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МЁССБАУЭРОВСКОЕ ИССЛЕДОВАНИЕ РЕДКОЗЕМЕЛЬНЫХ МЕТАЛЛОВ ВО ФТОРИДНЫХ И СИЛИКАТНЫХ СТЕКЛАХ

Методом мёссбауэровской спектроскопии на изотопах ¹⁵¹Eu, ¹⁶¹Dy и ¹⁵⁵Gd определено валентное состояние атомов европия, диспрозия и гадолиния во фторидных и силикатных стеклах. Европий в структуре стекол стабилизируется как в двухвалентном, так и в трехвалентном состояниях. Валентное состояние европия зависит от температуры расплава и от присутствия в составе шихты восстановителей. Атомы диспрозия в стеклах стабилизируются преимущественно в трехвалентном состоянии, однако введение в состав шихты восстановителя позволяет стабилизировать часть атомов диспрозия в двухвалентном состоянии. В структуре стекол атомы трехвалентного га*долиния образуют структурные единицы, характерные для смешанных оксидов гадолиния и алюминия.*

Ключевые слова: примесные атомы, электронный обмен, эмиссионная мёссбауэровская спектроскопия.

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Mössbauer Study of Rare Earth Metals in Fluoride and Silicate Glasses

The valence states of atoms of europium, dysprosium and gadolinium are determined by Mössbauer spectroscopy on isotopes ¹⁵¹Eu, ¹⁶¹Dy and ¹⁵⁵Gd in fluoride, silicate, borate and phosphatic glasses. Europium is stabilized both in bivalent and in trivalent states in structure of glasses. The valent states of europium depends on temperature melt and on the presence in the contents of mix material reducers. Atoms of dysprosium in glasses are stabilized mainly in a trivalent state, however the introduction into charge composition of a reducer allows to stabilize a part of atoms of dysprosium in a bivalent state. In structure of glasses atoms trivalent gadolinium form structural units, characteristic for mixed oxides gadolinium and aluminium.

Keywords: impurity atoms, electron exchange, Mössbauer emission spectroscopy.

1. Introduction

The optical properties of glasses containing rare-earth metals depend on the oxidation state of the rare-earth metal [1]. Mössbauer spectroscopy is an effective method for determining the oxidation state of rare-earth metal atoms in vitreous materials [2]. In particular, Mössbauer investigations have identified the oxidation states of europium in aluminosilicate and fluoride glasses [1; 3–8]. By varying the composition of the batch and synthesis conditions, it is possible to change the concentration ratio of europium in the oxidation states +2 and +3 over a wide range. However, data on the oxidation states of other rare-earth metals in similar glasses are not available. In this study, the oxidation states of europium, dysprosium and gadolinium in aluminosilicate and fluoroaluminate glasses were determined using ¹⁵¹Eu, ¹⁶¹Dy, and ¹⁵⁵Gd Mössbauer spectroscopy.

2. The valence state of europium in glasses

2.1. The glasses Al_2O_3 -SiO₂-MnO-Eu₂O₃

In this study, it will be demonstrated that the Eu^{2+} ions can be stabilized in glasses of the Al_2O_3 -SiO₂-MnO-Eu₂O₃ system without recourse to a reducing agent.

The glasses was synthesized from a mixture of the composition (mol %) $19.5Al_2O_3$, $31.5SiO_2$, 26.5MnO, and $22.5Eu_2O_3$ in zirconium crucibles in a nitrogen atmosphere at a temperature of 1573 K. The choice of the composition of the glass was motivated by the necessity of attaining the highest solubility of Eu_2O_3 . All the samples had a characteristic conchoidal fracture and were X-ray amorphous. No microinclusions were revealed in the samples under examination with an infrared microscope.

The ¹⁵¹Eu Mössbauer spectra were recorded at room temperature with a ¹⁵¹Sm₂O₃ source. The surface density of the absorbers with respect to the ¹⁵¹Eu isotope was equal to 2.5 mg/cm². The linewidth of the EuF₃ absorber with the ¹⁵¹Sm₂O₃ source was taken as the instrument linewidth [(3.9 ± 0.2) mm/s]. The isomer shifts are given relative to the spectrum of the Eu₂O₃ absorber.

