# New Light Emission Processes in Inorganic Materials

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*Abstract*: We synthesize new light-emitting inorganic materials. Emission is induced by photoexcitation and the photophysical processes are studied in detail by a variety of optical spectroscopic techniques. A focus of our research is on so-called upconversion processes and materials in which near-infrared radiation is transformed into visible emission. Potential applications of such processes are in lighting, imaging, display and laser devices. Both lanthanide and transition metal ion materials are investigated. Very interesting and novel behavior is observed in crystals containing both lanthanide and transition metal ions. We have chosen examples from this class of compounds to illustrate our research approach.

**Keywords:** Emission · Lanthanides · Luminescence · Transition metals · Upconversion

## Introduction

Light-emitting materials and processes are technologically very important; lighting, imaging, display, and laser devices are among the most important applications. Classically this area has been dominated by inorganic materials, but in the past decade organic light-emitting materials have been developed to very high degrees of efficiency and stability. Chemists are playing a significant role in the development of new materials.

In our research we combine chemical and physical concepts and techniques. The property of interest is the light emission of a material after photoexcitation. We are studying and trying to understand the photophysics behind the processes by applying a variety of optical spectroscopic laser techniques. The synthesis is always property-oriented and based on the principle of chemical and structural variation. How can we influence and tune the wavelength and the intensity of a light emission by a systematic variation of chemical and structural parameters? Photon upconversion (UC), *i.e.* the transformation of long-wavelength to short-wavelength radiation, has been and still is an important research topic in our group [1][2]. In the present paper we have chosen a specific example from an ongoing research project to illustrate our research strategy. Typical results from the spectroscopic studies are presented and the conclusions we draw from these results.

## 2. Results

Based on extensive experience in the field of UC in lanthanide materials [3] and some pioneering work on UC in transition metal ion systems [2] we decided to combine the f and d metal ions in the same compound to explore their UC behavior. So far we have studied the couples $Yb^{3+}/Mn^{2+}$, $Yb^{3+}/Cr^{3+}$, $Tm^{3+}/Re^{4+}$, $Tm^{3+}/Mo^{3+}$, $Er^{3+}/Os^{4+}$. Here we present some selected and representative results of $Yb^{3+}/Mn^{2+}$ systems. $Yb^{3+}$-doped $Mn^{2+}$ compounds such as $RbMnCl_3$, $CsMnCl_3$, $Rb_2MnCl_4$, and $CsMnBr_3$ all exhibit yellow-red luminescence at 15 K after near-IR excitation around 1μm [4–7]. Fig. 1 shows the 15 K upconversion luminescence spectra of $RbMnCl_3$:0.08%$Yb^{3+}$ and $CsMnCl_3$:0.9%$Yb^{3+}$ as examples. The efficiency of the process strongly depends on the temperature and the chemical and structural parameters of the $Mn^{2+}$ compound. Fig. 1 nicely illustrates the effect of an apparently trivial chemical variation: The $CsMnCl_3$:$Yb^{3+}$ luminescence is centered in the red while the $RbMnCl_3$:$Yb^{3+}$ luminescence is yellow. The luminescence is readily assigned to the $^4T_1 \rightarrow {}^6A_1$ transition of $Mn^{2+}$. Fig. 2a compares the 15 K crystal absorption of $CsMnCl_3$:$Yb^{3+}$ with the 15K UC excitation spectrum and Fig. 2b in the region of $^2F_{7/2} \rightarrow {}^2F_{5/2}$ excitations of $Yb^{3+}$. The coincidence of the sharp lines, which correspond to crystal-field components of $^2F_{5/2}$, clearly implicates the $Yb^{3+}$ ion in the upconversion process. Fig. 3 shows the temporal behavior of the 15 K UC luminescence intensity of $RbMnCl_3$:$Yb^{3+}$ (Fig. 3a) and $CsMnCl_3$:$Yb^{3+}$ (Fig. 3b) after an excitation laser pulse of 10 ns duration. The two materials behave differently: Whereas in $RbMnCl_3$:$Yb^{3+}$ the luminescence shows an exponential decay after the pulse, the UC intensity in $CsMnCl_3$:$Yb^{3+}$ first rises and then decays. This clearly tells us that two different mechanisms are at work in the two materials.

