Narrow Band Deep Red Photoluminescence of Y2Mg3Ge3O12:Mn4+,Li+ Inverse Garnet for High Power Phosphor Converted LEDs

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This work concerns a novel red emitting Mn4+ doped phosphor showing an extraordinarily high thermal quenching temperature. The composition Y2Mg3Ge3O12:Mn4+,Li+ exhibits efficient red photoluminescence peaking at 658 nm, which can be assigned to the 2Eg → 4A2g intraconfigurational transition of Mn4+ ([Ar]3d3 configuration) located at the octahedral site in the garnet structure. Photoluminescence properties, such as temperature dependence of the luminescence intensity and luminescence lifetime, are presented. Additionally, the band structure of the undoped host material were treated with Density Functional Theory (DFT) and evaluated with UV-reflectance spectroscopy. Furthermore, the energy levels of the Mn4+ ion in the Y2Mg3Ge3O12 host were calculated with the exchange charge model of crystal field theory and compared to those obtained experimentally from luminescence studies.

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The search for red emitting phosphors is of tremendous importance for the further optimization of solid-state light sources for indoor illumination applications. Most of the commercial white light emitting diodes (W-LEDs) are phosphor-converted LEDs (pLEDs) comprising a blue emitting (In,Ga)N chip and a yellow emitting phosphor, most commonly a garnet such as Y3Al5O12:Ce3+ (YAG:Ce3+) or Tb4Al12O19:Ce3+ (TAG:Ce3+). However, this approach suffers from major shortcomings such as cold white light and a low color rendering index (CRI), which results from the lack of red light. Therefore, red phosphors with outstanding luminescence performance and strong absorption in the near UV to blue spectral range are highly demanded. Compared with the established commercial red phosphors, for example, (Ca,Sr)AlSiN3:Eu2+ and (Ca,Sr,Ba)2Si5N8:Eu2+, which typically possess a broad emission band, Mn4+ activated oxide and fluoride phosphors exhibit an emission spectrum consisting of narrow lines in the red region.6–14 Moreover, the preparation of nitride phosphors requires harsh conditions, i.e. high temperature and pressure, which to a tremendous extent, increase the cost and difficulty of preparation.15,16 Additionally, rare earth elements as raw materials are too expensive for producing respective phosphors at a low cost-price. Recently, Mn4+ doped fluoride red emitting phosphors have attracted much attention because of the simple and efficient fabrication process, i.e. they can be prepared at room temperature or slightly above (20–80°C) by cation exchanger reaction.17 However, these types of materials have a huge drawback because toxic hydrofluoric acid is needed for their synthesis. Additionally, Mn4+ doped fluorides are rather sensitive toward high temperature, high humidity, and large excitation densities provided by LEDs.18–20 In general, Mn4+ doped oxide phosphors were prepared using conventional oxides, nitrates, and perchlorates as starting materials. All these disadvantages could be overcome by using an oxide type host material, if one is able to find a Mn4+ doped oxide host with a rather narrow emission band peaking at approximately 630 nm.9,21 So far, the closest emitting state to 630 nm in oxide based materials was observed for Mg14Ge5O24:Mn4+ (659 nm), CaAl12O19:Mn4+ (656 nm), SrAl12O19:Mn4+ (655 nm), and Sr4Al12O19:Mn4+ (654 nm), which have been studied thoroughly.22–24 PL properties of several other Mn4+ doped phosphors, such as ger- manates, arsenates, gallates, and other complex oxides, have been studied and results published so far.24–26 Accordingly, research activity and commercial interest is highly focused on Mn4+ based phosphors presently. This type of materials can emit in the desired red spectral region with a high quantum yield and thus meet the efficiency and color quality demands of the next generation warm white pLEDs. It is well known, that the Mg14Ge5O24:Mn4+ phosphor (also known as Mg-fluorogermanate due to the presence of some MgF2 as a flux) has extraordinary good properties in terms of the thermal quenching of the luminescence (T1/2 > 700 K).27 Due to this circumstance, the authors think this behavior might be expected for other Mg-germanates as well. From this perspective, it is reasonable to study other Mn4+ doped magnesium based germanates e.g. Y2Mg3Ge3O12:Mn4+,Li+.

