

## Kinetics of Crystallization of an Amorphous Film of $\text{Bi}_2\text{Te}_3(\text{Se}_3)$

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**Abstract.** Phase formation processes in Bi-Te system have been investigated by kinematic electron diffraction method. It is established that  $\text{Bi}_2\text{Te}_3$  and BiTe phases were formed on condensation plane in amorphous and crystalline state, respectively, at simultaneous and at consecutive evaporation of bismuth and tellurium, irrespective of the order of evaporation of components. Amorphous  $\text{Bi}_2\text{Te}_3$  phase is stable at room temperature and crystallizes at 423K temperature. It is shown that ordering of BiTe phase does not result in ordering of atom structure and is dependent on real structure. Kinetic parameters of crystallization of nanometric amorphous  $\text{Bi}_2\text{Te}_3(\text{Se}_3)$  films are determined. On experimental results it is defined that crystallization kinetics of  $\text{Bi}_2\text{Se}_3$  occur in accordance with Avrami-Kolmogorov law and is described by the analytic expression of  $V_t = V_0[1 - \exp(-kt^m)]$ .

**Keywords:** phase formation, amorphous layer, infrared, crystal, compounds

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### 1. Introduction

In works [1-5] on investigations of phase equilibrium in Bi-Te system the obtained results are not in agreement with one another and available discrepancies are especially connected with the region of a phase existence and type of state diagram. By microscopic and roentgen investigations and study of electro-resistance, thermal power, magnetic susceptibility, Hall effect and hardness  $\text{Bi}_2\text{Te}_3$  composition phase existence with wide range of homogeneity of the given phase has been established.  $\text{Bi}_2\text{Te}_3$  homogeneity boundaries according to the work [3] are at 36-40 and 53-55 in weight percents (48-52 and 65-67 at. %) of *Te*. In Bi-Te alloys except solid solutions forming by one of the components (Bi) in  $\text{Bi}_2\text{Te}_3$  there

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has been found out *NaCl* – typed cubic phase *BiTe* with  $a=0,647\text{nm}$  SSC B1. All alloys of Bi-Te system according to [1,4] are the alloys of changing composition therefore the problems of production and investigation of thin film specimens being as microstructural objects with their evaluable physical properties in massive specimens require the study of the given system compounds during their thermal treatment. Of scientific interest is the study of widening field of use of this system compounds as infrared radiation detectors, thermo-generators, power sources of space technology self – contained systems and implanted cardio stimulators [5-8].

In papers [9-12] there has been mainly considered the film formation of individual compounds of Bi-Te system with different orientation of dice. In [10,11] it is shown that films 30nm in thickness forming on previously heated different substrates up to 473K are texturized. With the increase of film thickness and substrate temperature texturization has been disturbed. By  $\text{Bi}_2\text{Te}_3$  conversation on NaCl substrate at room temperature fine-grained polycrystalline structures have been formed [12]. Laser evaporation of  $\text{Bi}_2\text{Te}_3$  on mica at  $T=623\text{K}$  leads to the strict orientation of (0001)  $\text{Bi}_2\text{Te}_3$  || (0001) – typed mica crystallites. Conditions of single crystal film production are established in [12].

However, the problems of phase formation on Bi-Te - based system compounds are not under consideration and data on phase transitions in thin layers in works which reference has rather a big number of titles are completely lacking. Method of kinematic electron diffraction examination can be the most productive problems referred to component solubility in Bi-Te system compound and also problems of phase formation and phase transformations in mentioned system. In present paper phase formation with different substructure because of reactions and processes of Bi-Te system nano-dimensional vacuum condensate interactions and kinetics of phase transitions in  $\text{Bi}_2\text{Te}_3$  thin layers have been studied.

To establish conditions of phase formation in Bi-Te system investigations have been carried out on films obtained by simultaneous and subsequent evaporation in vacuum  $\sim 10^{-4}\text{Pa}$  of individual components of bismuth and tellurium from two sources. Evaporation sources spaced at 120mm are composed of tungsten conical helixes. Freshly spalled crystals of NaCl and amorphous celluloid at room temperature are served as substrates. In this case on condensation plane the layer of films  $\sim 25\text{nm}$  in thickness has been formed. To get a full insight of phase composition in intimate range of temperatures and concentrations the obtained samples have been investigated at different temperatures: from room temperature and above. It has been carried out by method of kinematic electron-diffraction examination [13], by survey of a series of isothermal electron diffraction patterns. By electron diffraction patterns like these phases composition of specimen at any

