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OPTICAL PROPERTIES

Luminescence of Yttrium Aluminum Borate Single Crystals Doped with Manganese

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Abstract—The optical absorption and luminescence spectra of single crystals of yttrium aluminum borate $YAl_3(BO_3)_4$ doped with manganese ions are measured. It is established that the optical absorption spectra of yttrium aluminum borate single crystals doped with manganese ions are determined primarily by the contribution from the Mn^{4+} ions. The luminescence spectra of the $YAl_3(BO_3)_4$ single crystals doped with manganese exhibit narrow lines attributed to the Mn^{4+} ions and an extended multiband structure which is associated primarily with the contribution from the Mn^{2+} ions.

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1. INTRODUCTION

Luminescence of impurity crystals doped with manganese ions in various valence states has been extensively investigated. In the luminescence spectra of these crystals, the Mn^{2+} and Mn^{3+} ions each exhibit a single luminescence line associated with the $^4T_1$ and $^5T_2$ states, respectively. In the case of Mn^{2+} ions, this luminescence line can be observed either in the orange region or in the green region of the spectrum, depending on the crystal field [1]. Even with the excitation initiated under ultraviolet radiation through higher lying states, there can occur luminescence from the $^4T_1$ state. This phenomenon can be explained by radiationless relaxation of the aforementioned states toward the lowest lying excited state. The probability of relaxation in this case appears to be higher than the probability of spin-forbidden radiative transitions to the ground state. Luminescence of Mn^{2+} ions with the manifestation of two lines was observed only in $(Sr,Ba)F_2 : Mn^{2+}$ crystals by Diaz et al. [2]; however, in the authors' opinion, this specific luminescence can be explained by the presence of the $MnBaF_4$ impurity phase in the sample [3]. A complex structure of Mn^{2+} luminescence in willemite and β-cristobalite was noted by Sviridov et al. [1, p. 184]; however, no explanation for such a complex structure was offered by those authors. Unlike the manganese ions in the aforementioned valence states, the Mn^{4+} ions can have the spectrum of luminescence from the ^2E state in the form of two narrow lines in the red spectral region [4], which is similar to the luminescence spectrum of trivalent chromium ions isoelectronic with Mn^{4+}.

In this paper, we consider luminescence of trigonal single crystals of manganese-doped yttrium aluminum borate $YAl_3(BO_3)_4$: Mn (YAB : Mn), which were grown using the solution–melt method. Crystals of yttrium aluminum borate with a huntite structure have been intensively investigated in recent years, because these materials are very promising for use as matrices for rare-earth ions, especially for neodymium and ytterbium ions, and, moreover, have found wide applications in optoelectronics [5]. Rare-earth ions isovalently substitute for yttrium ions in the crystal lattice of huntites. At present, the properties of single crystals of the $YAl_3(BO_3)_4$ borate and its homologues doped with manganese ions are poorly understood [6, 7]. The results obtained have demonstrated that manganese ions are embedded in the crystal lattice of huntites in an unusual manner. In particular, Vorotynov et al. [7] studied single crystals of the manganese-doped yttrium aluminum borate with the use of electron paramagnetic resonance spectroscopy and revealed the valence state Mn^{2+}.

2. SAMPLE SYNTHESIS AND DESCRIPTION OF THE CRYSTAL STRUCTURE

Trigonal single crystals of the $YAl_3(BO_3)_4$: Mn compound were grown by the solution–melt method from the $Bi_2Mo_3O_{12}$–Li_2MoO_4–B_2O_3 solution melt on seeds in a regime with decreasing temperature. The growth temperature could be change in the range from 950 to 850°C by varying the composition of the initial solution melt. At the stage of dissolution, the temperature did not exceed 1000°C. The growth rates of crystals varied from 0.3 to 0.5 mm per day, which was

