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Photoluminescence studies of Mn⁴⁺ ions in YAlO₃ crystals at ambient and high pressure

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Abstract

Detailed investigations of the photoluminescence properties of Mn⁴⁺ (3d³) ions in YAlO₃ have been performed in the temperature range 10–600 K. The luminescence of Mn⁴⁺ ions due to the ²E → ⁴A₂ transition consists of two zero-phonon lines (*R* lines) at 691.3 and 692.7 nm, which became visible only at low temperature, and their vibronic sidebands that cover the range of 660–740 nm. The thermal quenching of the luminescence intensity due to the non-radiative decay occurs at temperatures above 420 K. The temperature dependence of the luminescence decay time shows a quasi-linear decrease from $\tau = 4.9$ to 1.6 ms in the temperature range from 90 to 420 K (with a temperature coefficient -0.01 ms K^{-1}) that makes YAlO₃:Mn a potentially good phosphor for a fibre optic fluorescence thermometer in this temperature range. The high-pressure low-temperature luminescence measurements in a diamond-anvil cell reveal similar pressure coefficients for Mn⁴⁺ and Cr³⁺ dopant ions in YAlO₃, equal to $1.16 \text{ cm}^{-1} \text{ kbar}^{-1}$ and $1.08 \text{ cm}^{-1} \text{ kbar}^{-1}$, respectively.

1. Introduction

The Mn⁴⁺ ions (3d³) in a crystalline host, as well as the Cr³⁺ ions with the same electronic structure, are of interest as an active lasing centre or as a luminescence co-activator for rare-earth ions. Therefore spectroscopic properties of the Mn⁴⁺ ions have been intensively studied in many crystals, mainly in ruby (Al₂O₃) and garnet (Y₃Al₅O₁₂, Gd₃Ga₅O₁₂, Ca₃Ga₂Ge₃O₁₂, etc) crystals [1–6]. Besides, Cr-doped crystals such as ruby and spinel (MgAl₂O₄) have been studied from the point of view of optical sensor applications, in particular, the fibre optic thermometry based on the temperature dependence of photoluminescence decay time [7]. Recently it was shown that the Cr-doped YAlO₃ crystal has a high potential to be applied as a fibre optic thermometer because of the large temperature coefficient of the photoluminescence lifetime [8].

Yttrium orthoaluminate (YAlO₃—also called yttrium aluminium perovskite (YAP)) is known as an anisotropic host material for solid-state lasers as an alternative to the most widely used Y₃Al₅O₁₂. Manganese-doped YAlO₃ became of interest during recent years after its high application potential was shown for holographic recording and optical data storage [9–11] as well as for thermoluminescent dosimetry of ionizing radiation [12].

At the same time the spectroscopic properties of Mn⁴⁺ ions in YAlO₃ remain rarely studied. However, the spectroscopic studies of Mn⁴⁺ ions in YAlO₃, performed by Noginov *et al* [13], showed some interesting peculiarities. In particular, three types of Mn⁴⁺ centre with different decay times were observed. On the other hand, the luminescence measurements described in [13] did not reveal emission lines sharp enough to be attributed to zero-phonon (the *R* lines) ²E → ⁴A₂ transitions in Mn⁴⁺ ions. The detailed temperature dependence of the luminescence properties of Mn⁴⁺ ions in YAlO₃ has not been studied, nor at high pressure. This stimulated us to perform additional spectroscopic studies of Mn⁴⁺ ions in YAlO₃.

In order to obtain Mn⁴⁺ ions in garnet crystals, e.g. Y₃Al₅O₁₂, in which manganese ions incorporate mainly in the trivalent state, divalent co-dopants such as Ca²⁺ or Mg²⁺ should be used for charge compensation. In the case of YAlO₃, manganese ions can be incorporated into the crystal as Mn⁴⁺ without any co-doping. Besides the Mn⁴⁺ ions in octahedral coordination (Al³⁺ positions), manganese ions can be present in as-grown YAlO₃ crystals also as Mn²⁺ ions in dodecahedral coordination (Y³⁺ positions) [14].

The present work is devoted to the detailed investigation of photoluminescence properties of Mn⁴⁺ ions in YAlO₃ and their temperature dependences in the temperature range from 10 K to 600 K. This paper also presents the results of high-pressure low-temperature measurements on Mn⁴⁺-doped YAlO₃ crystals. These measurements could be carried out due to the smaller sensitivity of our crystals to illumination, which does not completely recharge Mn⁴⁺ dopant ions. Previous attempts to perform such experiments were unsuccessful since the measured samples of different origin [13] underwent total recharging (Mn⁴⁺ → Mn⁵⁺ + *e* ionization) [15] in a very short time under illumination by a laser light, which resulted in complete Mn⁴⁺ luminescence quenching.

2. Crystal growth and experimental techniques

Single crystals of YAlO₃ doped with manganese were grown by the Czochralski method in the Institute of Physics, Polish Academy of Sciences. The crystals were grown in a pure nitrogen atmosphere from a melt containing 4 mol% more yttrium than aluminium oxide in comparison with the stoichiometric composition. The manganese concentration in the YAlO₃:Mn crystal studied corresponds to 0.2 mol% in the melt with respect to aluminium content. An as-grown crystal as well a crystal annealed in a hydrogen flow at 1300 K for 1 h were studied in the present work.

