

Effect of Annealing Temperature on the Structural Reorganization of Eu^{3+} Optical Centers in Al_2O_3 – Eu_2O_3 – BiOF Gel Films

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Abstract—The dependence of the structural reorganization of Eu^{3+} optical centers in Al_2O_3 – Eu_2O_3 – BiOF films on the annealing temperature has been investigated. It is shown by the methods of crystal field theory and computer simulation that the increase in the annealing temperature from 700 to 1100°C leads to removal of bismuth from Eu – O – Bi complex centers with the C_{3V} symmetry in the Al_2O_3 structure and the change in symmetry from D_3 to O_h for a large fraction of EuAlO_3 centers.

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INTRODUCTION

The formation of Eu – O – Bi chain centers in Al_2O_3 – Eu_2O_3 – BiOF gel films, which show a record peak luminescence intensity due to the ${}^5D_0 \rightarrow {}^7F_4$ transition ($\lambda \approx 700$ nm) in Eu^{3+} ions, has recently been reported [1]. Such centers are of interest both for studying the spectroscopic potential of Eu^{3+} ions and for a number of practical applications. In particular, light-converting coatings for silicon solar cells require increasing the fraction of photons emitted in the range of the maximum spectral sensitivity of these coatings (~ 700 – 900 nm). Therefore, further investigation of such centers is an urgent problem. Since it is fairly difficult to determine their nature in thin glasslike films by X-ray diffraction methods (if for no other reason than the absence of sufficiently large single-crystal regions), methods of optical spectroscopy can be more sensitive and informative [2]. In this paper, we report the results of studying the structural reorganization of Eu – O – Bi chain centers in such films caused by an increase in the annealing temperature. The study was performed using the methods of crystal field theory and computer simulation.

EXPERIMENTAL

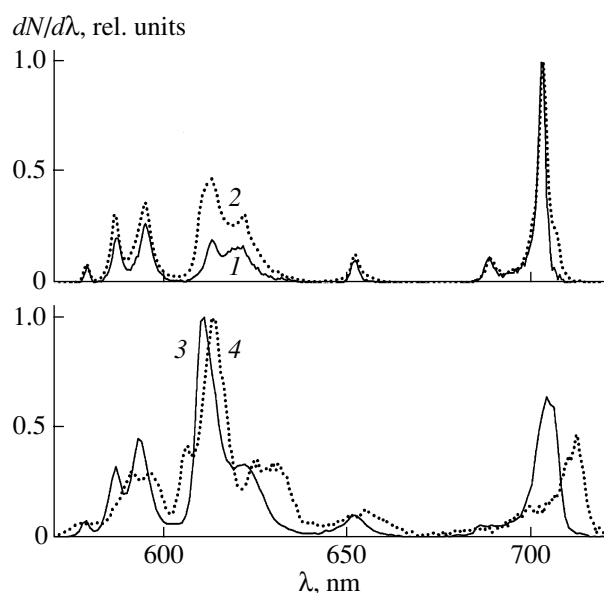
Films were formed using layer-by-layer deposition by centrifugation of multicomponent sols onto a quartz substrate, heating each layer at 150°C for 10 min. The initial Al_2O_3 sol was prepared using deposition of $\text{Al}(\text{NO}_3)_3$ by ammonia with subsequent washing until

the beginning of spontaneous peptization. An $\text{Eu}(\text{NO}_3)_3$ solution and a BiOF weight were added to the initial sol with intense stirring and then the mixture was subjected to ultrasonic treatment in order to obtain a homogeneous suspension. The films thus fabricated were annealed at different temperatures T_{an} .

Luminescence spectra were recorded with an SDL-2 spectrofluorimeter, corrected taking into account the spectral sensitivity of the recording system, normalized by reducing the peak spectral intensity to unity, and represented as a dependence of the number of photons per unit wavelength range ($dN/d\lambda$) on λ . Decomposition of complex spectral bands (recalculated in the number of photons per unit frequency range and frequency coordinates) into individual components modeled by Lorentzian profiles and determination of their barycenters were performed using the well-known methods of computer processing. The intensity I of an individual component was determined as the area under the corresponding profile. The crystal field parameters were found from splittings and intensities of individual components in the experimental spectra.