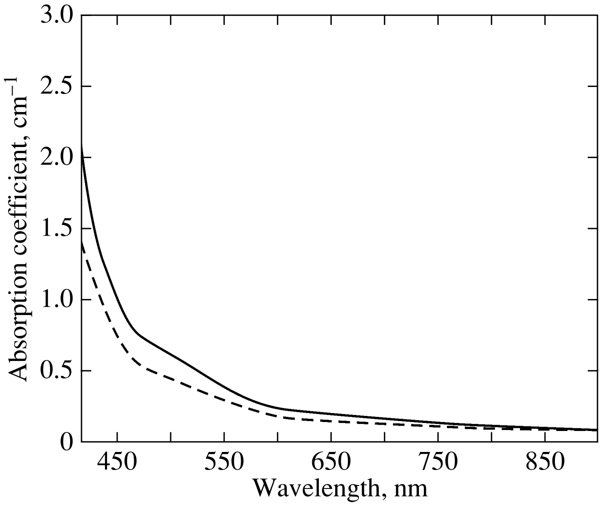

Fig. 1. Optical absorption spectra of the YAB : (Mn,Si) (solid line) and YAB : (Mn,Si,Zr) (dashed line) single crystals.

achieved by properly choosing the initial supercooling, the decrease in the temperature, and the hydrodynamic regime. Manganese sesquioxide Mn_2O_3 (up to 25% in terms of atomic percent with respect to aluminum) was added to the melt. Moreover, we synthesized samples from the initial solution melt but with an addition of zirconium dioxide and silicon dioxide in order to examine the possibility of controlling the valence of manganese ions through the formation of charge-compensating defects and the variation in their concentration.

In the crystals of the $YAl_3(BO_3)_4$ compound with a huntite structure (space group $R32$), the AlO_6 octahedra form helical chains extended along the threefold axis. The unit cell parameters of the $YAl_3(BO_3)_4$ crystal in the hexagonal setting are as follows: $a = 9.295$ Å and $c = 7.243$ Å. Slightly distorted trigonal prisms YO_6 are arranged between the chains of AlO_6 octahedra in such a way that each of these prisms links three helical chains of AlO_6 octahedra through common oxygen atoms. The distance between the yttrium ion and its nearest neighbor aluminum ion exceeds only insignificantly (by a factor of ~1.2) the distance between the nearest neighbor aluminum cations involved in the helical chain. Taking into account these structural features of the $YAl_3(BO_3)_4$ compound and the ionic radii of yttrium, aluminum, and manganese atoms (see [8, p. 26]), it can be expected that manganese ions in the valence state 4+ (the effective ionic radius $r = 0.54$ Å) can substitute for the aluminum ions ($r = 0.53$ Å) in the AlO_6 octahedra, whereas the Mn^{2+} ions ($r = 0.83$ Å) and the Mn^{3+} ions ($r = 0.65$ Å) can substitute for the yttrium ions ($r = 1.03$ Å) in the YO_6 trigonal prisms. Moreover, the zirconium ions Zr^{4+} ($r = 0.72$ Å) can be embedded in the crystal lattice instead of the yttrium ions, whereas the silicon ions Si^{4+} ($r = 0.40$ Å) can substitute for the aluminum ions.

The chemical composition of the grown crystals was determined on a Bruker S4 Pioneer x-ray fluorescence spectrometer with the use of a simplified technique without recourse to conventional reference substances (standards). According to the results obtained, the total concentration of manganese ions in all valence states amounts to approximately 1 at % per formula unit. The total concentrations of silicon and zirconium ions are equal to approximately 2.0 and approximately 0.1 at % per formula unit, respectively. Moreover, the x-ray fluorescence analysis revealed the presence of bismuth (for the Bi^{3+} ions surrounded by six oxygen ions, the effective ionic radius $r = 1.02$ Å) at a concentration of higher than 1% in the sample, which is explained by the fact that bismuth enters into the composition of the solvent. Other components of the solvent were not revealed.