The optical absorption spectra were measured with a Cary 5000 UV–vis–NIR spectrophotometer. The 514.5 nm line of an Ar⁺-laser or the light from a halogen lamp passing through a monochromator ($\lambda = 480$ nm) were used for optical excitation. The luminescence spectra were measured with a Jobin-Yvon Spex Triax 320 monochromator with a CCD camera. A Leybold cryogenerator with LTC60 temperature controller was used for low-temperature (10–320 K) photoluminescence measurements. A furnace equipped with a T-type thermocouple allowed photoluminescence measurements at temperatures up to 600 K. The luminescence decay kinetics were registered either at a certain wavelength or in an integral mode (broad band excitation), and were stored in a digital oscilloscope. The decay kinetics below room temperature were excited by the 514.5 nm laser line modulated by a mechanical chopper, while at elevated temperature they were excited by a spark lamp (IFSh-100/3 Russian made, 2 J in pulse, pulse duration about 10 μ s) with a proper green filter.

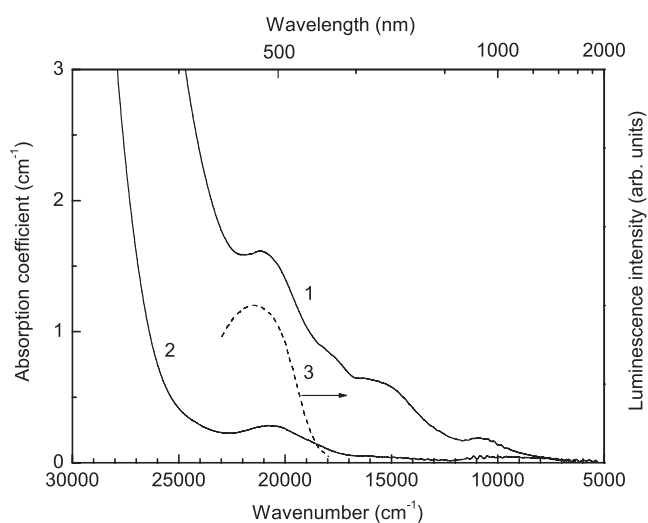


Figure 1. The room-temperature absorption spectra of the as-grown YAlO₃:Mn crystal (1) and the crystal annealed in hydrogen atmosphere (2) as well as the luminescence excitation spectrum registered near 710 nm for the as-grown crystal (3).

High-pressure measurements were performed with use of a low-temperature diamond-anvil cell (Diacell Products MCDAC-1). Argon was used as the pressure-transmitting medium. The diamond-anvil cell was mounted into an Oxford Optistat CF cryostat equipped with a temperature controller for low-temperature measurements. The polished samples of about 15 μm thicknesses were loaded into the cell along with a small piece of Nd-doped yttrium aluminium garnet (YAG) crystal, which served as a pressure sensor [16]. This pressure sensor was chosen since the strong ruby luminescence, typically used for pressure calibration, spectrally overlaps with much weaker luminescence of Mn⁴⁺-doped YAP. The changes of pressure were done at room temperature in order to minimize the effects of non-hydrostaticity. The half-widths of the ruby luminescence lines at highest applied pressures were not larger than 4 cm^{-1} (as compared with about 2 cm^{-1} at ambient pressure). This means that the non-hydrostatic effects were rather weak.

3. Experimental results and discussion

3.1. Spectroscopic properties of YAP:Mn⁴⁺ crystals at ambient pressure

The optical absorption spectra of the Mn-doped YAlO₃ crystals studied are presented in figure 1. As can be seen in the figure, besides Mn⁴⁺ ions that are responsible for the absorption band centred near 21 000 cm^{-1} (transition ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ in Mn⁴⁺ ions [13]), Mn⁵⁺ ions are present in the as-grown YAlO₃:Mn crystals and reveal themselves in absorption bands near 11 000, 15 000 and 18 000 cm^{-1} (transitions ${}^3\text{T}_1({}^3\text{F}) \rightarrow {}^3\text{T}_2({}^3\text{F})$ and ${}^3\text{T}_1({}^3\text{F}) \rightarrow {}^3\text{T}_1({}^3\text{P})$ in Mn⁵⁺ ions, in accordance with [17]). An intensive absorption above 26 000 cm^{-1} is caused by O–Mn charge transfer bands [13, 18]. The high-temperature annealing of the as-grown crystals in reducing atmosphere practically completely removes the absorption at 11 000, 15 000 and 18 000 cm^{-1} . One can suppose that such annealing reduces the amount of Mn⁵⁺ ions by means of the Mn⁵⁺ \rightarrow Mn⁴⁺ reaction that is charge compensated by the loss of oxygen from the crystal. An increase of the Mn⁴⁺ concentration in the crystal annealed in hydrogen has been confirmed by our x-ray luminescence measurements [19]. Traces of manganese ions with

