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CRYSTAL-CHEMICAL REGULARITIES IN THE FORMATION OF SPECTROMETRIC SCINTILLATORS BASED ON ALKALI-HALIDE CRYSTALS

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Among alkali-halide phosphors, only a few single crystals are used in scintillation counters owing to their unique properties. Scintillators make it possible to carry out efficient counting of high-energy particles and photons and to estimate their energy from the amplitude of fluorescence pulses. Under optimal conditions of application they do not store the light sum (S), which distinguishes them fundamentally from other typical phosphors. The conversion efficiency of scintillators does not depend on the energy of the ionizing particles, since the number of excited luminescence centers in each pulse changes in proportion to it. With increasing excitation power (from a monochromatic source), the amplitude of the scintillations remains constant; correspondingly, the number of fluorescence flashes per unit time increases. The maximum loading of the counter is determined only by the fluorescence decay time constant (τ).

In analyzing the structural model of scintillators and the mechanism of their excitation, two concepts are being developed. According to one of them (see, for example, ([1,2])), the luminescence center is created by an activator substituting cations in the host lattice. During scintillation these centers are excited by excitons or at the expense of the energy of recombination of electrons with ionized centers. Excitation by excitons, however, does not ensure the high scintillation yield achieved in practice ([2]), while recombination processes in alkali-halide crystals are inertial and are accompanied by large losses. To reconcile this with experiment it is assumed ([3]) that, upon excitation of scintillators, S is stored owing to the capture of electrons by the activator in the host lattice. Its subsequent emission increases the luminescence yield but does not lengthen τ, since the trap levels in these crystals are thermally rather unstable. To improve the quality of scintillators, a uniform distribution of activator ions in the host lattice is recommended ([2]).

Fig. 1. Epitaxial inclusion of TlJ in NaJ. A—nets (110) of the spatial lattice of NaJ; —distorted elementary cell of α-TlJ; —two-dimensional inclusion of a net (100) of α-TlJ between two nets (110) of NaJ; —quasimolecule of the first type; —quasimolecule of the second type

Figure 1: Fig. 1. Epitaxial inclusion of TlJ in NaJ. A—nets (110) of the spatial lattice of NaJ; —distorted elementary cell of α-TlJ; —two-dimensional inclusion of a net (100) of α-TlJ between two nets (110) of NaJ; —quasimolecule of the first type; —quasimolecule of the second type

These hypotheses, however, contradict the experiments. If the fluorescence yield depended on realization of the light sum, the pulse amplitude would vary with the excitation dose, and this would lead to loss by scintillators of the characteristic properties of spectrometers. The scintillation excitation time should be estimated from the rise of the luminescence pulses, and not from the emission time τ. The usual scheme of recombination luminescence does not make it possible to explain the high efficiency of energy transfer from the lattice to the luminescence centers in a time shorter than 10^{-7} sec, taking into account that the optimal activator concentration is small, while the length of elementary displacements of charge carriers (especially holes) is much less than the average distance between activator ions.

As follows from works ([4,5]), the creation in a crystal of electron–hole pairs (under excitation by light with $h\nu$ sufficient for the formation of charge carriers, or in the region of photon multiplication) does not lead to scintillations, since in the stationary regime phosphorescence predominates. Po-

therefore scintillators can be used only in counters of high-energy excitations. With decreasing energy, beginning at about 100 keV, the fluorescence yield falls sharply ([6,7]); at the same time the inertial component increases. The latter becomes stronger with increasing frequency of the excitation pulses. Evidently, in scintillators some other mechanism of excitation of luminescence is operating, unlike that in all other phosphors with recombination emission.

According to the second concept (see, for example, ([8])), scintillators are characterized by a fine substructure. It arises owing to two-dimensional epitaxial inclusions of the activator along certain planes of the host lattice, with the formation of anomalous mixed crystals. Here the activator creates the deepest electron-trapping levels ([9]). This was used to decorate the fine substructure by the method of additive coloration ([10]) and made it possible to observe it with an electron microscope ([11]). With increasing activator concentration, the distance between periodic inclusions decreases to a limiting value of the order of 0.5—1.0 μ.

