

Spectroscopic Properties of Nd³⁺ Ion in TbAlO₃ Single Crystals

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Growth of terbium aluminate single crystals and investigation of Nd³⁺ ion spectroscopic properties in them are described. Detailed investigation of absorption and luminescence spectra of Nd³⁺ ions in TbAlO₃ at T = 77 and 300°K permits obtainment of a complete diagram of the Stark components energy. The spectral-structural regularities of Nd³⁺ ions in orthoaluminate monocrystals are analyzed. The dependence on interionic distance of the position of the center of gravity of the ground terms of Nd³⁺ ion along with the nephelauxetic shift of ⁴F_{3/2} term of Nd³⁺ ion is investigated.

1. Introduction

Single crystals of rare-earth (RE) aluminates have recently become prospective materials for solid-state lasers (1-4). In this connection mixed systems are of particular interest, e.g. based on crystals with composition $A'_x A''_{1-x} B'_y B''_{1-y} O_3$ where A = RE ions, B = Al, Sc, Ga, etc. (8). However, in order to understand the processes of formation of activator centres one has to know how the spectroscopic properties of these centers vary depending on interatomic distances in these centers, while the symmetry remains practically unaltered. From this point of view, most fruitful and promising is the investigation of the behavior of the same activator ion in single crystals of compounds that form a "homologous" row. A number of convincing and important results obtained in this way during investigations of garnet structures (5-7), conditioned the tasks of the present paper, in which we intend to obtain information about spectral-structural properties of Nd³⁺ activator ion in single crystals with pervoskite structure.

It has been mentioned (1-4) that up to date the investigations of Nd³⁺ ions have been performed for yttrium, gadolinium, lutetium and lanthanum aluminates (1-4).

The purpose of the present paper is to describe the synthesis of new single crystals of terbium aluminates doped with neodymium ions, followed by a spectroscopic investigation of its properties and by an investigation of main laws governing the neodymium ion's behavior in single crystals of rare-earth aluminates.

During the working process single crystals of DyAlO₃ doped with neodymium ions were for the first time synthesized and optically examined. Some of these spectroscopic studies, required for analysis of spectral-structural properties of Nd³⁺ activator ion in single crystals of rare-earth aluminates, are described in this paper.

2. Experimental Procedure

The aluminate of the trivalent ion of Tb has the orthorhombic distortion of the ideal pervoskite structure found in GdFeO₃. This crystal belongs to space group $D_{2h}^{16}-Pb_{mn}$

with fair distorted perovskite units in the crystallographic cell (14–15). The results of X-ray examination showed that the values of lattice constants for single crystals of TbAlO_3 were: $a = 5.2317 \text{ \AA}$, $b = 5.3097 \text{ \AA}$, $c = 7.4196 \text{ \AA}$ (15).

The single crystals of terbium aluminate were grown by optical zone melting (OZM) in air (9, 10). The original materials were taken in the form Tb_2O_3 , Al_2O_3 and Nd_2O_3 with 99 999 wt% purity in an amount corresponding to composition $\text{Tb}_{0.97} \text{Nd}_{0.03} \text{AlO}_3$. After a thorough mixing, the charge was subjected to pressing. The seeds were preliminary roasted in air at 1250°C for 15–20 hr. The growth of TbAlO_3 single crystals was carried out at the rate of 4 mm/hr. After completion of the growth, the crystals appeared to contain a large number of F-centers, considerably in excess over that in YAlO_3 and GdAlO_3 crystals (11).

The investigation of the spectroscopic properties of Nd^{3+} ion in TbAlO_3 single

crystals was performed on a spectrometer DFS-12 and SF-8 at 300 and 77°K in the waverange 300 to 2500 nm. The specimens investigated were plates with $3 \times 10 \times 2$ mm size.