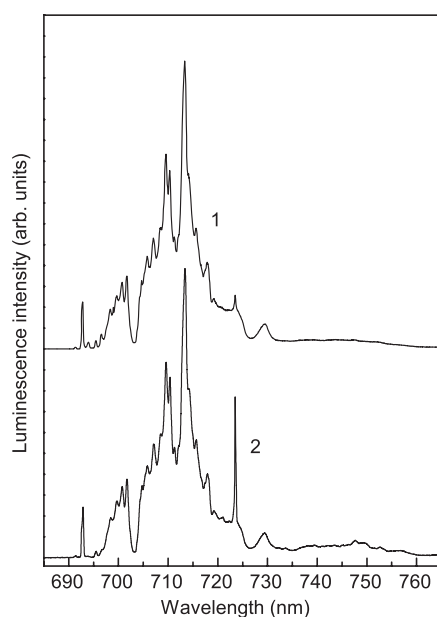


Figure 2. Luminescence spectra of the as-grown $\text{YAlO}_3:\text{Mn}$ crystal (1) and the crystal annealed in hydrogen atmosphere (2) using continuous Ar^+ -laser excitation ($\lambda = 514.5$ nm), recorded at $T = 10$ K.

various valence from Mn^{2+} to Mn^{5+} can be also present in our crystals, since they were also observed in YAlO_3 previously [20].

The low-temperature luminescence spectra of $\text{YAlO}_3:\text{Mn}$ crystals at $\lambda = 514.5$ nm laser excitation are shown in figure 2. The temperature dependence of the luminescence spectra is shown in figure 3.

The luminescence spectra of $\text{YAlO}_3:\text{Mn}$ crystals are similar to the spectra of Mn^{4+} ions in $\text{Y}_3\text{Al}_5\text{O}_{12}$ (see e.g. [2]) and are somewhat (about 40 nm) red-shifted in comparison with $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Mn}^{4+}$. The luminescence spectra of Mn^{4+} ions in YAlO_3 consist of two sharp lines peaked at 691.3 and 692.7 nm, which became discernible at the high-energy side of the spectrum at low temperature. As it will be shown later, these lines can be ascribed respectively to the R_2 and R_1 lines of the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition of Mn^{4+} ions. The broad structured band at the low-energy side of the R lines corresponds to the vibronic sidebands of the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition. The R lines are very small in comparison with their vibronic sidebands. At temperatures above 250 K the R lines disappear in a growing background of the vibronic sidebands and the anti-Stokes vibronic sidebands.

Comparing the luminescence spectra of the as-grown crystal and the crystal annealed in hydrogen, it can be seen that the spectrum shape in both cases is the same except for the sharp lines at 721.1 and 723.4 nm and the broad band at 735–760 nm, which become more pronounced in the crystal annealed in hydrogen. These lines can be ascribed to the R lines and vibronic sidebands of the Cr^{3+} ions. According to [21], the position of the R lines for the Cr^{3+} ions in YAlO_3 is 722.8 and 725.1 nm at room temperature. Apparently, the chromium ions are present in the studied crystals as an uncontrolled impurity, as was similarly observed by Noginov *et al* [13].

The rise of the Cr^{3+} lines in the crystal annealed in hydrogen denotes an increase of amount of Cr^{3+} centres in the crystal. By analogy with manganese ions it can be supposed

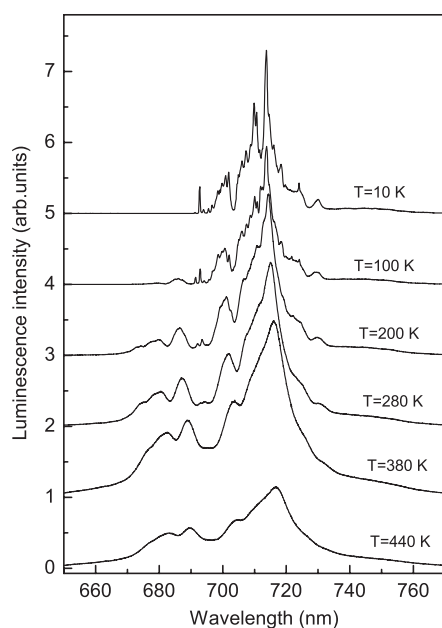


Figure 3. Temperature dependence of the luminescence spectra of the as-grown $YAlO_3:Mn$ crystal using continuous Ar^+ -laser excitation ($\lambda = 514.5$ nm).

