

Surface morphology and growth mechanisms of Pb-Cd-Te thin films

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Abstract— The analysis of the surface morphology of $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{Te}$: Pb (3 at.%) thin films obtained by the open evaporation in vacuum from pre-synthesized substances are performed. The quantitative composition and sizes of grains on the surface were analyzed. The films have a homogeneous composition and granular structure with individual grain sizes of several tens of micrometers. The introduction of Cadmium into the base matrix PbTe is the cause of the formation of defects such as grain boundaries due to the differ between crystal structure of CdTe and PbTe.

Keywords— Pb-Cd-Te, thin films, morphology, film growth

I. INTRODUCTION

IV-VI compounds are well known semiconductor materials for energy application [1]. The PbTe-based thin films are promising for manufacturing of miniature devices and flexible systems [2]. Reliable deposition and heat treatment technologies are used for their production for improving and stabilizing of application characteristics. One of the new types of thin-film materials, which are intensively studied for thermoelectricity in recent years, are compounds of the PbCdTe type [3],[4].

Another argument for the investigation of Pb-Cd-Te system is significantly different characteristics in compare to basic PbTe compound. In particular, the basic matrix of PbTe is a rock-salt type crystal structure with the lattice constant $a = 6.46 \text{ \AA}$, and the band gap is 0.16 eV at 0 K [5],[6]. CdTe is zink-blend structure crystal with lattice constant $a = 6.48 \text{ \AA}$ [7] or $a = 6.478 \text{ \AA}$ [8], and the band gap is 1.5 eV.

Structural studies are needed, in particular, for investigation of film-specific characteristics. Grain sizes can be determined by scanning electron microscopy (SEM). The density of dislocations can be determined by statistical

methods [9],[10]. Also, high-resolution SEM images allow to analyze the mechanisms of film growth, which are determined by technological factors of deposition (temperature modes, time of evaporation, the type of substrate material).

II. EXPERIMENT

A. Obtaining

The PVD technology is used for receiving thin films of the Pb-Cd-Te based system [11]. Initial compound $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{Te}$:Pb (3 at.%) was synthesized by direct melting of components for 10 h at 1073 K in sealed quartz ampoules evacuated to a residual pressure of 10^{-5} mbar. The classes of purity for Pb and Cd were 99.9996%, and for tellurium was 99.9997%.

The temperature of substrates at thin film deposition was $T_S = 473 \text{ K}$ and temperature of evaporator $T_E = 833 \text{ K}$. The thickness of the films was determined by the time of deposition in range (20-80) sec and measured using microinterferometer technique [12],[13].

B. Composition and structure

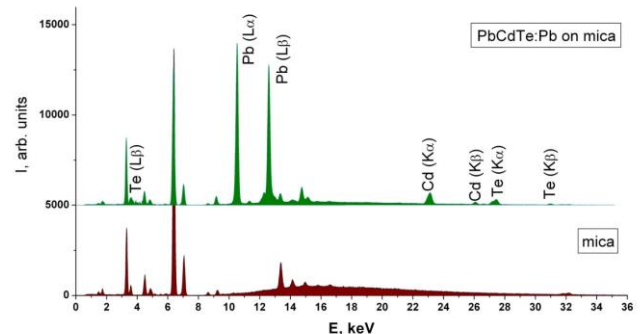


Fig. 1. X-ray fluorescence spectrum of $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{Te}:\text{Pb}$ (3 at.%) films deposited on mica substrate.

Chemical analysis of the film $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{Te}:\text{Pb}$ (3 at.%) was performed using X-ray fluorescence spectra [14]. The identification of chemical elements was performed by the energies at which the main peaks in the spectrum are observed and compared them with tabular data.

TABLE I. MASS CONTENT OF ELEMENTS FOR $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{Te}:\text{Pb}$ (3 AT.%) COMPOUND

Element	Mass. contribution, %
^{8}O	0.578 ± 0.115
^{48}Cd	11.463 ± 0.141
^{52}Te	25.691 ± 0.415
^{82}Pb	62.268 ± 0.366

No additional chemical elements are detected in the investigated film. Background peaks correspond to the chemical composition of the mica substrate. The mass ratio of Pb: Cd: Te for the film $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{Te}:\text{Pb}$ on a substrate of mica-muscovite may indicate the presence of Pb nanoinclusions (relative error ~ 3%) (table 1).

