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Spectroscopic Research of Interaction in the Systems Ge-In_2O_3-M_xO_y (M-Sn(IV), La, Sm, Eu)

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Using methods of IR transparency spectroscopy in a range of 1200 – 200 cm^{-1} and diffuse reflectance spectroscopy in a range of 200 – 2500 nm the character of interaction in the systems Ge-In_2O_3, Ge-In_2SnO_5, Ge-$LnInO_3$ (Ln - La, Sm, Eu) is investigated. Essential change in spectral characteristics of systems with the appearance of new bands and disappearance of previous ones is established at annealing of composites of Germanium - metal oxide composition which confirms the fact of oxidation-reduction interaction between components with formation of volatile products, mainly In_2O and GeO. Thermodynamic calculations well coincide with experimentally established values of conditional temperatures of evaporation. Systems are perspective for obtaining thin-film coatings interference optics of a IR range of a spectrum.

Keywords: the systems Germanium - metal oxide, spectral characteristics, interaction, thermal evaporation.

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Introduction

Systems of composition Germany - metal chalcogenide (oxide) are investigated recently as perspective materials for interference optics of an IR range of a spectrum [1-3]. The matter is that many of them reveal properties of so-called CVD ("Chemical Vapor Deposition") - composites, which are predisposed to interaction in a solid state with formation of volatile products in vacuum with the following condensation on a substrate and formation of a nano-structured coating. In details the CVD - mechanism of evaporation and condensation of such systems is considered earlier [4]. Among components of CVD - composites, in particular, metals oxides it was offered GeO_2, SnO_2, ZnO [3,5]. One of the most perspective also stand out Indium oxide and compounds on its basis due to ability to reduction with formation of volatile oxides such as In_2O and, possibly, InO [6].

It is necessary to notice that in many cases at interaction in CVD - composites X-ray amorphous products are formed which are hardly to identify by standard methods, for example, the X-ray diffraction analysis (XRDA). To such, in particular, belongs Germanium oxide of composition GeO in which Germany is in formal degree of oxidation +2. However, actually, it in a solid state is methastable and, as a rule, disproportioned on X-ray amorphous Germanium and vitreous matrix GeO_2. Therefore expediently such objects to investigate by spectroscopic methods, in particular, by methods of IR transparency spectroscopy and (or) spectroscopy of diffuse reflectance. It is necessary to notice that initial compounds, namely, Indium lanthanides earlier [7] are investigated by spectroscopic methods. In X-ray amorphous systems as usual broadening and certain shift (as a rule, bathochromic) of absorption bands in an IR range is observed. Besides, on occasion for favorable coincidence of the sizes of particles and optical parameters of substances of a composite and a matrix (KBr and CsI) oscillations on spectral curves appear meanwhile of not clear nature.

I. Synthesis and experimental research techniques

Indium (III) oxide, In_2O_3 is a compound of light yellow color, which crystallizes in cubic structure. Compound In_2SnO_5 is received by co-precipitation with ammonia from a solution of nitrates $In(NO_3)_3$ and $Sn(NO_3)_4$ with the following annealing at 600-700°C [8]; structure of compound is not yet studied. Lanthanide indates of composition $LnInO_3$ (Ln - La, Sm, Eu) are received by the co-precipitation with ammonia from a solution of nitrates, $In(NO_3)_3$ and $Ln(NO_3)_3$ with the following annealing of received hydroxides at 1200°C.

