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NEUTRON AND OPTICAL RESEARCHES OF MULTICOMPONENT CRYSTALLINE $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ AND $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ LUMINOPHORS

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Peculiarities in the crystal structure and spectral-luminescent properties of compound oxide systems $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ and $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ are studied using the neutron diffraction and optical spectroscopy methods. The influence of the introduced oxide on the structural and luminescent properties of those systems is shown to have a complicated character depending not only on the formation of a stable defect garnet structure and the diffusion of Ce^{3+} ions from the matrix into the oxide, but also on the interaction between the oxide and the matrix, which gives rise to the formation of new phases.

Keywords: neutron diffraction, luminophors, luminescence, crystalline structure, inter-atomic bond length.

1. Introduction

The development of methods and technologies for synthesizing luminophor materials is a challenging task for modern condensed matter physics and materials technology [1]. The most promising and widely studied materials for the laser and photoluminescent equipment are crystalline luminophors on the basis yttrium aluminum, $Y_3Al_5O_{12}$ (YAG), and lutetium aluminum, $Lu_3Al_5O_{12}$ (LuAG), garnets [2, 3]. Yttrium aluminum garnets activated with Ce^{3+} ions are very promising in the manufacture of light emitting diodes (LEDs) producing white light [3, 4]. At the same time, the luminophors on a basis of lutetium aluminum garnet, which is characterized by a high stopping power for x-ray radiation, find a wide application as optical converters in detectors of ionizing radiation for x-ray and positron emission tomogra-

phy, as well as in high-energy physics [5]. At present, the urgent task consists in creating an LED with the warm-white color of emission, which demands that the luminophor luminescence spectrum should be shifted toward the yellow-red range. As the simplest variant to solve this task, the simultaneous application of various ion-activators, which would allow an extra luminescence band to be obtained in the red spectral interval, is considered. An alternative variant is the influence on the crystallographic environment of ion-activators [6, 7] in the garnet structure, e.g., with the help of the formation of complex garnet/oxide systems.

The methods of colloid chemistry [8, 9] are among the most attractive ones to solve this task. They allow one to obtain materials characterized by a high uniformity in the distribution of optically active ions [10] and make their introduction into the crystalline matrix simpler [11]. Their main advantage consists in the capability of forming the complex composite systems with controllable redistribution of ion-activators between the components [12, 13]. The in-

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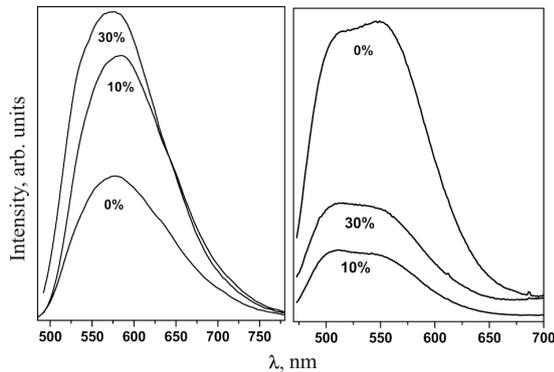


Fig. 1. Luminescence spectra of multicomponent luminophors $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ (left panel) and $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ (right panel) for various concentrations of Lu_2O_3 oxide

roduction of Lu_2O_3 as an additional component at the colloid-chemical synthesis of $Y_3Al_5O_{12}:Ce^{3+}$ was found to shift the maximum of its luminescence band into the red spectral interval down to $\lambda_{max} \approx 590$ nm [14]. In work [11], it was demonstrated that $Lu_3Al_5O_{12}:Ce^{3+}+Lu_2O_3$ composites in the form of optically transparent ceramics reveal an increase in the luminescence intensity and a shift of the luminescence band toward the long-wave region.

In this work, we report the results of detailed researches carried out for the crystal structure of complex oxide systems $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ and $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ with the use of the neutron diffraction method in order to determine probable mechanisms governing the formation of their optical properties. We emphasize that, in the case where complex oxide compounds are studied, the neutron diffraction analysis is the most informative method, which allows the atomic structure of crystals containing light elements, in particular, oxygen, to be analyzed. It is known that such an analysis is almost impossible to be made with the help of x-ray diffraction analysis.

