

**SYNTHESIS AND  
OPTICAL PROPERTIES  
OF  $\mathrm{YAIO}_3$   
CRYSTALS ACTIVATED  
BY  
 $\mathrm{Nd}^{3+}$   
IONS**

PHYSICS

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Fig. 1 and Fig. 2: spectra

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## Abstract

## Full Text

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## PHYSICS

# Kh. S. BAGDASAROV, A. A. KAMINSKII, G. I. ROGOV SYNTHESIS AND OPTICAL PROPERTIES OF $\text{YAlO}_3$ CRYSTALS ACTIVATED BY $\text{Nd}^{3+}$ IONS

(Presented by Academician A. V. Shubnikov on 28 XI 1968)

It is known <sup>(1)</sup> that in the  $\text{Y}_2\text{O}_3$ — $\text{Al}_2\text{O}_3$  system, besides the stable phase  $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$  ( $\text{Y}_3\text{Al}_5\text{O}_{12}$ ), there are two more stable compounds:  $\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  and  $2\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ , whose physical properties have practically not been studied. Of special interest among them is yttrium aluminate  $\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  ( $\text{YAlO}_3$ ), with a perovskite structure, stable in a very narrow temperature interval of 1875–1835° C. As our studies have shown, the synthesis of sufficiently large yttrium aluminate crystals is quite possible, since, unlike the phase  $2\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ , this compound has no polymorphic transitions down to room temperature.

**Fig. 1.** Absorption spectra at 300° K, corresponding to the transition  $^4I_{9/2} \rightarrow ^2P_{1/2}$ , of  $\text{Y}_3\text{Al}_5\text{O}_{12}$  crystals (a) and  $\text{YAlO}_3$  crystals (b) activated by  $\text{Nd}^{3+}$  ions.

**Fig. 2.** Luminescence spectra, corresponding to the transition  $^4F_{3/2} \rightarrow ^4I_{11/2}$ , of  $\text{YAlO}_3$  crystals at 300° K (a),  $\text{YAlO}_3$  at 77° K (b), and  $\text{Y}_3\text{Al}_5\text{O}_{12}$  at 300° K (c), activated by  $\text{Nd}^{3+}$  ions.

In contrast to garnet crystals  $\text{Y}_3\text{Al}_5\text{O}_{12}$  with rare-earth ions ( $\text{TR}^{3+}$ ), which are one of the principal materials for quantum electronics,  $\text{YAlO}_3$  crystals must possess certain distinctive features. Since the symmetry of yttrium aluminate is lower than the symmetry of  $\text{Y}_3\text{Al}_5\text{O}_{12}$  crystals, it should be expected that, under isomorphous substitution of  $\text{Y}^{3+}$  ions by  $\text{TR}^{3+}$  ions, the latter will enter mainly one type of optical centers, the optical properties of which will differ by large values of the probabilities of electronic transitions.

The incorporation coefficient of impurity  $\text{TR}^{3+}$  ions and of the iron group is considerably higher than in garnet and is close to unity. This circumstance makes it possible to grow crystals with a high activator concentration. At the same time, the lower melting point of this substance (1865°), compared with garnet

Figure 3. Schemes of the crystal-field splitting of the terms  ${}^2P_{1/2}$ ,  ${}^4F_{3/2}$ ,  ${}^4I_{11/2}$ , and  ${}^4I_{9/2}$  of  $\text{Nd}^{3+}$  ions in  $\text{YAlO}_3$  and  $\text{Y}_3\text{Al}_5\text{O}_{12}$  crystals at 77 and 300°K. The positions of the levels are indicated in  $\text{cm}^{-1}$ , and the transitions between them in Å.

Figure 2: Figure 3. Schemes of the crystal-field splitting of the terms  ${}^2P_{1/2}$ ,  ${}^4F_{3/2}$ ,  ${}^4I_{11/2}$ , and  ${}^4I_{9/2}$  of  $\text{Nd}^{3+}$  ions in  $\text{YAlO}_3$  and  $\text{Y}_3\text{Al}_5\text{O}_{12}$  crystals at 77 and 300°K. The positions of the levels are indicated in  $\text{cm}^{-1}$ , and the transitions between them in Å.

(1930°), simplifies the synthesis conditions. In this connection, the preparation of  $\text{YAlO}_3$  crystals activated by  $\text{TR}^{3+}$  is of unquestionable interest.

