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Interaction Studying in System GeO - B_2O_3 by Spectroscopic Methods

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Because of X-ray amorphous character of GeO and B_2O_3 for study of interaction between them methods of IR transmission spectroscopy and spectroscopy of diffuse reflectance are applied. Essential change of position and intensity of bands of absorption in system GeO-B_2O_3 (H_3BO_3) at heating and thermal evaporation in vacuum is established. It is observed essential gypsochromic shift of short-wave border and bathochromic shift of long-wave border of domain of an optical transparency of a coating compared with initial GeO that testifies in favour of change of the nature of a material. A coating from Germanium (II) oxide exhibits high optical and operational parameters and are perspective for interference optics of an IR range of a spectrum.

Keywords: Germanium (II) oxide, Boron oxide, spectroscopic methods, thin-film coatings.

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Introduction

Oxide compounds of Germanium, as well as element substance, cause indefatigable interest in researchers. First, it is connected with their unusual chemical and physical properties, not characteristic for analogues of Germanium, namely, Silicium and Tin compounds. So, for example, α – and β – modifications of GeO_2 behave themselves as they are different compounds; nevertheless, high-temperature β – (that is hexagonal) modification of GeO_2 is received much easier, than α-(tetragonal) modification, under usual conditions [1].

As to Germanium monooxide, GeO, it is metastable (on difference, for example, from SnO) in a solid state, especially at the raised temperatures [2], turning to composite Ge-GeO_2 (vitreous substance); through its such structure is always received in X-ray amorphous state. For this reason instead of the X-ray analysis is the most effective method of research of GeO and systems on its basis of spectroscopic method. Being qualitatively similar among them, IR transmission spectra of GeO_2 (hex.) and GeO essentially differ in details [3]. So, bands of absorption of the first of substances are much more intensive, expressed and well divided; instead of that in GeO they are indistinct and, worse divided and their intensity almost on an order the lower and is. Prominent feature as GeO, and systems in which its formation takes place (Ge-GeO_2, Ge-SnO_2, etc.) there is a superposition of oscillations on certain intervals which reminds a picture of imposing of rotating movements on oscillation spectra [4]. The nature of this phenomenon which also, by the way, reveals some other nanostructured systems, meanwhile remains not clear.

Possibility of their practical application - for manufacturing elements for IR optics with use in the thermovision techniques, manufacturing of an optical fibre, photo-electric converters (mainly of space basing) is the second reason of interest in elemental Germanium and its compounds, especially oxide. Recently, monocrystalline Germanium is widely used for reception of coatings with a high refractive index (~4.0 [5, 6] in an interference optics of an IR range of a spectrum up to 20 microns. However, wider application of Germanium in multilayered coatings is something prevented by not rather kind compatibility of layers of Germanium and any another substances with the lower refractive index. It should seem that an ideal variant could be Germanium monooxide, which refractive index (~2.1-2.2) not rather differs from an optimum parity, namely $n_l = \sqrt{n_h}$, where n_l, n_h – refractive index of materials with low and high values, accordingly. In view of potentially high mutual adhesion of layers through affinity of the chemical nature of substances, for such multilayered coatings it should be expected high mechanical durability. However, application attempts of either GeO or composites GeO-GeO_2, Ge-GeO_2, Ge-SnO_2 for reception of coatings from Germanium oxide have appeared not rather successful [4]. In first two cases coatings of low durability and in the last - rather thin coatings through necessity for current application of the considerably higher power and consequent birth-out of the evaporator were formed. The similar picture took place at application of system GeO_2-SiO which besides has appeared not technological through sprinkling of a material (mainly parts on the basis of SiO) in process of evaporation and, accordingly, their sticking to a substrate [7]. Obviously, the way out would have to consist in formation of ternary system on acid-basic principles. Really, for stabilisation of valency state of Ge(II) in oxide, which owns amphotermic properties (with prevalence of the basic ones) it is necessary to pick up as the partner oxide with expressive, but not rather strong acid properties. Thus it should have low enough melting temperature and at the same time - high (much more the higher for such for GeO) temperature of boiling (sublimation), average value of viscosity - only not to allow for melt to be splashed out of the evaporator or a target and at the same time to promote interaction with GeO or components of more complicated systems. Such ideal "partner" for GeO had appeared Boron oxide with temperatures of melting (460°C) and boiling (2100°C) which differ more than by 1600°C. By the acidity factor (χ) B_2O_3 concedes only P_2O_5, SO_3 and some other oxides which besides are volatile and instable [8]. Character of interaction in system GeO-B_2O_3 till now is not investigated. Recognizing that GeO reveals the mainly basic properties, and B_2O_3 is acid anhydride, that is owns considerably expressed acid properties, it is possible to expect appreciable chemical interaction between components system of via the acidic-basic mechanism. As an initial Boron-containing component acts H_3BO_3, one of interaction products should be water (through high temperature of heat treatment (above 700°C) - in a vaporous state). Thus, schemes of reactions can be written down in a kind:

$$mGeO + nH_3BO_3 \xrightarrow{t} mGeO\,nB_2O_3 + 3n/2H_2O\uparrow, \quad (1)$$

Proceeding from possible anionic forms, it is possible to provide formation of compounds of type $Ge_3(BO_3)_2$, GeB_2O_4, GeB_4O, etc. The experimental method picked up as an optimum parity of components GeO: B_2O_3 = 3:1 which corresponds to first of compounds which it is possible to name due hypothetical composition as Germaniun (II) orthoborate. As stability of compounds of Boron, as well as acidic properties of corresponding hydroxides, increase from orthoborates to methaborates and, further, to tetraborates, it should be expected that in system of the offered composition, equilibrium between GeO and GeB_4O_7, most likely, will take place. In last from compounds should occur (due to the expressed acid-basic interaction) stabilisation of valency state Ge(II), from which at enough high temperature will take place volatization GeO in the molecular form (omitting interaction of Ge with GeO_2, characteristic for solid "GeO") under the scheme:

$$GeB_4O_7 \xrightarrow{t} GeO(г)\uparrow + 2B_2O_3(p), \quad (2)$$

It should provide high stoichiometry of compounds in vapor, and, consequently, its preservation at condensation on a substrate in a metastable (however, strong enough) state:

$$GeO(g)\cdot \underset{\textbf{substrate}}{\overset{t}{\rightarrow}} GeO\ (s) \quad (3)$$

without disproportionation or with its minimum effect and formation of a nano-structured coating.

Its kind solubility in water, and also hygroscopy is certain lack of B_2O_3, but it is worth to hope for decrease in this factor due to its interaction with GeO with formation more or less stable compounds.

I. Synthesis and experimental research techniques

As the base material – Germanium (II) oxide is used GeO of a qualification preparation "chemically pure" (manufactures of IN "Khimreaktiv" (Donetsk)) and as the initial material for reception B_2O_3 - boric acid H_3BO_3 which is more suitable in handling (a soft peeks, instead of that melted B_2O_3 is rather firm and hygroscopic), of mark 14-3 (content of the basic substance not less than 99.5 % (a preparate is available in wide sale).

Samples of system GeO-B_2O_3 (3: 1) are received by mixing of initial components (GeO and H_3BO_3) in the necessary parity and the following heat treatment in high-temperature tubular (horizontal) furnace RHTC 804-450 (firm Nabertherm, Germany) in the medium of the cleared inert gas (Argon). Heat treatment was carried out in two stages. At the first stage heat treatment is carried out in vacuum at pressure 10^{-2} bar at 250°C – for 10 min, at 300°C – for 10 min, at 350°C – for 10 min, at 400°C–10 min. The heat treatment termination in vacuum occurs after a total disappearance of water vapour. Visually revealed it is shown as absence of a condensate on the cold ends of the quartz - glass reactor. At the second stage of heat treatment which is carried out in the inert gas medium of Argon (at superfluous pressure of 1.05-1.1 bar), annealing is carried out at slow rise in temperature of the furnace. Heating stages were 500, 600, 700°C – each for 10 min, 750°C – 30 min till appearance of a dark touch on cold parts of the reactor. Then a slow cooling of the furnace to room temperature is carried out. A film-forming material GeO-B_2O_3 (3: 1) represents itself a stiffened melt of black colour with glass shine. Initial reagents, a batch and both received melts and the residue after thermal evaporation in vacuum are investigated, in view of vitreous or X-ray amorphous character of products of interaction, by spectroscopic methods. As research methods IR transmission spectroscopy and electronic spectroscopy of diffuse reflectance are used.