Experimental

Precursors for the synthesis of all samples were prepared by a sol-gel method using citric acid as the complexing agent. The gels were obtained by using Mg(NO3)2·6 H2O (Merck 99.99%), LiNO3 (Aldrich 99.9%), Y2O3 (Treibacher 99.99%), GeO2 (Acros Organics 99.999%), Mn(ClO4)2·6 H2O (Aldrich 99.9%), and citric acid (Merck 99.9%) as starting materials. The educts, except GeO2, were dissolved in appropriate molar ratios in dilute Nitric Acid (Bernd Kraft 53–55%) i.e., 1 mol-% manganese with respect to Mn4+ content and heated to 65–75°C. Germanium oxide was separately dissolved in diluted Ammonia (Bernd Kraft 20%). The solutions were then carefully mixed. Under continuous stirring, citric acid was added with a molar ratio of 2:1 in regards to the sum of all metal ions. After concentrating the mixtures by slow evaporation, solids turned into transparent, highly viscous gels. The gels were dried in an oven at 160°C overnight. During dehydration, the gels turned into foams, which were completely ground to fine powders and heated at 1000°C for 4 hours in air to
remove any organic residue. Finally, the precursors were calcined at 1350 °C for 6 hours each in air.

The phase purity of all samples was investigated by powder X-ray diffraction (XRD). Required XRD patterns were recorded on a Rigaku MiniFlex II diffractometer working in Bragg-Brentano geometry using Cu Kα radiation.

Particle size and morphology were investigated by using scanning electron microscopy (SEM). To this purpose, a scanning electron microscope Zeiss EVO MA10 equipped with a LaB6-cathode was applied. Pressure in the sample chamber was $5 \times 10^{-2}$ Pa and acceleration voltage was 20 kV.

Photoluminescence (PL) as well as PL excitation (PLE) spectra were recorded on an Edinburgh Instruments FLS920 spectrometer equipped with a Xenon arc lamp (450 W) and a cooled ($-20$ °C) single-photon counting photomultiplier (Hamamatsu R2658P). Spectral resolution for the PL and PLE spectra measurements was typically set to value of 0.1 nm. The recorded PL spectra were corrected by applying a spectral sensitivity function obtained from a tungsten incandescent lamp certified by the National Physics Laboratory, UK.

Temperature dependent PL measurements upon 288 nm excitation were recorded using a microsecond pulsed Xe flash lamp (Heraeus µF920H) attached to the same Edinburgh Instruments FLS920 spectrometer.

Temperature dependent PL measurements from 80 to 500 K were performed using an Oxford Instruments cryostat Microstat N2, where liquid nitrogen was applied as the cooling agent. Typical temperature stabilization time was 60 s and the tolerance was set to ±3 K. PL measurements at 3 K were performed in a closed cycle cryocooler Optistat AC-V12 from Oxford Instruments, where helium was used as the cooling agent. Diffuse reflectance spectra (DRS) were carried out on an Edinburgh Instruments F9290 spectrometer equipped with a Xe arc lamp (450 W), a cooled ($-20$ °C) single-photon counting photomultiplier (Hamamatsu R928) as well as with a Spectralon integrating sphere. BaSO₄ (99.998%, Sigma Aldrich) or MgF₂ (99.995%, optical grade, Sigma Aldrich) powder was used as the reflectance standard. External quantum efficiencies (EQE) were determined using the approach of Kawamura et al.²⁸ Reflectance measurements in the UV spectral range (150–300 nm) were carried out on an Edinburgh Instruments FLS 920 spectrometer equipped with a deuterium lamp (DS-775) and a cooled ($-20$ °C) single-photon counting photomultiplier. MgF₂ (99.995%, optical grade, Sigma Aldrich) was used as the reflectance standard.

The Raman studies were performed using an Jobin Yvon HR 800 dispersive Raman spectrometer equipped with a frequency-doubled Nd:YAG laser ($\lambda = 532$ nm; $P = 20$ mW) as a radiation source.