3. EXPERIMENTAL TECHNIQUE, RESULTS, AND DISCUSSION

The optical absorption spectra of the grown single crystals of the $YAl_3(BO_3)_4$ compound doped with manganese ions were recorded on a Kontron UVIKON 943 spectrophotometer with a resolution of up to 0.3 nm. Figure 1 shows the optical absorption spectra of the YAB : Mn single crystals grown from fluxes of different compositions. It can be seen from Fig. 1 that the optical absorption spectra in the ultraviolet region exhibit an intense absorption band with the wing partially covering the visible spectral range. Another absorption band is observed on the slope of the intense absorption band in the wavelength range 460–570 nm, which can be assigned either to the transition to the $^4T_2$ state of the Mn^{4+} ion in the octahedral environment at the crystal field parameter $Dq = 1890$ cm^{-1} or to the transition to the $^5T_2$ state of the Mn^{3+} ion (with the same value of the crystal field parameter Dq). It is worth noting that, in Fig. 1, the optical absorption spectrum as a whole more closely resembles the optical absorption spectrum of Mn^{4+} ions in oxide crystals [4], in which the aforementioned intense ultraviolet band is attributed to the charge-transfer transition. The charge-transfer transitions of Mn^{3+} ions in oxide crystals are usually observed in the wavelength range near 300 nm [9, 10] and have no effect on the formation of the absorption spectrum in the visible spectral range. If the Mn^{2+} ions were present in the crystal lattice of the compound under investigation, the spin-forbidden absorption lines associated with these ions would not be seen in the optical absorption spectrum because of their lower intensity as compared to the intensity of the absorption lines attributed to manganese ions in other valence states. Therefore, we can draw the conclusion that the optical absorption spectrum of the single crystals of the $YAl_3(BO_3)_4$ compound doped with manganese ions is completely determined by the contribution from the Mn^{4+} ions. The observed difference in the optical absorption spectra of the YAB : Mn single crystals suggests that the concentration of Mn^{4+} ions slightly decreases when zirconium ions are embedded in the crystal. Judging from the optical absorption spectra of the YAB : Mn single crystals, the Mn^{4+} concentration in this case decreases by 25%, whereas the ratio of the concentration of zirconium ions to the total concentration of manganese ions is equal to 10%. It should be noted that, since the zirconium ions cannot substitute for the Mn^{4+} ions in the AlO_6 octahedra, the absorption coefficient does not necessarily linearly decrease with an increase in the concentration of zirconium ions. The mechanism of variation in the concentration of Mn^{4+} ions has a more complex nature and is associated with the presence of noticeable amounts of zirconium ions in the solution melt.

Figure 2 depicts the luminescence spectra of the YAB : Mn single crystals upon excitation with an argon laser at a wavelength of 514.5 nm in the absorption band of the transition of the Mn^{4+} ion to the $^4T_2$ state. It can be seen from this figure that the luminescence spectra have a complex multiband structure in the wavelength range 515–710 nm and a structure consisting of narrow peaks in the range 680–687 nm, including at least three components with maxima at wavelengths of 682, 684, and 686 nm. The latter components are characteristic of luminescence of Mn^{4+} ions in the ^2E state. It should be noted that the positions of these features correspond to those calculated in the framework of the Tanabe–Sugano diagram for the crystal field parameter Dq = 1890 cm^{-1} and the absorption coefficient B = 755 cm^{-1}. These values are in agreement with the corresponding quantities obtained for the Mn^{4+} ions in the $Gd_3Ga_5O_{12}$ crystal [4], as well as with the crystal field parameter Dq evaluated above from the optical absorption spectrum of the YAB : Mn single crystal. Thus, it has been established that the YAB : Mn single crystals under consideration contain the Mn^{4+} ions which substitute for the aluminum ions in the crystal structure. However, the mechanism of compensation for an excess charge of these ions remains unclear because no chemical elements that would inherently reside in the valence state 2+ have been identified in the crystal. Consequently, we believe that, in this situation, the most probable scenario is the formation of charge-compensating ion pairs Mn^{4+}/Mn^{2+} (Fig. 3). In this case, the manganese concentration of the order of 1 at % per formula unit, most likely, can be considered to be a limiting concentration, because an increase in the concentration of manganese ions in the melt does not lead to an increase in the manganese content in the crystal. However, some part of the divalent manganese ions can enter into the composition of charge-compensating defects with silicon or zirconium.