IR transmission spectra are recorded for samples, pressed in a matrix of CsI preliminary dried by heating at 180°C of qualification of special purity (manufacture of Institute of single crystals of NAS of Ukraine, Kharkiv)

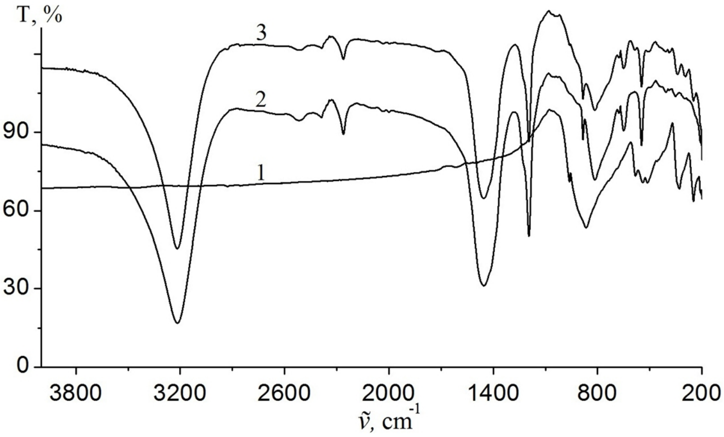

Fig. 1. IR spectra of the transmission of GeO-H_3BO_3 system: 1 - GeO; 2 - H_3BO_3; 3 - GeO-H_3BO_3 (batch).

in a mass parity the sample: a matrix 1:20. Record of spectra are carried out on the spectrophotometer with Fourier transformation Frontier (firm Perkin-Elmer, the USA) in a range of wave numbers ($\tilde{\nu}$) 4000-200 cm^{-1}.

Record of spectra of diffuse reflectance (DR) in co-ordinates F(R) = f(λ), where F(R) – is Kubelka–Munk function that is described by the equation:

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{k}{s}, \tag{4}$$

where R – is relative reflexion of the sample, k – absorption factor, s – dispersion factor, was carried out on spectrophotometer Lambda 9 (firm Perkin Elmer, the USA) with a special attachment in ditches with thickness of a layer of an investigated powdery material of 3 mm relatively to the sample of comparison (MgO) in the range of wave lengths of 200-2200 nanometres. All materials were pounded in an agate mortar directly ahead of record of DR – spectra. Reproducibility of measurements of values of wave lengths were ±0.05 nanometres for UV and visible ranges, ±0.2 nanometres for a near IR range.

Thin-film coatings are received by thermal evaporation (a resistive variant) in vacuum on installation VU-1A. The material was crushed on fragments and put in the molybdenum evaporator. A mode of evaporation and coating drawing: a current power through the molybdenum evaporator was 100A; duration of evaporation and coating drawing – near 5 min; substrate temperature – 200°C. Coatings were obtained on the substrates from following materials: germanium (a planar parallel plate); quartz glass (a planar parallel plate); glass K-8 (a wedge-shaped plate, a wedge corner – 12°).

Definition of refractive index (n) of a coating was carried out on a wedge-shaped plate made from glass K-8. Definition of n of coating was carried out by definition of factor of reflexion (R) from a wedge-shaped plate by measuring extreme values of R on an interference picture. Optical (d_{opt}) and physical (d) thicknesses are connected one with another via n, i.e., $d_{opt} = nd$.

II. Results and their discussion

On fig.1 are presented IR transmission spectra of initial reagents, GeO and H_3BO_3, and also their mechanical mixture (batch) in the ratio 3:1 at recalculation on B_2O_3. IR spectra of components essentially differ among them: so, bands of absorption of H_2O in GeO – both of valency, and deformation oscillations are essentially (~ by 250 and 150 cm^{-1}, accordingly) shifted sideways the higher frequencies rather from such to bands O–H in H_3BO_3. It is connected, obviously, with more acidic character of the specified groups in a case of boric acid. Other bands in GeO, on the contrary, are shifted bathocromically compared to bands of valency and deformation oscillations of B–O bands. Thus intensity of all bands in H_3BO_3 is considerably – on an order – the higher. Therefore in batch which consists of initial components, basically, bands of absorption of H_3BO_3 are exhibited; on their background the bands of absorption of GeO bonds seem to be a little appreciable.