3. Results

The overall absorption spectrum observed at 300 K is shown on Fig. 1. At the considered concentrations the absorption bands of Nd^{3+} ions are rather intensive. A superposition of a group of lines is observed in the range of 450 to 500 nm, associated with the transitions $^4I_{9/2} \rightarrow ^4G_{9/2}$ and $^4I_{9/2} \rightarrow ^2D_{3/2}$ for Nd^{3+} ion and $^7F_6 \rightarrow ^5D_4$ for Tb^{3+} ion. This gives an opportunity to consider the interaction of the ionic pair $\text{Nd}^{3+} \leftrightarrow \text{Tb}^{3+}$ from the viewpoint of excitation transmission.

The absorption spectra of Nd^{3+} ion corresponding to transitions $^4I_{9/2} \rightarrow ^2P_{1/2}$ and $^4I_{9/2} \rightarrow ^4F_{3/2}$ at $T = 77 \text{ K}$ are shown in Fig. 2.

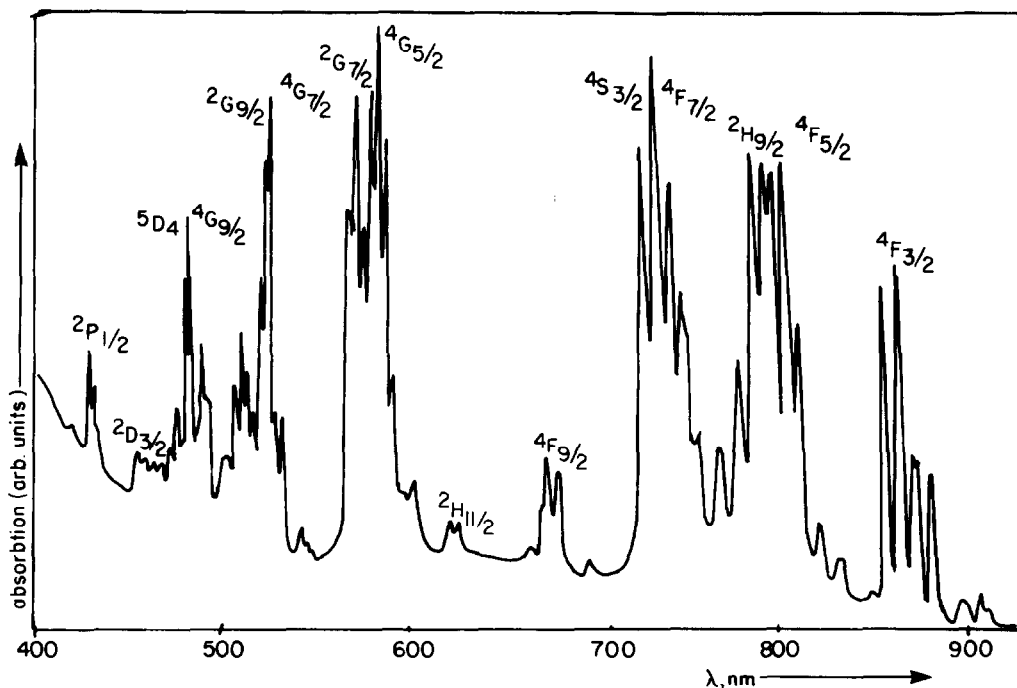


FIG. 1. Overall absorption of Nd^{3+} ion in TbAlO_3 single-crystals at $T = 300^\circ\text{K}$.

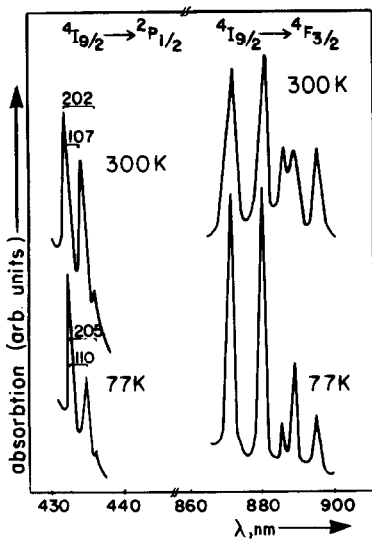


FIG. 2. Absorption spectra of Nd^{3+} ions in TbAlO_3 single-crystals corresponding to transitions ${}^4I_{9/2} \rightarrow {}^2P_{1/2}$ and ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$ at $T = 77$ and 300 K.