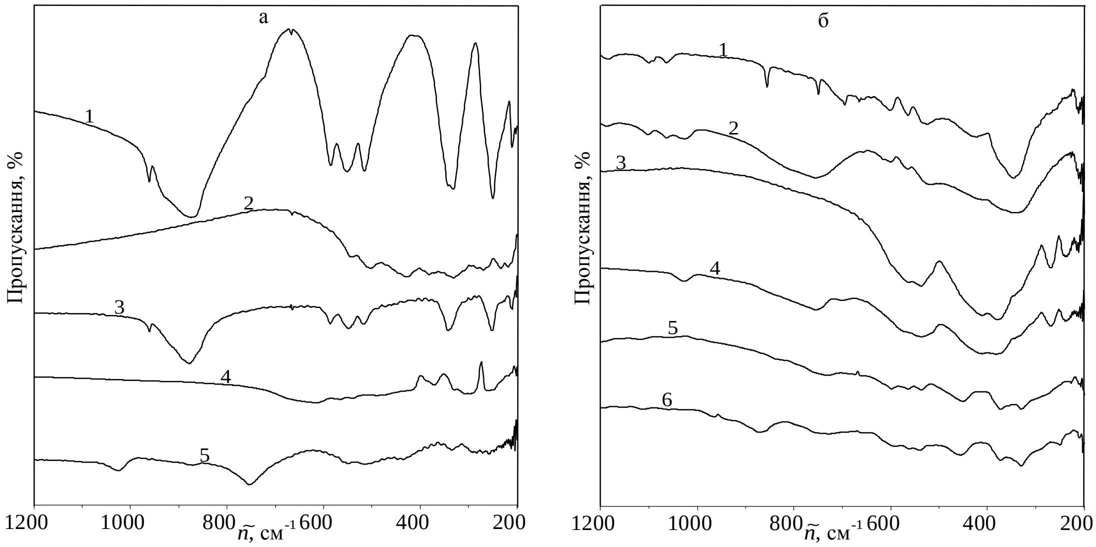

Fig. 1. IR spectra of transparency of the systems Germanium - metal oxide in a middle and far IR ranges of a spectrum: a: 1 – GeO_2, 2 – In_2O_3, 3 – Ge-In_2O_3, 4 – In_2SnO_5, 5 – Ge-In_2SnO_5; b: 1 – $LaInO_3$, 2 – Ge-$LaInO_3$, 3 –$SmInO_3$, 4 – Ge-$SmInO_3$, 5 –$EuInO_3$, 6 – Ge-$EuInO_3$.

All compounds crystallize in structure of rhombic perovskite (D_{2h}^{16}–*Pbnm*). Parameters of lattices naturally decrease from $LaInO_3$ (a = 0.5772 nm) to $EuInO_3$ (a = 0.5567 nm) [9] due to reduction of ionic radii of Ln^{3+} (so-called lanthanide compression).

CVD - composites on the basis of systems of specified oxides are prepared by sintering of the thin ground powders of Germanium and corresponding oxides in following parities: Ge : In_2O_3 =2 : 1; Ge : In_2SnO_5=3 : 1; Ge-$LnInO_3$ (Ln - La, Sm, Eu) =1 : 1 at temperature at which departure process of volatile components has just begun; endurance term represented ~ 1 hour. Annealing is carried out in the medium of in additionally cleared Argon, and the sample held in a pipe from quartz glass in the same place, which, in turn, was placed in the horizontal furnace RHTC80-450 (Nabertherm) with the regulated heating.

IR spectra of transparency of samples, pressed in a matrix of preliminary dehydrated by heating at 180°C CsI of os.ch. qualification (Institute of Single Crystals of NAS of Ukraine, Kharkiv) in a mass parity of the sample: a matrix, equal to 1 : 20, recorded in a range of wave numbers ($\tilde{\mathrm{V}}$) 1200-200 cm^{-1}. Records of spectra are carried out on spectrophotometer Frontier (Perkin-Elmer) with Fourier - transformation).

Diffuse reflectance spectra in a range of wavelengths of 200-2500 nm were recorded down in coordinates F(R) =f(λ), where F(R) - Kubelka-Munk function that is described by the equation:

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

where R - relative reflectance of the sample, k - absorption factor, s - dispersion factor,

on spectrophotometer Lambda 9 (Perkin Elmer) in ditches with thickness of a layer of an investigated powdery material of 3 mm concerning the sample of comparison (MgO). All materials were pounded in an agate mortar directly ahead of record of diffuse reflectance spectra.