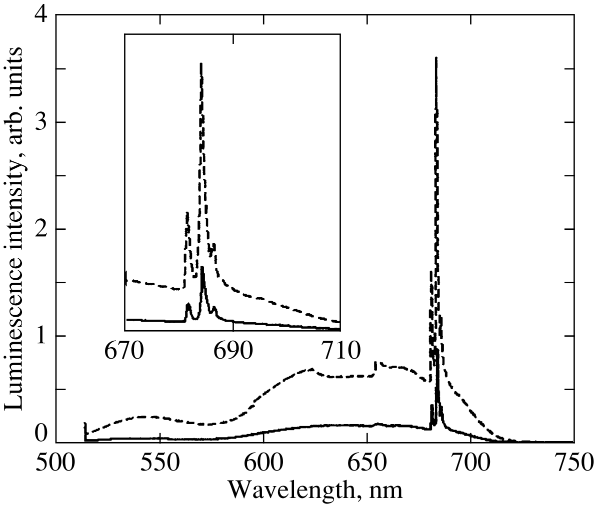

Fig. 2. Overall luminescence spectra of the YAB : Mn single crystals upon excitation with an argon laser at a wavelength of 514.5 nm. Exciting radiation is polarized either in the plane perpendicular to the C_3 axis (dashed line) or in the plane parallel to the C_3 axis (solid line).

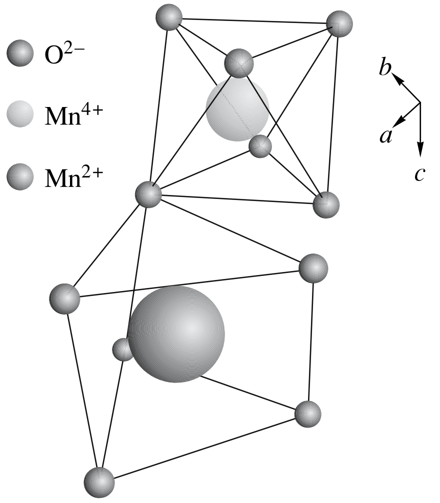

Fig. 3. Relative positions of Mn^{2+} and Mn^{4+} ions in the crystal lattice of the yttrium aluminum borate.

Figure 4 shows in greater detail the luminescence bands of the YAB : Mn single crystals upon excitation with an argon laser at a wavelength of 514.5 nm. It can be seen from this figure that the luminescence spectrum contains at least three different broad bands with maxima at wavelengths of 544, 637, and 670 nm. The luminescence observed at a wavelength of 700 nm can be treated as a phonon wing of narrow lines associated with the Mn^{4+} ions. Moreover, the luminescence spectrum also contains at least two components with maxima at wavelengths of 624 and 656 nm. The broad

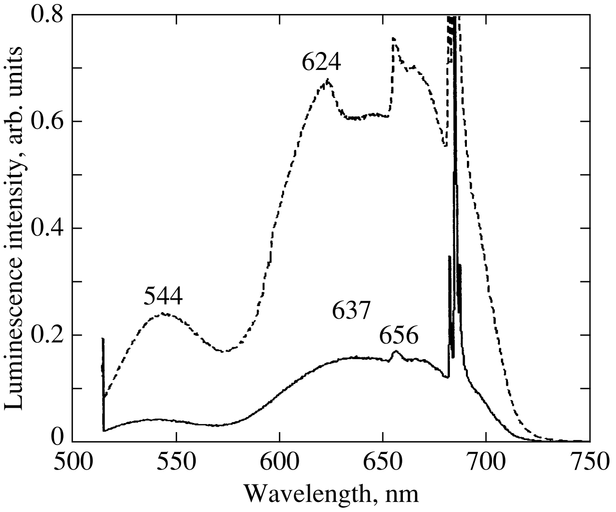

Fig. 4. Polarized luminescence spectra of the YAB : Mn single crystal upon excitation with an argon laser at a wavelength of 514.5 nm. Exciting radiation is polarized either in the plane perpendicular to the C_3 axis (dashed line) or in the plane parallel to the C_3 axis (solid line). The luminescence is polarized perpendicular to the C_3 axis.