Crystal Structure and Band Structure Calculation

Description of the crystal structure of inverse garnet $Y_2Mg_3Ge_3O_{12}$—Although silicates adopting the garnet structure of the general formula $A_2B_2X_3O_{12}$ are relatively well investigated, knowledge about the germanium based garnets is still insufficient. Garnets crystallize in a body centered crystal system with eight formula units per unit cell. The respective space group is $Ia\overline{3}d$ (230). The investigated structure is an inverse garnet with a mixed $\text{Mg}^{2+}/\text{Y}^{3+}$ occupancy of the dodecahedral site A where the cations are surrounded by 8 oxygen atoms, forming a polyhedron with point symmetry $D_2$. The atoms located onto site B, occupied by $\text{Mg}^{2+}$, are surrounded by 6 oxygen atoms in a slightly trigonal distorted octahedral coordination with the point symmetry of $C_3v$. The representation of the crystal structure is depicted in Fig. 1. Incorporation of $\text{Mn}^{4+}$ into the host structure will lead to a substitution of the $\text{Mg}^{2+}$ ions in octahedral coordination. It is well known, that $\text{Mn}^{4+}$ can be stabilized only in octahedral coordination. This is due to the large gain of crystal field stabilization energy of $\text{Mn}^{4+}$ ($|\text{Ar}\text{Mn}^4\text{F}^4|$) in an octahedral crystal field. The charge compensation was accomplished by the incorporation of $\text{Li}^+$. It is assumed, that the $\text{Li}^+$ ions will substitute either the B or the C site in the garnet. Several Garnets are known from literature, wherein lithium occupies the C site e.g. in $Y_3\text{Te}_2\text{Li}_3\text{O}_{12}$. On the other hand, $\text{Li}^+$ has an effective ionic radius of 0.76 pm in octahedral coordination and $\text{Mg}^{2+}$ has an effective ionic radius of 0.72 pm in octahedral coordination.²⁹ Additionally, it cannot be fully excluded that lithium substitutes A site. Even though this might be rather improbable due to the relatively long M-O distances ($M = \text{Y, Mg}$) of 239.4 pm.³⁰ From this considerations it is not obvious, which site lithium will preferentially occupy.

A Rietveld refinement was performed to obtain detailed crystal structure information on the $\text{Mn}^{4+}$-doped $Y_2\text{Mg}_3\text{Ge}_3\text{O}_{12}$ phosphor. The single crystal structure data of $Y_2\text{Mg}_3\text{Ge}_3\text{O}_{12}$, as reported by Lévy and Barbier were used as the starting structure model for the refinement.³⁰ Fig. 2 shows the recorded, calculated, and difference XRD patterns for the Rietveld refinement of $Y_2\text{Mg}_3\text{Ge}_3\text{O}_{12}:\text{Mn}^{4+}(1\%)\text{Li}^+(1.5\%)$ phosphor. The reliability factors are also listed in Table I indicating the quality of the refinement process. The refinement results designate that the $Y_2\text{Mg}_3\text{Ge}_3\text{O}_{12}:\text{Mn}^{4+}(1\%)\text{Li}^+(1.5\%)$ phosphor crystallizes in the garnet structure type with the $Ia\overline{3}d$ space group and unit cell parameters $a = b = c = 12.2184$ Å, $V = 1824.0763$ Å³, and $Z = 8$. The crystallographic data and atomic coordinates are also collected in Table I.

SEM images of the synthesized phosphors (Figs. 3a and 3b) show that the size of distinguishable particles formed is typically in the micrometer range ($\sim 20–200$ μm). Smaller structural subunits of the agglomerates revealed are in the range of a few hundred nanometers. The chemical composition according to the formula $Y_2\text{Mg}_3\text{Ge}_3\text{O}_{12}$...
Table I. Crystallographic data for $\text{Y}_2\text{Mg(Mg}_{0.99}\text{Mn}_{0.01})_2\text{(Ge}_{0.9956}\text{Li}_{0.0044})_3\text{O}_{12}$ as obtained from Rietveld refinement.

| Composition | $\text{Y}_2\text{Mg(Mg}_{0.99}\text{Mn}_{0.01})_2\text{(Ge}_{0.9956}\text{Li}_{0.0044})_3\text{O}_{12}$ |
|-------------|-------------------------------------------------------------------------------------------------|
| Crystal system | Cubic |
| Space group | $\text{Ia} \bar{3}d$ (230) |
| Cell parameters | $a = b = c = 12.2184 \, \text{Å}$; $\alpha = \beta = \gamma = 90^\circ$ |
| $Z$ | 8 |
| $R_{wp}$ | 3.91 |
| $R_p$ | 2.51 |
| $\chi^2$ | 5.810 |

Atomic coordinates

| Wyckhoff position | Atom | x | y | Z | SOF |
|------------------|------|---|---|---|-----|
| 24c              | Y    | 1/8 | 0 | 1/4 | 2/3 |
| 24c              | Mg1  | 1/8 | 0 | 1/4 | 1/3 |
| 16a              | Mg2  | 0  | 0 | 0  | 1  |
| 24d              | Ge   | 0.375 | 0 | 1/4 | 1  |
| 96h              | O    | -0.03297 | 0.05369 | 0.15693 | 1  |

was confirmed by EDX spectra (Fig. 3c). The quantification led to the following composition: Mg 16.9%, Y 10.3%, Ge 14.1%, O 58.6%.