2. Experiment

Specimens of crystalline luminophors $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ and $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ were fabricated within the colloid-chemical method, which was described in works [11, 12, 15] in detail. In the current series of experiments, specimens with 0, 10, and 30 wt.% Lu_2O_3 were used.

Photoluminescence spectra were measured at room temperature on a SDL-2 spectrofluorimeter. The lu-

minescence excitation wavelength in the experiment was $\lambda_{exc} = 440$ nm. The obtained spectra were corrected with regard for the spectral sensitivity of the measuring system.

Neutron diffraction experiments were carried out on a DN-2 spectrometer [16] of the IBR-2 pulsed reactor at I.M. Frank Laboratory of Neutron Physics (the Joint Institute for Nuclear Research, Dubna, Russia). Diffraction spectra were obtained at the scattering angle $2\theta = 90^\circ$, with the corresponding diffractometer resolution amounting to $\Delta d/d = 0.02$ at a wavelength of 2 Å. The characteristic time of the measurement of one spectrum was 1 h. The volume of examined specimens was $V \sim 50$ mm³. Diffraction data were analyzed using the Rietveld method [17] with the help of the software programs VMRIA [18].

3. Results and Their Discussion

In Fig. 1, the luminescence spectra of $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ and $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ are shown. The analysis of this figure testifies that the addition of Lu_2O_3 to $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ stimulates a shift of the luminescence band maximum toward the red range (~ 580 nm) and a substantial growth of the luminescence intensity at higher contents of Lu_2O_3 . In the case of $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$, the luminescence spectra are characterized by a weakly pronounced doublet with maxima at $\lambda_{max} \approx 510$ and 550 nm [19]. No appreciable shifts in the maximum positions of this doublet with the increase of Lu_2O_3 concentration were observed. At the same time, the change of the relative intensities of the doublet maxima did take place. Note that the long-wave component intensity is higher in the case of the $Lu_3Al_5O_{12}:Ce^{3+}$ (0 wt.% Lu_2O_3) specimen, whereas the short-wave component is more intense for $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ specimens. Moreover, the luminescence intensity decreases as Lu_2O_3 is added. The largest (four-fold) reduction was observed for the specimen $LuAG:Ce + 10\% Lu_2O_3$. As the concentration of Lu_2O_3 increases to 30%, an insignificant growth in the integral luminescence intensity was observed; nevertheless, it remained much lower than that for the $Lu_3Al_5O_{12}:Ce^{3+}$ (0 wt.% Lu_2O_3) specimen. The registered modification of optical properties in the studied systems associated with the introduction of lutetium oxide can testify to a distortion of the local crystallographic environment around the ion-activator [20].

In Figs. 2 and 3, the neutron diffraction spectra of the systems $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}/\text{Lu}_2\text{O}_3$ and $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}/\text{Lu}_2\text{O}_3$, respectively, are depicted. The spectra for $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}/\text{Lu}_2\text{O}_3$ with the maximum Lu_2O_3 content reveal a diffraction maximum at $d_{hkl} \approx 1.9 \text{ \AA}$, which is associated with the most intense reflex of the phase Lu_2O_3 with the cubic structure (spatial group $I2_13$). In the spectra of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}/\text{Lu}_2\text{O}_3$, one can observe the appearance of a weakly intense shoulder near the diffraction peak at $d_{hkl} \approx 2.0 \text{ \AA}$, which may correspond to the most intense reflex of the $(\text{Y}_{3-x}\text{Lu}_x)\text{Al}_5\text{O}_{12}$ phase formed in the course of synthesis as a result of the interaction between the components $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ and Lu_2O_3 [12, 13]. Neutron diffraction data were analyzed in the framework of the structural model for garnet compounds: cubic symmetry with spatial group $Ia3d$ [12, 21], in which Y and Lu atoms are in crystallographic positions 24(c) $(1/8, 0, 1/4)$, aluminum atoms in two nonequivalent positions Al1 (16(a) $(0, 0, 0)$) and Al2 (24(d) $(3/8, 0, 1/4)$), and oxygen atoms in positions 96(h) (x, y, z) . The cubic structure of garnets is characterized by three types of the nonequivalent oxygen environment: a complex dodecahedral one around the Y or Lu atoms, and the octahedral and tetrahedral ones for aluminum atoms Al1 and Al2 [12]. By analyzing the diffraction data, we determined the structural parameters and the interatomic bond lengths for $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}/\text{Lu}_2\text{O}_3$ and $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}/\text{Lu}_2\text{O}_3$.

