV and a current of 16 mA.
The morphology of the samples $Co_xGe_{35}Te_{65-x}$ has been studied by the scanning electron microscope (SEM) JEOL JSM-6380LV.
The content of each element in prepared samples was determined by energy-dispersive X-ray microanalysis (EDXMA) using a set-top box for microanalysis JEOL JSM-6380LV at an accelerating voltage of the primary electron beam of 20 kV.
Electron diffraction patterns were obtained using a transmission electron microscope (TEM) EMB-100BR, at an accelerating voltage of 100 kV.
In order to study the surface morphology was used atomic force microscope (AFM) P47-PRO AFM Solver. At the same time, the piezoelectric response of AFM microscopy was performed in contact mode AFM by the same high resolution using a cantilever type "golden" Silicon NSG11 series with TiN conductive coating.

Magnetic force microscopy (MFM) of the samples was carried out using a high-resolution non-contact "golden" silicon cantilever type NSG01 with a radius of curvature of 35 nm and a magnetic coating CoCr.

3. Results and discussion.

The atomic composition of the samples by the EDXMA data show, that the actual values of the atomic composition of the obtained samples are $Co_{34,5}$ $Ge_{32,5}Te_{33}$ and Co_{32} Ge $_{33}Te_{35}$ and similar or identical with the calculated compositions in accordance with the portion of cobalt, germanium and tellurium.

Identification of phase composition by XRD performed by comparing of its interplanar spacings and diffraction lines intensities with a worldwide database JCPDS –ICDD shows, that the alloy $Co_{32}Ge_{33}Te_{35}$ consists of two phases in equilibrium with each other.

One of these phases - known ternary compound $Co_2Ge_3Te_3$ cubic system [7]. However, this is not the main phase. The main unknown phase, decoded later as a tetragonal CoGeTe, has 32 lines on the diffractogram, among which the most intense line is d = 2.778 Å.

SEM of a two-phase sample $Co_{32}Ge_{33}Te_{35}$ shows two different types of grains: against the background of a clearly defined crystal phase are reviewed fines of second phase.

The results of XRD of the another ternary alloy $Co_{34,5}Ge_{32,5}Te_{33,}$ present on the Fig.1 and in the Table 1.

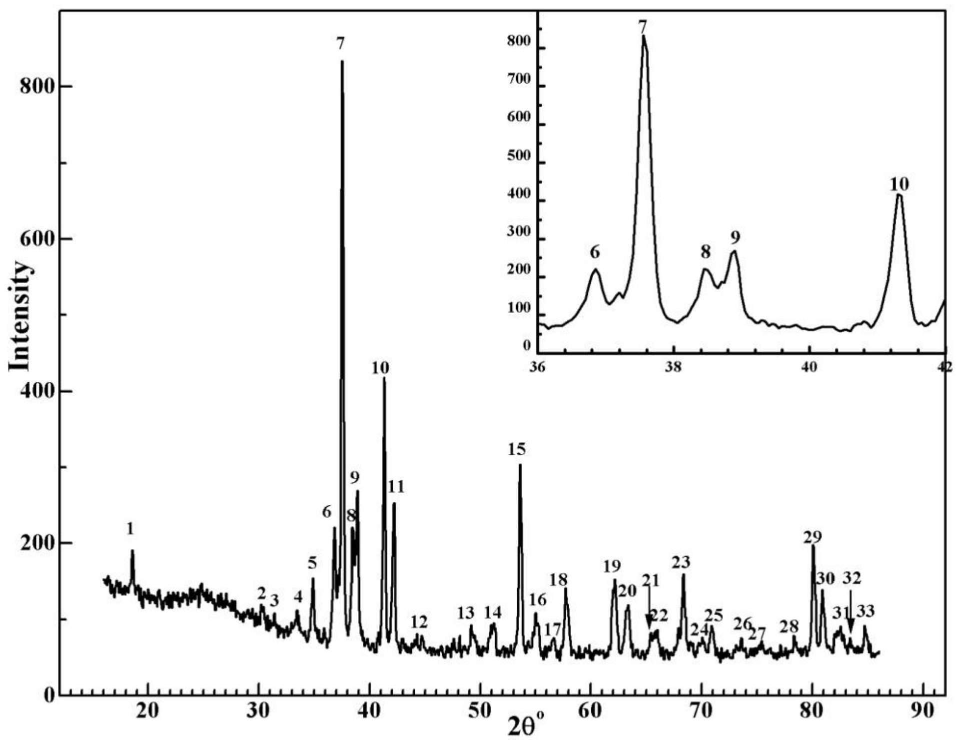

Fig.1. Diffractogram of the $Co_{34.5}Ge_{32.5}Te_{33}$ alloy, obtained at room temperature for Co-K_{α}-radiation, representing the tetragonal phase of ternary compound CoGeTe.

Table1. The interplanar spacing's d (Å**)** and diffraction lines intensities I/I_0 of the alloy Co $_{34,5}$Ge $_{32,5}$Te$_{33}$ belong to tetragonal ternary compound CoGeTe.