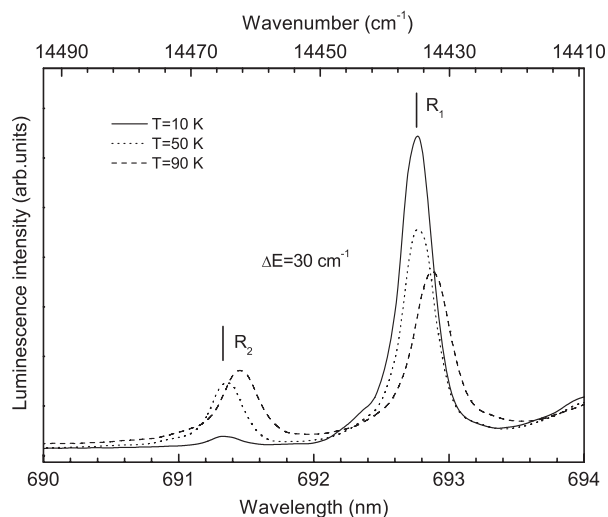


Figure 4. Luminescence spectra of Mn^{4+} ions in the region of R lines using Ar^+ -laser excitation ($\lambda = 514.5$ nm).

the $Cr^{4+} \rightarrow Cr^{3+}$ reduction process is a result of hydrogen annealing of the crystals. An increase of the amount of Cr^{3+} ions in the $YAlO_3$ crystal annealed in reducing atmosphere was also observed by the electron spin resonance (ESR) technique [22].

The detailed spectra of Mn^{4+} luminescence in the region of R lines at low temperatures are shown in figure 4. The spectral separation of these two lines is about 30 cm^{-1} . Note that such splitting of the 2E level for Mn^{4+} is about 80 cm^{-1} and 60 cm^{-1} for Al_2O_3 [1] and

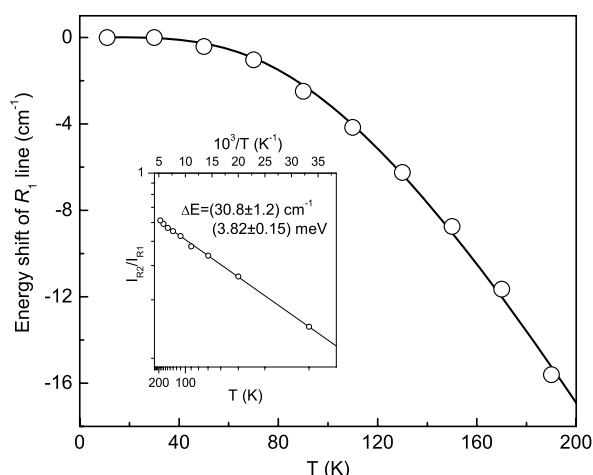


Figure 5. Temperature dependence of the R_1 line position and its theoretical approximation (see text for details). The inset shows the temperature dependence of the R_2/R_1 intensity ratio.

$\text{Y}_3\text{Al}_5\text{O}_{12}$ [2], respectively. This means that the oxygen octahedron surrounding the Mn^{4+} ions is not strongly distorted.

Figure 5 shows the temperature dependence of the R_1 line position relative to its value at 10 K. This dependence was approximated by the equation [23]

$$\varepsilon(T) = \varepsilon(0) + \alpha(T/T_D)^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx, \quad (1)$$

where $\varepsilon(0)$ is the R_1 line position (in energy units) at $T = 0$ K, T_D is the Debye temperature, and α is a coefficient. The fit of the experimental data by this equation gives the following values: $T_D = 465 \pm 15$ K, $\alpha = -309 \pm 10 \text{ cm}^{-1}$ (the theoretical curve is shown as a solid line in figure 5). The estimated value $T_D \approx 465$ K is close to the values of 540–550 K recently reported for isostructural rare-earth orthogallates (LnGaO_3 , $\text{Ln} = \text{La}, \dots, \text{Gd}$) [24].

The temperature dependence of the R lines' intensity ratio (R_2/R_1) corresponds to the Boltzmann rule with a thermal activation energy that agrees with the spectral distance between the R lines (see the inset in figure 5). This unambiguously confirms that these lines are the R lines of Mn^{4+} ions.

The figure 6 shows the temperature dependence of the Mn^{4+} luminescence intensity registered near 710 nm with lamp excitation through a monochromator ($\lambda = 480$ nm) while heating the sample above room temperature. As is seen from the figure, the luminescence intensity remains fixed at temperatures up to 420 K. After that the luminescence intensity is sharply reduced. An approximation of the intensity dependence by the equation

$$I = \frac{1}{1 + C \exp\left(\frac{-\Delta E_2}{kT}\right)}, \quad (2)$$

which describes the thermal quenching as a result of non-radiative transitions, gives an activation energy ΔE_2 of about 1.5 ± 0.1 eV ($12000 \pm 1000 \text{ cm}^{-1}$).

The luminescence decay kinetics of Mn^{4+} ions have been measured at 692.7 nm (R_1 line) as well as at a certain number of wavelengths (about 10) in the region of vibronic sidebands (695–720 nm) at temperatures from 10 to 320 K. All of them are single exponential like in figure 7(a) with $\tau = 5.1$ ms at $T = 10$ K and $\tau = 2.8$ ms at room temperature. The