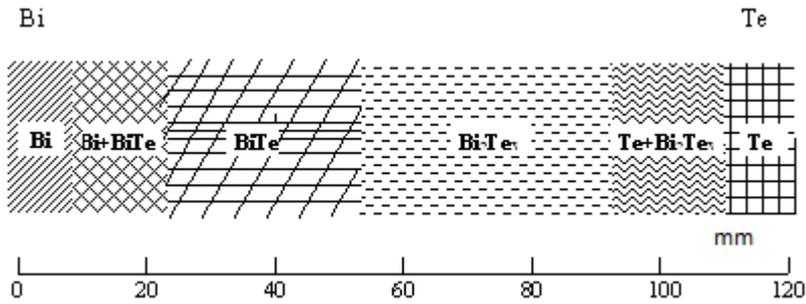
temperatures is determined and several isothermal cross-sections of region “composition-temperature” are derived.

## 2. Result and Discussion

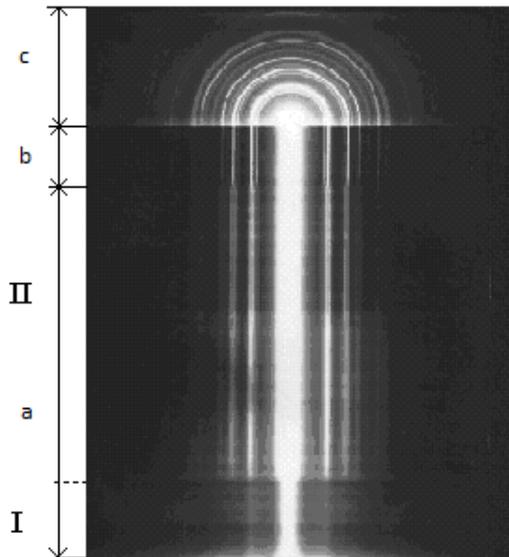
Specimen analysis obtained by binary field method shows that there have been formed several regions on condensation plane (fig.1): region of  $\text{Bi}_2\text{Te}_3$  composition compound, region of pure face-centered cubic phase  $\text{BiTe}$  with periods established in [3] and region of their mixture in the immediate vicinity of pure compounds. Resulting films as viewed from Te sources are amorphous which crystallization allows them as thin layers of  $\text{Bi}_2\text{Te}_3$  composition to be identified. Substantial extent of resulting phases on condensation plane is likely to be related to big mobility of Bi atoms in molecular beam during the evaporation, concentration compensation by their migration on condensation plane. Electron diffraction patterns obtained from films being immediately below Bi and Te sources involve lines of pure unreacted chemical elements.

As it is known a big body of fundamental results obtained from experiments on phase transformations, i.e. continuous or jump-like change of energy, high or low value of activation energies essential to complete process of phase transition and its rate are due to thermodynamic lows. An understanding of many experimental facts observed at phase transition involves two types of phase transitions: reconstructive one and transitions of shift type. By the first one two structures going into each other or states (amorphous or crystalline) are quite different. In the second case one structure is different from another by small shift of one or a big number of atoms in crystalline lattice. Complicity of kinetics study of amorphous film crystallization processes is that mechanism of new phase dice formation and their further growth is unknown which data can be obtained later due to establishing time-temperature dependencies of thin amorphous layer crystallization. Kinematic electron – diffraction examination featuring processes of phase transformations in  $\text{Bi}_2\text{Te}_3$  compound plays a decisive role in studying these problems.

Distinctive kinematic electron diffraction pattern derived from  $\text{Bi}_2\text{Te}_3$  films is given in fig.2. Fragment “a” comprises 2 parts: the first part of electron diffraction pattern appropriate to room temperature falls into blurred diffraction lines being indicative of film dispersity. Amorphous phase with values  $S = 4\pi \sin \theta / \lambda = 19,3; 27,67; 37,16 \text{nm}^{-1}$ , corresponding to diffusion lines on electron diffraction patterns at temperature 423K goes into polycrystalline state.