№	2θ	d Å	I/I_0	h	k	l
1	18,5374	5,637	7	0	0	2
2	30,18	3,462	3	1	1	2
3	33,431	3,102	4	2	0	0
4	34,8832	2,991	9	2	0	1
5	36,8085	2,854	16	1	1	3
6	37,1722	2,818	5	0	0	4
7	37,5397	2,774	100	2	1	0
8	38,4677	2,717	17	2	0	2

N	2θ	d Å	I/I_0	h	k	l
18	57,6901	1,853	12	3	1	2
19	57,9577	1,823	7	2	0	5
20	61,9442	1,739	10	3	1	3
21	62,1804	1,731	8	2	2	4
22	63,1509	1,720	7	3	2	0
23	63,3751	1,701	4	3	2	1
24	65,3812	1,667	4	3	0	4
25	65,8562	1,645	3	3	2	2

9	38,8563	2,694	24	2 1 1
10	41,33	2,566	48	1 0 4
11	42,1764	2,489	25	2 1 2
12	44,775	2,371	2	1 1 4
13	49,1411	2,153	3	2 2 1
14	51,0019	2,086	4	2 0 4
15	53,5861	1,977	38	2 1 4
16	54,9629	1,941	6	3 0 2
17	56,672	1,879	3	0 0 6
26	67,9213	1,607	4	2 0 6
27	68,3239	1,572	15	2 2 5
28	70,921	1,536	5	4 0 1
29	73,5991	1,495	3	4 0 2
30	78,322	1,415	4	3 3 2
31	80,0744	1,390	21	3 0 6
32	80,9158	1,377	11	4 2 1
33	84,72	1,327	5	4 1 4

Next, we performed the calculations using the program PDwin, designed to identify the phases and indexing of powder X-ray, which showed that this alloy is a single phase, and all diffraction lines belong to a single new tetragonal phase CoGeTe. Calculations showed that the sample has a tetragonal structure with lattice parameters a = 6.204 ± (0.01) Å, c = 11.274 ± (0.04) Å and the unit cell volume V = 433,32 ± (1.74) Å^3. That tetragonal phase of ternary compound CoGeTe with these parameters we have registered in an international database ICDD PSC: № 101925 [8]. The tetragonal crystal structure CoGeTe with the given parameters was confirmed by TEM investigations. Then we compare our results of X-ray studies with the results obtained by the authors of works [2,3], which was obtained the orthorhombic structure of the alloy CoGeTe with a percentage of the elements 32.9 % Co, 32.5)% Ge and 34.49)% Te. To identify the structure of the obtained alloy orthorhombic system with the parameters a = 6.1892 (4), b = 6.2285 (4), c = 11.1240 (6) Å authors of [2,3] using only 20 from the 268 diffraction lines reflections obtained in accordance with the program DICLVOL 04. All these 20 lines are arranged in the diffraction pattern before the line d = 2.774 Å, which is the most intense line in our new tetragonal phase (see. Tab.1). Based on these data, we can assume that the authors of [2.3] determined incorrectly crystal structure of obtained by them ternary alloy. Otherwise, a ternary compound CoGeTe may have two modifications: tetragonal, as in our case, and an orthorhombic, as in [2,3].

SEM images of alloy $Co_{34.5}Ge_{32.5}Te_{33}$ show well-faceted microcrystals of varying sizes from 4 to 11 microns. TEM analysis show that the sample $Co_{34.5}Ge_{32.5}Te_{33}$ consists of one phase having a tetragonal crystal lattice with parameters a = 6.21 Å and c = 11.28 Å.

TEM microdiffraction of a two-phase alloy $Co_{32}Ge_{33}Te_{35}$ showed the presence of two phases: the tetragonal CoGeTe and cubic $Co_2Ge_3Te_3$, which corresponds XRD data [1].

***Ferroelectric properties* of CoGeTe.**

The most common way to identify the properties of ferroelectric materials is to study the characteristics of the hysteresis loops, which can be registered by a low-frequency circuit Sawyer-Tower. In this paper we would like to answer the question about the presence of ferroelectric properties in the ternary compound CoGeTe with atomic composition $Co_{34.5}Ge_{32.5}Te_{33}$.

The presence of hysteresis loops in the sample $Co_{34.5}Ge_{32.5}Te_{33}$, shown in Fig.2, proves the existence of ferroelectric properties in tetragonal CoGeTe.