However, as it follows from fig.2, after heat treatment of the batch intensity of peaks of components are substantially equalised: bands of absorption of B_2O_3 that is formed from H_3BO_3 after annealing, become much weaker compared to such for H_3BO_3, and also less expressive. Obviously, it is connected with vitrification of both most B_2O_3, and, partially, all system GeO-B_2O_3. Due to it, on IR spectra of absorption the bonds, inherent in both components, are revealed if not to the same extent, but almost commensurately (tab.1).

The additional information about on character of interaction in investigated system can be got, comparing DR spectra of initial GeO and its alloy with B_2O_3 (fig.3). Spectral dependences of GeO (a curve 1) and its alloy with B_2O_3 (a curve 2) in a near IR range of a spectrum have similar, the S–shape form and by their occurrence stipulated by electronic transitions through the forbidden zone in fine-crystalline elemental Germanium; in both cases in the range of 1400-1900 nanometres the flexure is observed, and the point of the flexure which lies in case of GeO at 1570 nanometres, shifts more close to 1550 nanometres at transition to allay GeO-B_2O_3. Absorption bands of the allay GeO-B_2O_3 and initial GeO are close

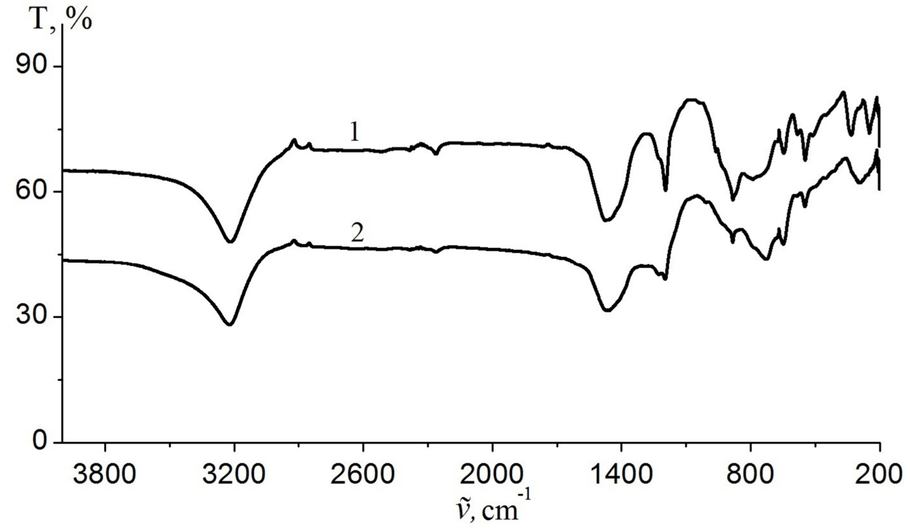

Fig. 2. IR spectra of the transmission of GeO-B_2O_3 system: 1 – after heat treatment; 2 – the residue after thermal evaporation in vacuum.