The Mössbauer spectra of the glasses under investigation represent a superposition of two lines, namely, the line with an isomer shift of $-(0.65 \pm 0.07)$ mm/s, which corresponds to the Eu³⁺

ions, and the line with an isomer shift of $-(13.10 \pm 0.07)$ mm/s, which corresponds to the Eu²⁺ ions (Fig. 1, curve *a*).



Fig. 1. ¹⁵¹Eu Mössbauer spectra at a temperature of 295 K: (a) the glass in the Al₂O₃–SiO₂–MnO–Eu₂O₃ system, (b) the polycrystal prepared from the AlN + SiO₂ + MnO + Eu₂O₃ mixture,
(c) the Eu₂O₃ polycrystal, and (d) the polycrystal prepared from the MnO + Eu₂O₃ mixture

When we replaced Al_2O_3 in the initial mixture by the corresponding amount of AlN, the material obtained after calcining of this mixture at a temperature of 1573 K turned out to be polycrystalline and the ¹⁵¹Eu Mössbauer spectrum in this case corresponded to the presence of Eu²⁺ ions alone (Fig. 1, curve *b*).

It is worth noting that the synthesis of glasses in the Al₂O₃-SiO₂-MnO-Eu₂O₃ system in a nitrogen atmosphere makes it possible to stabilize ~25% Eu in the reduced form in the structural network of the glass. The reduction of Eu³⁺ to Eu²⁺ can proceed either by the reaction Eu₂O₃ \rightarrow 2EuO + 1/2O₂ or by the reaction Eu₂O₃ + MnO \rightarrow 2EuO + Mn₂O₃. We carried out the annealing of the Eu₂O₃ compound and the Eu₂O₃ + MnO mixture at a temperature of 1573 K in a nitrogen atmosphere. However, the Mössbauer spectra of the materials thus prepared corresponded to the presence of Eu³⁺ ions alone (see Fig. 1, curves *c*, *d*). In other words, the reduction of Eu³⁺ to Eu²⁺ in the glass is favored by a combination of conditions, namely, the high temperature, the presence of a reducing agent, and the formation of a liquid phase during the synthesis of the glass.

It should be emphasized that the isomer shifts in the ¹⁵¹Eu Mössbauer spectra of the glasses differ from those of the Eu₂O₃ and EuO compounds (specifically, the spectra of the glasses are shifted toward negative velocities by ~0.6 mm/s), although it is evident that, in the structural network of the glass, as in the lattices of the Eu₂O₃ and EuO compounds, the local environment of the europium atoms involve only oxygen atoms. The difference in the isomer shifts of the ¹⁵¹Eu Mössbauer spectra of the glasses and europium oxides can be explained in terms of the induction effect, i. e., the effect exerted by the manganese and aluminum atoms (not bound directly to the europium atoms) on the electron density at the ¹⁵¹Eu nuclei.

The specific feature of the Mössbauer spectra of the Eu^{2+} ions in the glasses is their anomalously large broadening (~5 mm/s). This broadening is caused by the nonuniform isomer shift (because the structure of the glasses involves europium ions in oxidation states that are close to each other). Since the range of isomer shifts for the Eu^{2+} -containing compounds is considerably wider than that for the Eu^{3+} -containing compounds, the Mössbauer spectra of the Eu^{2+} ions are more broadened than the spectra of europium(III).

2.2. Fluoride glasses

The purpose of the present work was to attain the stabilization of europium atoms involved in fluoride glasses in an Eu^{2+} state.

