Luminescence upconversion under hydrostatic pressure in the 3d-metal systems Ti\(^{2+}\):NaCl and Ni\(^{2+}\):CsCdCl\(_3\)

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We present a study of upconversion materials and processes under external hydrostatic pressure. The near-infrared to visible photon upconversion properties of Ti\(^{2+}\)-doped NaCl and Ni\(^{2+}\)-doped CsCdCl\(_3\) at 15 K are studied as a function of external hydrostatic pressure. It is found that in Ti\(^{2+}\):NaCl pressure can be used to switch on an efficient upconversion mechanism, which is inactive at ambient pressure, leading to an order-of-magnitude enhancement of the overall upconversion efficiency of this material. For Ni\(^{2+}\):CsCdCl\(_3\) it is demonstrated that upconversion luminescence excitation spectroscopy can be used to study the pressure dependence of excited state absorption transitions. The results demonstrate the ability to tune upconversion properties by altering the local crystal field of active ions, in addition to probing the pressure dependence of excited state absorption transitions via upconversion spectroscopy.

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In this report we combine two active fields of condensed matter research, namely, upconversion spectroscopy and pressure studies. Upconversion is a nonlinear optical process, which converts low-energy light into higher-energy light. This process does not require coherent input radiation. Thus, upconversion materials have great application potential as luminescent materials for enhancing the efficiency of fluorescence lamps by converting their undesired near-infrared output into visible radiation.\(^1\) Additionally, upconversion materials have found use, for example, as solid state lasers,\(^2\) imaging phosphors,\(^3\) and quantum counters in IR detection systems.\(^5\) Intensive research efforts are therefore devoted to the design and control of the properties of upconversion materials. In the first half of our paper we demonstrate, for a specific example, how pressure can be used to tune the efficiency of such a near-infrared to visible photon upconversion process. From this we obtain fundamental insight into how crystal field changes affect the optically active ions in doped inorganic systems. In the second example, we demonstrate that upconversion techniques can be used to study the pressure dependence of more fundamental processes such as excited state absorption (ESA) transitions. Understanding such ESA processes is very important in laser materials research since they are detrimental for laser action, and the tuning range of many solid state lasers is limited by their occurrence.\(^5\) By studying their pressure dependence we obtain valuable information about their crystal field dependence.

As specific examples for our study we have chosen the 3d transition metal (TM) ions Ti\(^{2+}\) and Ni\(^{2+}\) instead of the more commonly used lanthanide ions. Due to the larger spatial extension of the spectroscopically active d electrons, the energy level structure of TM doped systems is particularly sensitive to environmental perturbations. These can be chemical or structural modifications,\(^6,7\) and here we study the effect of hydrostatic pressure on the upconversion properties of 0.8% Ti\(^{2+}\):NaCl and 5% Ni\(^{2+}\):CsCdCl\(_3\). We show that in 0.8% Ti\(^{2+}\):NaCl pressure can be used to switch on an efficient UC mechanism, which is inactive at ambient pressure, and this leads to an order-of-magnitude enhancement of the overall UC efficiency of this system. The example of Ni\(^{2+}\):CsCdCl\(_3\) shows that by UC luminescence excitation spectroscopy information about the pressure dependence of excited state absorption transitions can be obtained.

Ti\(^{2+}\) is a d\(^2\) ion. When doped into NaCl, it substitutes for Na\(^+\) and is thus in octahedral Cl\(^-\) coordination.\(^8\) Charge compensation was found to occur very likely as a Na\(^+\) vacancy.\(^5\) Figure 1(a) shows the relevant energy levels for octahedrally coordinated d\(^2\) ions as a function of the crystal field strength.\(^8\) For Ti\(^{2+}\):NaCl the energy level structure corresponds to the vertical dashed line. Figure 1(b) shows the 15 K ambient pressure absorption spectrum of 0.8% Ti\(^{2+}\)-doped NaCl. Two broad bands centered at 8200 and 15500 cm\(^{-1}\) are observed, and according to Fig. 1(a) they are assigned to the spin-allowed 3\(T_{1g} \rightarrow 3T_{2g}\) and 3\(T_{1g} \rightarrow 3T_{1g}\) transitions, respectively.\(^8\) Due to their weakness, no spin-forbidden tran-