In Fig. 4, the Lu_2O_3 -concentration dependences of the relative Al–O bond lengths are exhibited for the tetra- and octahedral oxygen environments of aluminum. The analysis of Fig. 4 testifies that, irrespective of the system concerned, the increase in the amount of Lu_2O_3 gives rise to an appreciable growth of the Al–O bond length in the octahedral oxygen environment. This fact can be explained by the formation of a stable defect structure in the oxide sublattice of the examined luminophors, which were obtained within the colloid-chemical method [10, 12]. This defect structure has to be characterized by the presence of oxygen vacancies and antistructural defects $[\text{Lu}(\text{Y})^{3+}\text{Al}]$ —here, $\text{Lu}(\text{Y})^{3+}$ cations occupy the positions of Al^{3+} cations—as well as their associates [22, 23].

When adding Lu_2O_3 to $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, an insignificant increase of the larger interatomic bond Y–O1 and a reduction of bond Y–O2 are observed. In

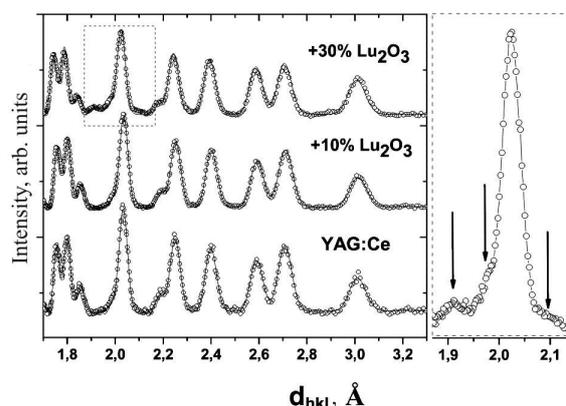


Fig. 2. Neutron diffraction spectra of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}/\text{Lu}_2\text{O}_3$ at various concentrations of added Lu_2O_3 oxide (0, 10, and 30 wt.%). Experimental points and the spectrum profile calculated by the Rietveld method are depicted. The right panel shows the scaled-up section of the neutron diffraction spectrum for $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}/\text{Lu}_2\text{O}_3$ with a Lu_2O_3 concentration of 30 wt.%. Arrows mark additional reflexes from the crystalline phase $\text{Y}_{3-x}\text{Lu}_x\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ formed in the course of synthesis

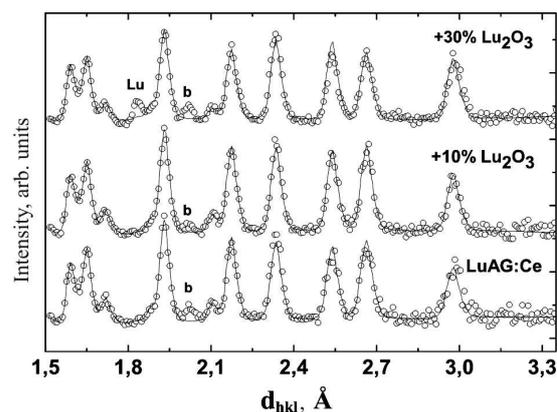


Fig. 3. Neutron diffraction spectra of multicomponent luminophors $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}/\text{Lu}_2\text{O}_3$ at various concentrations of added Lu_2O_3 oxide (0, 10, and 30 wt.%). Experimental points and the spectrum profile calculated by the Rietveld method are depicted. Symbol “b” is used to mark a reflex from aluminum, the material of the specimen container. Symbol “Lu” marks a weak peak from the crystalline Lu_2O_3 phase

