High pressure spectroscopy study of SCF Tb$_3$Al$_5$O$_{12}$:Mn

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Abstract. Single crystal film of Tb$_3$Al$_5$O$_{12}$:Mn, with concentration of Mn approximately equal to 0.07 at%, has been grown by liquid phase epitaxy on Y$_3$Al$_5$O$_{12}$ substrate. We have measured the absorption, luminescence, luminescence excitation spectra and luminescence kinetics of the film. To analyze the energetic structure and to estimate the crystal field strength we have measured the photoluminescence spectra under high hydrostatic pressure applied in diamond anvil cell up to 110 kbar. To characterize the Mn charge state we performed calculations of Tanabe –Sugano diagrams for 3d$^5$, 3d$^4$ and 3d$^3$ system. The negative pressure shift of the 16800 cm$^{-1}$ band yields attribution of this band to the $^2T_1$→$^2A_1$ transition in dodecahedrally coordinated Mn$^{4+}$ ion. We have estimated quantity of $Dq/B$ equal to 1.8±0.2. The configurational coordinate diagram of the Mn$^{4+}$(3d$^5$) has been calculated to analyze the nonradiative deexcitation processes $^4T_1$→$^2T_2$→$^4A_1$.

1. Introduction
The Tb$_3$Al$_5$O$_{12}$ (TbAG) garnet is considered as a promising host for luminescent materials, [1]. The advantage of TbAG results form effective energy transfer from Tb$^{3+}$ cation sublattice to the luminescence centers of impurity ions. Up to present the TbAG doped Ce$^{3+}$ ions [1-4] and simultaneously Ce$^{3+}$ and Eu$^{3+}$ ions [3, 4] were analyzed. In this work we focus on spectral investigations of TbAG:Mn single crystal film (SCF) deposited on deposited on Y$_3$Al$_5$O$_{12}$ (YAG ) monocystal.

Manganese is a well-known activator in garnet host used mainly for tunable solid-state laser media [5]. Since in Mn$^{3+}$ bound 4 electrons at the unfilled 3d shell the activation energy for creation of Mn$^{4+}$ (3d$^3$ system) and Mn$^{2+}$ (3d$^5$ system) is small enough that in many materials the ground and the first excited states of the Mn$^{3+}$, Mn$^{2+}$ and Mn$^{4+}$ can be located in the bandgap of the host and can contribute to the luminescence. Actually the luminescence related to Mn ions in different charge states (2+, 3+ and 4+) in garnets was studied in several works [5-10]. Luminescence of Mn$^{3+}$ consisting of broad band emission with maximum at 590 nm attributed to $^4T_1$→$^6A_1$ transition has been reported in Y$_3$Sc$_2$Ga$_5$O$_{12}$ and YAG, [7, 8, 10]. The Mn$^{3+}$ intensive luminescence related to the $^5T_2$→$^5E$ and $^3T_2$→$^3E$ transitions in the range 650 nm and 700-900nm respectively have been observed in several garnets [4, 7, 10]. The relative intensity of $^5T_2$→$^5E$ and $^3T_2$→$^3E$ transitions strongly depends on the crystals field strength and temperature [6]. Luminescence of Mn$^{4+}$ ions was investigated in details in YAG [7, 8] and in Ca-co-doped Gd$_3$Ga$_5$O$_{12}$ (GGG) crystals, [11]. The luminescence spectrum of the Mn$^{4+}$ ion in octahedral coordination consists the sharp R-lines around 640-670 nm related $^2E$→$^4A_2$ transition. It is considered that existence of Mn$^{4+}$ in octahedral coordination in YAG is accompanied by Mn$^{2+}$ ions occupying dodecahedrally coordinated Y$^{3+}$ sites, [10].
The energetic structure of the transition metal ion system can be analysed in the strong crystal field approximation by means of Tanabe –Sugano diagrams [12, 13]. According to this model the energetic structure is determined by Racah parameters $B$ and $C$ that describe Coulomb and exchange interaction of electrons in the d shell and crystal field parameter $Dq$ that describes the splitting of d level in the cubic crystal field. In ionic crystals the quantity of $Dq$ is proportional to the -5 power of central ion ligands distance, $R$, and therefore can be significantly different in different lattices. On the other hand quantities $B$ and $C$ are diminished with respect to the free ion quantities by nephelauxetic effect related to mixing of 3d wave functions with valence ones and are less depend on the lattice host.