Thermodynamic estimation of processes of evaporation of volatile components which are formed at annealing, were carried out by means of the equation:

$$G^o_T = \Delta H^o_T - T_{ум.}\, \Delta S_T = 0, \qquad (2)$$

where T_c - conditional temperature.

Value of ΔH^o_T and ΔS_T, in turn, are calculated by means of the equations:

$$\Delta H^{o}_{T} = \Delta H^{o}_{298} + \int_{o}^{T} \Delta C^{o}_{p} dT, \qquad (3)$$

$$\Delta S_{T} = \Delta S^{o}_{298} + \int_{o}^{T} \frac{\Delta C^{o}_{p}(T)}{T} dT - R \ln \prod_{i=1}^{n} P_i^{\gamma}, \qquad (4)$$

where ΔH^o_T, ΔS_T, ΔG_T – accordingly, enthalpy, entropy and free Gibbs energy of process of evaporation, ΔC^o_p – the algebraic sum of heat capacities of products and initial components (of a CVD - composite), P_i - partial pressure of gaseous products of evaporation provided that $\sum_{i=1}^{n} P_i \approx 10^{-5}$ bar.

Experimental values of T_c were defined as average arithmetic value between temperature of which obvious condensation of a touch on cold walls of the reactor, and the lower by 10°C temperature behind which sintering was carried out.

II. Results and their discussion

System Ge-In_2O_3

The absorption band in an IR range of a spectrum of In_2O_3 occupies an interval of wave numbers of 200-550 cm^{-1} (fig.1, and tab.1). After interaction between Germanium and In_2O_3 at temperature 740-750°C the specified band almost fully disappears and is replaced with a spectrum very similar to those for GeO_2 of hexagonal modification (fig.1, curves 1,3) with characteristic bands at ~ 880 cm^{-1} (valence oscillations of Ge–O bonds), and also at 450-550 cm^{-1} (deformation oscillations of Ge–O bonds). Obviously, it grows out of

Table 1

Position of the absorbance bands in an IR spectra of the systems Germanium – oxide

Oxide, system	$\tilde{\nu}$, cm^{-1}															
In_2O_3							666.6		540.1	502.9	427.3	383.0	332.7	270.3	234.5	219.3
Ge–In_2O_3		960.3	878.1				664.9	586.9	548.7	518.2	512.4		343.5		251.6	210.2
GeO_2		961.3	875.1				668.0	586.2	552.1	516.8			333.5		251.1	210.8
In_2SnO_5							614.5	566.0	539.1		485.9	371.4	329.8	307.0	261.7	
Ge–In_2SnO_5	1025.1	961.5	873.8	754.4					549.2	512.4	440.8	434.8	334.9			214.9
$LaInO_3$	1063.3		855.0	749.5	694.8	655.1	601.6	564.1	524.1			422.7	346.8			
Ge–$LaInO_3$	1026.5		859.2	755.3			600.9	564.2		518.9	413.7	343.1	335.1			207.1
$SmInO_3$							573.8	564.2	537.8		410.0	378.9	335.5	267.5	238.9	207.1
Ge–$SmInO_3$	1026.3			755.5	699.7		573.2		536.0		410.9	383.0	341.5	267.3	238.9	227.1
$EuInO_3$				730.8	675.6		597.3	536.4	539.6		450.9	368.6			230.1	207.2
Ge–$EuInO_3$		961.5	871.9	726.8		657.5	597.3	564.2	539.6		455.5	368.6			227.1	210.2