Theoretical calculations.—For ab initio calculations, we used the CASTEP module of the Materials Studio Package (v. 8.0). The linear density approximation (LDA) with the CA-PZ functionality, based on the Ceperley and Alder data as parameterized by Perdew and Zunger, was applied to treat the exchange-correlation effects.31–33 The dodecahedral site is partly occupied by yttrium and magnesium atoms in $\text{Y}_2\text{Mg}_3\text{Ge}_3\text{O}_{12}$. Therefore, the virtual crystal approximation (VCA) was applied.34 Ultrasoft pseudo-potentials were employed for a description of the interaction between the ionic cores and the valence electrons. The electronic configurations used in the band structure calculations were as follows: $4s^24p^64d^1$ $5s^2$ for Y, $2s^22p^63s^1$ for Mg, $4s^24p^2$ for Ge and $2s^22p^4$ for O ions, respectively. The energy convergence parameter was set to $5 \times 10^{-6}$. The Monkhorst-Pack k-points were set as $10 \times 10 \times 10$. The calculations were performed for a cubic unit cell.

Calculations of the Mn$^{4+}$ energy levels in $\text{Y}_2\text{Mg}_3\text{Ge}_3\text{O}_{12}$ host were performed using the exchange charge model of crystal field. Details of the model, including all pertinent equations and explanations, have been explained earlier in a number of publications and, therefore, are not repeated here for the sake of brevity.35 A significant advantage of the model is that it allows for calculating the crystal field parameters based on the experimental crystal structure data. It also accounts for the effects of the chemical bond formation between the impurity ion and ligands by evaluating the overlap integrals of their wave functions. A large cluster consisting of 92247 ions was built to achieve convergence of crystal lattice sums, especially for the second rank crystal field parameters. The calculated values of the crystal field parameters and energy levels of the Mn$^{4+}$ ions in $\text{Y}_2\text{Mg}_3\text{Ge}_3\text{O}_{12}$ are presented below in Table II.

Table II. Calculated energy levels (in cm$^{-1}$) for Mn$^{4+}$ in $\text{Y}_2\text{Mg}_3\text{Ge}_3\text{O}_{12}$.

| $\text{Oh}$ group notation | $\text{LS}$ Term | Energy (cm$^{-1}$) |
|-----------------------------|------------------|------------------|
| $4A_2g$ (4F)               | 0                |
| $2E_g$ (2G)                | 15829            |
| $2T_{1g}$ (2G)             | 16881, 17658     |
| $4T_{2g}$ (4F)             | 23434, 24564     |
| $2T_{2g}$ (2G)             | 23285, 25273     |
| $4T_{1g}$ (4F)             | 33247, 35031     |
| $2A_{1g}$ (2G)             | 36283            |
| $2T_{2g}$ (2H)             | 39321, 39660     |
| $4T_{1g}$ (4P)             | 52025, 56945     |

Results and Discussion

Diffuse reflectance and band structure.—The diffuse reflectance spectrum (DFR) of an undoped $\text{Y}_2\text{Mg}_3\text{Ge}_3\text{O}_{12}$ powder is depicted in Fig. 4. The significant decrease of the DFR signal intensity below 400 nm spectral region points to the beginning of intrinsic absorption of the studied garnet. The inset of Fig. 4 depicts the optical bandgap estimation of the undoped host material which is derived by the aid of the Tauc relation:

$$[F(R_{\infty}h\nu)]^n = A(h\nu - E_g),$$

where $E_g$ is the optical bandgap of the material. The inset shows the extrapolation of the bandgap energy for the undoped host material according to the Tauc relation.36,37
where $\hbar \nu$ is the photon energy, $A$ is a proportional constant, $E_g$ is the value of the bandgap, $n$ is 2 for direct a transition or 1/2 for an indirect transition and $F(R_w)$ is the Kubelka-Munk function, which is defined as follows:\(^{38}\)

$$F(R_w) = \frac{(1 - R)^2}{2R} = \frac{K}{S},$$  \hspace{1cm} [2]

Where $R$, $K$, and $S$ are the reflection, absorption and scattering coefficient, respectively. From the linear extrapolation $[F(R_w \hbar \nu)]^2 = 0$ in Fig. 4 (see red line), the optical bandgap $E_g$ was estimated to be 5.5 eV.

