ELECTRON SPECTRA OF Me₇Eu₂UO₂(PO₄)₅ CRYSTALS

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Absorption and luminescence spectra of Me₇Eu₂UO₂(PO₄)₅ crystals (Me represents Na, Rb, or Cs) are investigated. It is established that the luminescence of Eu³⁺ ions in these crystals is sensitized by uranyl. The effect of the outer-sphere cation Me⁺ on the spectroscopic properties and structural features of the compounds under study is considered.

Key words: spectrum, crystal, uranyl, europium, energy transfer.

Sensitization of the luminescence of rare-earth ions (REIs) in highly concentrated materials opens up fresh opportunities for spectral matching of luminophors and laser media and increasing lasing efficiency. Of particular interest is the use as a donor of uranyl complexes with high absorption coefficients in which the lower excited state is above the levels of the excited states of trivalent REIs involved in luminescent and laser transitions.

The luminescence of trivalent REIs in condensed media sensitized by the uranyl UO₂²⁺ was investigated earlier [1-24]. It was noted that even with an extremely high concentration of active ions the quantum efficiency of the transfer of electron-excitation energy from UO₂²⁺ to Ln³⁺ in crystal phosphate matrixes attains practically 100%. Very high efficiencies of REI sensitization by uranyl (∼90%) are obtained for glasses.

Since the maximum rate of the transfer of electron-excitation energy is attained (all other things being equal) for the minimum "donor-acceptor" distance, which is ensured by the minimum possible length of the ligand molecule, it is appropriate to consider orthosystems among phosphate materials. We planned possible structures in terms of dynamic crystal chemistry [25, 26] under the assumption of isolation of the uranyl and lanthanide coordination polyhedrons. What was implied was that the coordination saturation of active ions is attained in the presence of at least 4 ligands in UO₂²⁺ and 8 ligands in Ln³⁺. Phosphorus was considered as the third coordination center, with a coordination number (c.n.) of 4. The condition of the division of the vertices in the coordination polyhedrons leads to orthophosphate skeletons of the type

\[ \text{[Ln}_{m_1}\text{(UO}_2)_m\text{P}_{m_2}\text{O}_{m_3}]_{m_1}^{Z} \],

whose parameters are related in the following manner:

\[ m_0 = m_1 \left( \frac{p_{11}}{a_1} + \frac{p_{13}}{2} \right) + 2m_2 + m_3 \left( \frac{p_{31}}{2} + \frac{p_{32}}{2} + \frac{p_{33}}{a_3} \right), \]

\[ Z = m_1 \left[ 3 - 2 \left( \frac{p_{11}}{a_1} + \frac{p_{13}}{2} \right) \right] - 2m_2 - m_3 \left[ 5 - 2 \left( \frac{p_{31}}{2} + \frac{p_{32}}{2} + \frac{p_{33}}{a_3} \right) \right], \]

\[ m_1 \left( \frac{p_{11}}{a_1} + \frac{p_{13}}{2} \right) + 2m_2 + m_3 \left( \frac{p_{31}}{2} + \frac{p_{32}}{2} \right) = 4m_3. \]
where $m_i$ is the number of the $i$-type complexing agents, while $p_{ij}$ is the $j$-vertex of its polyhedron,

$$
\sum_j p_{ij} = p_i
$$

($p_i$ is the number of the vertices of the $i$th complexing agent's polyhedron); $Z$ is the total charge compensated by the corresponding number of the outer-sphere cations. Allowance for the concentration dependence of the energy-transfer efficiency on the ratio of the components in glasses showed that, from the viewpoint of the efficiency of donor-acceptor interaction, the optimum ratio $U:Ln = 1:2$. This enabled us to propose the formula $\text{Me}_7\text{Eu}_2\text{UO}_2(\text{PO}_4)_5$ for crystals of triple orthophosphates produced by solid-phase synthesis in a $\text{Me}_7\text{Eu}_2\text{UO}_2(\text{PO}_4)_5$ series with different outer-sphere cations ($\text{Me}$ represents Na, Rb, and Cs).

Absorption spectra for the crystals investigated are satisfactorily described in the model of additive chromophores — $\text{Eu}^{3+}$ and $\text{UO}_2^{2+}$ ions, while the excitation spectra in the region above 21,000 cm$^{-1}$ recorded in the lines of $\text{Eu}^{3+}$ and $\text{UO}_2^{2+}$ luminescence coincide and correspond to the absorption of the uranyl chromophore (Fig. 1). The intensity of $\text{Lu}^{3+}$ luminescence exceeds by two orders of magnitude the intensity of $\text{UO}_2^{2+}$ luminescence. Furthermore, the quantum yield of $\text{Eu}^{3+}$-ion luminescence is higher by two orders of magnitude than in uranyl-free analogs. All this shows that, as in the systems studied earlier [1-24], the luminescence of $\text{Eu}^{3+}$ in the $\text{Me}_7\text{Eu}_2\text{UO}_2(\text{PO}_4)_5$ crystals is sensitized by uranyl.

The luminescence spectra for uranyl in the $\text{Me}_7\text{Eu}_2\text{UO}_2(\text{PO}_4)_5$ crystals are similar to a considerable degree to the spectra in $\text{Cs}_4\text{Eu}_2\text{UO}_2(\text{P}_2\text{O}_7)_3$ [14, 16, 22, and 24] (Fig. 2). However they differ significantly from the luminescence spectra of the corresponding crystal uranyl phosphates by higher diffusion and are similar to the luminescence spectra of uranyl-phosphate glasses and glasses coactivated simultaneously by $\text{UO}_2^{2+}$ and $\text{Ln}^{3+}$ ions. The spectra themselves are represented by a line of pure electronic transition and its vibrational repetitions with the frequency of fully symmetric stretching vibrations of the uranyl ion $\nu_s(\text{O-U=O})$. Other frequencies of the vibrations of the uranyl complex in the luminescence spectra are not found. The half-widths of the spectral lines of $\text{UO}_2^{2+}$ luminescence lie in the range of 250-400 cm$^{-1}$. The Stokes parameters are $\sim 1.3$. This, as the spectral diffusion mentioned, points to a rather significant interaction of the uranyl ion with the phosphate matrix.