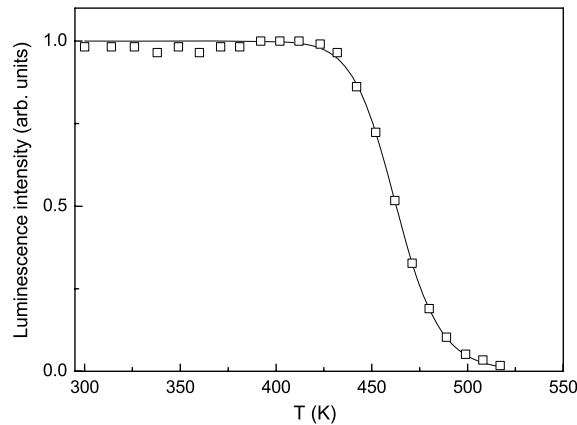


Figure 6. Temperature dependence of the luminescence intensity of the as-grown YAlO₃:Mn crystal registered near 710 nm with lamp excitation ($\lambda = 480$ nm) and its theoretical approximation (see text for details).

decay kinetics measured at 723.4 nm (R_1 line of Cr³⁺ ions) represent a two-exponential decay behaviour that is shown in figure 7(b). Besides the short component due to Mn⁴⁺ ions, the long component ($\tau \approx 50$ ms at $T = 10$ K) corresponding to Cr³⁺ ions is observed. The intensity of this component is increased in the hydrogen-annealed sample. According to [8], the lifetime of Cr³⁺ ions in YAlO₃ is 41.5 ms at room temperature, which agrees very well with our data.

The single exponential decay kinetics of Mn⁴⁺ ions indicate a single type of Mn⁴⁺ centre, unlike the results reported in [13], where three types of Mn⁴⁺ centre with different decay times (5.4; 0.54 and 0.41 ms at $T = 77$ K) were observed. It should be noted that our decay time is close to the decay time of 5.4 ms (3.0 ms at room temperature) observed in [13], which was attributed to the non-distorted octahedral Mn⁴⁺ sites.

The temperature dependence of the luminescence decay time of Mn⁴⁺ centres in YAlO₃ is shown in figure 8. As is seen from the figure, the decay time remains unchanged from its initial value $\tau = 5.1$ ms at $T = 10$ K up to 90 K. Above 90 K the decay time starts to decrease and shows a quasi-linear decrease in the temperature range between 90 to 420 K. Above 420 K, where the thermal quenching of the luminescence intensity occurs, the decay time sharply decreases.

The decay time dependence in the temperature range below 400 K was approximated by the following equation that describes the decay time shortening as a result of both the phonon-induced transitions with effective phonon energy $h\omega$ and the thermalization effect between the ²E level and the upper lying ⁴T₂ level, separated by the energy ΔE_1 [25]:

$$\tau^{-1} = \tau_0^{-1} \coth\left(\frac{h\omega}{2kT}\right) + \tau_1^{-1} \exp\left(\frac{-\Delta E_1}{kT}\right). \quad (3)$$

Here τ_0^{-1} is the initial radiative decay probability of the ²E level at $T = 0$ K, and τ_1^{-1} is the effective radiative decay probability of the ⁴T₂ \rightarrow ⁴A₂ transitions. The fit of the experimental data by this equation gives the following values: $h\omega = 0.032 \pm 0.001$ eV (257 ± 4 cm⁻¹), $\tau_0 = 5.05$ ms, $\Delta E_1 = 0.27 \pm 0.02$ eV (2140 ± 150 cm⁻¹), $\tau_1 = 3.1$ μ s.

The obtained value of ΔE_1 is commensurate with the energies of phonons (see e.g. [26]) and can be interpreted as an effective energy of phonons responsible for the decay time shortening at temperature above 90 K. A relatively small value of the separation energy, ΔE_1 , between the ²E and the ⁴T₂ levels, smaller than can be estimated from the absorption spectra,

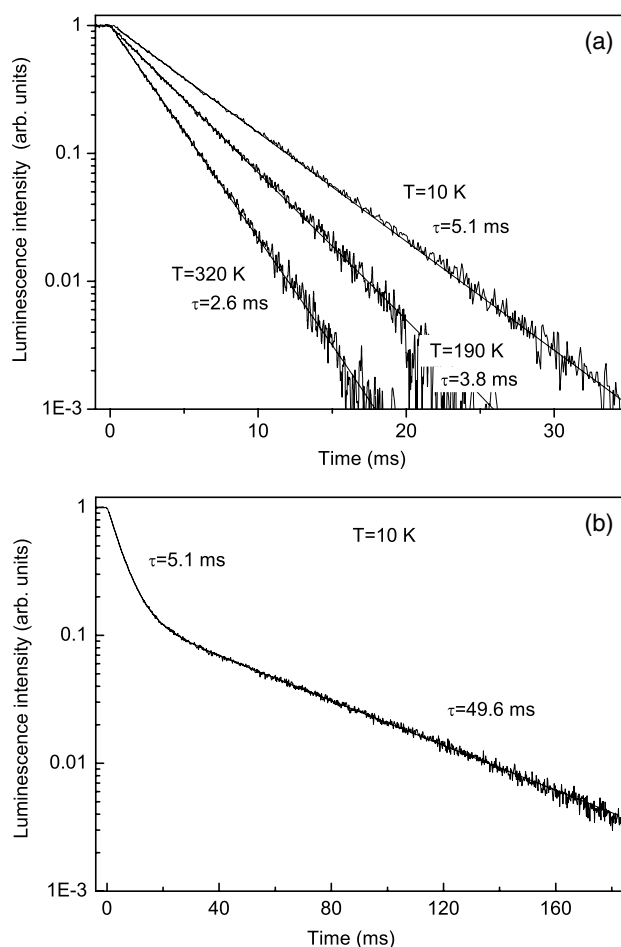


Figure 7. Luminescence decay curves registered for the as-grown $\text{YAlO}_3:\text{Mn}$ crystal at 692.7 nm (a) and 723.4 nm (b) at different temperatures.

testifies to a strong electron–phonon coupling of the ${}^4\text{T}_2$ level of the Mn^{4+} ions, and appropriate large Stokes shift of this level.