One of the most effective tool for characterisation of transition metal ion in crystal lattice is high pressure spectroscopy. High pressure compresses materials and causes the increase of crystal field strength $Dq$. As the result one observes the shift of the emission bands related to the transitions between the states belonging to different electronic configurations. High pressure spectroscopy has been successfully used to analyze materials doped with Cr$^{3+}$, Cr$^{4+}$, Ti$^{3+}$ and Mn$^{4+}$. The broad reviews of this topic can be finding in the papers, [14, 15]. The main purpose of presented contribution is to characterise of the Mn ions that incorporated into TbAG SCF. We have applied the high-pressure luminescence spectroscopy for determination of the valence state of manganese ions. Analysis of luminescence lineshape and luminescence kinetics obtained at high hydrostatic pressure confirmed existence of Mn$^{2+}$ in the investigated host.

2. Samples preparation and experimental technique

The TbAG:Mn films with thickness in the 19-64 µm range was crystallised by LPE onto YAG substrates from melt-solutions of Tb2O3 and Al2O3 in PbO–B2O3(12:1) . The growth temperature was varied between 970 and 1000 0C. Concentration of Mn ions varied from 0.019 to 0.07 at%. Details of the sample preparation are described in the paper [16].

Steady state luminescence has been excited by Ar laser with 457 nm and He-Cd laser with 325nm. The emission has been dispersed by PGS 2 spectrometer working as a monochromator and collected by an R943-02 Hamamatsu photomultiplier working in the photon counting regime. The luminescence kinetics was measured at room temperature using a Hamamatsu C4334-01 model Streak Camera. The luminescence was spectrally separated with a Bruker Optics 2501S model monochromator. The optical parametric generator PG401/SH pumped by the tripled output of a Nd:YAG pulse laser has been used for excitation of luminescence. High hydrostatic pressure has been applied in a diamond anvil cell (DAC) of the Merrill–Bassett system, [17]. Pressure appears when diamonds are moved and is transmitted to the fluid medium (dimethylsiloxane oil). A ruby crystal is used as the pressure detector.

3. Results and discussion

3.1. Luminescence spectra

Luminescence spectra of the TbAG:Mn (0.07 at. %) SCF on YAG obtained at different temperatures under excitation 457 nm are presented in Fig.1 a. The spectra consist of two broad bands at 18700 cm$^{-1}$ and 16800 cm$^{-1}$ which have been attributed to d-f transition of Ce$^{3+}$ in YAG [18, 19] and to Mn emission, respectively. The sharp lines around 14550cm$^{-1}$ correspond to the $^{2}E \rightarrow ^{4}A_{2}$ transition accompanied by phonons side-band in octahedrally Cr$^{3+}$ ions in YAG [20, 21].

Luminescence spectra obtained at different temperatures under excitation at 325 nm are presented in Fig.1 b. One notices that the spectrum lineshape depends strongly on temperature. At 10K one observes the sharp lines at 18420 cm$^{-1}$, 17080 cm$^{-1}$ and 16500 cm$^{-1}$ related respectively to $^{5}D_{2} \rightarrow ^{7}F_{6}$, $^{5}D_{2} \rightarrow ^{7}F_{4}$ and $^{5}D_{1} \rightarrow ^{7}F_{4}$ transitions in Tb$^{3+}$ ions and broad band with maximum at 16800 cm$^{-1}$ attributed to the Mn ion emission. The Tb$^{3+}$ emission is strongly quenched when temperature increases. Considering Mn luminescence by means of electron –lattice coupling one notices that the band consists with zero-phonon line (band) and one phonon repetition with phonon energy
approximately equal to 600 cm\(^{-1}\) and Huang–Rhys factor smaller than unity. The similar emission has been related to the \( ^4T_1 \rightarrow ^6A_1 \) transition of the Mn\(^{2+}\) ion, [6, 10].

![Figure 1](image.png)

**Figure 1.** Steady state luminescence spectra of TbAG:Mn (0.07 at. %) SCF obtained at different temperatures under excitation at 457 nm (a) and 325 nm (b)

3.2. High-pressure luminescence and luminescence kinetics

Ambient temperature luminescence excited with 325 nm, obtained at different pressures are presented in Fig. 2 a. In Fig. 2 b the energies of the emission peaks versus pressure are presented. One notices that increasing pressure causes the significant red shift of the emission. The shift rate of the maximum of the emission is constant and is equal to -9 cm\(^{-1}\)/kbar.

