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Journal of Luminescence 94–95 (2001) 331–335

JOURNAL OF
LUMINESCENCE

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Upconversion phenomena in the Yb^{3+} doped transition metal compounds Rb_2MnCl_4 and CsMnBr_3

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Abstract

Crystals of Yb^{3+} doped Rb_2MnCl_4 and CsMnBr_3 show orange-red $\text{Mn}^{2+} {}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$ upconverted luminescence under near-infrared Yb^{3+} excitation. By short 10 ns pulse excitations the upconversion (UC) process for both compounds has been determined to consist of a sequence of ground and excited-state absorption steps. This mechanism can gain nonzero probability by assuming an exchange mechanism between Yb^{3+} and Mn^{2+} . The efficiency of the UC process is dependent on the structural nature of the $\text{Yb}^{3+}\text{--Mn}^{2+}$ connection. It is three orders of magnitude more efficient in $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$ with a corner-sharing $\text{Yb}^{3+}\text{--Cl--Mn}^{2+}$ arrangement than in the face-sharing $\text{Yb}^{3+}\text{--Br}_3\text{--Mn}^{2+}$ arrangement of $\text{CsMnBr}_3 : \text{Yb}^{3+}$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Upconversion; Exchange interaction

1. Introduction

Upconversion (UC) is established in rare earth compounds as well as in a small number of transition metal ion systems [1,2]. A new type of UC process has recently been observed in mixed $\text{Yb}^{3+}/\text{Mn}^{2+}$ systems which includes cooperative electronic transitions based on exchange interactions between the two ions [3–5]. In the following, we describe the two title compounds which differ in their bridging geometry, ligand field strength and magnetic behavior. We are interested in the underlying upconversion mechanisms and the trends in UC efficiency when the chemical environment and the bridging geometry is changed.

2. Experimental section

Single crystals of $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$ and $\text{CsMnBr}_3 : \text{Yb}^{3+}$ were grown by the Bridgman technique using stoichiometric amounts of the corresponding chlorides and bromides, respectively, and a trace of Yb^{3+} , as described in Ref. [6]. The real ytterbium concentration is 0.5 ± 0.1 mol% measured by ICP-OES for the $\text{CsMnBr}_3 : \text{Yb}^{3+}$ compound. From absorption measurements it was concluded, that the concentration of Yb^{3+} in $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$ is $< 0.1\%$. The spectroscopic measurements were carried out as described in Ref. [4].

3. Results

In both crystals near-IR (NIR) excitation into a ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ absorption band of Yb^{3+} leads to

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orange-red broadband UC luminescence at 10 K, which is readily assigned to the $\text{Mn}^{2+} {}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$ transition. Fig. 1 shows the corresponding optical spectroscopic results for $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$. In Fig. 1b both the downconverted $\text{Yb}^{3+} {}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ luminescence consisting of sharp lines around $10,000 \text{ cm}^{-1}$ and the upconverted broadband luminescence centered around $16,000 \text{ cm}^{-1}$ are seen. Note the different scales of the two spectra. For a laser power of 140 mW focused with a 53 mm focal lens on the crystal the ratio of VIS : NIR emitted photons is 30% at 15 K. Fig. 1a shows the excitation spectrum in the NIR of the UC luminescence. It correspond to the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ absorption bands.

Fig. 2a shows the σ -polarized absorption spectrum of $\text{CsMnBr}_3 : \text{Yb}^{3+}$ in the NIR and VIS. Both the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ absorption lines above $10,000 \text{ cm}^{-1}$ and the first d-d bands of $\text{CsMnBr}_3 : \text{Yb}^{3+}$ are recognized. Fig. 2b shows the downconverted NIR luminescence of Yb^{3+} and the upconverted luminescence at 12 K after Yb^{3+} excitation around $10,600 \text{ cm}^{-1}$. In this figure the scaling factor is three orders of magnitude