TABLE II. THICKNESS OF $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{Te}:\text{Pb}$ (3 AT.%) SAMPLES

No sample	Thickness	Average size of surface objects, μm
1	405	1.2
2	340	1.1

The composition and structure are investigated by scanning electron microscope (Tescan Vega3) equipped with energy dispersive X-ray spectroscopy Quantax (Bruker Nano GmbH, Germany). For each sample, SEM studies were performed at three different points, where the presence of defects or inclusions was visually observed.

III. RESULTS AND DISCUSSION

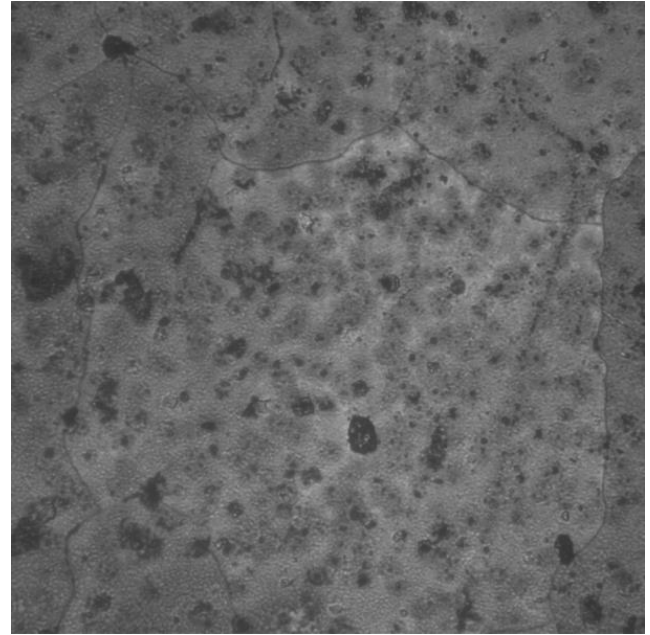
The lattice constant (a) of the substrate surface and the deposited material are slightly different. For mica $a = 0.518 \text{ nm}$ [15]. The studied $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{Te}:\text{Pb}$ (3%) is characterized by a lattice constant $a = 0.643 \text{ nm}$.

Differences in the values of the lattice constant of the substrate and condensate cause of internal stresses. Such internal stresses cause breaking of chemical bonds and forming of individual grains. It should be noted that the grain sizes are tens of micrometers, while the film thickness is only a few hundred nanometers. Therefore, such deformations will be noticeable on the surface of the studied films.

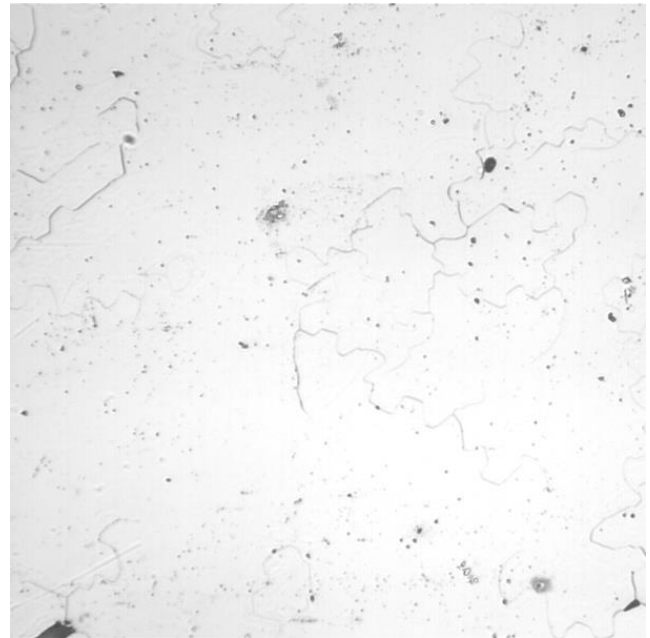
The clear borders of grains shown on Figure 2. Grains of the same size are observed for both samples. These images were obtained by NEXUS 412A hardmeter. Accordingly, it was decided to investigate in more details the boundaries of the observed grains. Therefore, the next step was SEM studies.