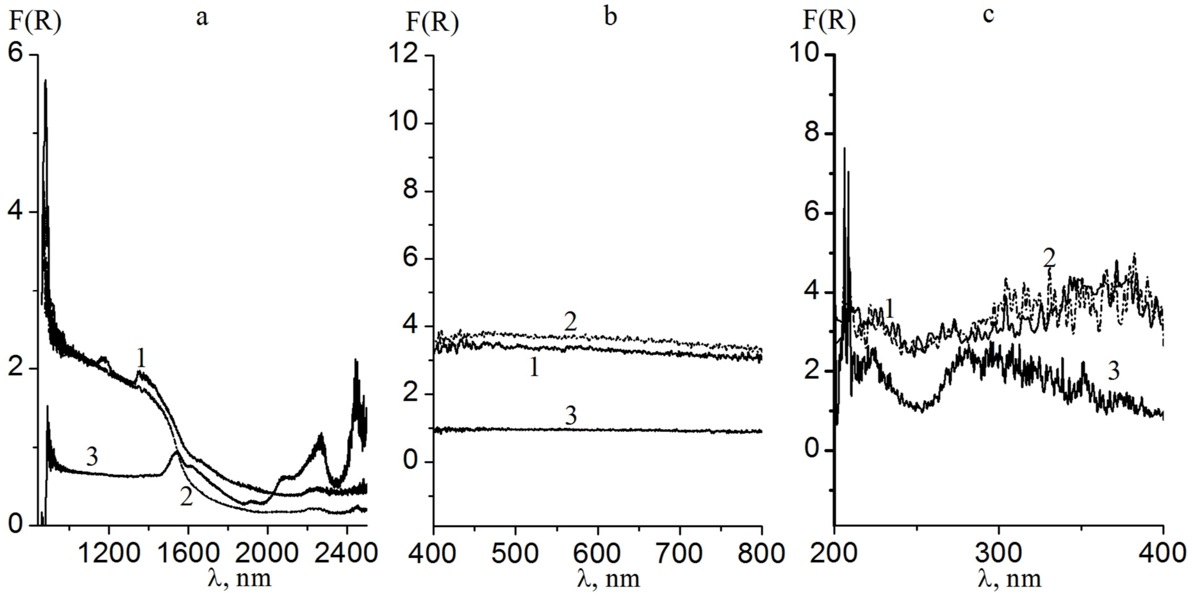

Fig. 3. Spectra of diffuse reflectance of GeO-B_2O_3 system in a near IR range (a), visible (b) and UV (c) ranges of a spectrum: 1 – initial GeO; 2 – after heat treatment; 3 – the residue after thermal evaporation in vacuum.

Table 1

Position and intensity of characteristic bands of absorption in an IR range of spectrum of GeO-B_2O_3 system

Specimen	Peaks position (wave numbers, cm^{-1})									
GeO	*3480.4*	*1617.7*	***961.9***	***866.8***	***582.4***	***540.1***	***513.0***	*458.9*	*329.5*	***248.1***
H_3BO_3	**3216.4**	**1455.5**	**1195.3**	**884.2**	**816.4**	678.6	**651.2**	**548.0**	495.0	410.7 **350.5**
GeO-H_3BO_3 batch	**3216.7**	**1455.0**	**1195.6**	958.5	**884.1**	**817.5**	678.6	**651.2** *567.0*	*585.3* 410.7	**547.9** 386.6
GeO–B_2O_3*	**3224.8**	**1425.9**	**1197.8**	***961.8***	883.3 ***579.3***	***866.0*** ***545.1***	814.0 *516.1*	777.9 *449.8*	735.8 *328.7*	651.5 *247.5*
GeO-B_2O_3**	**3222.5**	**1470.9**	**1197.6**	1006.7	**884.4**	790.0	**727.3**	**649.2**	*585.3*	**548.2** **296.7**

The note: *after heat treatment; **the residue after thermal evaporation in vacuum; by a direct font it is designated