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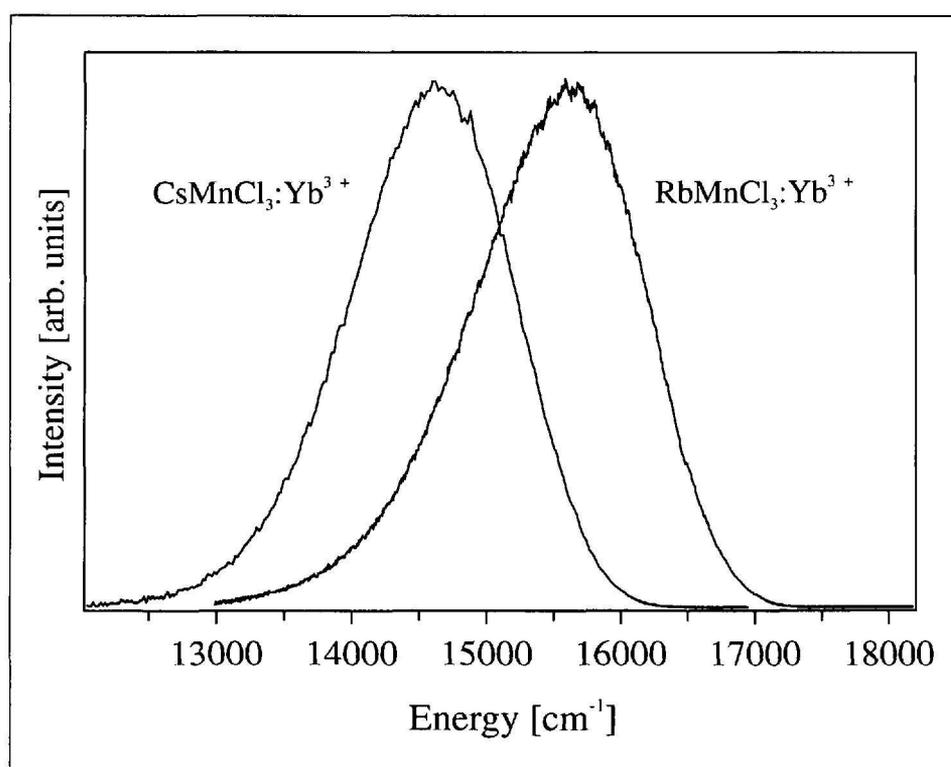Fax: +41 31 631 43 99
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Fig. 1. Upconversion luminescence spectra at 15 K of $Yb^{3+}$ doped crystals of $CsMnCl_3$ and $RbMnCl_3$ after 10680 $cm^{-1}$ and 10688 $cm^{-1}$ excitation into a $Yb^{3+}$ absorption band, respectively. The crystals were grown by the Bridgman technique and the spectra were taken as described in [5].
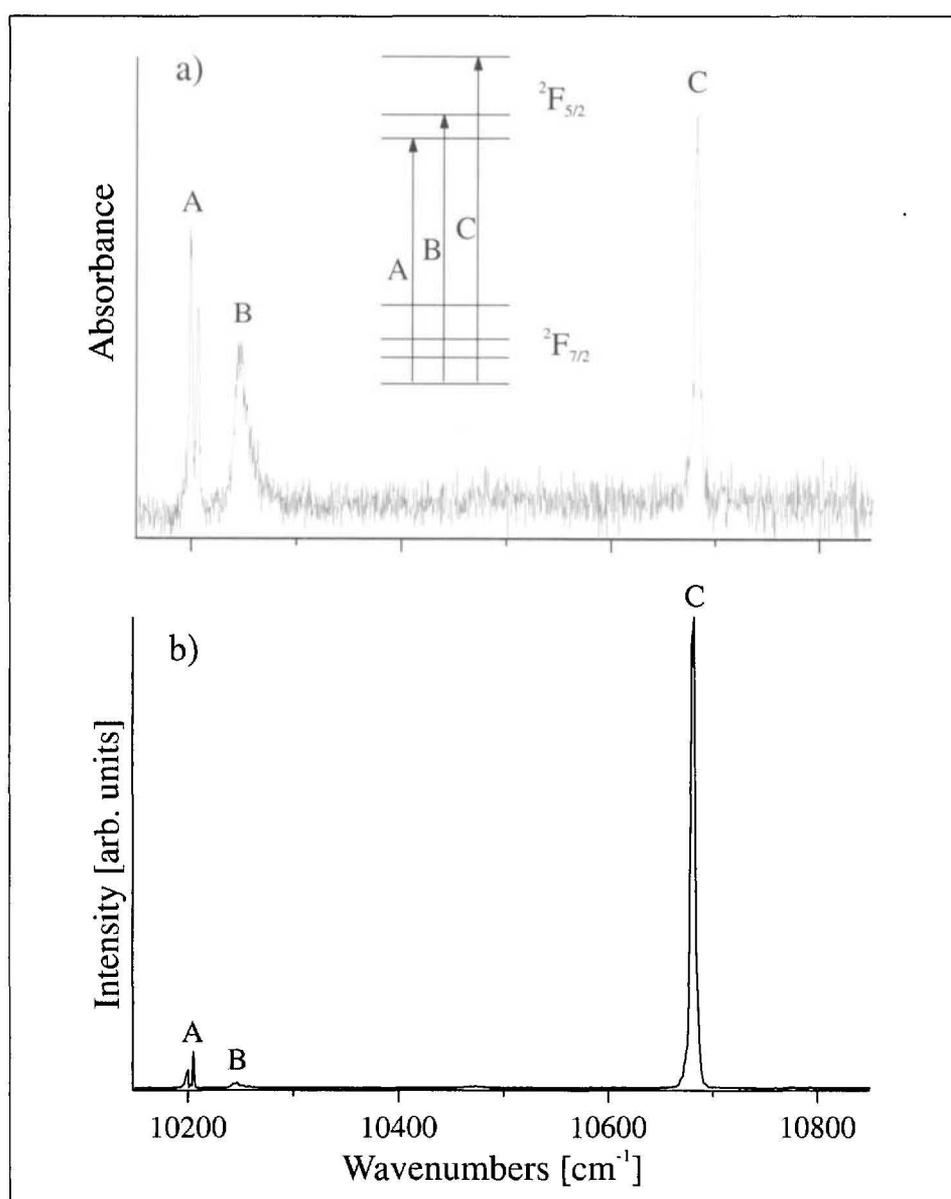