In this communication we present preliminary results of a study of some spectroscopic properties of  $\text{YAlO}_3$  crystals activated by  $\text{Nd}^{3+}$  ions, which were synthesized from the melt by a method developed at the Institute of Crystallography of the USSR Academy of Sciences. For the experiments, use was made—

**Fig. 3.** Schemes of the crystal-field splitting of the terms  ${}^2P_{1/2}$ ,  ${}^4F_{3/2}$ ,  ${}^4I_{11/2}$ , and  ${}^4I_{9/2}$  of  $\text{Nd}^{3+}$  ions in  $\text{YAlO}_3$  and  $\text{Y}_3\text{Al}_5\text{O}_{12}$  crystals at 77 and 300°K. The positions of the levels are indicated in  $\text{cm}^{-1}$ , and the transitions between them in Å.

single crystals of  $\text{YAlO}_3\text{—Nd}^{3+}$  of good optical quality with dimensions  $12 \times 8 \times 6$  mm were formed. The concentration of the active impurity was 1.5 and 3 wt.%. Identification of the obtained specimens by X-ray structural analysis showed that they consist entirely of the  $\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  phase.

The experimental technique used to study the spectroscopic characteristics of  $\text{YAlO}_3\text{—Nd}^{3+}$  crystals did not differ in any way from that described in work (2). Figure 1 shows the absorption spectra of  $\text{YAlO}_3\text{—Nd}^{3+}$  crystals and, for comparison,  $\text{Y}_3\text{Al}_5\text{O}_{12}\text{—Nd}^{3+}$ , corresponding to the transition  ${}^4I_{9/2} \rightarrow {}^2P_{1/2}$ , obtained at 300° K; Fig. 2 shows their luminescence spectra associated with transitions between the terms  ${}^4F_{3/2}$  and  ${}^4I_{11/2}$ . As can be seen, the spectral properties of these crystals differ substantially. Thus, the splitting of the term  ${}^4F_{3/2}$  at 77° K in  $\text{Y}_3\text{Al}_5\text{O}_{12}\text{—Nd}^{3+}$  crystals is  $\sim 84 \text{ cm}^{-1}$ , whereas for yttrium aluminate with  $\text{Nd}^{3+}$  ions it is  $129 \text{ cm}^{-1}$ . For a more detailed comparison, Fig. 3 gives schemes of the crystal-field splitting of the terms  ${}^2P_{1/2}$ ,  ${}^4F_{3/2}$ ,  ${}^4I_{11/2}$ , and  ${}^4I_{9/2}$  of these compounds. It is evident that the splitting of the term  ${}^4I_{9/2}$  in the  $\text{YAlO}_3\text{—Nd}^{3+}$  crystal is considerably smaller and has a different character (it is also seen that in the garnet the fifth Stark component,  $859 \text{ cm}^{-1}$ , of the term  ${}^4I_{9/2}$ , and the two upper levels, 2463 and  $2517 \text{ cm}^{-1}$ , of the term  ${}^4I_{11/2}$ , are significantly removed from the others).

Spectroscopic studies also showed that at concentrations of  $\text{Nd}^{3+}$  ions of  $\sim 3$  wt.% the spectra of yttrium aluminate crystals are characterized primarily by

one type of optical center. The accuracy of the measurements was  $\pm 3 \text{ cm}^{-1}$ .

The results of our spectroscopic studies of  $\text{YAlO}_3$  crystals and their comparison with analogous data for garnet crystals indicate that yttrium aluminate can be used as an active medium in optical quantum generators, and induced emission should be expected on one (or several) of three lines: 10640, 10723, and 10795 Å (transition  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ ). It should also be noted here that, for rapid analysis of the synthesized phases in the  $\text{Y}_2\text{O}_3\text{—Al}_2\text{O}_3$  system, as our experiments have shown, the method of studying absorption or luminescence spectra can be successfully applied, since the X-ray structural characteristics, in particular of the phases  $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ , differ little from one another <sup>(1)</sup>.

Measurement of the lifetime of the excited state ( ${}^4F_{3/2}$ ) of  $\text{Nd}^{3+}$  ions (3.0 wt.%) in  $\text{YAlO}_3$  crystals gave a value of  $\tau_{\text{em}}$  at 65° K of about 300 μsec.

In conclusion, we express our gratitude to G. A. Bogomolova and V. N. Shpakov for their participation in the spectroscopic measurements, and to B. P. Sobolev for carrying out the X-ray structural analysis.

*Proof note.* We have recently obtained induced emission from an optical quantum generator with  $\text{YAlO}_3\text{—Nd}^{3+}$  crystals (1.5 and 3 wt.%) both at 77° K and at 300° K. At room temperature the optical quantum generator emits on the line 1097 Å with an excitation threshold below 0.5 J, and at 77° K on the line of 10725 Å.

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