The glasses were synthesized from fluorides of alkaline-earth metals (BeF₂, CaF₂, SrF₂, MgF₂), aluminum (AlF₃), and europium (EuF₃) in an electrical furnace under an argon atmosphere in SU-2000 glassy carbon crucibles. The composition of the fluoride glasses was varied over a wide range, and the content of the EuF₃ europium fluoride was in the range from 0.5 to 6.0 mol %. The ¹⁵¹Eu Mössbauer spectra were recorded at temperatures 295 and 80 K with a ¹⁵¹Sm₂O₃ source (which was kept at 295 K). The surface density of the absorbers with respect to the ¹⁵¹Eu isotope was equal to 2.5 mg/cm². The linewidth of the EuF₃ absorber with the ¹⁵¹Sm₂O₃ source was taken as the instrument linewidth [(3.9 ± 0.2) mm/s]. The isomer shifts are given relative to the spectrum of the EF₃ absorber.

The Mössbauer spectra of the fluoride glasses synthesized from the batch composed only of the metal fluorides have the form of single lines [the half-width at half-maximum is equal to (3.9 \pm 0.3) mm/s], irrespective of the glass composition, the europium content, or the measurement temperature. The isomer shift of these lines [0.55 \pm 0.07) mm/s] corresponds to Eu³⁺ ions (Fig. 2 a).



Fig. 2. ¹⁵¹Eu Mössbauer spectra of the fluoride glasses containing (*a*) Eu³⁺ ions, (*b*) a mixture of Eu³⁺ and Eu²⁺ ions, and (*c*) Eu²⁺ ions. The measurement temperature is 295 K

It should be emphasized that, although the isomer shifts of the Mössbauer spectra of the fluoride glasses and the EuF_3 compound differ from each other, it seems likely that only the fluorine atoms can be involved in the local environment of the europium atoms both in the structure of the fluoride glass and in the lattice of the EuF_3 compound. The difference between the isomer shifts of the Mössbauer spectra of the fluoride glasses and the EuF_3 compound can be explained by the induction effect. This effect implies that the alkaline-earth metal and aluminum atoms, which are not bound directly to the europium atoms, affect the electron density at the ¹⁵¹Eu nuclei.

In order to prepare fluoride glasses containing europium in the reduced state, the AlF₃ aluminum fluoride in the batch was partially replaced by the AlN aluminum nitride, which exhibits clearly pronounced reducing properties. The Mössbauer spectra of these glasses can be represented as a superposition of two lines (Fig. 2 b). One of these lines, which lies in the range of velocities ~0.5 mm/s, corresponds to Eu³⁺ ions. The parameters of this spectrum, as before, are in-

dependent of the glass composition, the europium content, or the measurement temperature and coincide with the parameters of the Mössbauer spectra of the Eu^{3+} ions in the fluoride glasses synthesized from the batch composed only of the metal fluorides. The second line, which lies in the range of velocities ~ -14 mm/s, corresponds to Eu^{2+} ions. In the Mössbauer spectra, one or the other of the components predominates, depending on the concentration ratio of AlF₃ and AlN in the batch; therefore, it is possible to prepare a glass containing only Eu^{2+} ions (Fig. 2 c).

The parameters of the Mössbauer spectrum of the Eu^{2+} ions, more precisely, the isomer shift and the linewidth, depend on the concentration ratio of Eu^{2+} and Eu^{3+} ions in the glass. As the Eu^{2+} content increases, the isomer shift increases [from $-(14.31 \pm 0.05)$ to $-(15.13 \pm 0.07)$ mm/s], whereas the linewidth decreases [from (6.4 ± 0.2) to (5.0 ± 0.2) mm/s]. Let us compare the isomer shift of the Mössbauer spectrum of the Eu^{2+} ions in the glass with the isomer shift of the spectrum of the EuF_2 compound [$-(13.95 \pm 0.05)$ mm/s]. As in the case of europium atoms in the oxidation state +3, the isomer shift of the Mössbauer spectrum of the Eu^{2+} ions in the glass differs from that of the crystal, which, apparently, can also be explained in terms of the induction effect.

The specific feature of the Mössbauer spectra of the Eu^{2+} ions in the fluoride glasses is their anomalously large broadening. This broadening of the ¹⁵¹Eu Mössbauer spectra of the fluoride glasses is associated with the nonuniform isomer shift (because the structure of the glasses involves europium ions in oxidation states that are close to each other). Since the range of isomer shifts for the Eu^{2+} -containing compounds is considerably wider than that for the Eu^{3+} -containing compounds, the Mössbauer spectra of the Eu^{2+} ions are more broadened than the spectra of the Eu^{3+} ions.