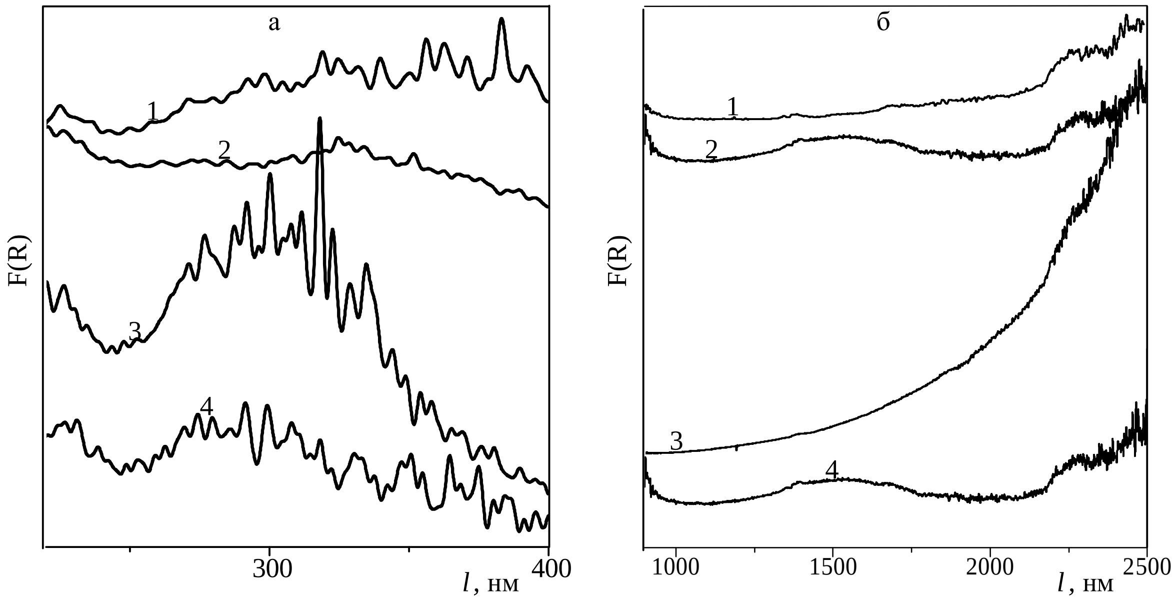

Fig. 2. Spectra of diffuse reflectance of the systems Germanium - metal oxide in an UV (a) and near IR (b) ranges of a spectrum: 1 – In_2O_3, 2 – Ge-In_2O_3, 3 – In_2SnO_5, 4 – Ge-In_2SnO_5.

interaction under the scheme:

$$Ge(s) + In_2O_3(s) \xrightarrow{t} GeO_2(s) + In_2O(g). \qquad (5)$$

Also there can be an additional process with another equation:

$$2Ge(s) + In_2O_3(s) \xrightarrow{t} 2GeO(g) + In_2O(g). \qquad (6)$$

Occurrence in an IR spectrum of products of reaction characteristic for GeO oscillations in a range of 200-600 cm^{-1} is acknowledgement of possibility of last scheme. By the way, the scheme (5) is closer to typical CVD - process. In favor of a course of reactions diffuse reflectance spectra (fig.2, a) testify. Really, instead of spectrum In_2O_3 with "tail" in dark-blue domain (450-500 nm), in visible and near IR ranges of F(R) for products there is poorly structured band of permanent absorption.

System Ge-In_2SnO_5

The IR spectrum of transparency of In_2SnO_5 represents wide, continuous domain with bands of absorption which combine in them spectral characteristics of In_2O_3 and SnO_2 (fig.1, a). However, after annealing of mixes of components (the temperature is something lower, than in the previous system, namely, 720-730°C) the spectrum essentially changes: there are new bands, in particular, with maxima at 1025 and 754 cm^{-1} which do not belong to any modification of GeO_2. Their arrangement is more inherent for germanates (most likely, metha-germanates). Therefore it is possible to write down the process scheme in a following kind:

$$2Ge(т) + In_2SnO_5(т) \xrightarrow{t}$$
$$\xrightarrow{t} SnGeO_3(т) + GeO(г) + In_2O(г) \qquad (7)$$

To presence of GeO in reaction products testify characteristic oscillations in an IR spectrum in a range of 200-600 cm^{-1}. Thus, in the given reaction, possibly takes place oxidation of Ge to Ge(IV) and Ge(II) and reduction of In(III) to In(I) and Sn(IV) to Sn(II). For stoichiometry and phase composition of products of interaction the specified system partially meets the requirements, which concern to CVD - composites.