**Figure 1.** Diagram of Bi-Te binary field distribution.

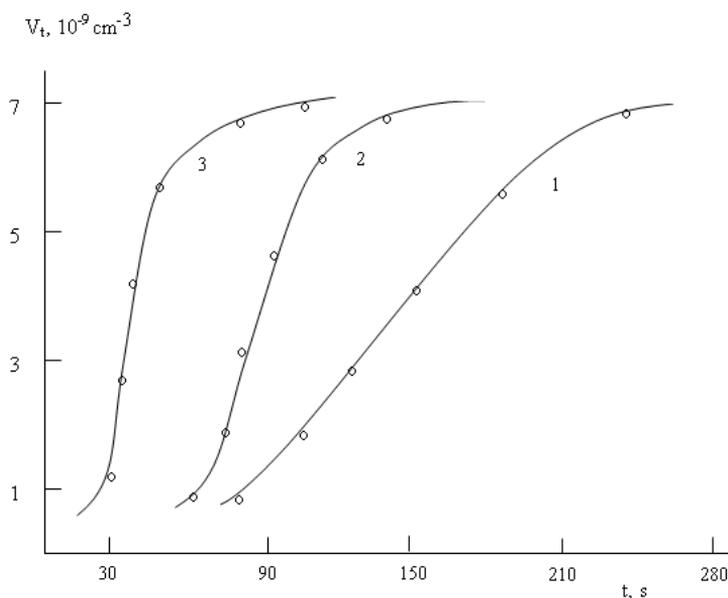


**Figure 2.** Kinematic electron diffraction pattern evidencing transformation of amorphous phase  $\text{Bi}_2\text{Te}_3$  into crystalline one.

Crystallized phase  $\text{Bi}_2\text{Te}_3$  is stable and further annealing at 523K and above for 4-5 minutes and more does not lead to any fixed structural changes. To describe kinetics of growth as in the case of constant rate of new phase nucleus generation and their subsequent growth about statistical behavior of overlapping nucleus of growing phase as in intermediate cases (decreasing rate of generation) kinetic equation [14-15] is general

$$V_t = V_0[1 - \exp(-kt^m)] \quad (1)$$

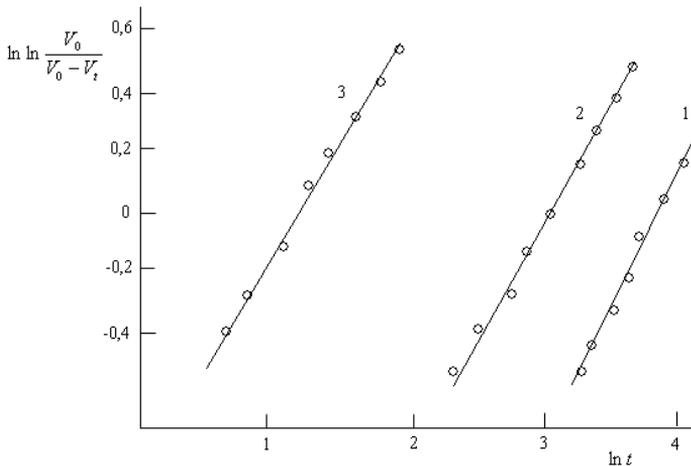
where  $V_t$  is the fraction of substance volume, undergone transformation to instant  $t$ ;  $V_0$  is the initial volume,  $k$  – constant of reaction rate. Magnitude  $m$  is variable for dissimilar possible types of transformations and depends on growth dimension. On the base of  $m$  exponent magnitude, one can conclude of possible mechanism of transformation. However, should be noted that to gain reliable results one must have accurate experimental data about magnitude  $Vt$ .



**Figure 3.** Kinetic crystallization curves of amorphous  $\text{Bi}_2\text{Te}_3$ . Values of  $T_{\text{cryst}}$ : 1- 423K, 2-438K, 3- 453K

To establish kinetic parameters of  $\text{Bi}_2\text{Te}_3$  amorphous film crystallization there have been obtained isothermal kinetic electron diffraction patterns at 423, 438, 453K. Line intensities of growing crystal phase  $\text{Bi}_2\text{Te}_3$  corresponding to different instants of time have been determined micro photometrically on the base of micro photograms of kinematic electron diffraction patterns. Diffraction line intensities with Miller indices (1120), (2240), (3030) of crystal due to annealing time have been determined. Within temperature range under investigation there have been plotted kinetic crystallization curves of amorphous  $\text{Bi}_2\text{Te}_3$ , i.e. dependence of  $\text{Bi}_2\text{Te}_3$  crystallized portion volume on time at different temperatures (fig.3).