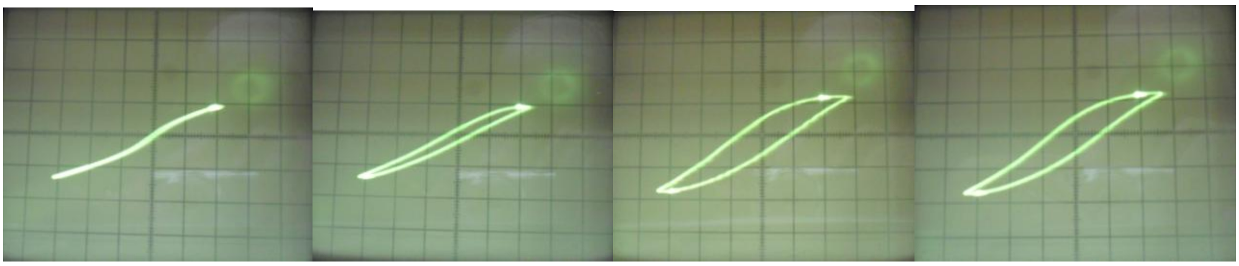

Fig.2. Hysteresis loops of the ferroelectric alloy $Co_{34.5}Ge_{32.5}Te_{33}$ (tetragonal CoGeTe); a) 50 Hz, b) 500 Hz, c) 1.0 k Hz and d) 1.1 k Hz.

The asymmetry of its hysteresis loops and offset the negative region increases with the value of the supplied electric field. We got a similar result and for a two-phase sample $Co_{32}Ge_{33}Te_{35}$ containing tetragonal CoGeTe and cubic $Co_2Ge_3Te_3$ phases. The scanning force microscopy confirm the ferroelectric characteristics $Co_{34.5}Ge_{32.5}Te_{33}$ and $Co_{32}Ge_{33}Te_{35}$ by measuring the gradient of the electrostatic forces and the piezoelectric response of the samples on the AFM Solver P47-PRO.

***Magnetic response of* CoGeTe.**

The results of research MFM of binary ferroelectric material GeTe confirmed that GeTe truly non-magnetic material, as in the surface topographic image does not appear any magnetic domains (Figure 3 (c)).

At the same time, the results for the ternary tetragonal compound CoGeTe
show, that this sample is a novel magnetic material which can be characterized by specific magnetic domains parallel to belt-like shape as shown in Fig. 3 (f).

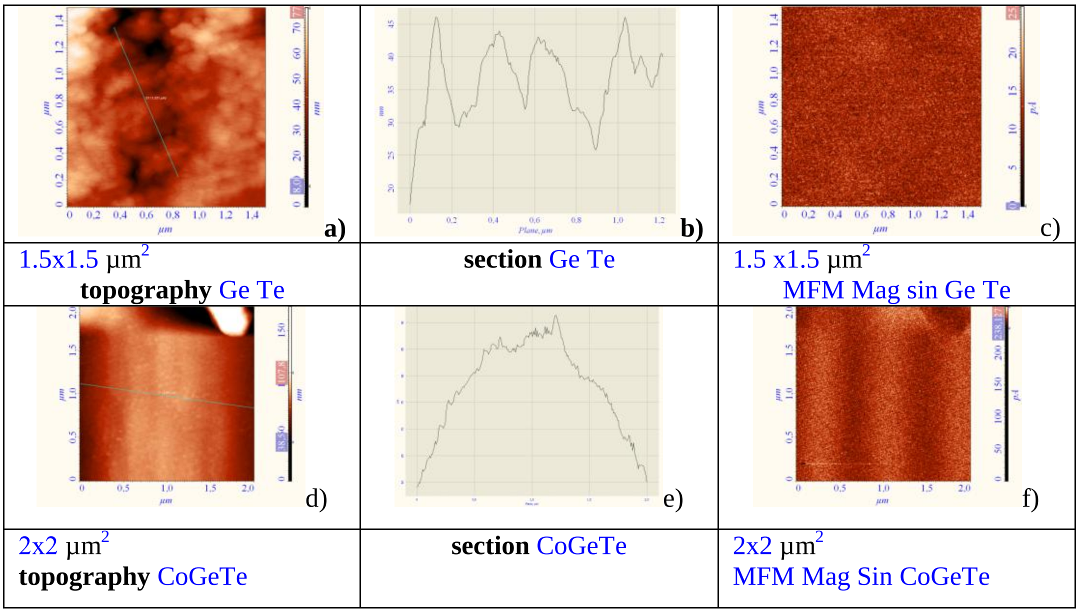

Fig. 3. Magnetic force microscopy MFM of samples GeTe (a, b, c) and $Co_{34.5}Ge_{32.5}Te_{33}$ alloy (tetragonal phase CoGeTe) (d, e, f).

4.Conclusion.

Thus, summing up the work done on the preparation and characterization of ternary compound CoGeTe containing almost equal proportions of significantly different nature elements such as metal cobalt, semiconductor germanium and nonmetal tellurium, we can formulate the following conclusions:

1. The ternary compound CoGeTe with atomic composition $Co_{34.5}Ge_{32.5}Te_{33}$ was obtained as well faceted microcrystals with sizes ranging from 4 to 11 microns.
2. The parameters of the new tetragonal ternary phase CoGeTe are: a = 6.204 ± 0.01 Å and c = 11.273 ± 0.03 Å.
3. Tetragonal phase CoGeTe is a ferroelectric material and demonstrates a magnetic response in the form of magnetic domains parallel belt-like shape.

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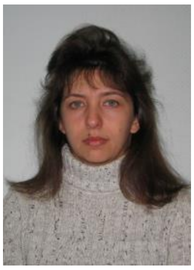

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