The spectrum of diffuse reflectance of system displays multi-component structure and a variety of valence states of products of interaction and is poor informative (fig.2, a).

Systems Ge-$LnInO_3$ (Ln - La, Sm, Eu)

System Ge-$LaInO_3$

In an IR spectra of the transparency of initial compounds, $LaInO_3$ absorption bands in domain of 750-1060 cm^{-1} obliged of their occurrence by valence oscillations of bonds Si-O and deformation oscillations of bonds C-O in CO_3^{2-} - groups which are admixtures to the basic phase are shown. Bands in a range of 520-695 cm^{-1}, most likely, display valence oscillations of bonds In-O, while bands at 347 and 423 cm^{-1} - valence oscillations of bonds La-O. Interaction with Germanium does not bring essential changes in the general spectral picture, only characteristic bands at 755 and 1026 cm^{-1} appear that reveal also in system Ge-$SmInO_3$ (fig.1, tab.1). Spectrum diffuse reflectance of system is poor expressive in all range; the exception, as well as for other of systems, represents an UV range in which there are intensive bands of absorption thanks to electronic transitions $O^{2-} \rightarrow In^{3+}$ and $In^{+} \rightarrow In^{3+}$ (fig.3).

In the given system, obviously, there are partially oxidation-reduction processes under the scheme:

$$Ge(т) + 2LaInO_3(т) \xrightarrow{t} La_2GeO_5(т) + In_2O(г), \quad (8)$$

with preservation of a considerable part of initial components.

System Ge-$SmInO_3$

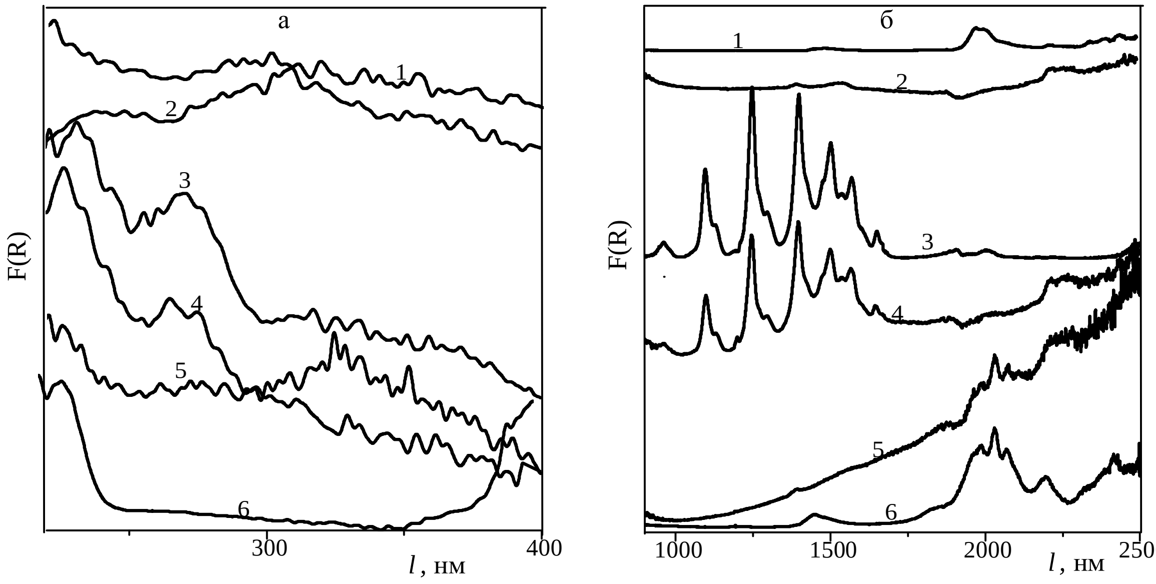

Fig. 3. Spectra of diffuse reflectance of the systems Germanium – lanthanide indates in an UV (a) and near IR (b) ranges of a spectrum: 1 – $LaInO_3$, 2 – Ge-$LaInO_3$, 3 –$SmInO_3$, 4 – Ge-$SmInO_3$, 5 –$EuInO_3$, 6 – Ge-$EuInO_3$.