The analysis of these transitions permitted a precise determination of the Stark components of Nd^{3+} ion's ground state ${}^4I_{9/2}$. The splitting of the three lowest energy levels is equal to $0.110, 205 \text{ cm}^{-1}$ at 77 K and $0.107, 202 \text{ cm}^{-1}$ at 300 K. The splitting of term ${}^4F_{3/2}$ was determined as well at $T = 77$ K and 300 K, and it turned out to be equal to 122 cm^{-1} and 119 cm^{-1} , respectively.

We investigated also the luminescence of Nd^{3+} ions in TbAlO_3 , corresponding to transitions from level ${}^4F_{3/2}$ to levels ${}^4I_{9/2}$ and ${}^4I_{11/2}$ at 77 K (Fig. 3). The transition ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ was the most intensive one (1060 nm). The luminescent analysis confirms the results on splitting obtained from absorption spectra for state ${}^4F_{3/2}$ (122 cm^{-1}). A detailed analysis of the absorption and luminescence spectra permitted the determination of positions of energy levels for the terms of Nd^{3+} ions in TbAlO_3 (see Table 1).

4. Discussion

Experiments (16, 17) present detailed theoretical analysis of crystalline field (CF) in

crystals YAlO_3 doped with thulium and erbium ions. This paper also gives analysis of main properties of CF in crystals TbAlO_3 , doped with neodymium ions, and of certain spectral-structural regularity of Nd^{3+} ion's behavior in rare-earth aluminates row.

Comparing the splitting of the term ${}^4F_{3/2}$ for Nd^{3+} ion (ΔE) at 77 K in crystal of our own growth. $\text{TbAlO}_3:\text{Nd}^{3+}$ ($\Delta E = 122 \text{ cm}^{-1}$), $\text{EuAlO}_3:\text{Nd}^{3+}$ ($\Delta E = 110 \text{ cm}^{-1}$), $\text{DyAlO}_3:\text{Nd}^{3+}$ ($\Delta E = 124 \text{ cm}^{-1}$)—with that in crystals $\text{YAlO}_3:\text{Nd}^{3+}$ ($E = 129 \text{ cm}^{-1}$) (12), $\text{GdAlO}_3:\text{Nd}^{3+}$ ($\Delta E = 116 \text{ cm}^{-1}$) (2), and $\text{LuAlO}_3:\text{Nd}^{3+}$ ($\Delta E = 131 \text{ cm}^{-1}$) (3), one can conclude that the local symmetry of surroundings changes insignificantly on replacing the rare-earth ion in the matrix by a Nd^{3+} ion. A change in the splitting ($\Delta E = 23 \text{ cm}^{-1}$) from that for the above mentioned crystals is observed only for $\text{LaAlO}_3:\text{Nd}^{3+}$ single crystals (4). The dependence $E_{{}^4F_{3/2}} = J(R_{\text{RE}}/R_{\text{Nd}})$ is shown in Fig. 4a where R_{RE} and R_{Nd} are the effective ionic radii of the RE matrix ion and neodymium ion respectively: the values of effective ionic radii are obtained from (12) at eight-fold coordination.