There have been plotted dependencies  $\ln \ln \frac{V_0}{V_0 - V_t}$  on  $\ln t$  for temperature 423, 428 and 523K (fig.4). For all temperatures experimental points fall on straight lines. Value exponent of  $m$  in equation (1) defined from the slope of straight lines given in fig.4 appears to be close to three ( $m=2,82$ ; 2,91 and 2,98 for 423, 438 and 453K, respectively). At indicates that in the case of  $\text{Bi}_2\text{Te}_3$  amorphous film crystallization within temperature range under investigation two-dimensional growth of dice has been taken place. In the given case constant  $k$  being included in equation (1) is equal to  $1/3\pi\sigma_3\sigma_p^2$ . Here  $\sigma_3$  is the rate of crystallization center formation has been determined as the number of nucleus changing into crystallization centers in per unit of time in unit of metastable phase volume;  $\sigma_p$  is the linear crystallization rate defined as the rate of graving center linear dimensions changes in new phase [14-15].



**Figure 4.** Dependence  $\ln \ln \frac{V_0}{V_0 - V_t}$  on  $\ln t$  for crystallization.

On the base of mentioned data there has been plotted diagram of  $\ln K$  dependence on reverse temperature which appears to be linear. Dependence like these points to the fact that rates of nucleus generation and linear growth of dice can be described by Arrhenius - typed expression

$$\ln K = A - \frac{1}{RT} (E_3 + 2E_p) \quad (2)$$

where  $E_3$  is the activation energy of nucleus generation;  $E_p$  is the activation energy of die growth;  $R$  is the universal gas constant;  $A$  is the constant temperature – independent.

By slope of straight line of  $\ln K$  dependence on  $1/T$  there has been determined total activation energy of crystallization being to 75,5kcal/mol. Activation energy of nucleus generation  $E_3$  calculated by slope of straight line of dependence  $1/\tau$  on  $\ln t$  ( $\tau$  is the experimentally observed time of crystallization onset – incubation time [18] established by isothermal kinematic electron diffraction patterns obtained at T423, 438 and 453K) appears to be equal to 28,7kcal/mol.

As it is seen from fragment “b” thermal treatment of film for 30min. at temperature 573K brings about re crystallization of object and diffraction field lines on electron diffraction patterns become sharper: there has been taken place further coarsening of dice. Set of diffraction lines (fig.2 fragment “b”) on electron diffraction pattern from discrete part (fig.2 fragment “c”) on the base of hexagonal syngamy  $\text{Bi}_2\text{Te}_3$  with periods of elementary cell of crystal lattice  $a=0,438$ ;  $c=3,05\text{nm}$ ; SSC  $D_{3d}^5$  and agree with data [16]. Annealing of thin films at  $T \approx 423\text{K}$  leads to appearance of additional, very weak lines in intensities on electron diffraction patterns. Appearance of new lines is likely to be related to the process of ordering as there have been remained main diffraction lines of initial face-centered cubic lattice. Ordered phase is stable at T 503-523K which line intensity line increases with temperature rise of thermal treatment. Since additional diffraction lines which intensity reinforces with temperature rise and become sharper, indexes with the periods of FCC lattice as well it should be suggested that ordering is due to the read structure of object, die coarsening and is not the result of atomic ordering of structure.

Electron-microscopic investigations also allow microcrystalline structure of  $\text{Bi}_2\text{Te}_3$  hexagonal phase to be revealed and first be observed (fig 5.)

It is revealed that in thin layers crystallized on different single crystal ( $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{LiF}$ ) and isotropic substrates (amorphous celluloid) in the case of  $\text{Bi}_2\text{Te}_3$  hexagonal phase formation the orientation by plane  $(1\bar{1}20)$  or  $(10\bar{1}0)$  parallel to substrate are always dominated.



**Figure 5.** Microcrystalline structure of  $\text{Bi}_2\text{Te}_3$  hexagonal phase.

In paper [17] similar orientations have been established for TIS, TIS and TLTe composition compounds by their epitaxial growth on *NaCl* and *KCl* single crystal substrates, respectively.

Phase formation processes in Bi-Se system films have been investigated in [18] which results are generalized in fundamental work [19]. It is established that by Bi deposition on Se thin layer due to reactive diffusion between them the moment  $\text{Bi}_2\text{Te}_3$  composition compound in high disperse state is formed. No prolonged annealing of films at temperature 473K promotes die coarsening and leads to sharpness of diffraction reflections. By further annealing of  $\text{Bi}_2\text{Te}_3$  in vacuum there has been volatilized the part of Se atoms having weak bond in crystal lattice hence *BiSe* is formed.