Fig. 2. Crystal absorption (a) and upconversion excitation spectrum (b) at 15 K of $Yb^{3+}$ doped $CsMnCl_3$. The luminescence was monitored at the maximum around 14500 $cm^{-1}$, see Fig. 1. See [5] for experimental details.
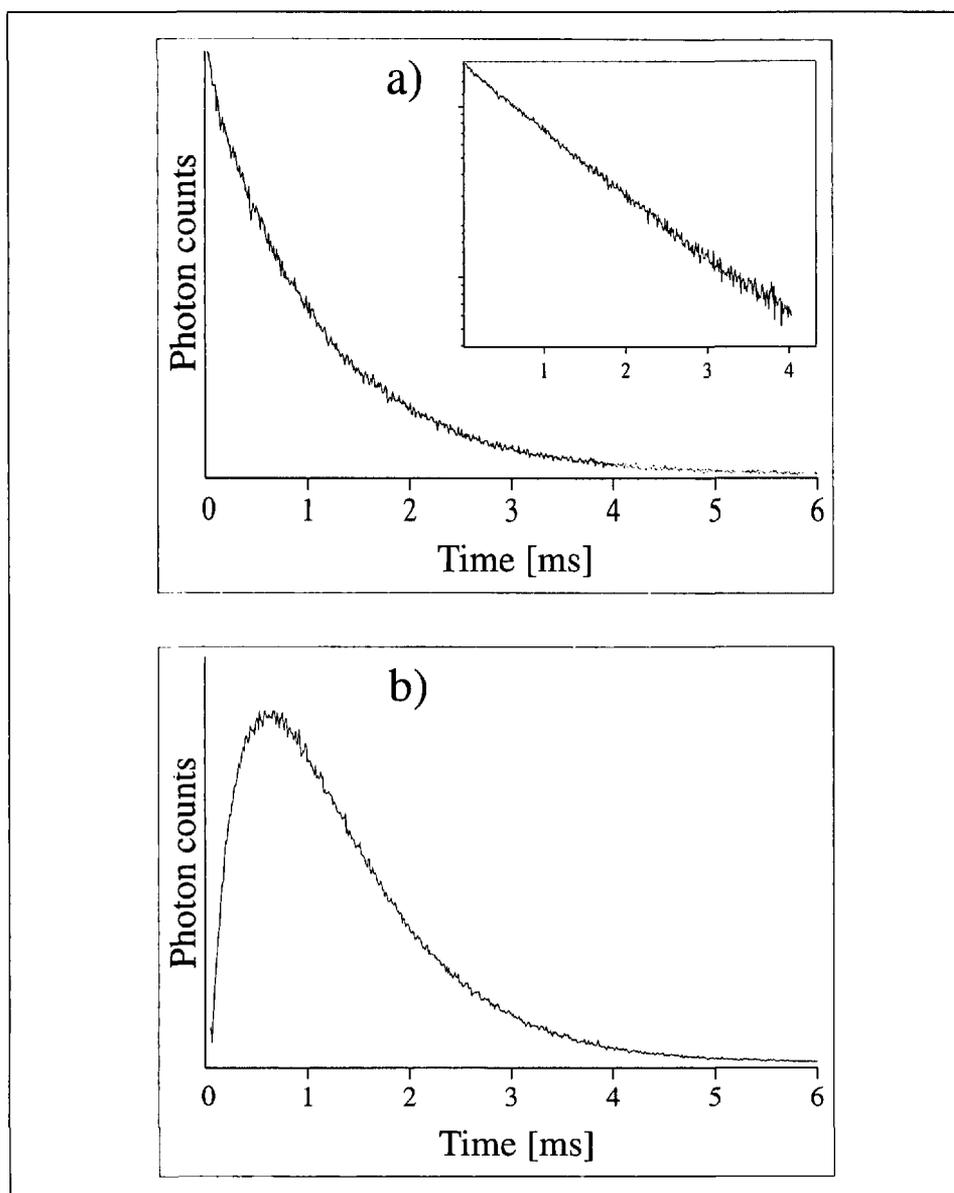
Fig. 3. Upconversion transients of RbMnCl$_3$:Yb$^{3+}$ (a) and CsMnCl$_3$:Yb$^{3+}$ (b) at 15 K after a 10 ns pulse excitation around 10700 cm$^{-1}$ into a $^2F_{7/2} \rightarrow ^2F_{5/2}$ Yb$^{3+}$ excitation. The inset in (a) shows a semilogarithmic representation of the same decay curve. See [5] for experimental details.