RESULTS AND DISCUSSION

The figure shows the luminescence spectra of a $45\text{Al}_2\text{O}_3$ – $30\text{Eu}_2\text{O}_3$ – 25BiOF (mol %) film annealed at different temperatures; the excitation wavelength $\lambda_{\text{exc}} = 280$ nm. It can be seen that the peak luminescence intensity in the ${}^5D_0 \rightarrow {}^7F_4$ band at $T_{\text{an}} = 700^\circ\text{C}$ (curve 1) multiply exceeds the corresponding intensi-



Luminescence spectra of the 45Al₂O₃-30Eu₂O₃-25BiOF (mol %) film annealed at $T_{\text{an}} = (1) 700$, (2) 900, (3) 1000, and (4) 1100°C. $\lambda_{\text{exc}} = 280$ nm; the half-widths of the excitation and detection bands are 4.0 and 1.5 nm, respectively.

ties for other bands. With an increase in T_{an} to 900 and 1000°C (curves 2 and 3, respectively), the fraction of photons emitted in the $^5D_0 \rightarrow ^7F_1$ ($\lambda \sim 590$ nm) and $^5D_0 \rightarrow ^7F_2$ ($\lambda \sim 615$ nm) transitions significantly increases. At $T_{\text{an}} = 1100^\circ\text{C}$, the shape of the spectral bands radically changes. Such a character of changes in the luminescence spectra with a change in T_{an} , indicating structural reorganization of Eu³⁺ optical centers, is

retained with the change in the film composition within (40–60)Al₂O₃–(20–40)Eu₂O₃–(10–30)BiOF and the change in λ_{exc} from 250 to 395 nm. The decrease in the Al content to 10 mol % due to the increase in the BiOF content under similar annealing conditions leads to a significant change in the shape of the spectral bands; in this case, the integrated and peak intensities of the $^5D_0 \rightarrow ^7F_2$ band significantly exceed the intensities of other $^5D_0 \rightarrow ^7F_j$ bands. However, even at 1 mol % Al₂O₃, Eu³⁺ optical centers with the spectra similar (in the first-order approximation) to curves 1–3 can be formed; however, the optical quality of such films is low.

Due to the absence of a clear structure of spectral bands at $\lambda > 640$ nm, we restricted ourselves to the $^5D_0 \rightarrow ^7F_1$, 7F_2 and $^5D_0 \rightarrow ^7F_0$ transitions ($\lambda \sim 570$ nm) in determination of the symmetry of Eu³⁺ optical centers. The Stark level energies E and the relative intensities of the transitions from the 5D_0 multiplet of Eu³⁺ ions in a 45Al₂O₃-25BiOF-30Eu₂O₃ film at different T_{an} , obtained using the calculated profiles, are listed in Table 1. According to the theory of groups [4], the experimentally observed splitting of the 7F_1 and 7F_2 multiplets into two and three Stark components, respectively, should occur in trigonal fields. Europium oxo-complexes with a coordination number of 6 and approximate local symmetry C_{3V} (as in Al₂O₃) or a coordination number of 12 and approximate symmetry D_3 (as in LaAlO₃) satisfy this condition. Therefore, the data in the literature on E for Al₂O₃ and LaAlO₃ crystals are also listed in Table 1 for comparison.

Table 1. Experimental values of the Stark level energies and the relative intensities of the transitions from the 5D_0 state of Eu³⁺ ions

$^{2S+1}L_J$	Symmetry	Gel film at $T_{\text{an}}, ^\circ\text{C}$								Al ₂ O ₃ : Eu ³⁺ [2]	LaAlO ₃ : Eu ³⁺ [3]
		700		900		1000		1100			
		E, cm^{-1}	$I, \text{rel. un.}$	E, cm^{-1}	$I, \text{rel. un.}$	E, cm^{-1}	$I, \text{rel. un.}$	E, cm^{-1}	$I, \text{rel. un.}$		
7F_0	A_1	0	0.15	0	0.17	0	0.05	0	0.50	0	0
7F_1	A_2	256	1.30	230	1.10	241	0.75	265	0.18	202	314
	E							378	1.87		380
		480	2.61	456	2.57	438	2.09	544	3.06	458	
7F_2	A_1/E		0.94	895	0.87	901	2.13			898	
		945		967	2.85	978	2.21	942	2.30		959
	E/A_1	1011	1.34					1006	5.57	943	1004
				1169	4.09	1174	3.62	1214	2.13	1294	1.54
	E							1086	1.40		
								1452	4.18	1268	