The luminescence decays obtained at various pressures are presented in Fig. 3 a. The emission decays almost exponentially for all pressures and emission lifetime decreases with pressure from 0.62 ms to 0.01 ms, for ambient pressure and 125 kbar, respectively. The luminescence decay times measured as the ratio \( \tau = \frac{\int I(t) dt}{\int I(t) dt} \) versus pressure are presented in Fig. 3 b. The decreasing of the luminescence lifetime can be attributed to pressure induced increase of the nonradiative internal-conversion process.
3.3. Energetic structure of the Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ in garnet lattice
We have considered the possibility of existence of Mn ions in the Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ charge states and therefore have analyzed our experimental data by means of respective Tanabe –Sugano diagrams. The Tanabe –Sugano diagrams presenting the lowest states of octahedrally coordinated Mn$^{3+}$ (3d$^4$) system, octahedrally (positive $Dq/B$) and tetrahedrally (negative $Dq/B$) coordinated Mn$^{4+}$ (3d$^3$) system, and dodecahedrally coordinated Mn$^{2+}$ (3d$^5$) system are presented in Fig. 4 a, b and c, respectively. The expected radiative transitions in all cases are represented by arrows. One notices

![Figure 2](image2.png)

**Figure 2.** Steady state luminescence spectra of TbAG:Mn (0.07 at. %) SCF obtained at different pressures at ambient temperature under excitation at 325 nm (a). Energy of the emission spectra versus pressure (b).

![Figure 3](image3.png)

**Figure 3.** (a) Luminescence decay for ambient temperature obtained at different pressures. Luminescence has been excited with 325 nm laser pulse and monitored at 16800 cm$^{-1}$. (b) Luminescence decay times versus pressure.
that in the reasonable range of the quantity $1.8 < Dq/B < 2.8$ the ground state of Mn$^{3+}$ is the $^5$E state belonging to $t_2$ electronic configuration, whereas the luminescent states are $^5T_2$ from $t_2^2e^2$ electronic configuration and $^1T_2$ from the $t_2^4$ electronic configuration. It is expected that similarly like in YAG:Mn$^{3+}$ the ground state is splitted by strong static Jahn–Teller effect of $E(\oplus)\bar{e}$ type with stabilization energy $E_{st} = \frac{L^2}{\hbar \omega} = 1850$ cm\(^{-1}\) [10]. According to the diagram in Fig. 4 a only the spin forbidden $^1T_2 \rightarrow ^5E$ transition can be characterized by negative pressure shift of the luminescence.

![Figure 4](image-url)  

**Figure 4.** (a) Tanabe–Sugano diagram of Mn$^{3+}$ (3d\(^4\)) system in octahedral coordination. (b) Tanabe–Sugano diagram of Mn$^{4+}$ (3d\(^3\)) system in octahedral (positive $Dq/B$) and tetrahedral (negative $Dq/B$) coordination. (c) Tanabe–Sugano diagram of Mn$^{2+}$ (3d\(^5\)) system in dodecahedral coordination.

and long luminescence lifetime. The spin allowed $^5T_2 \rightarrow ^5E$ transition yields luminescence that should shift toward the blue region with increasing pressure. If one would attribute the luminescence presented in Fig. 2 a to the Mn$^{3+}$ to $^1T_2 \rightarrow ^5E$ transition the crystal field parameter $Dq/B$ should be greater than 2.5. In this case one expects the emission energy at ambient pressure to be smaller than 14000 cm\(^{-1}\), whereas we have obtained this energy 16800 cm\(^{-1}\). This discrepancy excludes the ascription of obtained emission to the $^1T_2 \rightarrow ^5E$ transition in Mn$^{3+}$.

In the case of Mn$^{4+}$ in octahedral coordination the ground state is the $^4A_2$ state of ground electronic configuration $t_2^3$, whereas the first excited state depends on the crystal field strength. For $Dq/B > 2.4$ it is the $^5E$ state and for $Dq/B < 2.4$ it is $^5T_2$ state of the first excited electronic configuration $t_2^2e$. One expects that the energy of the spin –allowed $^4T_2 \rightarrow ^4A_2$ emission would increase with increasing pressure, whereas the energy of the $^2E \rightarrow ^4A_2$ spin forbidden transition is pressure independent. We have obtained the large negative pressure shift of the emission that is contradict to the assumption that we deal with Mn$^{4+}$ in octahedral coordination. In the case of tetrahedrally coordinated Mn$^{4+}$ one expects the spin allowed emission related to $^4A_2 \rightarrow ^2T_1$ and/or spin –forbidden emission related to $^2T_1 \rightarrow ^2T_1$ transitions. However it is very probable that this emission is quenched by non-radiative transitions to the $^4T_2$ and $^5E$ states.