3. The valence state of dysprosium in glasses

In this study, the oxidation states of dysprosium in aluminosilicate and fluoroaluminate glasses were determined using ¹⁶¹Dy Mössbauer spectroscopy.

Aluminosilicate glasses were synthesized from Al₂O₃, SiO₂, MnO, and Dy₂O₃ in zirconium crucibles in a nitrogen atmosphere at temperatures of 1200 and 1300°C. Fluoroaluminate glasses were synthesized from alkaline-earth metal fluorides (BeF₂, CaF₂, SrF₂, MgF₂), aluminum fluoride (AlF₃), and dysprosium fluoride (DyF₃) in an electric furnace in glassy-carbon crucibles in an argon atmosphere at temperatures of 950 and 1050°C. The composition of the glasses was varied over a wide range. The dysprosium content in the glasses was varied from 2 to 5 mol %. The synthesis of the glasses was performed with the use of the ¹⁶¹Dy isotope enriched to 80%. The Mössbauer spectra were recorded with a Gd₂O₃: ¹⁶¹Tb source at a temperature of 295

The Mössbauer spectra were recorded with a Gd_2O_3 : ¹⁶¹Tb source at a temperature of 295 K. The isomer shifts are given relative to the spectrum of the DyF₃ absorber. The errors in the determination of the isomer shifts were equal to ± 0.06 mm/s.

Preliminarily, we measured the ¹⁶¹Dy Mössbauer spectra of individual chemical compounds of dysprosium, namely, dysprosium oxide (Fig. 3 a), dysprosium silicate (Fig. 3 b), and dysprosium fluoride (Fig. 3 a). All the Mössbauer spectra of these compounds have the form of single lines with the isomer shifts (IS = +0.56, -0.22, and 0.00 mm/s for dysprosium oxide, dysprosium silicate, and dysprosium fluoride, respectively) lying in the range of zero velocities, which is typical of compounds with dysprosium in the oxidation state +3. The linewidth of the Mössbauer spectra at half-height is equal to ~10 natural widths, which is explained by the relaxation processes characteristic of dysprosium compounds.



 and (*c*-*e*) the Al₂O₃-SiO₂-MnO glasses containing 5 mol % Dy₂O₃. The temperatures of the melt are (*c*) 1200 and (*d*, *e*) 1300°C.
(e) ¹⁶¹Dy Mössbauer spectrum of the glass synthesized from the batch in which Al₂O₃ was partially replaced by AlN

The ¹⁶¹Dy Mössbauer spectra of the aluminosilicate glasses have the form of single lines (Figs. 3 c, d, and e). The isomer shift of these spectra is virtually independent of the composition of the glass (IS = -0.15 mm/s) and corresponds to the presence of dysprosium only in the oxidation state +3 in the structure of glasses. The parameters of the Mössbauer spectra (the isomer shift and the linewidth at half-height) turned out to be close to those for dysprosium silicate, and, most likely, dysprosium enters into the composition of the aluminosilicate glass in the form of structural units characteristic of dysprosium silicate.

The investigation of europium-containing aluminosilicate glasses revealed that an increase in the temperature of the melt leads to the stabilization of a part of the europium atoms in the oxidation state +2 in the structure of the glass. However, as can be seen from Figs. 3 c, d, the synthesis of the glasses at temperatures of 1200 and 1300° C has virtually no effect on the fine structure of the Mössbauer spectra and, in both glasses, dysprosium occurs in the oxidation state +3 (as follows from the results of the processing of the experimental Mössbauer spectra in Fig. 3 with the use of the least-squares method, the fraction of dysprosium in the oxidation state +2 is less than 0.05).

Another method used for determining the oxidation state of rare-earth metals in the structure of silicate glasses consists in introducing an effective reducing agent (AlN) into the batch. However, in the case of dysprosium-containing glasses, the partial replacement of Al_2O_3 by AlN in the batch does not lead to the appearance of dysprosium in the oxidation state +2 in the structure of the glass (Fig. 3 e).