Table 2. Crystal field parameters and strengths calculated from the data of Table 1

Crystal field parameters and strengths	Gel film at T_{an} , °C						$Al_2O_3 : Eu^{3+}$ [2]	$LaAlO_3 : Eu^{3+}$ [3]
	700		900		1100			
	symmetry						C_{3V}	D_3
	C_{3V}	D_3	C_{3V}	D_3	C_{3V}	D_3		
B_0^2	-850.7	-738.7	-866.7	-727.8	-753.8	-616.6	-965	-214
B_0^4	-420.1	711.8	-405.2	989.4	-392.1	1191.9	1	451
B_3^4	1140.0	664.6	1514.2	873.8	1753.2	983.1	1914	314
S	476	363	582	438	637	473	707	163

It was shown in [1] that at $T_{an} = 700^\circ\text{C}$ the diffraction patterns of $50Al_2O_3-40Eu_2O_3-10BiOF$ powders contain only reflections corresponding to the $EuAlO_3$ phase; however, they do not manifest themselves in the luminescence spectrum due to effective excitation transfer to $Eu-O-Bi$ chain centers. It was also suggested in [1] that such centers are formed in the Al_2O_3 structure and, according to the calculation performed, such a center should contain a Bi^{3+} ion in an empty octahedral position on the C_3 symmetry axis at a distance of $\sim 2 \text{ \AA}$ from the Eu^{3+} ion. It was also found in [1] that, at an insignificant increase in T_{an} (to 800°C), the Bi_2O_3 phase is also formed in powders. Taking into account the proximity of the ionic radii of Bi^{3+} and Eu^{3+} (1.02 and 0.947 Å, respectively) [5], one cannot exclude the possibility of formation of similar centers in the Bi_2O_3 structure. However, our search for Eu^{3+} optical centers (which would induce a trigonal field) at partial substitution of oxygen atoms with fluorine in the Bi_2O_3 structure [6] did not reveal any such centers; they were not found either in the bismuth oxyfluoride structure, described in [7]. On the basis of these data, we excluded from analysis the scenario of substitution of Bi^{3+} ions with Eu^{3+} ions in Bi_2O_3 and $BiOF$ crystallites and considered only incorporation of Eu^{3+} and Bi^{3+} ions into Al_2O_3 or $EuAlO_3$.

Comparison of the energies of Stark levels of a gel film with the energies of the corresponding levels of $Al_2O_3:Eu^{3+}$ or $LaAlO_3:Eu^{3+}$ does not allow an unambiguous choice between the C_{3V} and D_3 symmetries. Therefore, to refine the symmetry of optical centers, we will determine the crystal field parameters. In trigonal fields, the crystal field Hamiltonian has the form [4]

$$H_{CF} = B_0^2 C_0^2 + B_3^4 (C_3^4 - C_{-3}^4) + B_0^6 C_0^6 + B_3^6 (C_3^6 - C_{-3}^6) + B_6^6 (C_6^6 + C_{-6}^6), \quad (1)$$

where B_q^k are the crystal field parameters and C_q^k is a spherical tensor of rank k . Splitting of the 7F_1 and 7F_2

multiplets is set by the parameters B_0^2 , B_0^4 , and B_3^4 [8] of Hamiltonian (1). The $J-J$ mixing effects significantly influence the splitting of multiplets and, therefore, the crystal field parameters. Hence, diagonalization of the matrix of Hamiltonian (1) was performed in the basis of the states of the multiplets under consideration.

The crystal field parameters calculated by the least-squares method according to the data of Table 1 in the approximation of the C_{3V} and D_3 symmetries, as well as the values of these parameters for $LaAlO_3$ and Al_2O_3 crystals, are listed in Table 2. This table contains also the values of the crystal field strength S calculated from the formula [9, 10]

$$S = \sqrt{1/3 \sum_{k=2,4,6} 1/(2k+1) \left[(B_0^k)^2 + 2 \sum_{q>0} |B_q^k|^2 \right]}. \quad (2)$$

Since it is possible to determine only the parameters of tensors of ranks two and four in the case under consideration, instead of formula (2), we used the following expression to calculate the crystal field strength:

$$S = \sqrt{1/2 \sum_{k=2,4} 1/(2k+1) \left[(B_0^k)^2 + 2 \sum_{q>0} |B_q^k|^2 \right]}.$$