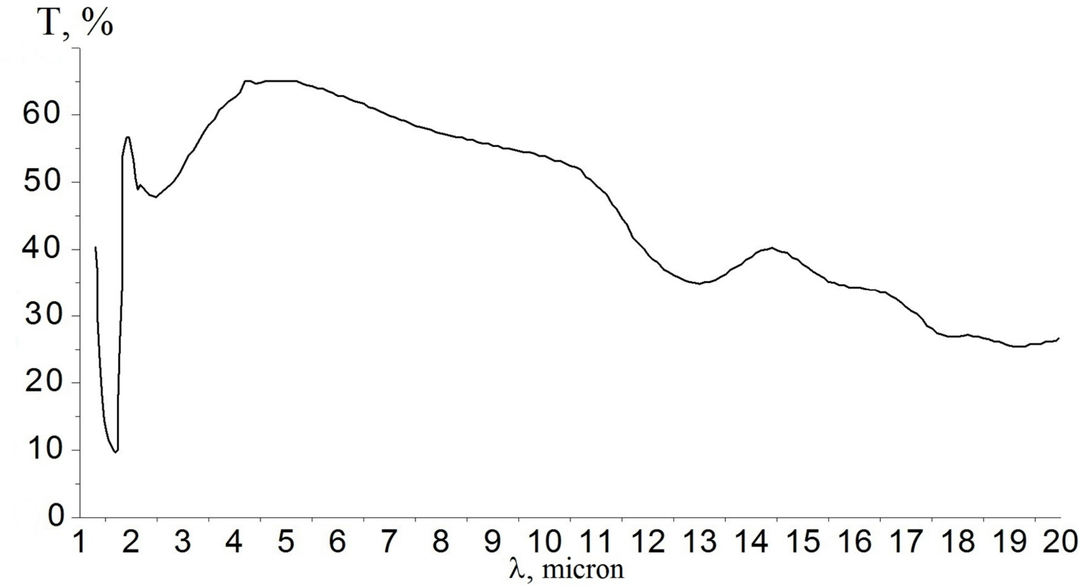

Fig. 4. The spectrum of the transmission of a planar parallel plate from Germanium with the coating from GeO.

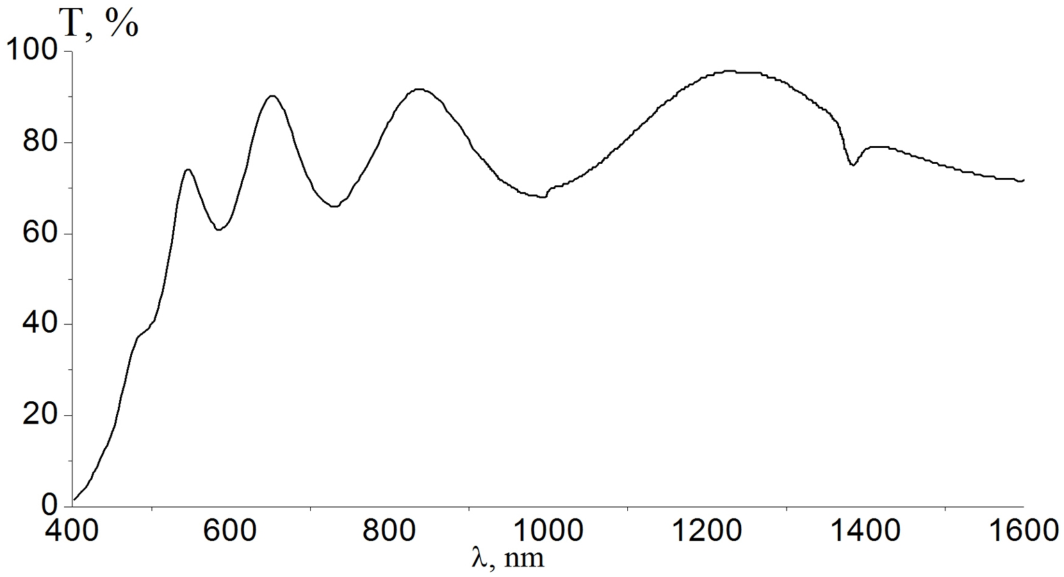

Fig. 5. A transmission spectrum of a planar parallel plate from quartz glass with a coating from GeO.

enough on intensity though in a point of an excess they differ - F(R) is bigger for GeO in ~1.5 times. Obviously, the last is connected with effect of dilution of absorbing substance (GeO) at melting with B_2O_3 not absorbing in this range. However, at transition in a short-wave (visible and, further, UV) range the picture changes: intensity of a band of absorption of pure GeO becomes the lower for such for alloy GeO-B_2O_3, probably, through partial replacement of GeO_2 in the nano-composite Ge-GeO_2 which is as a matter of fact GeO, for B_2O_3 with the lower refractive index.

As in the course of thermal evaporation the main (almost uniform) component which takes off, is GeO due much lower volatility of B_2O_3, it is worth to expect that in the residue after thermal evaporation a content of GeO would have to be considerably the lower compared with the initial sample of system GeO-B_2O_3. Really, on IR spectra of the transmission of the sample after evaporation bands of absorption, characteristic for GeO, almost do not remain (tab.1, fig.2). The same concerns DR a spectrum (fig.3) from which considerable decrease in intensity of a band of absorption of GeO with a characteristic flexure follows. Instead of that the bands of absorption in the domain of 1500-2500 nanometres, inherent to absorbed water, because of growth of content of B_2O_3 in melt (B_2O_3,as already was marked, is rather hygroscopic substance) become more expressive. Essential decrease in level of absorption of GeO (F(R) falls from 3.5-4.0 and above to 0.9÷1.0 in a visible range and from 2.5-5.0 to 1.0÷2.5 in an UV range) is observed and in other domains of a spectrum too.