Fig. 1. Epitaxial inclusion of TlJ in NaJ. **A** —nets (110) of the spatial lattice of NaJ; —distorted elementary cell of α-TlJ; —two-dimensional inclusion of a net (100) of α-TlJ between two nets (110) of NaJ; —quasimolecule of the first

type; —quasimolecule of the second type.

Activator impurities localized in the form of periodic inclusions can be excited and luminesce at the expense of the energy of electron–hole pairs and excitons delivered into the region of the fine substructure by ionizing particles. The latter, in moving through the crystal, create along the track a cascade of electron–hole pairs and excitons. An increase in the scintillation yield is promoted by near-defect excitons (odexes), which arise near periodic activator inclusions. In contrast to ordinary anionic excitons, less energy is required for the formation of odexes. They can move only along the fine substructure and efficiently excite the luminescence centers present there*.

In scintillators, the activator ions in the host lattice must not create deep levels for trapping charge carriers and be excited by the recombination mechanism. Therefore, in growing spectrometric scintillators one should not seek to increase the concentration of activator in the host lattice and to distribute it uniformly in the crystal according to the type of isomorphous substitution. This conclusion is also confirmed by the fact that the light yield of scintillations does not depend on the activator dosage—

* The formation of near-defect excitons is confirmed by studies of the excitation spectrum of the scintillator CsJ—Na. Here additional excitation bands appear, $\lambda_{max} = 274$ and $299\,m\mu$ ($\Delta E = 0.38$ eV). They are equidistant from the doublet in the absorption spectrum of CsJ (206 and $219\,m\mu$), which corresponds to the formation in the CsJ lattice of anionic excitons.

of the activator when it is added in excess of the necessary minimum ([12,13]), or when an impurity with good solubility in the host lattice is introduced ([14]).

To clarify the conditions for the formation of periodic activator intergrowths, their orientation in the single crystal, and the structure of the centers formed here, we present a crystal-chemical analysis of the regularities in the distribution of impurity centers during the growth of scintillators. NaI—TlI. The lattice parameter of NaI is $a = 6.462$ Å. TlI is known in three modifications: 1) rhombic α-TlI with unit-cell parameters 5.24; 4.57 and 12.92 Å; 2) cubic β-TlI with a CsCl-type structure with $a = 4.20$ Å; and 3) cubic with a NaCl-type structure with $a = 6.94$ Å. The volumes of the unit cells of NaI and TlI with the NaCl-type structure differ by 24%. Therefore the solubility of TlI in NaI is small. However, in the NaI—TlI system the formation of anomalous mixed crystals is favored by periodic two-dimensional intergrowths of α-TlI with flat (100) nets on the (110) face of NaI. In NaI, along the c axis, two loops of the (110) net have the parameters: $4.568 \times 6.462 \times 2 = 59.04$ Å^2, coinciding with the parameters of the elementary (100) face of α-TlI, $4.57 \times 12.92 = 59.04$ Å^2. In the region of epitaxial intergrowths, Tl^+ ions form two types of complexes with anions: surrounded by 9 iodine ions at the vertices of a hexahedron and at the center of one of its faces, and also surrounded by 3 anions (Fig. 1). These centers create deep electron-capture levels, as well as effective traps for excitons.

Fig. 2. Epitaxial intergrowth of α-TlI in CsJ.

Fig. 2

Figure 2: Fig. 2

A —unit cell of α-TlI; —nets (011) of the spatial lattice of CsJ; —two-dimensional intergrowth of the (100) net of α-TlI between two (011) nets of CsJ; —quasi-molecule of the first type; —quasi-molecule of the second type