In order to describe the strong luminescence quenching which occurs above 400 K, an additional term should be added to equation (3). This term has the following form:

$$\tau_2^{-1} \exp\left(\frac{-\Delta E_2}{kT}\right). \quad (4)$$

The fit of this term to the decay time data above 400 K gives a value of the activation energy ΔE_2 close to 1.35 eV ($\sim 11\,000\text{ cm}^{-1}$) and a value of the non-radiative transition probability $\tau_2^{-1} = 10^{17}\text{ s}^{-1}$. The activation energy value ΔE_2 obtained from the luminescence decay measurements agrees very well with the activation energy calculated from the temperature dependence of the luminescence intensity. This energy can be interpreted as the energy distance from the minimum of potential energy of the ${}^2\text{E}$ state to the level where it overlaps with the potential energy of the ${}^4\text{A}_2$ ground state in the configurational coordinates. Another possible explanation is the energy distance from the ${}^2\text{E}$ level to the charge transfer levels of Mn^{4+} ions.

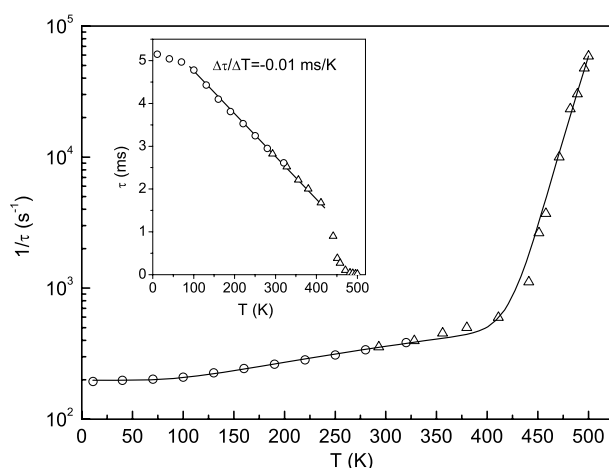


Figure 8. Temperature dependence of the luminescence decay time of Mn⁴⁺ centres in the as-grown YAlO₃:Mn crystal measured at 692.7 nm (R_1 line) (marked as circles) and in integral mode (marked as triangles) and their theoretical approximation (see text for details).

This means that the thermally activated transition from the ²E level to the charge transfer levels results in the de-excitation of the Mn⁴⁺ centres that is apparent in both the thermal quenching of the luminescence intensity and in the sharp decrease of the decay time. Moreover, an excitation of Mn⁴⁺ ions into the charge transfer levels can result in the delocalization of electrons from Mn⁴⁺ ions (i.e. the Mn⁴⁺ → Mn⁵⁺ + e ionization) [17]. The model presented above fits the experimental data very well in the whole range of temperatures; this is shown in figure 8 as a solid line.

The linear dependence of the decay time in the 90–420 K temperature range (see the inset in figure 8) should be mentioned separately. Here the decay time decreases from $\tau = 4.9$ to 1.6 ms with the temperature coefficient $\Delta\tau/\Delta T = -0.01$ ms K⁻¹. The value of -0.01 ms K⁻¹ is less than -0.075 ms K⁻¹ for YAlO₃:Cr³⁺, but the temperature range of the linear dependence is wider than the range of 270–350 K reported for YAlO₃:Cr³⁺ [8]. In such a way YAlO₃:Mn is a potentially good phosphor for a fibre optic thermometer in the 90–420 K temperature range.

3.2. Spectroscopy of YAP:Mn⁴⁺ crystals at high hydrostatic pressure

The pressure dependence of luminescence spectra of the Mn⁴⁺-doped YAP crystal annealed in hydrogen in order to increase the luminescence intensity of non-intentional Cr³⁺ dopant at $T = 10$ K is presented in figure 9 in the range of pressure up to 130 kbar. The spectra were taken at this low temperature in order to observe the pure electronic transition lines of Mn⁴⁺ and Cr³⁺ ions. The spectral resolution of these spectra is slightly worse than of those presented in figure 3 due to the very small size of samples measured in the diamond-anvil cell and also due to the small intensity of the luminescence of Mn⁴⁺ and Cr³⁺ ions in YAP.