A spectrum of the transmission of the coating put on a plate from Ge is presented on fig.4. The experimental curve of the transmission of a coating on a substrate lies above a curve for a substrate (the transmission almost 0.65 while the substrate has the transmission near 0.47)

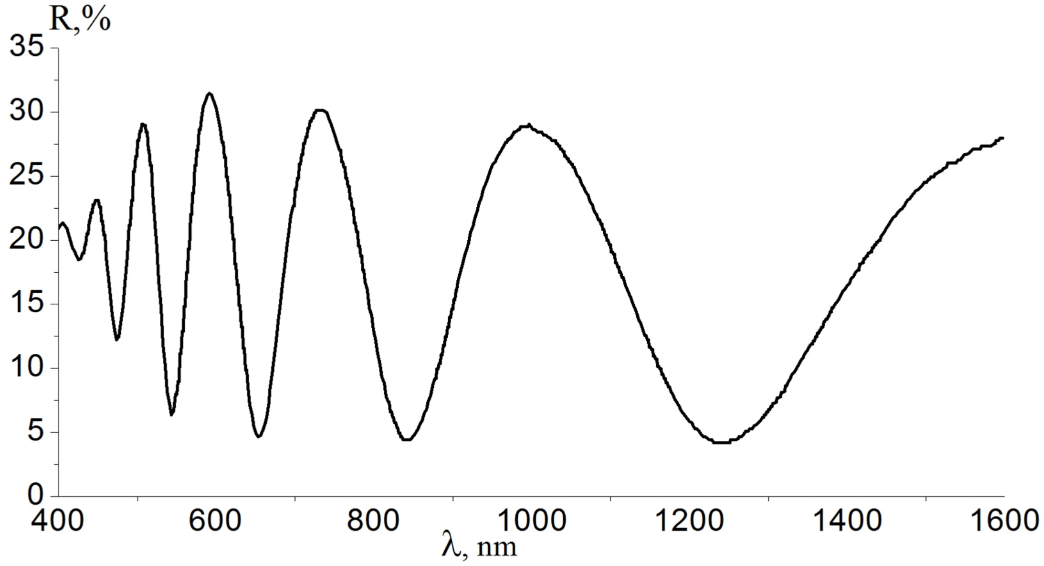

Fig. 6. The reflectance spectrum from of a wedge-shaped plate from glass К-8 with a coating from GeO.

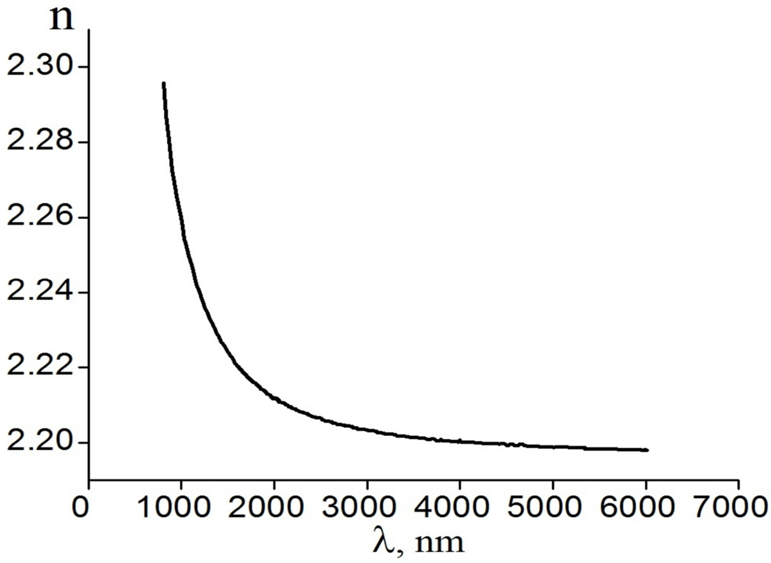

Fig. 7. The dispersion of refractive index of coating GeO calculated from reflexion of a wedge-shaped plate from glass К-8.

with a maximum at 4.5-5.0 microns. In the middle IR range (~11.1-11.3 microns) experimental values of the transmission of a coating become the lower than the transmission of a substrate which testifies to achievement of a long-wave border of domain of its transparency. The border of domain of the transmission of a coating specified above correlates with position of the basic peak of absorption in GeO (13.0 microns) that is due to the occurrence of valency oscillation of bonds Ge–O. Some bathocromic shift of minimum, obviously, testifies to formation on a surface of a substrate of "genuine" compounds of Ge(II) or nano-composite with its participation.