It can be seen in Table 2 that the crystal field strength of gel films ranges from 476 to 637 cm^{-1} and from 363 to 473 cm^{-1} on the assumption of the C_{3V} and D_3 symmetries, respectively. The different-symmetry values $S = 476$ and 363 cm^{-1} for the gel films at $T_{an} = 700^\circ\text{C}$ can be assigned to $S = 707 \text{ cm}^{-1}$ in Al_2O_3 (C_{3V} symmetry) and $S = 163 \text{ cm}^{-1}$ in $LaAlO_3$ (D_3 symmetry). However, with an increase in T_{an} , S approaches the values characteristic of the Al_2O_3 structure. For example, the value $S = 637 \text{ cm}^{-1}$ at $T_{an} = 1000^\circ\text{C}$ unambiguously indicates the presence of such centers.

These conclusions are confirmed by the analysis of the relative intensities of luminescence transitions from

Table 3. Experimental values of the Stark level energies and the relative intensities of the ${}^5D_0 \rightarrow {}^7F_0, {}^7F_1$ transitions

$2S+1L_J$	Symmetry	Gel film at $T_{\text{an}} = 900^\circ\text{C}$	
		E, cm^{-1}	$I, \text{rel. un.}$
7F_0	A_1	0	0.55
7F_1	$A_2(C_{3V})$	229	1.10
	$B_2(O_h)$	380	0.28
	$E(C_{3V})$	462	2.23

the 5D_0 multiplet to the Stark components A_2 and E of the 7F_1 multiplet. The ${}^5D_0 \rightarrow {}^7F_1$ transition is of magnetic-dipole type. The degeneracy of the E component exceeds that of the A_2 component by a factor of 2. Therefore, the intensity of the transitions to E should also exceed the intensity of the transition to A_2 by a factor of 2. Indeed, the ratio of intensities in gel films is 2.01 at $T_{\text{an}} = 700^\circ\text{C}$. However, at $T_{\text{an}} = 900$ and 1000°C , the ratios of intensities are, respectively, 2.34 and 2.79, i.e., much larger than 2.

To explain this effect, we will take into account that with an increase in temperature the symmetry of optical centers of the LaAlO_3 type increases from trigonal to cubic [3]. In cubic fields, the 7F_1 multiplet is unsplit. Therefore, with an increase in T_{an} from 700 to 900°C , optical centers of different systems (trigonal and cubic) should be formed in gel films and three lines should be observed in the band due to the ${}^5D_0 \rightarrow {}^7F_1$ transition. Spectral analysis of this band confirms this suggestion (Table 3). With allowance for the formation of the third component, the ratio of the intensities of the transitions to the E and A_2 components is 2.03; i.e., close to the theoretical value 2. The ratio of the intensity of the transition to the B_2 component of the cubic system to the total intensity of the ${}^5D_0 \rightarrow {}^7F_1$ band should approximately coincide with the relative fraction of EuAlO_3 cubic centers. This circumstance makes it possible to estimate this fraction for films annealed at different T_{an} as 8, 21, and 37% at 900, 1000, and 1100°C , respectively. A significant increase in the fraction of such centers at $T_{\text{an}} = 1100^\circ\text{C}$ is confirmed by the comparison of the Stark level energies at this temperature with the spectrum reported in [3]. In Table 1, the energies of these levels are printed in italics. Because of ambiguous assignment of the energy levels to the centers of Al_2O_3 or LaAlO_3 types, the crystal field parameters for the gel film at $T_{\text{an}} = 1100^\circ\text{C}$ were not determined.

To analyze the geometry of optical centers in more detail, we will apply the methods of computer simulation. To this end, it is necessary to calculate the crystal field parameters according to the microscopic model (for example, using the model of exchange charges, which was proposed in [11] and developed in [12, 13]).

According to this model, the crystal field parameters can be written as

$$B_q^k = -e^2 \langle r^k \rangle \sum_j \rho_j (2\beta_j)^{k+1} g_j / R_j^{k+1} (C_q^k(\theta_j, \varphi_j))^*, \quad (3)$$

where e is the elementary charge; $\langle r^k \rangle$ is the mean calculated on the $4f$ functions; $-eg_j$ and R_j, θ_j , and φ_j are, respectively, the charge and spherical coordinates of the j th ion;

$$\beta_j = \frac{1}{1 + \rho_j} \quad \text{and} \quad \rho_j = \rho_0 \left(\frac{R_0}{R_j} \right)^n. \quad (4)$$

Here, R_0 is the least distance R_j ; $n = 3.5$; and, for the Eu^{3+} ion, $\rho_0 = 0.05$.