It is well known that the splitting magnitude (ΔE) of the state ${}^4F_{3/2}$ can serve as measure of the deviation of the CF symmetry from cubic. At $R_{\text{RE}} < R_{\text{Nd}}$ (see Fig. 1) the structure of rare-earth aluminates, the study of which is described in this paper, is orthorhombic (14). In this case, upon increase in R_{RE} we observe monotonic decrease in non-cubic component of CF, reaching the least value in EuAlO_3 . Values of splitting term ${}^4F_{3/2}$ in TbAlO_3 and DyAlO_3 are close to similar value in YAlO_3 which confirms an insignificant difference of non-cubic components of CF in these crystals. The sharp decrease in the splitting magnitude $\Delta E_{{}^4F_{3/2}}$ for $R_{\text{RE}} > R_{\text{Nd}}$ corresponds to the structural transition from orthorhombic to rhombohedral (14). The splitting of the ${}^4F_{3/2}$ level of Nd^{3+} must decrease drastically in LaAlO_3 (point symmetry: D_3) which is nearly cubic since this splitting depends only

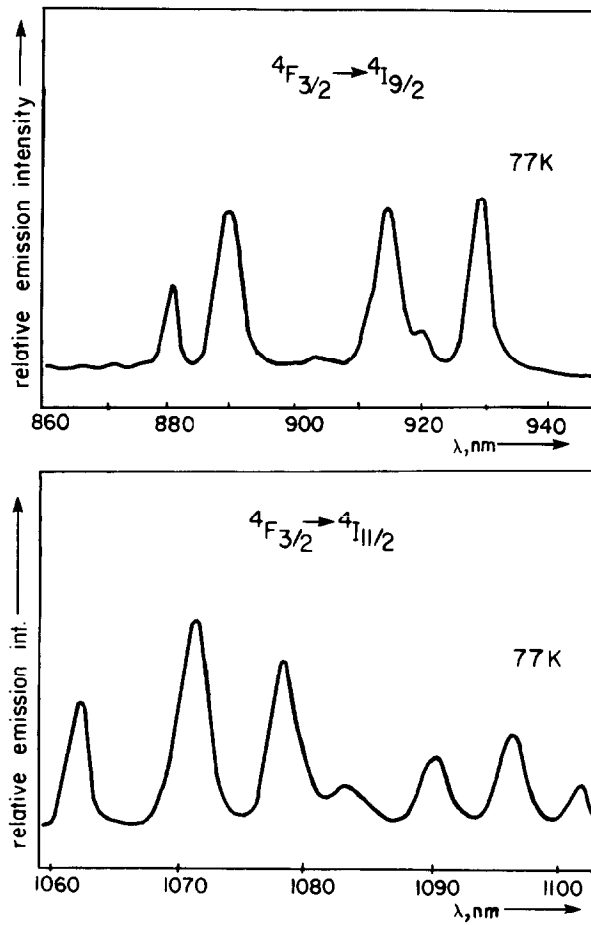


FIG. 3. Luminescence spectra of Nd^{3+} ions in TbAlO_3 corresponding to transitions ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ at $T = 77\text{ K}$.

TABLE I
THE VALUES OF STARK COMPONENTS ENERGY FOR Nd^{3+} ION IN TbAlO_3 AT 77°K

Terms	Energy levels of Nd^{3+} ion in TbAlO_3 at 77 K (cm^{-1})	ΔE (cm^{-1})
${}^4I_{9/2}$	0, 110, 205, 510, 669	669
${}^4I_{11/2}$	2027, 2106, 2164, 2269, 2320, 2371	344
${}^4I_{15/2}$	5731, 5790, 6127 ^a , 6152, 6254, 6309 ^a , 6402, 6766	1035 ^a
${}^4F_{3/2}$	11565, 11443	122
${}^4F_{5/2}, {}^2H_{9/2}$	12310, 12425, 12459, 12527, 12572, 12601, 12723, 12894	584
${}^4F_{7/2}, {}^4S_{3/2}$	13337, 13459, 13572, 13594, 13609, 13661	324
${}^4F_{9/2}$	14945, 14817, 14771, 14749, 14704	241
${}^2H_{11/2}$	15898, 15924, 15949, 16000, 16026, 16129	231
${}^2G_{7/2}, {}^4G_{5/2}$	16878, 16998, 17036, 17129, 17316, 17385, 17467	589
${}^4G_{7/2}, {}^2G_{9/2}$	18875, 18929, 18997, 19099, 19238, 19327, 19361, 19440, 19550	675
${}^4G_{9/2}, {}^2D_{3/2}$	20747, 20877, 20921, 20986, 21053, 21106	239
${}^2P_{1/2}$	23175	

^a Energy levels and ΔE -values require more accurate definition.