In a spectrum of the transmission of a coating on a substrate made of quartz glass (fig.5) is revealed a characteristic interference picture located more low for the transmission of the substrate. Thus, in this case takes place formation of the reflectance system. The beginning of appreciable absorption of a coating lies near 550 nanometres that proves to be true due to its yellow colour.

From a curve of reflexion from wedge shaped plates with a coating (fig.6) that also has a characteristic periodic appearance, the dispersion of a refractive index of the coating (fig.7) is calculated. In the domain of a spectrum close to short-wave border, value of refractive index is 2.3 and above, essentially decreasing at transition into an IR range till 2.15-2.20.

All coatings have kind adhesion to a substrate from any material both satisfactory thermal and climatic firmness. The mechanical durability estimated according to OST3-1901-85 on device SM-55, represents near 20000 turns to occurrence of a scratch which corresponds to group of durability 0.

Essential shift of a band of absorption at 13.0 microns compared to such for initial is the certificate in favour of preservation in a coating of compound GeO, instead of nano-composite Ge_{nano}-$GeO_{2\ vitr.}$, the initial material is which as a matter of fact. Really, as the size of Ge^{2+} ion (0.087 nanometres) is essentially bigger compared to those for Ge^{4+} ion (0.067 nanometres) also lengths of corresponding bonds Ge(II)-O should be bigger, than such for bonds Ge(IV)–O. So, the parity of the specified lengths of bonds is 1.11 that is close to a parity of positions of maxima of bands of absorption (1.12). In favour of presence of "true" compound GeO in a coating considerable distinction in positions of short-wave borders of absorption of an initial material (1550 nanometres) and a coating from it (550 nanometres), and also unusually low values of an refractive index of the last testifies also.

Conclusions

1. Essential change of IR transmission spectra of the annealed sample of system GeO-B_2O_3 compared to a batch which testifies to a course of reaction with possible formation of Ge(II) compounds is observed. Instead of that spectra of diffuse reflectance of system are similar to such for GeO.
2. Thermal evaporation in vacuum of the sample of system GeO-B_2O_3 causes cardinal change of spectral curves which testify to decrease of content of GeO because its departure.
3. The thin-film coating received from system GeO-B_2O_3, obviously, contains Ge(II) compounds, instead of a composite which proves to be true sharp change of borders of domain of a transparency (0.55÷11 microns) compared to an initial material (1.55÷9 microns), and also values of refractive index (2.15÷2.25).
4. The material on the basis of GeO-B_2O_3 is necessary to be considered as perspective for interference optics of an IR range of a spectrum.

Work is executed within the framework of the scientific and technical project "Working out a material on the basis of Germanium compounds for interference coatings with the improved characteristics, transparent in a range 3-5 microns" with SE of Special instrument making "Arsenal" (Kiev).

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Вивчення взаємодії у системі GeO – B_2O_3 спектроскопічними методами

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Через рентгеноаморфний характер GeO та B_2O_3 для вивчення взаємодії між ними застосовані методи ІЧ спектроскопії пропускання та спектроскопії дифузного відбиття. Встановлено суттєву зміну положення й інтенсивності смуг поглинання у системі GeO–B_2O_3 (H_3BO_3) при нагріванні та термічному випаровуванні у вакуумі. Спостерігається суттєвий гіпсохромний зсув короткохвильової межі і батохромний зсув довгохвильової межі області оптичної прозорості покриття порівняно з вихідним GeO, що свідчить на користь зміни природи матеріалу. Покриття з оксиду Германію(ІІ) володіють високими оптичними й експлуатаційними параметрами та є перспективними для інтерференційної оптики ІЧ діапазону спектру.

Ключові слова: оксид Германію(ІІ), оксид Бору, спектроскопічні методи, тонкоплівкові покриття