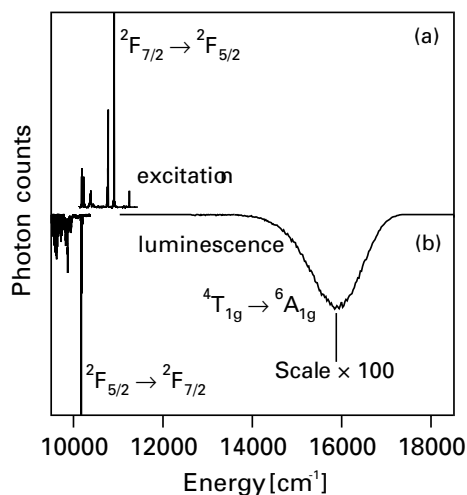


Fig. 1. (a) 15 K excitation spectrum monitoring the orange $\text{Mn}^{2+} {}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$ upconversion luminescence centered at $16,000 \text{ cm}^{-1}$. (b) Survey luminescence and upconversion luminescence spectra at 15 K of $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$ (<0.1%) excited with $E//c$ at $10,777 \text{ cm}^{-1}$. Note the magnification of the upconversion by a factor of 100.

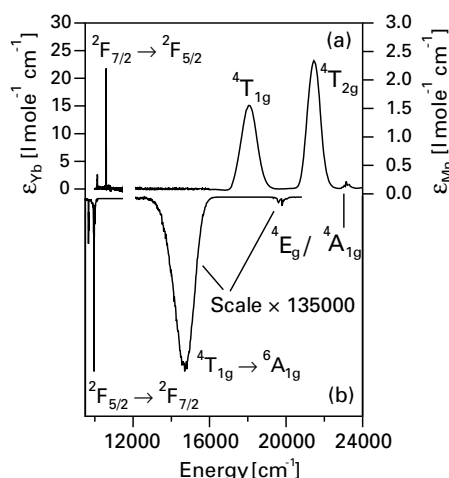


Fig. 2. (a) $E \perp c$ polarized absorption spectrum of $\text{CsMnBr}_3 : \text{Yb}^{3+}$ (0.5%) at 12 K. (b) 12 K luminescence and upconversion spectra after NIR excitation at $10,596 \text{ cm}^{-1}$ showing the Yb^{3+} luminescence around $10,000 \text{ cm}^{-1}$, the red $\text{Mn}^{2+} {}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$ upconverted luminescence centered at $14,500 \text{ cm}^{-1}$ and the green cooperative Yb^{3+} pair UC luminescence around $20,000 \text{ cm}^{-1}$. The UC luminescences are scaled up by a factor of 135,000.

larger than in Fig. 1, indicating that for equivalent excitation power at 12 K the ratio of VIS : NIR photons is three orders of magnitude smaller in this crystal than in $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$. In Fig. 2b we also recognize a very weak structured luminescence band around $20,000 \text{ cm}^{-1}$. This is assigned to a cooperative UC luminescence of Yb^{3+} pairs, which are present in small concentration in this crystal. This type of UC process has been described in numerous Yb^{3+} compounds [7]. We note that in $\text{CsMnBr}_3 : \text{Yb}^{3+}$ this luminescence can only be observed because it happens to lie in the absorption window between the ${}^4\text{T}_{1g}$ and ${}^4\text{T}_{2g}$ absorption bands of Mn^{2+} .

Fig. 3 shows the time dependence at 12 K of the upconverted luminescence intensity in a semilogarithmic representation after a 10 ns laser pulse into the Yb^{3+} absorption in the NIR for both crystals. We notice that the curves have no rise and correspond to single exponential decays. Decay times of 9.8 ms and 337 μs are derived for $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$ and $\text{CsMnBr}_3 : \text{Yb}^{3+}$ at 12 K, respectively.

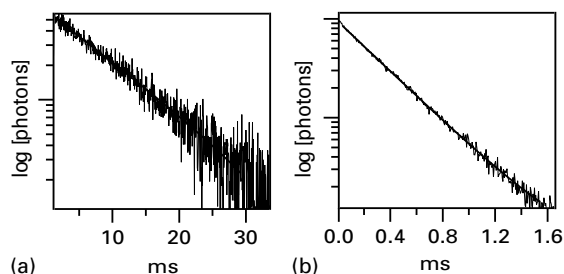


Fig. 3. Temporal behavior of the upconverted Mn^{2+} ${}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$ 12 K luminescence intensity exciting with a 10 ns laser pulse at $10,201.7\text{ cm}^{-1}$ and at $10,596\text{ cm}^{-1}$ in (a) $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$ and (b) $\text{CsMnBr}_3 : \text{Yb}^{3+}$, respectively. The straight lines show the single exponential fits to the experimental data.