The Mössbauer spectra of the fluoroaluminate glasses have the form of single lines (Fig. 4 a). The isomer shifts of these spectra are independent of the composition of the glass or the syn-

thesis temperature (IS = +0.12 mm/s) and correspond to the presence of dysprosium only in the oxidation state +3 in the structure of the glass. The parameters of the Mössbauer spectrum of dysprosium fluoride, and, most likely, dysprosium enters into the composition of the fluoroaluminate glasses in the form of structural units characteristic of dysprosium fluoride. An increase in the temperature of the melt does not lead to the appearance of dysprosium in the oxidation state +2 in the structure of the glass (Fig. 4 b, c). The partial replacement of AlF₃ by AlN in the composition of the batch is accompanied by the appearance of an additional line in the Mössbauer spectrum (Fig. 4 d) with the isomer shift (IS = +6.10 mm/s) corresponding to dysprosium in the oxidation state +2 (as judged from the areas under the spectra corresponding to dysprosium in the oxidation state +3 and +2, the fraction of dysprosium in the oxidation state +2 is equal to 0.20 ± 0.05 . The specific feature of the Mössbauer spectra of dysprosium in the oxidation state +2 is their large broadening (the linewidth at half-height is equal to ~15 natural widths). This broadening can be caused not only by relaxation processes but also by a nonuniform isomer shift (due to the existence of dysprosium states having a similar chemical form in the structure of the glass).



Fig. 4. ¹⁶¹Dy Mössbauer spectra of (*a*) dysprosium fluoride and (*b*-*d*) the Al₂F₃-BeF₂-MgF₂-CaF₂-SrF₂ glasses containing 5 mol % DyF₃. The temperatures of the melt are (*b*) 950 and (*c*) 1050°C.
(*d*) ¹⁶¹Dy Mössbauer spectrum of the glass synthesized from the batch in which AlF₃ was partially replaced by AlN. The dotted line shows the decomposition of spectrum (*d*) into two components corresponding to dysprosium in the oxidation states +2 and +3

4. The valence state of gadolinium in glasses

The purpose of this work was to investigate the influence of the composition of glasses in the $(BaGeO_3)_{1-x-y}(Al_2O_3)_x(0.45CaF_2 \cdot 0.55MgF_2)_y$ (x = 0.25, y = 0; x = 0.17, y = 0.17; x = 0, y = 0.45) system on the local structure of the gadolinium centers. The oxidation state of gadolinium atoms and the degree of homogeneity of their local environment in the glasses under investigation were determined using ¹⁵⁵Gd Mössbauer spectroscopy. The content of the Gd₂O₃ activator in all the studied glasses was equal to 5 wt % over and above 100% (however, the activator content in the glass with x = y = 0.17 was varied from 2 to 5 wt %). The glasses were synthesized from the following initial reactants: Al₂O₃, GeO₂, BaO, CaF₂, MgF₂, and Eu₂O₃ (all of the compounds used were of the reagent grade). The synthesis of the glasses was performed at a temperature of 1300°C in an argon atmosphere in glassy-carbon crucibles with the use of the ¹⁵⁵Gd₂O₃ compound enriched to 90%.

The ¹⁵⁵Gd Mössbauer spectra were recorded with a $Pd(^{155}Eu)$ source at a temperature of 80 K. The isomer shifts are given relative to the spectrum of the GdF₃ absorber. The surface density of the absorbers with respect to the ¹⁵⁵Gd isotope was equal to 10 mg/cm².