EDX spectra and SEM images of the samples are shown in fig. 3 (sample #1) and fig. 4 (sample #2). First of all, it should be pointed out that Fig. 1b demonstrates the grains

whose sizes are consistent with those observed earlier (Fig. 2), and were about $30\text{-}50 \mu\text{m}$ for sample #1 and $20\text{-}40 \mu\text{m}$ for sample #2. For comparison, the same increase in the scale is considered for both samples (fig. 3, c and fig. 4, b).



(a)



(b)

Fig. 2. Surface images of samples #1 (a), #2 (b) (magnitude x 100).

It was also found that grain sizes decrease slightly with the film thickness increase. The paper considered thin films with slightly different thicknesses (335 nm (#1) and 400 nm (#2)). The substrate is a single crystal mica muscovite.

It is important to note that the surface of all samples is fairly uniform. Moreover, layer-by-layer growth of condensate is clearly observed. This is the so-called layer by layer overlayer growth material on the substrate (Frank-van-der-Merve growth mode). This indicates that the substrate-

material interaction is much greater than the inter-cluster interaction.

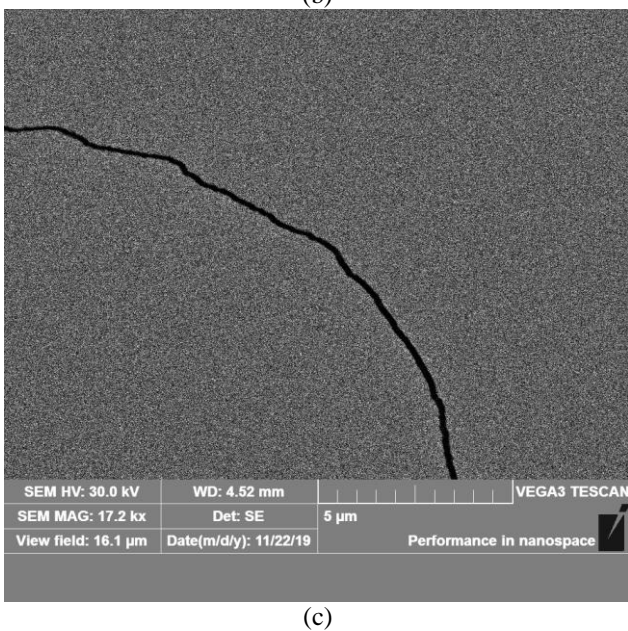
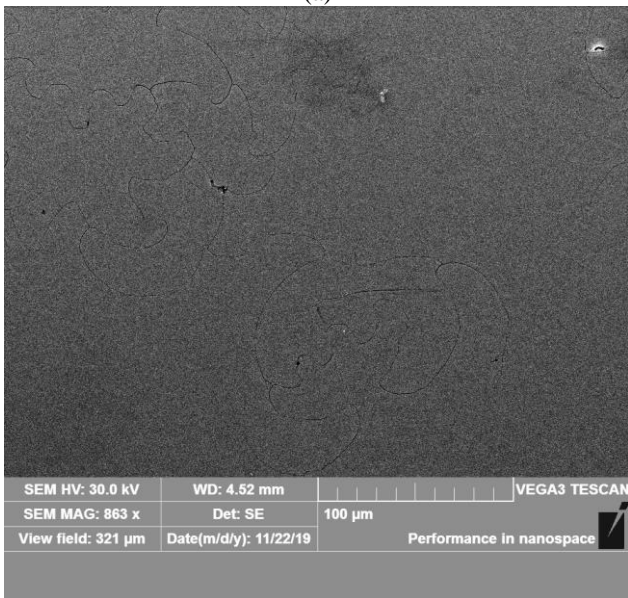
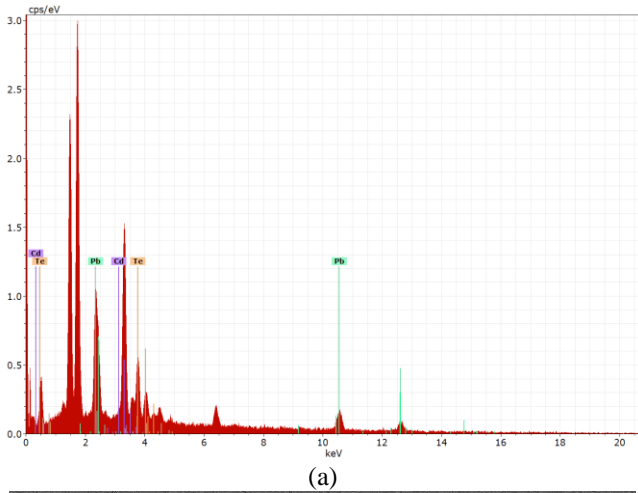


Fig. 3. EDX spectrum (a) and SEM images for $Pb_{0.9}Cd_{0.1}Te: Pb$ (3%) thin films for sample #1 with different scale: 100 μm (b), and 5 μm .