According to [18-19] processes of  $\text{Bi}_2\text{Te}_3$  lattice rearrangement in BiSe lattice can be explained from structural point of view: the base of  $\text{Bi}_2\text{Te}_3$  compound structure comprises 9 – layered rhombohedral packing of the atoms where 2/3 octahedral vacancies are occupied by Bi atoms.



Atoms of Se and Bi are the capital and small letters, respectively. The shortest interatomic distances in  $\text{Bi}_2\text{Te}$  structure where two layers of occupied vacancies alternate with one layer of free ones are the following:

$$Se - Se = 0,330nm; Bi - SeI = 0,307nm; Bi - SeII = 0,299nm.$$

Selenium with selenium (AC, CB, BA) has a weak residual bond as a result the part of Se atoms related to one another weakly by compassion volatilizes and rhombohedral crystal lattice with periods  $a=0,9832nm$ ,  $a=24^{\circ}10'$  with space

symmetry of crystals (SSC)  $R\bar{3}m - D_{3d}^5$  rearranges in hexagonal lattice of BiSe with periods  $a=0,418\text{nm}$ ;  $c=2,28\text{nm}$ ; SSC  $P\bar{3}m - D_{3d}^5$  R.

However, it should be noted that in [18-19] there have not been established regularities and kinetic parameters of Bi<sub>2</sub>Te<sub>3</sub> film phase transformations and dimension of growth of resulting dice is not revealed.

Unlike typical electron – diffraction examination high – energy electron diffraction which allows only discrete electron diffraction patterns from diffraction field to be taken, kinematic electron – diffraction examination allows all intermediately-primary and forming on their basis the secondary phases generating due to phase transformations taking place because of artificial ageing of thin film to be fixed, i.e. by temperature rise and film annealing. In the case of kinematic survey diffraction field near the camera of electronograph closes flaps with narrow horizontal slit in the middle, as a result on the moving photographic plate with certain velocity instead of typical electron diffraction pattern in the form of concentric rings, electron diffraction pattern from the polycrystal there have been derived straight lines. By kinematic electron – diffraction examination for thin films of any compound there has been achieved and determined stationary values of activation energies necessary for completion of phase transitions when all the material of one or another compound taken place in the process goes from amorphous state into crystalline one or from one crystalline modification into another one.

Complicity of kinetics study of phase transformations in films is that it is often unknown mechanism of given processes, the data about them one can obtain by determining temperature – time dependencies, i.e. by establishing relationship between fraction of volume  $V$  and time of transformation  $t$  which defines both physical and chemical kinetics of any process.

As  $Bi$  and  $Si$  in vapor elasticity differ sharply from each other in order to obtain Bi – Se system alloys by method of simultaneous and consecutive evaporation of components of given system there have been previously set spaced at the height of 70mm above the condensation plane and behind each other at a distant of 100mm are as sources of evaporation. Amount of evaporated Bi and Se is 18,5 and 8,4mgm, respectively. Freshly spalled single crystals  $KCl$  are as substrates.

Electron diffraction patterns taken from films formed on the condensation plane by simultaneous evaporation of Bi – Se system components show that resulting films in the collector with big content of Se are amorphous and contain diffusion haloes with values  $S = 4\pi \sin \theta / \lambda = 14,14; 20,46; 30,34; 35,88\text{nm}^{-1}$ .

These objects after annealing for 10 minutes at 443K go into polycrystalline states, there have been observed sharp diffraction lines being among  $\text{Bi}_2\text{Te}_3$  on electron diffraction patterns.

By further annealing at 468K polycrystalline compound for 5 minutes it undergoes phase transformation and BiSe compound has been formed.