The IR spectrum of initial compound, $SmInO_3$, unlike $LaInO_3$, does not revenge bands which correspond to admixture phases, in the domain of 600-1060 cm^{-1} (fig.1, b). Instead the bands caused by valence oscillations of bonds In-O (410-574 cm^{-1}) and Sm-O (239-379 cm^{-1}), are preserved also after interaction between Ge and $SmInO_3$. In the last takes place occurrence of new bands of absorption at 755 and 1026 cm^{-1}, obviously, due to formation of ortho-germanate of composition of structure Sm_2GeO_5 under the scheme similar to the previous one:

$$Ge(т) + 2SmInO_3(т) \xrightarrow{t} Sm_2GeO_3(т) + In_2O(г), \qquad (9)$$

Expressive enough there are spectra of diffuse reflectance (fig.3) of the given system in visible, and, especially in a near IR ranges of a spectrum. On them accurately reveal absorption bands at wavelengths of 450 nm and 900-1700 nm that of the occurrence are obliged to intra-center 4f-4f transitions in Sm^{3+}. It is observed essential (~ in 1.5 times) decrease in intensity of the specified bands, possibly, due to dilution of initial compound by Germanium at essential growth of background absorption. It is necessary to note the fact of occurrence of additional bands at 850 and 2200-2300 nm, probably, due to appearance of insignificant amount Sm^{2+} [10] (fig. 3, b).

System Ge-$EuInO_3$

Prominent feature of IR spectra of samples of the given system, except presence of bands of absorption due to valence oscillations of bonds In-O (450-675 cm^{-1}) and Eu-O (369 cm^{-1}), are absorption bands due to deformation oscillations of C-O (groups CO_3^{2-}) at 727-731 cm^{-1} which do not disappear after heat treatment (fig. 1, b). At the same time certain unexpectedness occurrence of two bands at 962 and 872 cm^{-1}, characteristic for GeO_2 (hexagonal) after interaction between Ge and $EuInO_3$. The additional information spectra of diffuse reflectance of samples of system give (fig.3). Changes which occur after interaction with Germanium, in an UV range of a spectrum look especially expressive: instead of characteristic for Lanthanide indate enough dim band there appear well divided bands of absorption at wave lengths of 210-250 nm and 350-450 nm (with a maximum near to 400 nm). Such picture is characteristic for oxide compounds of Eu(II), in particular, Eu_2SiO_4 [9]. It is caused by 4f-5d electronic transitions in Eu^{2+} ions an in oxide matrix. Essential changes are observed also in a near IR range of a spectrum. The general background of absorption essentially increases because of the presence of Germanium. At the same time considerable (~ in 2-2.5 times) decrease of intensity of a band is observed, which is caused by intra-center 4f-4f electronic transitions in Eu^{3+} ions in the domain of 2100-2400 nm. Besides of dilution caused by an additive of Germanium, the important role in this case, obviously, plays the reduction process of Eu^{3+} ions to Eu^{2+} ions under the possible scheme:

$$2Ge(т) + 2EuInO_3(т) \xrightarrow{t} Eu_2GeO_4(т) + \\ + GeO(г) + In_2O(г), \qquad (10)$$

By analogy to Eu_2SiO_4 that has hexagonal structure, it is possible to consider certain structural similarity of Eu_2GeO_4 to GeO_2 (hexagonal) and for their IR spectra. Thus, interaction in system Ge-$EuInO_3$ should differ essentially from such in similar systems with another Lanthanide indates.