This layer-by-layer growth of the material is observed for Van der Waals epitaxy, when the adhesion energies are significant. The two-dimensional Van der Waals bonding is characterized by two completely different surface tensions, which are the Van der Waals plane (0001) and the plane of the ribs, for which covalent bonding is considered. Thus, the total surface tension of the Van der Waals nuclei is minimized for the minimum number of overhanging bonds in the planes of the ribs obtained by two-dimensional growth.

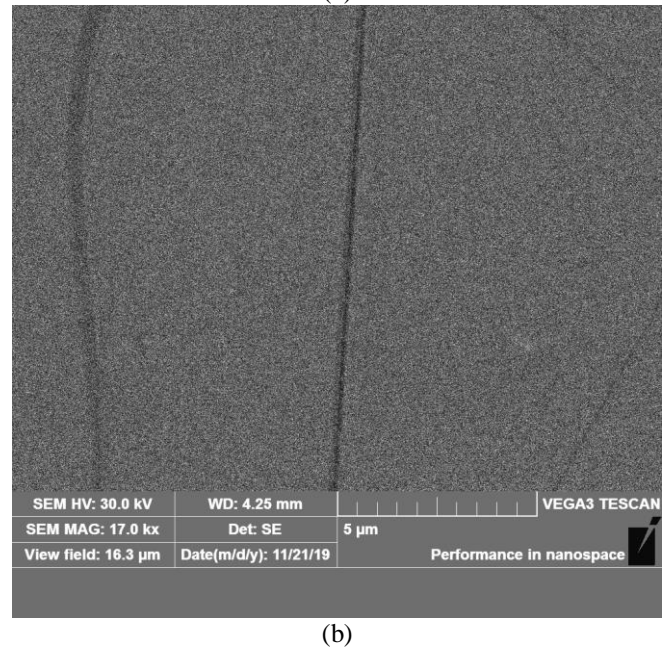
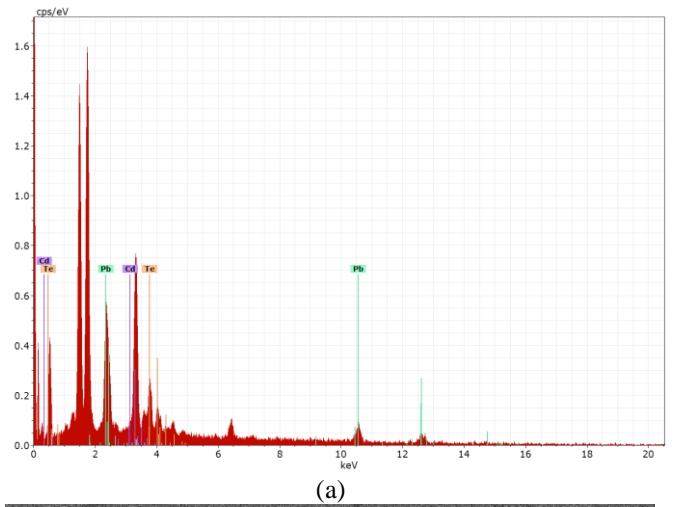
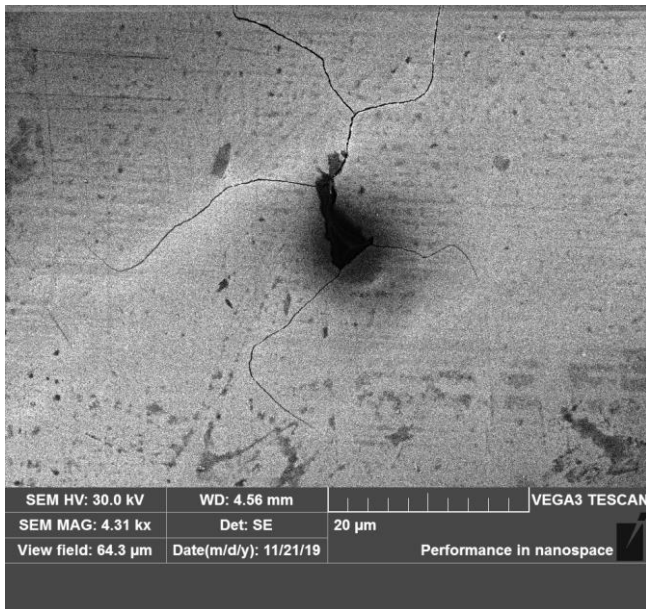