All luminescence lines undergo red shifts. The pressure coefficients of R_1 lines of Mn⁴⁺ and Cr³⁺ are equal to -1.16 cm⁻¹ kbar⁻¹ and -1.08 cm⁻¹ kbar⁻¹, respectively. The pressure coefficients of the vibronic sideband lines are of the order of -1.2 to -1.3 cm⁻¹ kbar⁻¹, except for the line which occurs at 732 nm at ambient pressure, for which the pressure coefficient is equal to about -2.0 cm⁻¹ kbar⁻¹. The spectral positions of various luminescence lines associated with Mn⁴⁺ dopant and Cr³⁺ impurity are shown in figure 10.

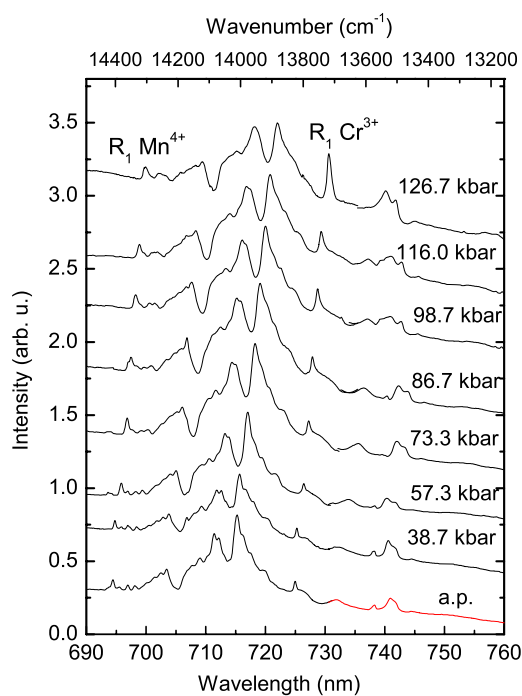


Figure 9. Pressure dependence of the YAP:Mn luminescence spectra at $T = 10$ K, excited by the 514.5 nm argon-ion laser line.

(This figure is in colour only in the electronic version)

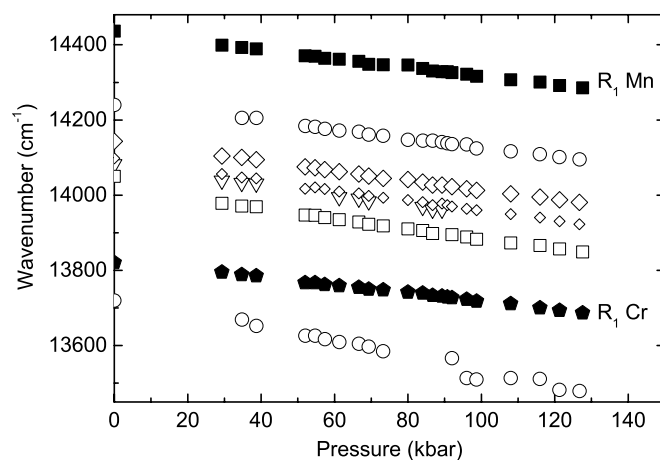


Figure 10. Spectral position of various luminescence lines of YAP:Mn crystals at $T = 10$ K. Full symbols: R_1 lines of Mn^{4+} and Cr^{3+} ions; open symbols: vibronic lines.

The pressure coefficient of the $Cr^{3+}R$ lines in YAP is slightly larger than that for Cr^{3+} in ruby. This is in good agreement with the difference in experimental values of bulk moduli of those materials: $B_0(\text{YAP}) = 192$ GPa [27] and $B_0(\text{ruby}) = 253$ GPa [28].

The pressure coefficients of the R_1 lines of Mn^{4+} and Cr^{3+} dopant ions are similar. This is surprising since the larger charge of Mn^{4+} should induce stronger overlap between the

wavefunctions of the cation and surrounding ligands. Such an overlap is a source of larger covalence of chemical bonds. Thus usually causes the pressure coefficients of Mn⁴⁺ to be much larger than the pressure coefficient of Cr³⁺ ions substituting the same host sites [29]. Apparently, this does not occur in YAP crystals. The influence of other defects located close to one of the dopant ions (Mn⁴⁺ or Cr³⁺) may be a source of this effect. Indeed, annealing of YAP crystals in hydrogen atmosphere increases the relative ratio of Cr³⁺/Mn⁴⁺ luminescence, as has been shown earlier. This is a proof that the annealing affects the system of point defects in YAP crystals.

The pressure coefficients of the vibronic sideband lines are slightly larger than the pressure coefficients of the pure electronic lines. This is in agreement with the typical pressure dependence of phonon energies in crystals.

4. Conclusions

The photoluminescence of Mn⁴⁺ ions originating from the ²E → ⁴A₂ transition has been studied in an YAlO₃ crystal in the temperature range 10–600 K at ambient pressure. Besides the vibronic sidebands that cover the range of 660–740 nm at room temperature, two zero-phonon lines (*R* lines) at 691.3 and 692.7 nm, which became apparent at low temperature, were revealed. The Debye temperature estimated from the peak shift of *R* lines versus temperature is about 465 K.