4. Discussion

Fig. 4 shows the relevant structure elements of the two lattices. Rb_2MnCl_4 crystallizes in a layer-type perovskite structure with corner-sharing $[\text{MnCl}_6]^{4-}$ octahedra in two dimensions perpendicular to the tetragonal c -axis, see Fig. 4a. It is not known how Yb^{3+} is incorporated and charge compensation is achieved in this lattice. From absorption experiments we know that our crystal contains less than 0.1% Yb^{3+} , even though 1% of Yb^{3+} was added to the melt. Incorporation of Yb^{3+} and charge compensation is evidently difficult in this system. The situation is

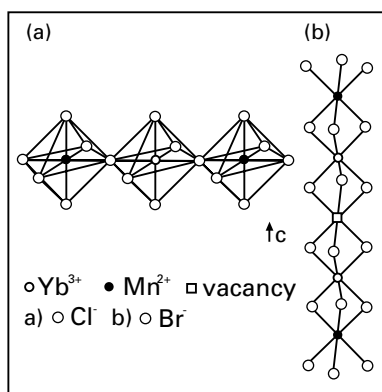


Fig. 4. Relevant elements of the $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$ and $\text{CsMnBr}_3 : \text{Yb}^{3+}$ structures representing schematically the corner-sharing (a) and face-sharing (b) connectivity between the Mn^{2+} ions.

very different in CsMnBr_3 , which crystallizes in a one-dimensional structure with face-sharing $[\text{MnBr}_6]^{4-}$ octahedra forming chains along the hexagonal c -axis. In this type of lattice the incorporation of trivalent ions such as Yb^{3+} is much easier and well established [8]. As shown in Fig. 4b, the most likely arrangement is one in which a sequence Yb^{3+} -vacancy- Yb^{3+} is replacing three Mn^{2+} ions. In this crystal the actual Yb^{3+} concentration of 0.5% is close to the one used in the melt for the crystal growth.

In the following, we will briefly discuss what we believe to be the main mechanism for the unusual UC phenomenon. In addition the question of the very different UC efficiencies in the two title systems will be addressed. Similar phenomena have very recently been reported for $\text{RbMnCl}_3 : \text{Yb}^{3+}$ and $\text{CsMnCl}_3 : \text{Yb}^{3+}$ [3]. In $\text{CsMnCl}_3 : \text{Yb}^{3+}$ the UC efficiency was found to be very high, similar to $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$ reported here, whereas in $\text{RbMnCl}_3 : \text{Yb}^{3+}$ it is significantly lower. The studies on the title compounds were motivated by these differences. We suspect a correlation with the structure, in particular the bridging between the incorporated Yb^{3+} ions and its Mn^{2+} neighbors. That is why we chose lattices with different bridging geometries between adjacent Mn^{2+} ions in the present study: corner-sharing octahedra in $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$ (Fig. 4a) and face-sharing octahedra in $\text{CsMnBr}_3 : \text{Yb}^{3+}$ (Fig. 4b).

From the UC excitation spectra in Figs. 1 and 2 it clearly follows that a ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ absorption is the first step in the upconversion process in both systems studied here. And the absence of a rise in the transient curves of Fig. 3 rules out an energy transfer UC mechanism. Both the ground-state absorption (GSA) step and the upconversion process occur within the 10 ns of the laser pulse. We conclude that the second step is an excited-state absorption (ESA) step from the intermediate level, and the total process thus a GSA/ESA sequence. Whereas the GSA is a normal Yb^{3+} absorption, the ESA causes considerable conceptual problems. It corresponds to an electronic transition from an intermediate state localized on Yb^{3+} to a final state localized on Mn^{2+} . This requires some kind of coupling between Yb^{3+} and Mn^{2+} . This could be either an exchange or an