the case of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, the increase of the Lu_2O_3 concentration also results in the growth of the larger interatomic distance Lu–O1 and a reduction of the Lu–O2 bond length. This fact points to an anisotropic character of the oxygen dodecahedron volume modifications around the Y and Lu atoms (Fig. 5). The anisotropic character of a change of the

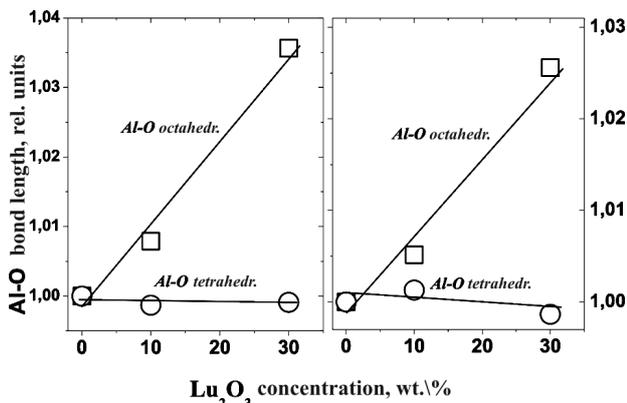


Fig. 4. Dependences of the relative variation of the Al-O bond length on the Lu₂O₃ concentration in the octa- and tetrahedral oxygen environments in the Y₃Al₅O₁₂:Ce³⁺/Lu₂O₃ (left panel) and Lu₃Al₅O₁₂:Ce³⁺/Lu₂O₃ (right panel) structures. The bond lengths are normalized by the corresponding values for undoped compounds Y₃Al₅O₁₂:Ce³⁺ and Lu₃Al₅O₁₂:Ce³⁺. Solid lines demonstrate linear approximations of experimental data

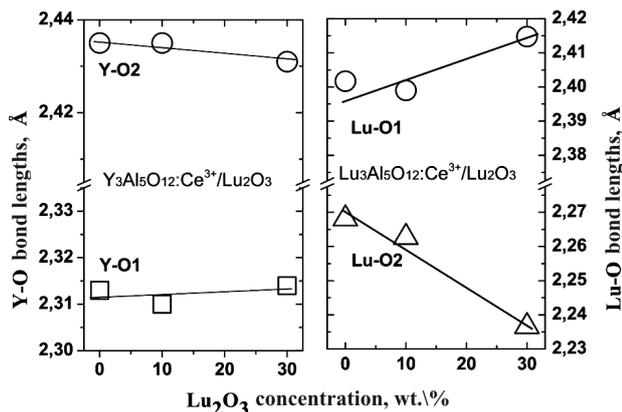


Fig. 5. Dependences of Y-O1 and Y-O2 bond lengths in Y₃Al₅O₁₂:Ce³⁺/Lu₂O₃ (left panel) and Lu-O1 and Lu-O2 bond lengths in Lu₃Al₅O₁₂:Ce³⁺/Lu₂O₃ (right panel) on the Lu₂O₃ concentration. Solid lines are linear approximations of experimental data

oxygen dodecahedron around Y or Lu has to result in modifications of the crystallographic environment around the optically active Ce³⁺ ion and, accordingly, give rise to a redistribution of the luminescence intensity between two relaxation channels, ⁵D₁ → ²F_{5/2} and ⁵D₁ → ²F_{7/2} (see Fig. 1).

The obtained experimental data make it possible to analyze the mechanism governing the formation of optical properties in the complex oxide systems

Lu₃Al₅O₁₂:Ce³⁺/Lu₂O₃ and Y₃Al₅O₁₂:Ce³⁺/Lu₂O₃ synthesized within the colloid-chemical method. It is found that a stable defect region is formed in both systems. This result is confirmed by the modification of all structural characteristics in the studied luminophors after the introduction of lutetium oxide. In particular, the lengths of Al-O bonds in the oxygen octahedron grow, which can testify to a considerable number of antistructural defects [Lu(Y)³⁺Al].