In the case of Mn$^{2+}$ presented in Fig. 4 c the ground state is $^6A_1$ form the $t_2^3e^2$ electronic configuration whereas the first excited state is $^4T_1$ form $t_2^4e$ electronic configuration. The spin forbidden transition $^4T_1 \rightarrow ^2A_1$ can yield the luminescence with peak at 16800 cm\(^{-1}\) that energy diminishes with increasing pressure.

The difference between energy of $^4T_1 (t_2^4e)$ and $^6A_1 (t_2^3e^2)$ states (labeled as $\Delta$ in Fig. 4c) can be used for calculation of Racah parameters and crystal field strength. For the case when $\frac{8Dq}{9}B >> B$, $C$ one can use following approximation:
\[ \Delta \approx 10B + 6C - 10Dq \frac{9B^2}{4(9B + C + \frac{80}{9}Dq)} - \frac{C^2}{160Dq} \]  \tag{1} 

The free Mn\(^{2+}\) ion Racah parameters are \(B = 860\) cm\(^{-1}\) and \(C = 3850\) cm\(^{-1}\) \[18\]. With these values relation (1) yields \(Dq = 1600\) cm\(^{-1}\). Usually values \(B\) and \(C\) in crystals are smaller than the free ion ones and therefore quantity \(Dq\) is smaller than 1600 cm\(^{-1}\). Considering the reasonable values \(B = 600\) cm\(^{-1}\) and \(C = 3500\) cm\(^{-1}\) one obtains \(Dq = 1060\) cm\(^{-1}\). Diminishing of energy \(\Delta\) with increasing pressure is caused mainly by increase of the value of \(Dq\). Obtained quantity of pressure shift \(-9\) cm\(^{-1}\)/kbar is similar like in other transition metal ions, where one has observed the transitions between states from different electronic configurations \[15\].

The effect of electron - lattice interaction is responsible for existence of vibrational broadening of the emission band. In the case of Mn\(^{2+}\) one should consider coupling in the excited states \(^4T_1\) and \(^5T_2\) to the one dimensional breathing mode \(a_1\), two dimensional mode \(e\) with coordinations \(Q_\alpha, Q_\beta\) and three dimensional mode \(\tau\) with coordinations \(Q_\alpha, Q_\beta, Q_\gamma\). Hamiltonian of the electron–lattice interaction can be expressed as follows

\[ H_{el-l} = \frac{1}{2} \hbar \omega \sum_{\alpha} Q^2_{\alpha} + \sum_{\alpha} \frac{dV}{dQ_{\alpha}} Q_{\alpha} = \frac{1}{2} \hbar \omega \sum_{\alpha} Q^2_{\alpha} + \sum_{\alpha} V_{\alpha} Q_{\alpha} \]  \tag{2} 

where \(V\) is the crystal field potential. As the result of electron–lattice interaction the system being in the \(l\) state reaches minimum energy after the shift of the ligands ions in the configurational space to the point defined by new minimum energy \((Q_{\alpha}^l, Q_{\beta}^l, Q_{\gamma}^l)\). One can define the stabilization energy, \(E_{st}^l\) as the energy which is released in the relaxation process.

\[ E_{st}^l = \frac{1}{2} \sum_{\alpha} (Q_{\alpha}^l)^2 \]  \tag{3} 

In the case of breathing mode stabilization energy is equal to \(Sh\omega = \frac{1}{2} \omega V_1^2\), where \(S\) is Huang–Rhyes factor and \(\hbar \omega\) is phonon energy, and in the case of Jahn–Teller effect stabilization energy is equal to \(\frac{(V_e^l)^2}{6h\omega}\) and \(\frac{(V_\tau^l)^2}{9h\omega}\) in the case of coupling with \(e\) and \(\tau\) mode, respectively, \[22\]. In general case the stabilization energy is a more complicated function of parameters \(V_{\alpha}^l\). One can consider the pressure effect on lattice relaxation and stabilization energy; \[15\];

\[ \frac{dE_{st}}{dp} = E_{st} \left[2(n + 1) - 6\gamma\right] \]  \tag{4} 

In relation (4) \(B_0\) is a local compressibility (bulk modulus), \(\gamma\) is Grüneisen parameter and \(n\) exponent describing the dependence of crystal field on central ion–ligand distance. Parameter \(n\) is equal 5 for symmetrical \(a_1\) mode (for Jahn–Teller mode \(n\) can be equal to 3). Typical values of Grüneisen parameter are between 1 and 2. Thus one notices that contribution related to increase the crystal field strength \(2(n + 1)\) and that related increase of material stiffness \(6\gamma\) cancel each other. Therefore rather small changes in the electron-lattice coupling and Jahn-Teller effect with increasing pressure are expected. This prediction is confirmed by our experiments since pressure does not change the bandwidth of the spectrum (see Fig. 2 a).