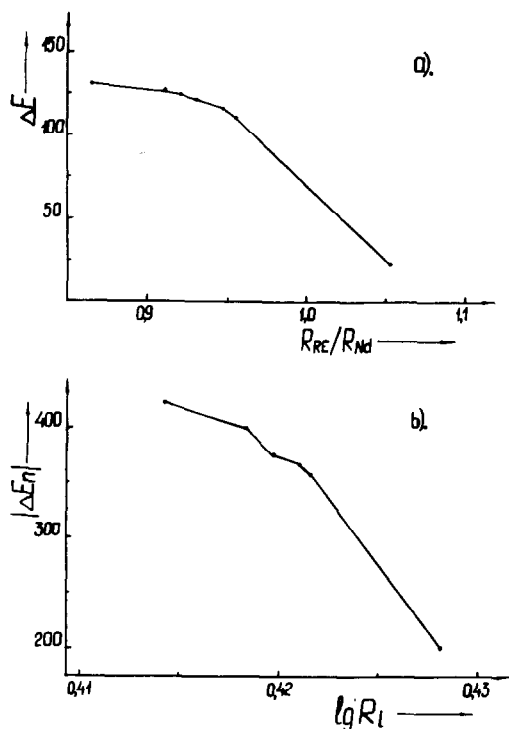


FIG. 4. Variation of Nd³⁺ term's position at 77 K in the group of orthoaluminates: (a) dependence of the splitting of the term ⁴F_{3/2} for Nd³⁺ ion (ΔE) on the effective ionic radius of the RE ion of the matrix; (b) dependence of nepheloxetic shift (ΔE_n) of the term ⁴F_{3/2} for Nd³⁺ on interionic distance R_i .

on the B_0^2 parameter, which falls to zero in a cubic symmetry. It explains the sharp decrease in the value $\Delta E_{F_{3/2}}$ in LaAlO₃ in Fig. 1.

Distance between centers of gravity of terms ⁴F_{3/2} and ⁴I_{9/2} of Nd³⁺ ion in

TbAlO₃, equal to 11205.2 cm⁻¹, is bigger than corresponding distances in YAlO₃ (11191 cm⁻¹) and LuAlO₃ (11157 cm⁻¹). Thus, nephelauxetic shift (ΔE_H) of the terms ⁴F_{3/2} (in relation to its place in aquo-ion—11580 cm⁻¹) is lesser in case of TbAlO₃ (-374.8 cm⁻¹), which means that connection of activator-nearby anions in this matrix is less covalent (13). For crystals EuAlO₃ + Nd³⁺ value ΔE_H of the terms ⁴F_{3/2} in the observed row of orthorhombic aluminates is the minimum (see Table No. 2).

Insignificant value ΔE_H of the terms ⁴F_{3/2} of Nd³⁺ ion in LaAlO₃ shows that for rhombohedral aluminates the activator-nearby anions connection is considerably less covalent as compared to aluminates of orthorhombic structure. Change in ΔE_H of the term ⁴F_{3/2} of Nd³⁺ ion in row of rare-earth aluminates depending upon the distance between ions-R_i (anion-cation distance) is shown in Fig. 4b.