The density functional theory calculations of the band structure for $Y_2Mg_3Ge_3O_{12}$ based on the crystal data (see Table I) are shown in Fig. 5. According to our calculations, this compound processes a bandgap of about 5.19 eV, with the valence band (VB) maximum and the conduction band (CB) minimum at the \( \Gamma \) point. Therefore, the material has a direct bandgap. It is expected that the value of the calculated bandgap is smaller than the experimental one as the LDA mostly underestimates the size of the bandgap. Perdew reported, that the LDA calculated bandgap is in most oxides up to 40% smaller than that from experimental data.\(^{38}\) Such small difference of the energy gap values (0.3 eV) arising from the calculations and the Tauc analysis may suggest that the latter method underestimates a real energy gap value and additional studies are needed for clarification of this question.

The upper part of VB predominantly originates from the O 2s and O 2p states with a smaller contribution arising from Y/Mg 5s, Y/Mg 4p states, respectively (Fig. 6). The VB consists of many very narrow sub bands due to all constituent ions covering 5 eV energy range. The bottom of CB is mostly composed of Ge 4s and 4p states. The wide bandgap of the host, taken together with the experimental excitation spectra exhibiting two well seen bands of the $^4A_2 \rightarrow ^4T_2$ and $^4A_2 \rightarrow ^4T_1$ transitions lead to the conclusion that the energy levels of the Mn$^{4+}$ ion including the $^4T_1$ (F) state are located in the bandgap.

**Excitation and emission spectra at 300 K.**—Fig. 7 shows the PLE, PL and DRS spectra of $Y_2Mg_3Ge_3O_{12}$:Mn$^{4+}$,Li$^+$ at room temperature. The PLE exhibits two excitation bands in the wavelength range 250–450 nm. The short-wavelength band below 350 nm is deconvoluted to a charge transfer transition (CT) $O^2-$Mn$^{4+}$ and to an intracutational transition of Mn$^{4+}$ ions. The Gaussian deconvolution of excitation spectra were performed in linear energy scale and afterwards transformed nm scale as presented in Fig. 7. The excitation bands peaking at 269 nm, 291 nm, and 421 nm are due to the fully allowed CT and to the spin-allowed intracutational transitions $^4A_2 \rightarrow ^4T_1$, and $^4A_2 \rightarrow ^4T_2$ ($^4T_1$ of Mn$^{4+}$ ions in octahedral coordination, respectively. The PL spectrum, which originates from the spin-forbidden $^2E \rightarrow ^4A_2$ transition is composed of several sharp lines centered at 658 nm. The feature at 639 nm is attributed to the zero phonon line (ZPL) (Fig. 7). Furthermore, phonon side bands at higher energies (anti-Stokes) and at lower energies (Stokes) of the ZPL can be identified. The efficiency of the prepared phosphor was examined by determining the $eQE$. The $eQEs$ was found to be about 51%.

The calculations of the crystal field parameters for the Mn$^{4+}$ ions at the Mg octahedral sites resulted in the following non-zero parameters (all in cm$^{-1}$, Stevens normalization): $B_{2g}^1 = 3917$, $B_{2g}^2 = -4532$, $B_{2g}^3 = 13574$, $B_{2g}^4 = 112404$. The structure of the Hamiltonian considering only these non-zero parameters emphasizes the trigonal symmetry of the octahedral Mg sites. Diagonalization of the crystal field
levels are compared with the experimental spectra in Fig. 7. As it turns out from this Figure, a good agreement between the calculated levels and main features of the excitation and emission spectra is achieved.