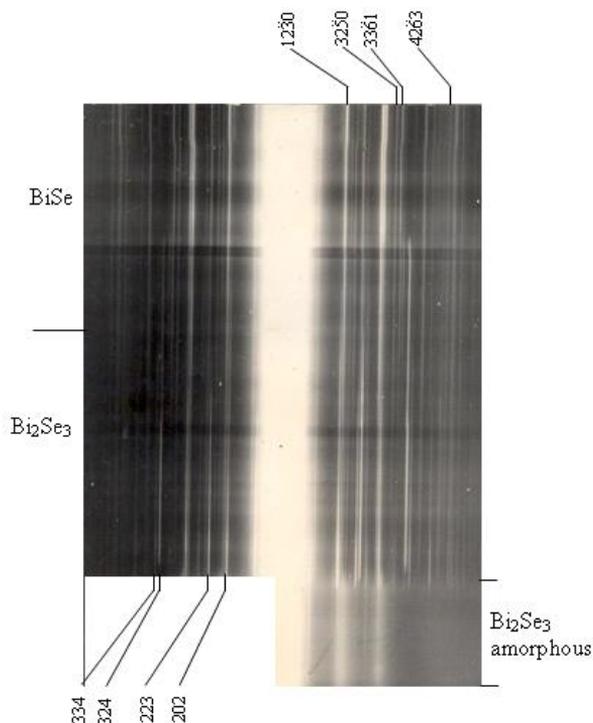
Electron diffraction patterns obtained from films condensed on substrates being in various points of condensation plane show only the presence of  $\text{Bi}_2\text{Te}_3$  amorphous phase, although in composition presence of BiSe can be expected. Portions of Se and Bi remain free and on electron diffraction patterns from films being on substrates placed immediately under the sources of evaporation there have been seen diffusion haloes and sharp diffraction lines being among Se and Bi, respectively.

By *Bi* condensation on Se layer and in the case of Se deposition on Bi only  $\text{Bi}_2\text{Te}_3$  compound is formed. Bismuth selenide of BiSe composition has not been formed. In both cases portions of Se and Bi as well as in the case of simultaneous evaporation of Bi and Se from two sources remain free unreacted. Selectivity at Bi – Se system phase formation can be explained by chemical bond between the components of the given system and as neutral atoms or ions of Bi have a bigger atomic weight than atoms of Se, by evaporation they have a bigger kinetic energy which are sufficient only for  $\text{Bi}_2\text{Te}_3$  compound.

To establish kinetic parameters of  $\text{Bi}_2\text{Te}_3$  amorphous film crystallization in 30nm thickness and  $\text{Bi}_2\text{Te}_3$  - BiSe –typed phase transformation isothermal kinematic electron diffraction patterns at 463; 478; 488 and 498K have been obtained. On kinematic electron diffraction patterns taken from films thermal-treated by special furnace in in the column of electronograph immediately during the survey it is seen that diffusion likes referring to the amorphous phase disappear and there have been appeared diffraction reflections of crystalline  $\text{Bi}_2\text{Te}_3$  which on expiration of certain time go into BiSe. One of these kinematic electron diffraction patterns taken at 498K is given in fig.6.

Line intensities of growing crystal phase with Miller indices (202); (223); (324); (334) corresponding to various instants of annealing are determined photometrically. Transition from values of intensity to the amount of crystallized substance have been carried out by normalization providing that in kinematic approximation according to the work [20] intensity of electron scattering is proportional to the volume of scattering substance and local intensity of Debye ring falling at a small fragment  $\Delta$  has the formula

$$I_{hkl} = I_o \lambda \left| \frac{\Phi_{hkl}}{\Omega} \right|^2 V \frac{d_{hkl}^2 \Delta P}{4\pi L \lambda} \quad (3)$$



**Figure 6.** Kinematic electron diffraction pattern taken at T498K

here  $I_o$  is the intensity of primary beam radiation,  $\lambda$  is the electron wavelength,  $\Phi$  is the structure amplitude of diffraction reflection which is in kinematic approximation is determined from atomic scattering factors,  $\Omega$  is the volume of crystal lattice elementary cell,  $V$  is the irradiated volume of polycrystalline specimen,  $d_{nkl}$  is the interplanar distance,  $\Delta$  is the small fragment of Debye ring;  $P$  is the factor of diffraction reflex amplification regularity,  $L\lambda$  is the constant of the instrument which is defined depending on applied voltage of accelerating electrons.

During kinematic survey of magnitude values including in the right part of equation (3) remain constant except  $V$ . Intensity of diffraction reflection with

indices  $hkl$  providing of  $I_0$  and  $L\lambda$  according to (3) is proportional to irradiated volume of polycrystal, i.e.  $I_{hkl} \sim V$ .