electric multipole coupling. We believe that it is based on exchange interactions, and the experimentally found strong dependence of the upconversion efficiency on the bridging geometry confirms this. We use a $\text{Yb}^{3+}\text{--Mn}^{2+}$ dimer picture to account for the observed effects. We are aware that this is approximate, because $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$ is magnetically ordered at 12 K [9] and, in addition, Yb^{3+} is likely to have more than one Mn^{2+} neighbor in $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$. But the dimer picture, which is shown in Fig. 5, does contain the essential features for an understanding. And since a great deal of work has been done on transition metal dimers, we can use some old concepts from these studies as a basis. As seen in Fig. 5 the dimer states have double labels, one part from each partner. And the second step in the upconversion process, which causes the complications in a picture with separate Yb^{3+} and Mn^{2+} chromophores, is quite a normal ESA step within the dimer. How does the ESA step gain intensity? We believe that it is the same mechanism which gives intensity to pair transitions of Cr^{3+} , which are forbidden in a single-ion mechanism [10]. Tanabe and coworkers proposed such a mechanism to account for the absorption spectra of magnetically coupled Mn^{2+} systems [11]. It has been shown that this mechanism can enhance the intensity of transitions which are spin-forbidden in the single ion, by several orders of magnitude. It can also account for the occurrence of so-called cooperative transitions, such as double excitations in a Cr^{3+} dimer, which cannot occur in single ions [12]. The

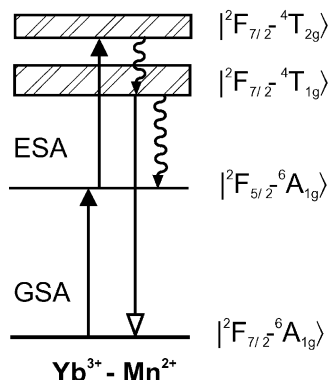


Fig. 5. Schematic representation of the UC mechanism in a $\text{Yb}^{3+}\text{--Mn}^{2+}$ dimer picture. Full arrow lines and curly arrows represent radiative and nonradiative relaxation processes.

ESA step in Fig. 5 is such a cooperative electronic transition, which takes the dimer from a nominally Yb^{3+} centered excited state to a nominally Mn^{2+} excited state.

For an exchange mechanism we expect a dependence of the efficiency of the process on the chemical and structural nature of the $\text{Yb}^{3+}\text{--Mn}^{2+}$ connection. For an electric multipole mechanism, on the other hand, we would expect a strong decrease of the efficiency with increasing $\text{Yb}^{3+}\text{--Mn}^{2+}$ distance. The present study very clearly shows a correlation with the nature of the $\text{Yb}^{3+}\text{--Mn}^{2+}$ bridge. If the $\text{Yb}^{3+}\text{--Mn}^{2+}$ distance was important we would expect a higher efficiency of the UC process in $\text{CsMnBr}_3 : \text{Yb}^{3+}$, because in this lattice the expected $\text{Yb}^{3+}\text{--Mn}^{2+}$ distance is 3.26 Å, much shorter than in $\text{Rb}_2\text{MnCl}_4 : \text{Yb}^{3+}$ with 5.05 Å. It appears safe to conclude that the corner-sharing $\text{Yb}^{3+}\text{--Cl--Mn}^{2+}$ arrangement is more efficient than the face-sharing $\text{Yb}^{3+}\text{--Br}_3\text{--Mn}^{2+}$ in promoting the cooperative ESA step in Fig. 5. This conclusion is in very good agreement with earlier suspicions based on $\text{RbMnCl}_3 : \text{Yb}^{3+}$ and $\text{CsMnCl}_3 : \text{Yb}^{3+}$. But it is only by the type of study presented here, i.e. a systematic variation of the bridging geometries, that we arrive at unambiguous conclusions.

In all the Yb^{3+} doped Mn^{2+} lattices studied so far this unusual UC is quenched at room temperature. We ascribe this to the occurrence of a nonradiative Mn^{2+} to Yb^{3+} multiphonon relaxation process which becomes efficient at high temperatures. Evidence for this is the observation of increasing Yb^{3+} luminescence with increasing temperature upon Mn^{2+} excitation in the VIS. Unfortunately, it is hard to circumvent this intrinsic loss channel by clever chemical engineering.

Acknowledgements

This work was financially supported by the Swiss Science National Foundation.

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