In the structure of the glasses studied in this work, the gadolinium atoms can form structural units characteristic of gadolinium oxide, gadolinium fluoride, and gadolinium oxyfluoride, as well as structural units characteristic of mixed gadolinium and aluminum oxides. In the first stage of our investigation, we measured the ¹⁵⁵Gd Mössbauer spectra of the aforementioned compounds. As can be seen from Fig. 5 a, b, the Mössbauer spectra of the cubic and monoclinic gadolinium oxides have the form of a superposition of two (cubic Gd₂O₃) or three (monoclinic Gd₂O₃) quadrupole doublets. This finding is in agreement with the X-ray structural data, according to which the structures of the cubic and monoclinic gadolinium oxides involve two and three nonequivalent positions of the gadolinium atoms, respectively. The Mössbauer spectra of the other compounds (Fig. 5 b, c, d, e, and f) have the form of quadrupole doublets. The isomer shifts of all the Mössbauer spectra measured in our work correspond to triply charged gadolinium ions. The parameters of the Mössbauer spectra are presented in the Table 1.



Fig. 5. ¹⁵⁵Gd Mössbauer spectra of (a) monoclinic Gd₂O₃, (b) cubic Gd₂O₃, (c) GdF₃, (d) GdOF, (e) GdAlO₃, and (f) Gd₃Al₅O₁₂. Dotted lines show the decomposition of spectra (a) and (b) into three and two quadrupole doublets, respectively

The ¹⁵⁵Gd Mössbauer spectra of all the glasses under investigation have the form of quadrupole doublets (Fig. 6). The parameters of the spectra depend neither on the composition of the glass (Figs. 6a, 6b, 6d) nor on the gadolinium concentration (Figs. 6b, 6c). The isomer shifts in the Mössbauer spectra of the glasses and crystalline compounds of gadolinium coincide within the limits of experimental error. Therefore, their values cannot be used as criteria for the determination of the structural units forming the structural network of the glass. However, the quadrupole splittings can serve as such criteria. A comparison of the fine structure of the Mössbauer spectra of the gadolinium oxides (the superposition of two or three quadrupole doublets) and the spectra of the lasses (one quadrupole doublet) allows us to conclude that, in the structure of the glasses under investigation, the gadolinium atoms do not form structural units characteristic of oxides.

Similarly, the difference between the quadrupole splittings of the Mössbauer spectra of the dysprosium fluoride and dysprosium oxyfluoride and the quadrupole splittings of the Mössbauer spectra of the glasses under investigation suggests that the structural units characteristic of GdF_3 and GdOF are absent in the structure of the glasses. This inference is also confirmed by the fact that the parameters of the Mössbauer spectra of the glasses (both containing alkaline-earth metal fluorides and free of them) coincide.

Table 1

Composition of the compound	Parameters			
	Isomer	Quadrupole	With	Area
	shift	splitting	at half-	Under
			height	The
				spectrum
	mm/s			rel. units
Crystalls				
Gd ₂ O ₃ , monoclinic	0.49	0.49	0.72	0.44
	0.46	2.78	0.73	0.36
	0.45	5.36	0.79	0.20
Gd_2O_3 , cubic	0.50	2.75	0.72	0.26
	0.52	5.26	0.71	0.74
GdF ₃	0.67	2.82	0.73	
GdOF	0.60	0.57	0.70	
GdAlO ₃	0.56	2.85	0.72	
$Gd_3Al_5O_{12}$	0.55	2.91	0.70	
Glasses				
$(BaGeO_3)_{0.55}(Al_2O_3)_{0.45}$	0.52	2.93	1.01	
$+ 5 \text{ wt } \% \text{ Gd}_2\text{O}_3$				
$(BaGeO_3)_{0.64}(Al_2O_3)_{0.17}(0.45CaF_2.0.55MgF_2)_{0.17}$	0.55	2.95	0.98	
$+ 5 \text{ wt } \% \text{ Gd}_2\text{O}_3$				
$(BaGeO_3)_{0.64}(Al_2O_3)_{0.17}(0.45CaF_2.0.55MgF_2)_{0.17}$	0.54	2.91	1.02	
$+ 2 \text{ wt } \% \text{ Gd}_2\text{O}_3$				
$(BaGeO_3)_{0.25}(0.45CaF_2.0.55MgF_2)_{0.75}$	0.51	2.87	0.96	
+5 wt % Gd ₂ O ₃				