Fig. 4. EDX (a) and SEM (b) images for $Pb_{0.9}Cd_{0.1}Te: Pb$ (3%) thin films for sample #2.

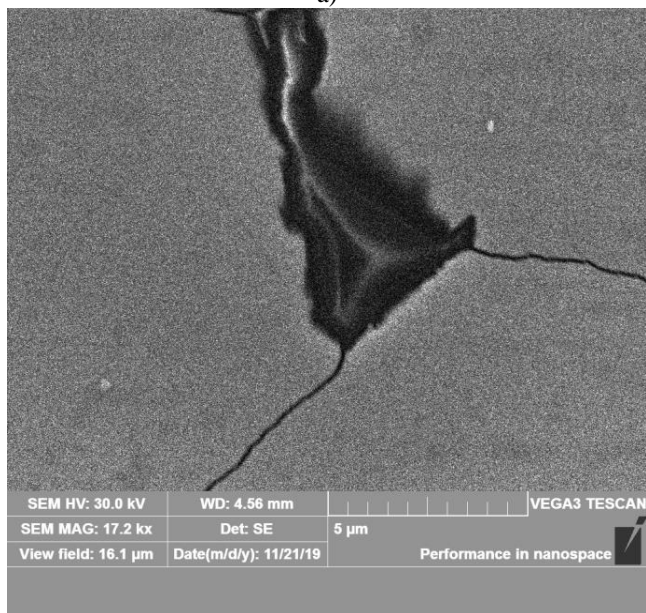
In the case of alloys, inside the film can occur its decomposition into its constituent components with release of a new phase nuclei and its subsequent evolution. Such processes are observed in certain areas of the studied films (Fig. 4). On the one hand, the surface of the film is quite homogeneous (gray). But on the surface, there are separate phases, EDS analysis of this area indicates a sharp increase in cadmium content and almost in the same proportion decreased tellurium content. The content of the components for sample #1 is distributed in quantities: Pb – 46.4 at.%, Cd – 28.4 at.%, and Te – 25.2 at.%.

In the next step, the region was investigated where three different grains are in contact with each other (Fig. 5). The

chemical composition of the elements is given in table. 3. As can be seen, this region is sharply depleted in lead.



a)



b)

Fig.5. SEM images for $Pb_{0.9}Cd_{0.1}Te$: Pb (3%) thin films for sample #2 with different scale: 20 μm (a), and 5 μm (b).

TABLE III.
WEIGHT AND ATOMIC CONTENT OF ELEMENTS FOR SAMPLE #2

Element	AN	[wt.%]	[norm. wt.%]	[norm. at.%]
Tellurium	52	19,52316	29,25798	34,12078
Lead	82	30,59619	45,85234	32,93041
Cadmium	48	16,6083	24,88968	32,94881
		66,72765	100	100

Accordingly, if we consider that the tellurium content at the point of contact of the grains is within the framework of the considered composition of the compound under study, it can be assumed that the presence of the CdTe phase is observed here.

Thus, separate zink-blend phases of CdTe create internal stresses in the base material PbTe (rock-salt). As a result, various types of structural defects arise, cause bond breaks and the formation of grains of certain sizes, depending on the quantitative content and distribution of such additional phases. In turn, a larger number of grain boundaries leads to a decrease in thermal conductivity θ due to the increase the scattering of phonons, that has good agree with data in [3], which makes such materials promising for thermoelectric applications.