Departure temperatures ($T_{c.}$), defined experimentally (after condensation of deposit of black-brown color on cool wall of the reactor), lay in limits of 700-770°C. Thu value of temperature in case of system Ge-$SmInO_3$ is highest, and the lowest - for system Ge-$EuInO_3$. This fact stands out strange enough as Sm and Eu are the neighbor

Table 2

Thermodynamics of the processes in systems Germanium – metal oxide

Systems	Equation of the reaction	$T_{c.}$ (appearance deposit), °C	ΔH^{o}_{298}, k/mole	ΔS_{298}, J/mole K	$T_{calc.}$, °C
Ge-In_2O_3 (2:1)	$Ge(s) + In_2O_3(s) \xrightarrow{t} In_2O(g) + GeO_2(s)$	745	316	308	753
Ge-In_2SnO_5 (3:1)	$2Ge(s) + In_2SnO_5(s) \xrightarrow{t}$ $In_2O(g) + GeO(g) + SnGeO_3(s)$	725	365	366	724
Ge-$LaInO_3$ (1:1)	$Ge(s) + 2LaInO_3(s) \xrightarrow{t}$ $In_2O(g) + La_2GeO_5(s)$	715	291	309	710
Ge-$SmInO_3$ (1:1)	$Ge(s) + 2SmInO_3(s) \xrightarrow{t}$ $In_2O(g) + Sm_2GeO_5(s)$	765	322	309	769
Ge-$EuInO_3$ (1:1)	$2Ge(s) + 2EuInO_3(s) \xrightarrow{t}$ $Eu_2GeO_4(s) + In_2O(g) + GeO(g)$	705	357	362	713

elements in a lanthanide series. The essence consists in different ability of compounds of lanthanides in degree of oxidation +3 to reduction. So, Eu(III) is capable easy enough to be reduced to Eu(II).

Instead of that for reduction of Sm(III) it is necessary powerful enough reducing agent. In turn, element of Germanium is oxidized, as a rule, under these conditions to Ge(IV), while In(III) always reduces to In(I).

On ability to formation complex oxide of metals and Ge(IV) it is possible to write down a series [11]: Eu(II) > La(III) > Sm(III) > Sn(II). As in case of system Ge-$EuInO_3$ (by the way, also for system Ge-In_2SnO_5) besides two volatile compounds (GeO and In_2O) should be formed in the given system, the last, obviously, have advantages concerned volatile components. Really, T_c.for it there is the lowest among all systems of the given type (tab.2). Something more low volatility and the higher for $T_{c.}$ step is occupied by system Ge-$LaInO_3$. Thermodynamic calculations give value of the temperatures, rather close to experimental values.

Conclusions

1. Research of systems Ge - metal oxide revealing perspective CVD - composites for drawing coatings for interference optics of an IR range of a spectrum are carried out.
2. Spectroscopic methods (IR spectroscopy of transparency and electronic spectroscopy of diffuse reflectance) establish character of interaction in systems Ge-(-In_2O_3, -In_2SnO_5, -$LnInO_3$ (Ln- La, Sm, Eu) that consists in oxidation-reduction reactions between components of systems and in following of interaction between products with formation of new complex and volatile compounds.
3. The estimation of volatility of formed compounds (In_2O and GeO) and balance shift in conditional temperature specifies in perspectives of system Ge - $EuInO_3$ for application as a material for IR optics.

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Спектроскопічне дослідження взаємодії у системах Ge-In_2O_3-M_xO_y (M-Sn(IV), La, Sm, Eu)

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Методами спектроскопії пропускання у діапазоні 1200 - 200 см$^{-1}$ та спектроскопії дифузного відбиття у діапазоні 200 - 2500 нм досліджено характер взаємодії у системах Ge-In_2O_3, Ge-In_2SnO_5, Ge-$LnInO_3$ (Ln – La, Sm, Eu). Встановлено суттєву зміну у спектральних характеристиках систем з появою нових смуг та зникненням попередніх при прожарюванні композитів складу германій – оксид металу, що підтверджує факт окисно-відновної взаємодії між компонентами з утворенням летких продуктів, переважно In_2O та GeO. Термодинамічні розрахунки задовільно збігаються з експериментально встановленими значеннями умовних температур випаровування. Системи є перспективними для одержання тонкоплівкових покриттів інтерференційної оптики ІЧ діапазону спектра.

Ключові слова: системи Германій – оксид металу, спектральні характеристики, взаємодія, термічне випаровування.