Note that a reduction of the luminescence intensity, when Lu₂O₃ is added to Lu₃Al₅O₁₂:Ce³⁺, can also be explained, besides making allowance for processes associated with the energy scattering at crystal lattice defects, by the diffusion of cerium ions from the Lu₃Al₅O₁₂:Ce³⁺ matrix into Lu₂O₃, which is accompanied by a decrease of their concentration in LuAG: Ce³⁺ and, as a consequence, by a reduction of the integral luminescence intensity, because Ce³⁺ does not luminesce in Lu₂O₃ [24]. When Lu₂O₃ is introduced into Y₃Al₅O₁₂:Ce³⁺, the redistribution of Ce³⁺ in the system also takes place,; however, it occurs not between Y₃Al₅O₁₂:Ce³⁺ and Lu₂O₃, but between the newly formed, additional phases Y_{3-x}Lu_xAl₅O₁₂ and/or Lu₃Al₅O₁₂ (see Fig. 3), in which the luminescence of Ce³⁺ ion is good. In this case, owing to the change in the matrix composition, the maximum of Ce³⁺ luminescence becomes shifted toward the long-wave region, which is really observed in the case of Lu₃Al₅O₁₂:Ce³⁺. Therefore, this scenario can be considered as one of the reasons for such a different influence of Lu₂O₃ on the spectral-luminescence properties of Y₃Al₅O₁₂:Ce³⁺/Lu₂O₃ and Lu₃Al₅O₁₂:Ce³⁺/Lu₂O₃.

Note that, while considering the optical properties of luminescent systems on the basis of the garnet-Lu₂O₃ system, it is necessary to consider the role of the processes of cerium ion diffusion from the initial garnet phase in the formation of new phases, in which the ion-activator can be in the optically active or inactive state. In addition, their optical properties depend substantially on the concentration of an ion-activator in the garnet matrix.

4. Conclusions

Here, the structural aspect of the formation of optical properties in complex oxide systems Y₃Al₅O₁₂:Ce³⁺/Lu₂O₃ and Lu₃Al₅O₁₂:Ce³⁺/Lu₂O₃ obtained with the help of the colloid-chemical method is analyzed. It is found that a stable defect structure is

formed in the oxygen sublattice of the examined luminophors, which is confirmed by the changes in their structural parameters after the introduction of lutetium oxide. The luminophor $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ demonstrates a substantial increase of the luminescence intensity, as the Lu_2O_3 concentration increases. At the same time, a luminescence intensity reduction was observed for $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ under the same conditions. In our opinion, this difference can be explained by the redistribution of cerium ions between the phases that are formed in the course of synthesis and in which Ce^{3+} ions either can emit (this is $Y_{3-x}Lu_xAl_5O_{12}$ in the case of $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$), which gives a contribution to the total luminescence spectrum, or can be in a non-emitting state (Lu_2O_3 in the case of $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$), which is experimentally observed as luminescence quenching.

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НЕЙТРОННІ ТА ОПТИЧНІ ДОСЛІДЖЕННЯ
БАГАТОКОМПОНЕНТНИХ КРИСТАЛІЧНИХ
ЛЮМІНОФОРІВ $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$
ТА $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$

Резюме

Особливості кристалічної структури і спектрально-люмінесцентні властивості складних оксидних систем $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ і $Lu_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$ досліджені методами дифракції нейтронів та оптичної спектроскопії. Обговорено вплив введеного оксиду на структурні і люмінесцентні властивості цих систем, який носить складний характер, і залежить не тільки від формування стійкої дефектної структури граната та дифузії іонів Ce^{3+} з матриці в оксид, а й від взаємодії оксиду з матрицею, що відбувається з утворенням нових фаз.