REFERENCES

- [1] N.K. Abrikosov, *Semiconducting II–VI, IV–VI, and V–VI Compounds*. Springer. 2013, pp. 6-7.
- [2] O. Kostyuk, B. Dzundza, Y. Yavorsky and Z. Dashevsky, “Development of Thermal Detector Based on Flexible Film Thermoelectric Module,” *Physics and Chemistry of Solid State*. Vol. 22, № 1, pp. 45-52, 2021. DOI: 10.15330/pcss.22.1.45-52.
- [3] M. Bukała, P. Sankowski, R. Buczek and P. Kacman, “Structural and electronic properties of $Pb_{1-x}Cd_xTe$ and $Pb_{1-x}Mn_xTe$ ternary alloys,” *Physical Review B*, vol. 86, № 8, p. 085205, 2012.
- [4] M. Szot, P. Pfeiffer, K. Dybko, A. Szczerbakow, L. Kowalczyk, P. Dziawa, R. Minikayev, T. Zajarniuk, K. Piotrowski, M.U. Gutowska, A. Szewczyk, T. Story and W. Zawadzki, “Two-valence band electron and heat transport in monocrystalline $PbTe$ - $CdTe$ solid solutions with Cd content up to 10 atomic percent,” *Physical Review Materials*, vol. 4, № 4, p. 044605, 2020.
- [5] E. Saucedo, L. Fornaro, V. Corregidor, E. Diéguez, “Some structural aspects of $Pb_xCd_{1-x}Te$ bulk material,” *The European Physical Journal-Applied Physics* vol. 27, pp. 427-430, 2004.
- [6] Z. Dashevsky, in: D. Khokhlov, Talor&Francis (Eds.), *The Applications of Lead Chalcogenides in Thermoelectric Devices, Lead Chalcogenides: Physics and Application*, New York, 2003.
- [7] D. Freik, T. Parashchuk, B. Volochanska, “Thermodynamic parameters of CdTe crystals in the cubic phase,” *Journal of crystal growth*, vol. 402, pp. 90-93, 2014.
- [8] S. Movchan, F. Sizov, V. Tetyorkin, “Photosensitive heterostructures CdTe-PbTe prepared by hot-wall technique,” *Semiconductor Physics Quantum Electronics & Optoelectronics*, vol. 2, N 2, pp. 84-87, 1999.
- [9] L.I. Nykyruy, T.O. Parashchuk, B.P. Volochanska, “Thermodynamic parameters of lead sulfide crystals in the cubic phase,” *Chalcogenide Letters*, vol. 13, № 6, pp. 239–245, 2016.
- [10] H. Il'chuk, A. Kashuba, R. Petrus, I. Semkiv and N. Ukrainets, “Simulation the spectral dependence of the transmittance for semiconductor thin films,” *Physics and Chemistry of Solid State*, vol. 21, № 1, pp. 57-60, 2020.
- [11] B. Naidych, T. Parashchuk, I. Yaremiy, M. Moysenchenko, O. Kostyuk, O. Voznyak, Z. Dashevsky and L. Nykyruy, “Structural and Thermodynamic Properties of Pb-Cd-Te Thin Films: Experimental Study and DFT Analysis,” *Journal of Electronic Materials*, vol. 50, № 2, pp. 580-591, 2021.
- [12] B. Dzundza, L. Nykyruy, T. Parashchuk, E. Ivakin, Y. Yavorsky, L. Chernyak and Z. Dashevsky, “Transport and thermoelectric performance of n-type PbTe films,” *Physica B: Condensed Matter*, p.412178, 2020.
- [13] L. Nykyruy, Y. Saliy, R. Yavorskyi, Y. Yavorskyi, V. Schenderovsky, G. Wisz, S. Górný, “CdTe vapor phase condensates on (100) Si and glass for solar cells”, In 2017 IEEE 7th International Conference Nanomaterials: Application & Properties (NAP) (pp. 01PCSI26-1). IEEE.
- [14] I. Yaremiy, S. Yaremiy, V. Fedoriv, O. Vlasii, A. Lucas, “Developing and programming the algorithm of refinement of the crystal structure of materials with possible isomorphous substitution,” *Eastern-European Journal of Enterprise Technologies*, vol. 5, № 5, pp. 61-67, 2018.
- [15] A.G. Betekhtin. *Mineralogy*, State Publishing House of Geological Literature, Moscow, 1950, p. 956.
- H. Wang, A.D. LaLonde, Y. Pei and G.J. Snyder, “The criteria for beneficial disorder in thermoelectric solid solutions,” *Advanced Functional Materials*, vol. 23, № 12, pp. 1586-1596, 2013.