Consequently, from kinematic electron diffraction pattern by determine change of line intensities one can find out the change of substance amount undergoing phase transformation. As it is mentioned above the kinetics is described by formula (3) in the case of three-dimensional growth of dice ( $\nu = 2/3$ ) but if the centers of new phase grow in the form of two-dimensional formations ( $\nu = 1/2$ ) for the volume of transmuted substance to instant  $t$  there has been held true the formula

$$V_t = V_0[1 - \exp(-0,8\nu_3 A^2 t^3)] \quad (4)$$

where  $A$  is the product of form factor into the linear rate of growth ( $k_s \cdot \nu_p$ ) (fig.7.)

There have been plotted dependencies  $\ln \ln \frac{V_0}{V_0 - V_t}$  on  $\ln t$  (fig.8) for T463, 478,

488 and 498K. For all temperatures experimental points fall on straight lines. Value of exponent  $m$  in equation (3) derived from slope of given straight lines appears to be close to four. It indicates that in the case of  $\text{Bi}_2\text{Se}_3$  amorphous film crystallization within the investigated temperature range three-dimensional growth of dice has been taken place. On the given case including in formula (3) constant

$k = \frac{1}{3} \pi \nu_3 \nu_p^3$ . Here  $\nu_3$  is the velocity of crystallization center formation which defines as the number of nuclei transforming into the centers in per unit of time in unit of metastable phase volume;  $\nu_p$  is the linear rate of crystallization defined as the velocity of new phase growing center linear size change.

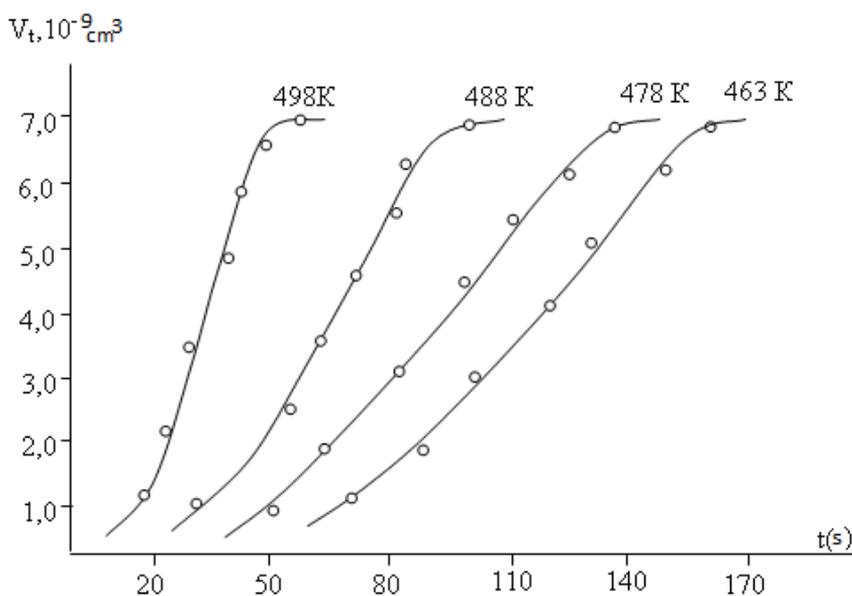
Taking into consideration that  $\nu_3$  and  $\nu_p$  obey Arrenius equation we take

$$\ln k = A - \frac{1}{RT} (E_3 + 3E_p) \quad (5)$$

i.e. total activation energy of crystallization process comprises of two components:  $E_{total} = E_3 + 3E_p$  where  $E_3$  and  $E_p$  are activation energy nucleus generation and dice growth, respectively.

Values  $\ln k$  set for the dependence  $\ln \ln \frac{V_0}{V_0 - V_t}$  on  $\ln t$  (fig.3) by the slope of straight lines which are plotted on the base of kinetic curves of crystallization (fig.2) appears to be the following:

$T, K$	463	478	488	498
$\ln k$	-19,2	-16,5	-13,4	-10,2

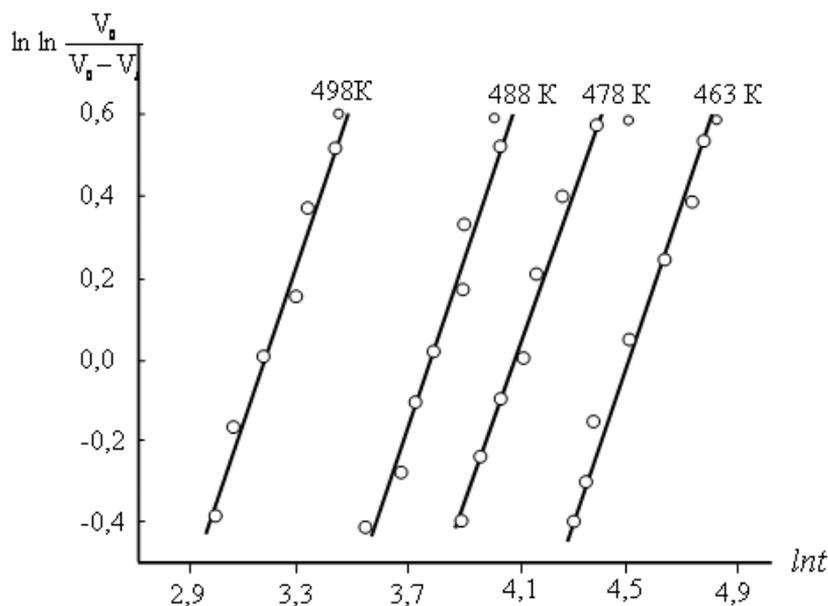


**Figure 7.** Crystallization isotherms of amorphous  $\text{Bi}_2\text{Te}_3$

Diagram of the dependence  $\ln k$  on  $1/T$  is linear. By the slope of straight line of the given dependence there has been determined total activation energy of crystallization equal to 87,3kcal/mol.

Determined total rate of crystallization on tangent angle slope to kinetic curves from the dependence  $\ln v$  on  $1/T$  there has been established activation energy equal to 28kcal/mol that is corresponding to activation energy of nucleus formation  $E_3$ . Activation energy of nucleus formation  $E_3$  calculated by the slope of straight line of the dependence  $1/\tau_0$  on  $\ln t$  (where  $\tau_0$  is experimentally observed time of

crystallization onset - on electron diffraction pattern) are also equal to 28kcal/mol. Activation energy of die growth  $E_p$  derived from relationship  $E_p=(E_{total}-E_3)/3$  is equal to 19,4kcal/mol.



**Figure 8.** Diagram of dependence  $\ln \ln \frac{V_0}{V_0 - V_t}$  on  $\ln t$

### 3. Conclusion

Crystallized phase  $\text{Bi}_2\text{Se}_3$  is unstable and further annealing on expiration of certain time leads to  $\text{Bi}_2\text{Se}_3 \rightarrow \text{BiSe}$  transformation. As it is seen on the kinematic electron diffraction pattern (fig.1) the further thermal treatment of film brings about recrystallization of  $\text{Bi}_2\text{Se}_3$  films and continuous registration of phase transformation by kinematic survey allows decrease of  $\text{Bi}_2\text{Se}_3$  initial phase reflection intensity and rise of growing BiSe to be followed.

To plot kinetic curves along with diffraction lines of decreasing phase  $\text{Bi}_2\text{Se}_3$  there have been also analyzed isolated lines of growing hexagonal phase BiSe not coinciding with lines of  $\text{Bi}_2\text{Se}_3$  just reflections  $(1\bar{2}\bar{3}0)$ ;  $(3\bar{2}\bar{5}0)$ ;  $(3\bar{3}\bar{6}1)$ ;  $(4\bar{2}\bar{6}3)$ . By micro-photogrames intensities of analyzed lines at various instants are determined. Going from intensity to volume by normalization there been plotted isotherms which correlation with analytical expression of kinetic curves of phase transformations (4) shows that better correlation is at  $m=3$ , i.e. there has been taken

place two-dimensional growth of dice and for the volume of transmitted substance to instant  $t$  expression (5) is held true. Total activation energy of phase transformation, i.e.  $E_{total}=E_3+2E_p$  estimated by linear dependence  $\ln k$  on  $1/T$  appears to be equal  $\sim 125,5$  kcal/mol. Value  $E_3$  calculated as well in the case of crystallization of amorphous Bi<sub>2</sub>Se<sub>3</sub> from dependence  $1/\tau_0$  on  $\ln t$  appears to be equal 37,3 kcal/mol. Determined from relationship  $E_{total}=E_3+2E_p$  activation energy of die growth is equal to 441 kcal/mol.

Thus, the use of kinematic electron – diffraction method along with the investigations of phase formation in Bi-Se system offer scope for following both phase transitions and establishing as kinetic parameters of Bi<sub>2</sub>Se<sub>3</sub> amorphous film crystallization as Bi<sub>2</sub>Se<sub>3</sub>  $\rightarrow$  BiSe phase transformation.

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