bands observed in the luminescence spectrum depicted in Fig. 2 could be assigned to the Mn^{2+} ions located in the tetrahedral (544 nm) and octahedral (637 nm) environments. However, according to the x-ray diffraction data, the YAB : Mn single crystal under investigation has the symmetry space group $R32$ and its structure does not include tetrahedral positions that can be occupied by manganese ions. The implantation of Mn^{2+} ions into the octahedral positions is unlikely because of the considerable difference between the radii of the Mn^{2+} ions and the aluminum ions. The luminescence band observed at a wavelength of 637 nm could be attributed to the luminescence of the Mn^{3+} ions in the $^5T_2$ state. However, as follows from the analysis of the optical absorption spectra, the concentration of trivalent manganese ions in the crystal should be substantially lower than the concentration of Mn^{4+} ions. Therefore, the most probable origin of this band is the luminescence from the $^4T_1$ state of the Mn^{2+} ions. The excitation of these ions most likely occurs through energy transfer upon absorption of exciting radiation by the Mn^{4+} ions.

At the same time, it is evident that the compensation for the charge of divalent manganese ions requires the formation of a pair of ions Mn^{2+}/R^{4+} (where R = Mn or Si) in the crystal lattice, which should be located in the nearest neighbor positions of the Y^{3+} and Al^{3+} ions separated by a distance of approximately 3.6 Å (Fig. 3). In this situation, there arises a low-symmetry component of the crystal field that should lead to a splitting of the $^4T_1$ state of the Mn^{2+} ion into several states. In the simplest case, when the trigonal component of the low-symmetry crystal field is predominant, it can be expected that the splitting of the $^4T_1$ state of the Mn^{2+} ion into two states, namely, the $^4A_1$ and ^4E states, will be observed in the luminescence spectrum. In our opinion, the observed peaks at wavelengths of 544 and 637 nm can be approximately described as a luminescence from the aforementioned two states. The large magnitude of the splitting (approximately 2700 cm^{-1}) can be explained by the fact that the Mn^{2+} ions have a large deficiency of the effective ionic radius as compared to the effective ionic radii of the ions substituted for by them in the crystal lattice. As a result, the former ions should be substantially shifted from their equilibrium positions in the oxygen environment and, consequently, the low-symmetry component of the crystal field should be enhanced. In this case, the luminescence from the $^4A_1$ state within the unit cell should be completely polarized in the direction perpendicular to the axis of the trigonal component of the low-symmetry crystal field. In actual fact, the polarizations of almost all components in the observed luminescence spectrum are incomplete (with the degree of polarization in the range from 0.05 to 0.40). This circumstance is associated with the averaging of the polarization over the six possible positions of the axis connecting the Mn^{2+} and Mn^{4+} (or Si^{4+}) ions with respect to the crystallographic axes. The completely polarized radiation is observed in a relatively narrow line with a maximum at a wavelength of 624 nm. The appearance of additional (including relatively narrow) spectral features is caused by the crystal-field components of even lower symmetry.

4. CONCLUSIONS

Thus, it has been established that the optical absorption spectra of single crystals of yttrium aluminum borate $YAl_3(BO_3)_4$ doped with manganese ions are determined primarily by the contribution from the Mn^{4+} ions. The luminescence spectra of the $YAl_3(BO_3)_4$ single crystals doped with manganese exhibit narrow lines attributed to the Mn^{4+} ions and an extended multiband structure which should be assigned to the Mn^{2+} ions. A strong splitting of the luminescence line associated with the $^4T_1$ state of the Mn^{2+} ion in the single crystals of yttrium aluminum borate doped with manganese is accounted for by the appearance of low-symmetry components of the crystal field upon the formation of Mn^{2+}/Mn^{4+} (Si^{4+}) ion pairs.

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