**Excitation and emission spectra at 3 K.**—To investigate the luminescence of Mn$^{4+}$ center in more detail, we recorded high resolution excitation and emission spectra at 3 K (Fig. 8). The 3 K measurement avoids thermal broadening of the spectral bands and allows a more reliable assignment of the energy levels. Furthermore, the excited state becomes narrow in energy and is of a well-defined parity. The radiative transition to the ground state takes place via one or more intermediate transitions of a pure electronic state of even parity and a vibronic state of odd parity. The intensity and the splitting of the ZPL is strongly influenced by the local site symmetry of the Mn$^{4+}$ ion. It is well established, that the octahedra sites in garnets reveal a trigonal distortion. The octahedra are stretched along the 3-fold axis. The faces of the equivalent triangles are plane parallel, which leads to a site symmetry of $C_3v$. However, this trigonal distortion does not cause the splitting of the $^3$E emitting state. The splitting of the $^3$E can be explained by spin-orbit coupling, which was found e.g. for YAG:Mn$^{4+}$ as well. The splitting of the ZPLs is about 16 cm$^{-1}$, which is comparable to YAG:Mn$^{4+}$ with $\sim$19 cm$^{-1}$ (see Fig. 9). The phonon fine structure observed will be further discussed in the next section.

**Fine structure of the phonon sidebands.**—The fine structure of the strong phonon sidebands as shown in the 3 K PL spectrum are originating from phonon states, which are directly excitable in the surrounding of the emitting center (i.e. local modes). In accordance to the work of Hurrel et al. we tried to assign the different vibrational modes as indicated in Fig. 9 with the help of the factor group analysis. The phonon energies, which are associated with the vibrations of the GeO$_2$ tetrahedra, agree very well with the fine structure, which was reported for $Y_2$Al$_5$O$_{12}$ before. The room-temperature Raman spectrum of $Y_2$Mg$_3$Ge$_3$O$_{12}$ is presented in Fig. 10. As described by Cavalli et al. for $Ca_3Sc_2Ge_3O_{12}$ we assigned the observed Raman active modes in a similar way in our germanate garnet (see Fig. 10). The $v_3$ local mode cannot be identified in the Raman spectrum, because in $T_d$ symmetry only $v_1$, $v_2$, $v_3$, and $v_4$ normal modes can occur.

**Temperature dependent emission spectra.**—The photoluminescence of Mn$^{4+}$ in $Y_2$Mg$_3$Ge$_3$O$_{12}$:Mn$^{4+}$ (1%)Li$^+(1.5\%)$ shows an extraordinarily high thermal quenching temperature above $T_{1/2} > 800$ K ($T_{1/2}$ is defined as the temperature, whereat PL integrals decrease to 50%). Two mechanisms for the thermal quenching of Mn$^{4+}$ luminescence were proposed so far. The first one is connected with a crossover of the Franck-Condon shifted $^4T_{2g}$ state with the $^4A_{2g}$ ($^4F$) ground state. (see the postulated quenching mechanism in Fig. 11b) as studied in YAG. The second is related to a low-lying O$^{2-}$-Mn$^{4+}$ CT state, which has been proposed responsible for quenching in pyrochlores. According to our study, the spectral position of the O$^{2-}$-Mn$^{4+}$ CT state in $Y_2$Mg$_3$Ge$_3$O$_{12}$ is below 300 nm (see the deconvolution of short-wavelength excitation bands in Figs. 7 and 8), which is very similar to $Mg_3Ge_2O_{12}$:Mn$^{4+}$, where analogous excitation band is covering the same spectral range. The reported $T_{1/2}$ value for $Mg_3Ge_2O_{12}$:Mn$^{4+}$ is about 700 K. Furthermore, the energy of the $^4A_{2g} \rightarrow ^4T_{2g}$ transition in $Y_2$Mg$_3$Ge$_3$O$_{12}$ is much higher (the band

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**Figure 8.** PL and PLE spectra of $Y_2$Mg$_3$Ge$_3$O$_{12}$:Mn$^{4+}$ (1%)Li$^+(1.5\%)$ at 3 K. The assignments of the intraconfigurational Mn$^{4+}$ and O$^{2-}$-Mn$^{4+}$ transitions are also shown.

**Figure 9.** Emission spectrum of $Y_2$Mg$_3$Ge$_3$O$_{12}$:Mn$^{4+}$ (1%)Li$^+(1.5\%)$ at 3 K with the assignment of the vibrational modes.

**Figure 10.** Raman spectrum of $Y_2$Mg$_3$Ge$_3$O$_{12}$:Mn$^{4+}$ (1%)Li$^+(1.5\%)$ at 300 K.
peaks at \(\sim 420\) nm) than e.g. in YAG (\(\sim 485\) nm). The experimental data available on the germanate garnet does not allow unique identification of thermal quenching mechanism. But considerably higher location energy levels of the Mn\(^{4+}\) ion (due to stronger crystal field in comparison with YAG) and CT state is obviously responsible for the observed high thermal quenching temperature of Mn\(^{4+}\) luminescence in Y\(_2\)Mg\(_3\)Ge\(_3\)O\(_{12}\). Obviously, the energetic position of the \(^4T_2\) level of Mn\(^{4+}\) and CT transition is crucial for obtaining red phosphors with high quenching temperature.