\[\text{FIG. 1. (a) Tanabe-Sugano energy level diagram for octahedrally coordinated } d^2 \text{ ions. The vertical dashed line represents the ligand field strength in Ti}^{2+}:\text{NaCl. The } 15 \text{ K ambient pressure absorption and luminescence spectra (excited at } 15454 \text{ cm}^{-1} \text{) are shown in (b) and (c). (d) shows the pressure dependence of the } 3T_{1g}(t_{2g}e_g) \rightarrow 3T_{1g}(t_{2g}e_g) \text{ (VIS, circles) and } 3T_{2g}(t_{2g}e_g) \rightarrow 3T_{1g}(t_{2g}) \text{ (NIR, squares) luminescence band maxima. The latter data points were shifted to higher energy by } 7300 \text{ cm}^{-1}. \text{ The straight lines are linear regression fits to the experimental data with slopes of } 9 \text{ cm}^{-1}/\text{kbar.}\]
FIG. 2. 15 K normalized UC luminescence spectra obtained after 9394 cm$^{-1}$ excitation at (a) ambient pressure and (b) 34 kbar. The temporal evolution of these spectra after 10 ns pulsed excitation is shown on linear scales in (c) and (d), respectively.

sitions to singlet states are observed. Figure 1(c) shows the 15 K ambient pressure luminescence spectrum (upside down) obtained after excitation at 15 454 cm$^{-1}$. Two broad luminescence bands centered at 5460 and 12 850 cm$^{-1}$ with 15 K lifetimes of 1.5 ms and $\approx20$ $\mu$s, respectively, are observed. They are due to luminescence transitions from the $^{3}T_{2g}$ and $^{3}T_{1g}$, respectively, to the ground state. With the existence of two metastable excited states this system fulfills the basic prerequisite for UC processes. The temporal evolution of these spectra after 10 ns pulsed excitation pulse. This so-called transient is shown on linear scales in (c) and (d), respectively.

$^{3}T_{2g}$ data points were arbitrarily shifted to higher energy by 7300 cm$^{-1}$, in order to emphasize the equal pressure dependence of the two luminescence bands. Both bands blueshift with 9 cm$^{-1}$/kbar. This is explained by Fig. 1(a): With increasing pressure the crystal field strength 10 Dq increases, and in the strong-field limit of the Tanabe-Sugano diagram increasing pressure the crystal field strength 10 Dq increases, and in the strong-field limit of the Tanabe-Sugano diagram the $^{3}T_{2g}$ and $^{3}T_{1g}$ excited states have identical slopes, since they both derive from the $(t_{2g},e_{g})$ electron configuration.

Figures 2(a) and 2(b) exhibit 15 K UC luminescence spectra of Ti$^{2+}$:NaCl obtained after 9394 cm$^{-1}$ excitation into $^{3}T_{2g}$ at (a) ambient pressure and (b) 34 kbar. Both spectra are identical to the respective luminescence spectra obtained by direct $^{3}T_{1g}$ excitation. Figures 2(c) and 2(d) plot the temporal evolution of the upconverted luminescence intensities in (a) and (b) after 10 ns short excitation pulses at 15 K. There is a fundamental difference between these two transients. At ambient pressure [Fig. 2(c)] the $^{3}T_{1g}$ population decays instantaneously and single exponentially with the $^{3}T_{1g}$ lifetime after the excitation pulse. This is typical behavior of an UC mechanism involving two consecutive absorption steps, i.e., ground state absorption (GSA) and excited state absorption (ESA), as illustrated in Fig. 3(a). At 34 kbar [Fig. 2(d)] there is a rise preceding the decay, which is typical for an UC mechanism involving radiative processes that proceed after the excitation pulse. This so-called energy transfer UC (ETU) process is illustrated in Fig. 3(b). Two nearby $^{3}T_{2g}$ excited Ti$^{2+}$ ions combine their energy to yield one ion in the $^{3}T_{1g}(t_{2g},e_{g})$ higher excited state and one ion in the $^{3}T_{1g}(t_{2g})$ ground state (dashed arrows). This process requires a spectral overlap of $^{3}T_{2g}-^{3}T_{1g}(t_{2g})$ emission with $^{3}T_{2g}-^{3}T_{1g}(t_{2g},e_{g})$ ESA, which, from simple energetic considerations, is zero at ambient pressure and 15 K. However, with increasing pressure, the $^{3}T_{2g}-^{3}T_{1g}(t_{2g})$ emission is blueshifted, whereas the $^{3}T_{2g}-^{3}T_{1g}(t_{2g},e_{g})$ ESA essentially remains at the same energy, Fig. 3, leading to a nonzero spectral overlap of the above luminescence and ESA transitions. Hydrostatic pressure at 15 K thus induces a change from a rather inefficient GSA/ESA to an efficient GSA/ETU process.