Let us emphasize that when a NaI–TlI single crystal is grown from the melt, a finely dispersed TlI phase does not arise, since crystallization is carried out at $T \approx 650^{\circ}$, whereas TlI already melts at 440°. Phase inclusions may appear in crystals with a high concentration of activator only during subsequent cooling or annealing. Then a supersaturated solid solution arises, from which excess impurities migrate into the region of the nearest intergrowths and transform them into three-dimensional inclusions. CsJ–TlJ. In this system the solubility of the activator in the host lattice is low, since the volumes of the unit cells of the components (in the CsCl-type structure) differ by 22%. As in NaJ–TlJ, two-dimensional epitaxial intergrowths of α-TlJ arise here on the $(0\bar{1}1)$ faces of CsJ. The elementary loops of the (011) nets in CsJ have the parameters $4.5667 \times 6.457 \times 2 = 58.97$ Å^2, while for α-TlJ along (100) they are $4.57 \times 12.92 = 59.04$ Å^2. The difference is only 0.12%. A thin substructure is created. In the region of the intergrowths, two types of association of Tl^+ ions with anions arise: surrounded by 9 and by 3 iodine ions (Fig. 2). CsJ–NaJ. The CsJ–Na scintillator is synthesized with additions of the activator in the form of NaJ. In this system the activating impurity is sparingly soluble in the host lattice, since the molar volume of NaJ ($Fm3m$) is 28.7% smaller than that of CsJ ($Pm3m$). Epitaxial intergrowths of NaJ in CsJ arise along (100) nets, rotated relative to one another by 45° (Fig. 3). Their equivalent param-

are, respectively, equal to: $a^2 = (6.462)^2 = 41.76$ Å^2 and $2a^2 = 2(4.5667)^2 = 41.71$ Å^2. The difference is 0.12%. In the region of periodic two-dimensional intergrowths, the Na^+ ions are surrounded by six anions at the center of a tetragonal dipyramid (Fig. 3), whose fourth-order axis is oriented along one of the $3L_4$ axes of the CsJ lattice.

Na^+ ions in CsJ–Na are not an activator in the usual sense of the term, since they cannot be excited by the energy of anion excitons or electron-hole pairs ([15]). Luminescence in this scintillator apparently arises through the annihilation of excitons on quasi-complexes existing in the region of the fine substructure.

Crystallochemical analysis of scintillators makes it possible to carry out a rational selection of new objects. As an example, let us give the parameters of the scintillator NaJ–Eu. It is formed when the activator is added in the form of $EuCl_2$. The latter has a rhombic structure of the $PbCl_2$ type with unit-cell parameters equal to 8.914, 7.50, and 4.493 Å. Epitaxial intergrowths of $EuCl_2$ may be realized by (010) nets on (100) nets of NaJ ($Fm3m$). The areas of the elementary meshes, rotated relative to one another by 45°, are: for (100) in NaJ,

Fig. 3. Epitaxial intergrowth of NaJ in CsJ. A —two-dimensional intergrowth of the (100) net of NaJ in the CsJ lattice; —projection of the (100) nets of CsJ and NaJ onto the plane; —quasi-molecule; Na+ at the center of a tetragonal dipyramid of iodine ions

Figure 3: Fig. 3. Epitaxial intergrowth of NaJ in CsJ. A —two-dimensional intergrowth of the (100) net of NaJ in the CsJ lattice; —projection of the (100) nets of CsJ and NaJ onto the plane; —quasi-molecule; Na+ at the center of a tetragonal dipyramid of iodine ions

$a^2 = 41.76$ Å^2, and for (010) in $EuCl_2$, $a \times c = 8.914 \times 4.493 = 40.05$ Å^2. The difference in area is 1.7%, and in linear dimensions 2.44 and 1.64%.

Fig. 3. Epitaxial intergrowth of NaJ in CsJ. **A** —two-dimensional intergrowth of the (100) net of NaJ in the CsJ lattice; —projection of the (100) nets of CsJ and NaJ onto the plane; —quasi-molecule; Na^+ at the center of a tetragonal dipyramid of iodine ions.

The solubility of $EuCl_2$ in NaJ is small, since the components differ in stoichiometry, lattice parameters and structure, and also in ionic radii.

The scintillator NaJ—Eu luminesces at 445 mμ. The half-width of the band at room temperature is ∼ 24 mμ. The decay time of the scintillation pulses is characteristic of intracenter luminescence of excited Eu^{2+} ions ($\tau_0 \approx 10^{-6}$ sec). Under x-ray or γ-excitation, no long component is observed. The samples obtained give good amplitude resolution of γ-scintillations.

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Note: Figure translations are in progress. See original paper for figures.