Temperature dependent decay curves.—Decay curves over the temperature range 75–700 K are shown in Fig. 12. At 300 K, the average lifetime revealed 3.2 ms for Y\(_2\)Mg\(_3\)Ge\(_3\)O\(_{12}\):Mn\(^{4+}\)(1%),Li\(^{+}\)(1.5%), respectively. At temperatures from 3 to 500 K, the decay curves of the investigated compound remain mono-exponential. The calculated lifetimes versus temperature are depicted in Fig. 12b.

The internal quantum efficiencies (iQE) have been calculated in accordance with Eq. 3,

\[
iQE = \frac{\tau_{300\,K}}{\tau_0} \tag{3}\]

wherein \(\tau_0\) is the radiative lifetime and \(\tau\) the radiative lifetime at 300 K. Since \(\tau_0\) is approximately \(\tau_{3K}\), the average lifetimes at 3 K have been applied for the calculations of the iQE. The obtained value for the iQE is 64%. Upon increasing the temperature, the PL lifetime of the spin-forbidden \(^2E \rightarrow ^4A_2\) transition starts to decline linearly. The \(T_{1/2}\) value is about 400 K. This decline of \(\tau\) is much stronger in comparison to the decrease of the PL integrals. Beside an increased probability of non-radiative transitions, which decreases the radiative lifetime, this observation can be explained by the progressive mixing of the 3d Mn\(^{4+}\) with the 2p O\(^-\) orbitals which weakens the parity rule and therefore additionally decreases the lifetime of the excited state.
Conclusions

A novel deep red emitting phosphor according to the composition Y₂Mg₂Ge₃O₁₂:Mn⁴⁺,Li⁺ was successfully synthesized via a sol-gel precursor and subsequently treated by a conventional solid state reaction. The band structure was investigated by DFT calculations and experimentally evaluated with UV/Vis reflectance spectroscopy. The optical bandgap (or the beginning of intrinsic absorption) of undoped Y₂Mg₂Ge₃O₁₂ was found to be at about 5.5 eV. Moreover, it was shown that Y₂Mg₂Ge₃O₁₂:Mn⁴⁺,Li⁺ absorbs efficiently broad-band near UV to blue light and provides bright narrow band red emission with a maximum at 658 nm. At very low temperature (3 K) a rather complicated vibronic structure of the PL, due to vibronic coupling with the host lattice, was revealed. The calculations of the Mn⁴⁺ energy levels in Y₂Mg₂Ge₃O₁₂ were performed using the exchange charge mixing model of the crystal field. The obtained values of energy level positions are in very good agreement with the experimental luminescence data. The PL measurements show an extraordinarily high thermal quenching temperature, which is explained by the large energy difference between the Franck-Condon shifted ⁴T₂g state and the ⁴A₂g ground state, which ensures high energy barrier for thermal quenching. Also the O²⁻–Mn⁴⁺ CT state is located at high energies. The PL lifetime of the spin-forbidden ⁴E → ⁴A₂ transition decreases linearly as a function of temperature. This can explained by the progressive mixing of the 3d Mn⁴⁺ with the 2p O²⁻ orbitals which weakens the parity rule and therefore decreases the lifetime of the emitting state and additionally by an increased probability of non-radiative transitions. In principle, this type of Mn⁴⁺ phosphor has a potential serving as a red component in phosphor blends for high power (brightness) pcLEDs, since this material possesses an extraordinary high thermal quenching temperature.