In the optical centers with the structure of the Al_2O_3 type, the coordinates of oxygen ions will be chosen as follows:

$$R_1, \theta_1, \varphi = \begin{cases} 0 \\ 2\pi/3 \\ 4\pi/3 \end{cases} \quad \text{and} \quad R_2, \theta_2, \varphi = \begin{cases} \pi/3, \\ \pi, \\ 5\pi/3. \end{cases}$$

The empty octahedral position on the C_3 axis contains a Bi^{3+} ion; i.e., this ion has the coordinates $(0, 0, 2R_1 \cos \theta_1)$.

In the optical centers with the LaAlO_3 structure, Bi^{3+} ions are absent and Eu^{3+} ions are surrounded with 12 O^- ions having the coordinates

$$R_1, \theta_1, \varphi = \begin{cases} 0 \\ 2\pi/3 \\ 4\pi/3 \end{cases}, \quad R_2, \theta_2, \varphi = \begin{cases} \pi/3, \\ \pi, \\ 5\pi/3, \end{cases}$$

$$\text{and} \quad R_3, \theta_3, \varphi = \pi/6 + n\pi/3$$

$$\text{at} \quad n = 0, 1, 2, 3, 4, 5.$$

The parameters R_1, θ_1, R_2 , and θ_2 for the centers with the Al_2O_3 structure and $R_1, \theta_1, R_2, \theta_2, R_3$, and θ_3 for the centers with the LaAlO_3 structure were chosen by the least-squares method so as to minimize the root-mean-square deviation of the crystal field parameters calculated using formulas (3) and (4) from the experimental values from Table 2. The root-mean-square deviation RMS Dev was estimated from the formula

$$\text{RMS Dev} = \sqrt{\sum_{k,q} (B_q^k(\text{calc}) - B_q^k(\text{expt}))^2}.$$

The results of the calculations are listed in Tables 4 and 5. On the basis of the obtained values of RMS Dev, we can conclude that the crystal fields observed in the gel films annealed at 700°C can be implemented in optical centers of both types, while in the gel films annealed at $T_{\text{an}} = 900$ or 1000°C , this implementation is possible

Table 4. Results of the crystal field calculation according to the model of exchange charges of optical centers with the Al_2O_3 structure. The Bi^{3+} ion is located on the C_3 axis and has the coordinates (0, 0, $2Z_1$)

Coordinates	$T_{\text{an}} = 700^\circ\text{C}$	$T_{\text{an}} = 900^\circ\text{C}$	$T_{\text{an}} = 1000^\circ\text{C}$
R_1	2.846	2.684	2.506
θ_1	44.8°	41.3°	40.6°
Z_1	2.020	2.016	1.904
R_2	2.620	2.462	2.381
$\pi-\theta_2$	70.3°	71.9°	73.5°
Z_2	-0.886	-0.765	-0.676
Crystal field parameters			
$B_0^2(\text{expt})/B_0^2(\text{calc})$	-850.7/-850.52	-866.7/-857.20	-753.8/-754.58
$B_0^4(\text{expt})/B_0^4(\text{calc})$	-420.1/-420.04	-405.2/-339.40	-392.1/-401.06
$B_3^4(\text{expt})/B_3^4(\text{calc})$	1140.0/1139.85	1514.2/1422.75	1753.2/1742.93
RMS Dev	0.24	113	13.65

Table 5. Results of the crystal field calculation according to the model of exchange charges of optical centers with the LaAlO_3 structure