## 3. Discussion

The phenomena reported here have no precedent, because chemical compounds of this composition and experiments of this type have never been combined so far. We thus have no direct guidance from the literature in our attempt to understand the observed behavior. Nevertheless, we must conclude that the process is cooperative, because the absorption occurs on the Yb$^{3+}$ ion and the luminescence originates from Mn$^{2+}$. The most simple model, and certainly a very simplistic one in these materials which are magnetically ordered at low temperatures, is a dimer model. This is shown in Fig. 4 for RbMnCl$_3$:Yb$^{3+}$: We consider an Yb$^{3+}$ ion with its nearest-neighbor Mn$^{2+}$ ion as the relevant chromophoric unit. Consequently we use double labels to indicate the electronic state of both partners in a given dimer state. In this picture the UC process is less mysterious, because there is a dimer state around 10000 cm$^{-1}$, which is accessed with the first photon in a ground-state absorption (GSA) step. The second step corresponds to an excited-state absorption (ESA) from this intermediate [$^2F_{5/2}$-$^6A_1$] to the [$^2F_{7/2}$-$^4T_2$] dimer state. This is followed by a fast relaxation to [$^2F_{7/2}$-$^4T_1$] and then the luminescence to the ground state. Such a GSA-ESA sequence is well established within the f-f energy levels of trivalent lanthanides [8]. The new feature in our systems is that the sequence has cooperative character and does not occur on a single ion.

The efficiency of the UC process is highest in CsMnCl$_3$:Yb$^{3+}$ and Rb$_2$MnCl$_4$:Yb$^{3+}$, and it is lower by orders of magnitude in CsMnBr$_3$:Yb$^{3+}$. We ascribe this primarily to structural differences. In both CsMnCl$_3$:Yb$^{3+}$ and Rb$_2$MnCl$_4$:Yb$^{3+}$ the bridging between Yb$^{3+}$ and the nearest Mn$^{2+}$ is through a linear Yb$^{3+}$-Cl-Mn$^{2+}$ arrangement (corner-sharing octahedra, see Fig. 5), whereas in CsMnBr$_3$:Yb$^{3+}$ there is a face-sharing arrangement. We conclude that the corner-sharing Yb$^{3+}$-Cl-Mn$^{2+}$ bridge is most efficient in promoting the necessary coupling between the two ions to enable the cooperative process. Based on our experience with dimers of transition metal ions we believe that the underlying mechanism is an exchange mechanism [9].

The temporal behavior of the UC intensity after a short laser pulse provides important additional information about the mechanism. In RbMnCl$_3$:Yb$^{3+}$ both the GSA and the ESA photons are absorbed during the 10 ns of the laser pulse. The transient in Fig. 3a is thus simply the exponential decay curve of the $^4T_1$ state of Mn$^{2+}$. The situation is different for CsMnCl$_3$:Yb$^{3+}$. There is little UC inten-
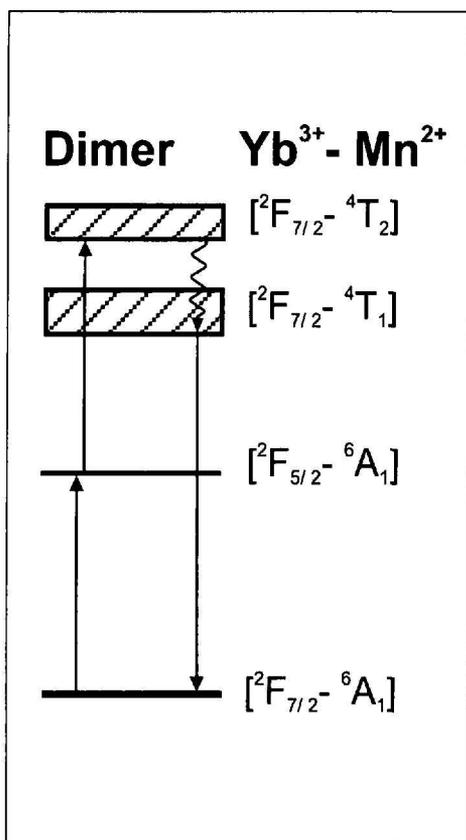
Fig. 4. Schematic representation of the upconversion process in $RbMnCl_3:Yb^{3+}$. GSA and ESA stand for ground-state and excited-state absorption, respectively. The dimer states are labeled with the respective electronic states of both partners.
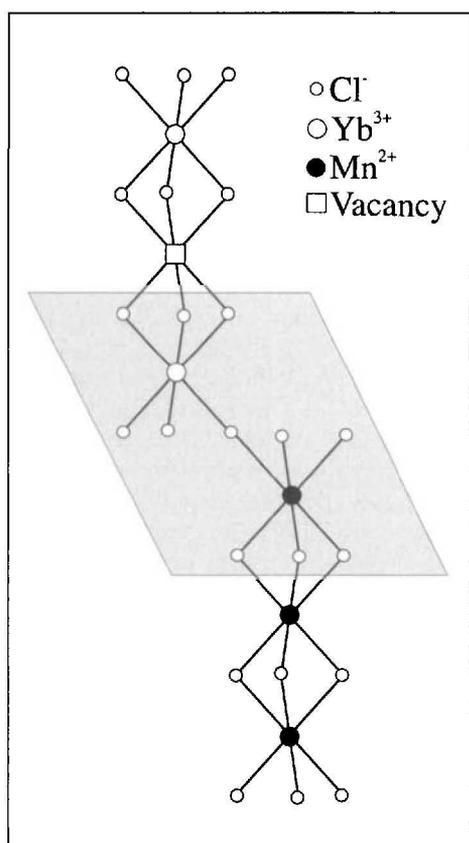
sity immediately after the laser pulse. This clearly indicates a relatively slow energy-transfer step, and the mechanism becomes more complicated than shown in Fig. 4 for $RbMnCl_3:Yb^{3+}$.