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References

1. C. Feldmann, T. Jüstel, C. R. Ronda, and P. J. Schmidt, Adv. Funct. Mater., 13, 511 (2003).
2. A. Katelnikovas et al., Opt. Mater. (Amst.), 34, 1195 (2012).
3. T. Jansen and T. Jüstel, Mater. Sci. Appl., 5, 1074 (2014).
4. G. Bisale and A. Bril, Appl. Phys. Lett., 11, 53 (1967).
5. Z. Xia and A. Meijerink, Chem. Soc. Rev., 46, 275 (2017).
6. S. Li, X. Liu, R. Mao, Z. Huang, and R. Xie, RSC Adv., 5, 7650 (2015).
7. R. Mueller-Mach et al., Phys. status solidi, 202, 1727 (2005).
8. H. A. Hoppe, H. Lutz, P. Morys, W. Schmick, and A. Seilmeier, J. Phys. Chem. Solids, 61, 2001 (2000).
9. T. Jansen and T. Jüstel, J. Phys. Chem. Solids, 110, 180 (2017).
10. M. G. Brik and A. M. Srivastava, J. Electrochem. Soc., 159, 1212 (2012).
11. R. Kasa and S. Adachi, J. Electrochem. Soc., 159, 189 (2012).
12. D. Chen, Y. Zhou, and J. Zhong, RSC Adv., 6, 66285 (2016).
13. Z. Zhou, N. Zhou, M. Xia, M. Yokoyama, and H. T. (Bert) Hintzen, J. Mater. Chem. C, 4, 9143 (2016).
14. M. G. Brik and A. M. Srivastava, J. Lumin., 133, 69 (2013).
15. T. Dueres, J. Plewa, and T. Jüstel, J. Alloys Compd., 693, 291 (2017).
16. R. J. Xie, Y. Q. Li, N. Hiroaki, and H. Yamamoto, Nitride Phosphors and Solid-State Lighting, p. 1, CRC Press, Boca Raton, FL, (2011).
17. H. Zha et al., Nat. Commun., 5, 4312 (2014).
18. J. Li et al., J. Mater. Chem. C, 4, 4611 (2016).
19. Q. Zhou et al., Mater. Chem. Phys., 170, 32 (2016).
20. H. F. Sijbom et al., ECS J. Solid State Sci. Technol., 5, R3040 (2016).
21. F. Baur, F. Glocker, and T. Jüstel, J. Mater. Chem. C, 3, 2054 (2015).
22. T. Murata, T. Tanoue, M. Iwamori, K. Morinaga, and T. Hase, J. Lumin., 114, 207 (2005).
23. L. Wang et al., Phys. status solidi, 210, 1433 (2013).
24. L. Thornton, J. Opt. Soc. Am., 40, 579 (1950).
25. W. Bischof and E. Kostiner, J. Solid State Chem., 6, 80 (1973).
26. O. M. Noginov, N. Bogutis, K. Babalab, and R. R. Alminov, MRS Proc., 602, 107 (1999).
27. G. Bisale and B. C. Grabmaier, Luminescent Materials, Springer Berlin Heidelberg, Berlin, Heidelberg, (1994).
28. Y. Kawamura, H. Nasabe, and C. Adachi, Jpn. J. Appl. Phys., 43, 7729 (2004).
29. R. D. Shannon, Acta Crystallogr. Sect. A, 32, 751 (1976).
30. D. Lévy and J. Barbier, Acta Crystallogr. Sect. C. Cryst. Struct. Commun., 55, 1611 (1999).
31. S. J. Clark et al., Z Krist., 220, 567 (2005).
32. D. M. Ceperley and B. J. Alder, Phys. Rev. Lett., 45, 566 (1980).
33. J. P. Perdew and A. Zunger, Phys. Rev. B, 23, 5048 (1981).
34. L. Bellaiche and D. Vanderbilt, Phys. Rev. B, 61, 7877 (2000).
35. N. M. Avram and M. G. Brik, Optical Properties of 1d Ions in Crystals: Spectroscopy and Crystal Field Analysis, Springer, Berlin and Heidelberg, (2013).
36. J. Taue, R. Grigorovici, and A. Vancu, Phys. status solidi, 15, 627 (1966).
37. J. Taue, Mater. Res. Bull., 5, 37 (1968).
38. P. Kubelka and F. Munk, Z. Tech. Phys., 12, 593 (1931).
39. J. P. Perdew, Int. J. Quantum Chem., 30, 451 (1986).
40. J. F. Donegan, T. J. Glynn, L. J. Imbusch, and J. P. Remeika, J. Phys. Rev., 61, 2001 (2000).
41. J. P. Hurrell, S. P. Porto, S. S. Mitra, and R. P. Bauman, J. Phys. Rev., 173, 851 (1968).
42. E. Cavalli et al., J. Phys. Condens. Matter, 12, 4665 (2000).
43. D. Chen et al., J. Mater. Chem. C, 4, 1704 (2016).
44. T. Senden, T. H. Broers, and A. Meijerink, Opt. Mater. (Amst.), 60, 431 (2016).