Coordinates	$T_{\text{an}} = 700^\circ\text{C}$	$T_{\text{an}} = 900^\circ\text{C}$	$T_{\text{an}} = 1000^\circ\text{C}$	[4]
R_1	2.613	2.837	2.828	3.220
θ_1	36.9°	33.0°	32.8°	34.8°
Z_1	2.089	2.379	2.376	2.645
R_2	2.916	2.662	2.676	3.039
$\pi-\theta_2$	33.8°	36.5°	34.9°	33.6°
Z_2	-2.423	-2.140	-2.195	-2.531
R_3	2.651	2.650	2.650	3.048
θ_3	92.1°	89.1°	90.4°	90.0°
Z_3	-0.088	0.042	-0.016	-0.001
Crystal field parameters				
$B_0^2(\text{expt})/B_0^2(\text{calc})$	-738.7/-740.37	-727.8/-694.77	-616.6/-564.70	-214.0/-214.01
$B_0^4(\text{expt})/B_0^4(\text{calc})$	711.8/707.71	989.4/840.32	1191.9/950.23	451.0/451.03
$B_3^4(\text{expt})/B_3^4(\text{calc})$	664.6/655.52	873.8/635.02	983.1/583.78	314.0/314.00
RMS Dev	10.10	283.43	469.63	0.03

only in the optical centers of the Al_2O_3 type. Note that the probability of existence of Eu–O–Bi optical centers sharply decreases at $T_{\text{an}} = 1000^\circ\text{C}$. The decrease in the distances R_1 and R_2 in the centers of the Al_2O_3 type, which follows from the calculation, is in agreement with the observed increase in the film density. The values of the Z coordinates of O^- ions (Table 4) indicate that optical centers are formed in a heavily deformed Al_2O_3 structure with a significant displacement of the Eu^{3+} ion to the three “lower” O^- ions with respect to the

position occupied by Al^{3+} . It was suggested in [2] that such deformation can be caused by incorporation of rare earth ions into corundum.

The existence of optical centers of the Al_2O_3 type is confirmed by comparison of the calculated ratios $I_4(^5D_0 \rightarrow ^7F_4)/I_2(^5D_0 \rightarrow ^7F_2)$ of the transition intensities with the experimental values at annealing temperatures of 700, 900, and 1000°C .

In neglect of the refractive index dispersion, the ratio of these intensities (the luminescence branching

ratio) depends on the frequency ν_i and transition line strength S_i as follows:

$$\frac{I_4}{I_2} \approx \frac{\nu_4^3 S_4}{\nu_2^3 S_2}. \quad (5)$$

The transitions under consideration are of electric-dipole type; therefore, the line strength is set by the intensity parameters Ω_k as follows:

$$S_i = e^2 \sum_{k=2,4,6} \Omega_k \langle {}^5D_0 \| U^k \| {}^7F_i \rangle^2, \quad (6)$$

where $\langle {}^5D_0 \| U^k \| {}^7F_i \rangle$ are the reduced matrix elements of the unit tensor U^k . The intensity parameters are determined through the crystal field parameters of B_i^p of odd ranks p using the formula [14]

$$\Omega_k = 4 \frac{(2k+1)}{\Delta_{fd}^2} \langle f|r|d \rangle^2 \langle f||c^1||d \rangle^2 \times \sum_{p,t} \left\{ \begin{matrix} 1 & k & p \\ f & d & f \end{matrix} \right\}^2 \langle d||c^p||f \rangle^2 |B_i^p|^2, \quad (7)$$

where Δ_{fd} is the energy of the excited $4f^{N-1}5d$ configuration and $\langle d||c^p||f \rangle$ is the one-electron reduced matrix element of the spherical tensor.

The ratios 1.08, 0.83, and 0.40, calculated from formulas (5)–(7), are in satisfactory agreement with the corresponding experimental values: 1.09, 0.76, and 0.53. Note that on the assumption of the LaAlO_3 structure, the ratio of intensities does not exceed 0.02 for all annealing temperatures.

CONCLUSIONS

The results reported above, with allowance for the data of [1], suggest that Eu–O–Bi complex optical centers with the C_{3V} symmetry in the heavily deformed Al_2O_3 structure and EuAlO_3 crystallites with the D_3 symmetry are formed in $(40\text{--}60)\text{Al}_2\text{O}_3\text{--}(20\text{--}40)\text{Eu}_2\text{O}_3\text{--}(10\text{--}30)\text{BiOF}$ films at $T_{\text{an}} = 700^\circ\text{C}$. However, EuAlO_3 crystallites do not exhibit luminescence due to the effective transfer of electronic excitations to the complex optical centers. The increase in T_{an} to 1100°C leads to complete removal of Bi from complex centers, appearance of the luminescence bands charac-

teristic of EuAlO_3 crystallites, and transformation of a large fraction of the latter into centers with the O_h symmetry. The fraction of photons emitted in the ${}^5D_0 \rightarrow {}^7F_4$ transition decreases from 45 to 20%.

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