At room temperature the UC process is essentially quenched in all the $Yb^{3+}$-$Mn^{2+}$ materials studied so far. We have identified a thermally activated relaxation process from $[^2F_{7/2}\text{-}^4T_1]$ to $[^2F_{5/2}\text{-}^6A_1]$ as the main loss process. This is an intrinsic loss process, which is not easy to circumvent. It is likely to be more efficient in oxides and fluorides than in the chlorides studied here. We are considering the use of lattices with tetrahedral $Mn^{2+}$ sites instead of the octahedral ones reported here. We have also made first attempts to replace $Mn^{2+}$ by other transition metal ions emitting in the visible range. First experiments on $Yb^{3+}$ and $Cr^{3+}$ co-doped garnet lattices demonstrate the feasibility of UC processes also for this couple [10]. But again there is a competitive loss pathway at room temperature, and we have to further tailor our materials to reduce this.

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[1] D.R. Gamelin, H.U. Güdel, *Acc. Chem. Res.* **2000**, *33*(4), 235–242.
[2] D.R. Gamelin, H.U. Güdel, *Topics in Current Chemistry* **2001**, *214*, 1–56.
[3] H.U. Güdel, M. Pollnau, *J. of Alloys and Compounds* **2000**, *303-304*, 307–315.
[4] R. Valiente, O.S. Wenger, H.U. Güdel, *Chem. Phys. Lett.* **2000**, *320*, 639–644.
[5] R. Valiente, O.S. Wenger, H.U. Güdel, *Phys. Rev. B.* **2001**, 63, 165102.
[6] P. Gerner, O.S. Wenger, R. Valiente, H.U. Güdel, *Inorg. Chem.* **2001**, 40, 4534–4542.
[7] C. Reinhard, P. Gerner, R. Valiente, O.S. Wenger, H.U. Güdel, *J. Lumin.*, accepted.
[8] M.F. Auzel, *C.R. Acad. Sc. Paris* **1966**, 262, 1016.
[9] J. Ferguson, H.J. Guggenheim, Y.J. Tanabe, *J. Phys Soc. Jpn.* **1966**, 21, 692.
[10] S. Heer, M. Wermuth, K. Krämer, H.U. Güdel, *Chem. Phys. Lett.* **2001**, 334, 293–297.



Fig. 5. Relevant structural unit of $Yb^{3+}$ doped $CsMnCl_3$. The part in the frame corresponds to the $Yb^{3+}\text{-}Mn^{2+}$ dimer used in the model.