The relatively long luminescence lifetime results form the fact that the \(^4T_1 \rightarrow ^6A_1\) transition is forbidden with respect to parity and spin. Decrease of the luminescence lifetime with pressure is accompanied by diminishing of the luminescence intensity. This correlation suggests that the increase
of nonradiative internal conversion process is responsible for this effect. The luminescence lifetime in presence of nonradiative internal conversion is given by following relation

\[
\tau = \left[ \frac{1}{\tau_{rad}} + P_{nr} \cdot e^{-\frac{E_{nr}}{kT}} \right]^{-1}
\]

(5)

where \(\tau_{rad}\) is the radiative lifetime, \(P_{nr}\) is probability of the nonradiative internal conversion to the ground state \(^6A_1\) and \(E_{nr}\) is activation energy of the nonradiative processes.

To analyze the nonradiative pathway one considers the diagram presented in Fig. 5, where the electronic manifolds representing the \(^6A_1\) \((t_3^3e^2)\), \(^4T_1\) \((t_2^4e)\) and \(^2T_2\) \((t_2^5)\) states are presented. Energy barrier for nonradiative processes is defined as a difference between energy of parabolas cross-over and minimum energy of the excited electronic manifold. Considering the \(^6A_1\) \((t_3^3e^2)\) and \(^4T_1\) \((t_2^4e)\) states one obtains quantity of energy barrier given by following relation:

\[
E^0_{nr} = \frac{\Delta^2}{4E_{st}^2}
\]

(6)

One notices that stabilization energy in the \(^4T_1\) \((t_2^4e)\) state is small and therefore energy of crossing of the \(^6A_1\) \((t_3^3e^2)\) and \(^4T_1\) \((t_2^4e)\) parabolas obtained from (6) is very high (actually is not indicated in Fig. 5). On the other hand the electron-lattice interaction and shift in the configurational state is much larger in the \(^2T_2\) \((t_2^5)\) state since this quantity depends on difference in electronic configuration between the \(^6A_1\) \((t_3^3e^2)\) and \(^2T_2\) \((t_2^5)\). Thus one considers the nonradiative process that involves the transition of the system from \(^4T_1\) \((t_2^4e)\) to the \(^2T_2\) \((t_2^5)\) state and then to the ground state \(^6A_1\) \((t_3^3e^2)\). In Fig. 5 energy \(E_{nr}\) is the activation energy of this three step process.

Considering Tanabe–Sugano diagram presented in Fig. 4c one notices that energy of the \(^2T_2\) \((t_2^5)\) state should strongly diminish with pressure. Therefore pressure diminishes also the energy of the barrier \(E_{nr}\) and shortens the luminescence lifetime.

4. Conclusions

The effective energy transfer from TbAG host to Mn ions takes place in TbAG:Mn and results in the intensive orange Mn\(^{2+}\) luminescence. It has been found that the manganese in the TbAG:Mn film locate mainly in the Mn\(^{2+}\) state in the dodecahedral positions of the lattice. We have not observed luminescence related to Mn\(^{3+}\) in octahedral coordination. Also we have not observed Mn\(^{4+}\) in octahedral coordination, however we cannot exclude the existence of Mn\(^{3+}\) ions in tetrahedral coordination replacing Al\(^{3+}\) ions, that compensate Mn\(^{2+}\) replacing Tb\(^{3+}\).
Considering the ionic radiuses of Mn$^{4+}$, which are 0.53 Å and 0.39 Å, [23] in octahedral and tetrahedral positions, respectively one notices that they are almost equal to the respective quantities of ionic radiuses of Al$^{3+}$ which are equal to 0.535 Å and 0.39 Å. Thus Mn$^{4+}$ can easy replace Al$^{3+}$ in octahedral and tetrahedral sites as well. As it has been discussed in this contribution tetrahedrally coordinated Mn$^{4+}$ ions are not seen in the luminescence due to the effective nonradiative processes involving the $^4T_2$ and $^2E$ states.

Acknowledgements.
The work was supported by Gdansk University, grant no 5200-5-0049-8.

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