Parameters of the ¹⁵⁵Gd Mössbauer spectra of the glasses under investigation



*Fig. 6.*¹⁵⁵Gd Mössbauer spectra of (*a*) (BaGeO₃)_{0.55}(Al₂O₃)_{0.45} + 5 wt % Gd₂O₃, (*b*) (BaGeO₃)_{0.64}(Al₂O₃)_{0.17}(0.45CaF₂·0.55MgF₂)_{0.17} + 5 wt % Gd₂O₃, (*c*) (BaGeO₃)_{0.64}(Al₂O₃)_{0.17}(0.45CaF₂·0.55MgF₂)_{0.17} + 2 wt % Gd₂O₃, and (*d*) (BaGeO₃)_{0.25}(0.45CaF₂·0.55MgF₂)_{0.75} + 5 wt % Gd₂O₃ glasses

5. Conclusions

Triply and doubly charged states of europium are revealed by 151 Eu Mössbauer spectroscopy in the structure of glasses of the composition (mol %) 19.5Al₂O₃, 31.5SiO₂, 26.5MnO, and 22.5Eu₂O₃. The isomer shifts in the Mössbauer spectra of Eu³⁺ and Eu²⁺ ions in the structure of glasses differ from the isomer shifts in the spectra of the Eu₂O₃ and EuO compounds. This difference is explained by the fact that the electron density at ¹⁵¹Eu nuclei is affected by the manganese and aluminum atoms, which are not bound directly to the europium atoms. The broadening of the spectra of the Eu²⁺ ions in glasses is caused by the nonuniform isomer shift.

The structure of glasses based on fluorides of alkaline-earth metals, aluminum, and europium, in which aluminum fluoride is partially replaced by aluminum nitride, is investigated by 151 Eu Mössbauer spectroscopy. It is found that these glasses contain europium atoms in two oxidation states (+2 and +3). The isomer shifts of the Mössbauer spectra of Eu³⁺ and Eu²⁺ ions entering into the composition of the fluoride glasses are somewhat different from the isomer shifts of the Mössbauer spectra of EuF₃ and EuF₂ compounds. This difference is explained by the effect of the alkaline-earth metal and aluminum atoms (not bound directly to the europium atoms) on the electron density at the ¹⁵¹Eu nuclei. The broadening of the Mössbauer spectra of the Eu²⁺ ions in the fluoride glasses is explained by the nonuniform isomer shift.

In the structure of the aluminosilicate and fluorosilicate glasses, dysprosium is stabilized in the oxidation state +3 and only the introduction of the reducing agent AlN into the batch makes it possible to transform a part of the dysprosium atoms into the oxidation state +2 in the fluoroaluminate glasses.

The revealed correlation between the parameters of the ¹⁵⁵Gd Mössbauer spectra of the GdAlO₃ and Gd₃Al₅O₁₂ compounds and the $(BaGeO_3)_{1-x-y}(Al_2O_3)_x(0.45CaF_2 \cdot 0.55MgF_2)_y$ glasses allows us to draw the conclusion that, in the structure of the glasses under investigation, the trivalent gadolinium atoms form structural units characteristic of mixed gadolinium and aluminum oxides.

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МОДЕЛИ U-МИНУС-ЦЕНТРА ОЛОВА В ХАЛЬКОГЕНИДНЫХ КРИСТАЛЛИЧЕСКИХ И СТЕКЛООБРАЗНЫХ ПОЛУПРОВОДНИКАХ

Рассмотрены результаты исследования донорных U-минус-центров в халькогенидах свинца и амфотерных U-минус-центров в стеклообразных халькогенидах мышьяка и германия методом мёссбауэровской спектроскопии.

Ключеые слова: мёссбауэровская спектроскопия, U-минус-центры.

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Models of Negative U-Tin-Centers in Chalcogenide Crystalline and Glassy Semiconductors

The results of the study of donor negative U-centers in lead chalcogenides and amphoteric negative U-centers in glassy arsenic and germanium chalcogenides using Mössbauer spectroscopy are regarded.

Keywords: Mössbauer spectroscopy, U-centers.