Splitting of terms of ⁴I_{9/2} and ⁴I_{11/2}, contrary to splitting of term ⁴F_{3/2}, besides B_0^2 , depends also on parameters B_0^4 ; B_0^6 ; B_2^4 ; B_2^6 ; B_4^4 ; B_4^6 ; B_6^6 , which maintain values different from zero at symmetry O_h. In orthorhombic aluminates under observation the values of energies of gravity centers of Nd³⁺ ion's levels in relation to lower Stark's level of each term ⁴I_j (j = 9/2 : 11/2) with increase in R_i are monotonically decreased. For rhombohedral LaAlO₃ a sharp decrease in values of center gravity energies of terms ⁴I_j (see Fig. 5) has been observed.

TABLE II
POSITION OF ENERGIES OF GRAVITY CENTERS OF TERMS (ΔE g.c.) AND NEPHELOXETIC SHIFT (ΔE_n) OF TERM ⁴F_{3/2} OF Nd³⁺ ION AT 77 K IN ROW OF ORTHOALUMINATES

Term	Matrix	LuAlO ₃	YAlO ₃	TbAlO ₃	GdAlO ₃	EuAlO ₃	LaAlO ₃
ΔE g.c. (cm ⁻¹)	⁴ I _{9/2}	301.0	300.2	298.8	294.5	294.0	216.6
	⁴ I _{11/2}	185.5	184.2	182.5	180.7	—	138.2 ^a
	⁴ F _{3/2}	66.5	64.5	61.0	58.0	55.0	11.5
ΔE_n (cm ⁻¹)		-423.0	-394.7	-374.8	-367.5	-358.0	-202.1

Energy of centers of gravity of terms 4I_j is expressed as under:

$$\Delta E_{g.c.} = A'_{A_1} \cdot B_0 \cdot C_0,$$

where $B_0 : C_0 = \text{const}$,

$$A'_{A_1} = \text{central symmetric component of CF}(A'_{A_1} \sim 1/R_i)$$

The angle of inclination of the straight lines in Fig. 5, contrary to the theoretically calculated value, which is one unit, equals -1.2 . It shows that actual value of central symmetric component of CF in orthorhombic aluminates differs from theoretical value.

5. Summary

Thus, the results of the performed investigation are as follows:

1. New single-crystals of TbAlO_3 , EuAlO_3 , DyAlO_3 , doped with neodymium ions, have been synthesized.

2. A spectroscopic investigation of these crystals has been carried out; diagrams of Nd^{3+} energy levels in TbAlO_3 single-crystals have been constructed.

3. The variation of Nd^{3+} ion's main spectroscopic properties along the row of rare-earth orthoaluminates is examined.

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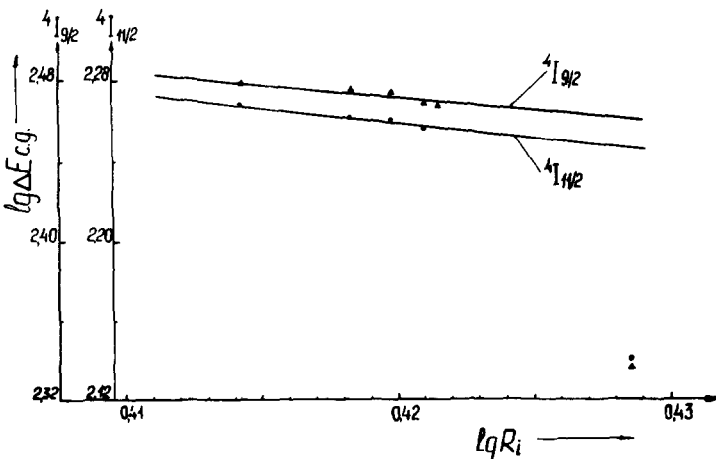


FIG. 5. Dependence of positions of center of gravity for the terms ${}^4I_{9/2}$ and ${}^4I_{11/2}$ for Nd^{3+} at 77 K in the group of orthoaluminate single-crystals: on interionic distance R_i .

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