The temperature dependence of the luminescence decay time shows a quasi-linear decrease from $\tau = 4.9$ to 1.6 ms in the temperature range from 90 to 420 K (with a temperature coefficient -0.01 ms K⁻¹) that makes YAlO₃:Mn a potentially good phosphor for a fibre optic fluorescence thermometer in this temperature range.

The decay time shortening without decrease of the luminescence intensity at temperature above 90 K is associated with phonon-induced transitions. The decay time shortening at temperatures above 420 K correlates well with the thermal quenching of the luminescence intensity caused by the non-radiative decay.

The high-pressure luminescence measurements show that the pressure coefficients of intentional Mn⁴⁺ dopant ions and Cr³⁺ impurity ions are similar, most probably due to the influence of another point defect on those ions.

Acknowledgments

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References

- [1] Geschwind S, Kisliuk P, Klein M P, Remeika J P and Wood D L 1962 *Phys. Rev.* **126** 1684
- [2] Riseberg L A and Weber M J 1971 *Solid State Commun.* **9** 791
- [3] Petermann K and Huber G 1984 *J. Lumin.* **31/32** 71
- [4] Brenier A, Suchocki A, Pedrini C, Boulon G and Madej C 1992 *Phys. Rev. B* **46** 3219
- [5] Bulyarskii S V and Prikhodko V V 2000 *Phys. Status Solidi b* **222** 563
- [6] Eremenko V V *et al* 2001 *Appl. Phys. Lett.* **79** 734
- [7] Grattan K T V and Zhang Z Y 1995 *Fiber Optic Fluorescence Thermometry* (London: Chapman and Hall)
- [8] Uchiyama H, Aizawa H, Katsumata T, Komuro S, Morikawa T and Toba E 2003 *Rev. Sci. Instrum.* **74** 3883
- [9] Loutts G B, Warren M, Taylor L, Rakhimov R R, Ries H R, Miller G, Noginov M A, Curley M, Noginova N, Kukhtarev N, Caulfield H J and Venkateswarlu P 1998 *Phys. Rev. B* **57** 3706

- [10] Noginov M A, Noginova N, Curley M, Kukhtarev N, Caulfield H J, Venkateswarlu P and Loutts G B 1998 *J. Opt. Soc. Am. B* **15** 1463
- [11] Kukhtarev N and Kukhtareva T 2003 *Opt. Memory Neural Networks* **12** 75
- [12] Zhydachevskii Ya, Durygin A, Suchocki A, Matkovskii A, Sugak D, Bilski P and Warchol S 2005 *Nucl. Instrum. Methods Phys. Res. B* **227** 545
- [13] Noginov M A and Loutts G B 1999 *J. Opt. Soc. Am. B* **16** 3
- [14] Rakhimov R R, Wilkerson A L, Loutts G B, Noginov M A, Noginova N, Lindsay W and Ries H R 1998 *Solid State Commun.* **108** 549
- [15] Zhydachevskii Ya, Durygin A, Suchocki A, Matkovskii A, Sugak D, Loutts G B and Noginov M A 2004 *J. Lumin.* **109** 39
- [16] Kobayakov S, Galanciak D, Kamińska A, Suchocki A and Malinowski M 2006 *Appl. Phys. Lett.* **88** 234102
- [17] Noginov M A, Loutts G B, Noginova N, Hurling S and Kuck S 2000 *Phys. Rev. B* **61** 1884
- [18] Noginov M A, Loutts G B, Ross K, Grandy T, Noginova N, Lucas B D and Mapp T 2001 *J. Opt. Soc. Am. B* **18** 931
- [19] Zhydachevskii Ya, Suchocki A, Sugak D, Luchechko A, Berkowski M, Warchol S and Jakiela R 2006 *J. Phys.: Condens. Matter* **18** 5389–403
- [20] Noginov M A, Loutts G B and Warren M 1999 *J. Opt. Soc. Am. B* **16** 475
- [21] Weber M J and Varitimos T E 1974 *J. Appl. Phys.* **45** 810
- [22] Sugak D, Matkovskii A, Savitskii D, Durygin A, Suchocki A, Zhydachevskii Y, Solskii I, Stefaniuk I and Walraffen F 2001 *Phys. Status Solidi a* **184** 239
- [23] McCumber D E and Sturge M D 1963 *J. Appl. Phys.* **34** 1682
- [24] Senyshyn A, Ehrenberg H, Vasylechko L, Gale J D and Bismayer U 2005 *J. Phys.: Condens. Matter* **17** 6217
- [25] Powell R C 1998 *Phys. Solid State Laser Materials* (New York: AIP)
- [26] Suda J, Kamishima O, Hamaoka K, Matsubara I, Hattori T and Sato T 2003 *J. Phys. Soc. Japan* **72** 1418
- [27] Ross N L, Zhao J and Angel R J 2004 *J. Solid State Chem.* **177** 1276
- [28] Goto T, Anderson O L, Ohno T and Yamamoto S 1989 *J. Geophys. Res. B* **94b** 7588
- [29] Galanciak D, Grinberg M, Gryk W, Kobayakov S, Suchocki A, Boulon G and Brenier A 2005 *J. Phys.: Condens. Matter* **17** 7185