When Ni$^{2+}$ is doped into CsCdCl$_3$ it enters a site of trigonally distorted octahedral Cl$^-$ coordination. A schematic energy level diagram for Ni$^{2+}$ in a hexachloro environment
is displayed in Fig. 4(a). The \( ^3T_{2g} \) and \( ^1T_{2g} \) excited states are metastable and emit light in a wide variety of \( \text{Ni}^{2+} \)-doped inorganic hosts. \( ^3A_{2g} \) and \( ^1A_{2g} \) luminescence bands with \( 19 \text{ cm}^{-1} \) blueshift from \( 1 \text{ bar} \) to \( 34 \text{ kbar} \), and \( 29 \) and \( 41 \text{ kbar} \). The luminescence band maxima shifts. Thus, the UC luminescence changes color from red at \( 1 \text{ bar} \) to yellow at \( 34 \text{ kbar} \).

Figure 5(a) shows the excitation spectra of the UC luminescence bands from Fig. 4(b). These spectra are comprised of a relatively sharp feature on the low-energy side and a broader feature towards higher energies. A detailed previous ambient pressure study of \( \text{Ni}^{2+}:\text{CsCdCl}_3 \) has demonstrated that in this system UC occurs via a GSA/ESA mechanism as illustrated in Fig. 4(a). \( ^3A_{2g} \rightarrow ^1E_{g} \) GSA is followed by rapid nonradiative (multiphonon) relaxation to \( ^3T_{2g} \) (wavy arrow) and \( ^3T_{2g} \rightarrow ^1T_{2g} \) ESA. As Eq. (1) indicates for this mechanism, the UC excitation spectrum is given by the product of the GSA and ESA spectra. The sharp feature on the low-energy side in the top spectrum of Fig. 5(a) has been assigned to \( ^3T_{2g} \rightarrow ^1T_{2g} \) ESA by means of two-color experiments. With increasing pressure, this band undergoes a redshift with \( 4 \text{ cm}^{-1}/\text{kbar} \). As indicated in Fig. 4(a) both the \( ^1T_{2g} \) and \( ^3T_{2g} \) excited states derive from the \( (t_{2g}^2e_{g}^0) \) electron configuration. Their energy difference \( \Delta E \) is given by Eq. (3): \( \Delta E = E(1T_{2g}) - E(3T_{2g}) \) is given by Eq. (3) for \( B = 10D_q \) and \( B = 10D_gB + (10D_gq)^2 \).

\[
\Delta E = \frac{33}{2}B + \frac{1}{2}10D_qB + \frac{1}{2}10D_gB + (10D_qg)^2, \tag{3}
\]

where \( B \) is the so-called Racah interelectron repulsion parameter, which is a measure for the covalency of metal-ligand interactions. Figure 5(b) shows that \( \Delta E \) increases as a function of \( 10D_q \) for constant \( B \) and can thus not explain the observed redshift with pressure. Only a simultaneous pressure-induced reduction of \( B \) can account for the observed behavior. This is illustrated by Fig. 5(c), which plots \( \Delta E \) for decreasing \( B \) values at constant \( 10D_q \). Thus, for this ESA transition the decrease in \( B \) has a greater impact than the increase in \( 10D_q \). Pressure increases the covalency of the \( \text{Ni}^{2+}-\text{Cl}^{-} \) bond, resulting in the observed redshift of the \( ^3T_{2g} \rightarrow ^1T_{2g} \) ESA transition. For the same reason the most efficient UC excitation occurs at decreasing energies [Fig. 5(a)], whereas the UC luminescence is shifted towards higher energies [Fig. 4(b)]. Thus, the amount of excitation energy converted into heat during the UC process decreases with increasing pressure.

In summary, we have demonstrated that external hydrostatic pressure can be used to tune UC properties and efficiencies. The example of \( \text{Ti}^{2+}:\text{NaCl} \) shows that an increase of the ligand field strength activates a new efficient UC mechanism which leads to a substantial increase in the overall \( \text{Ti}^{2+} \) UC efficiency. The example of \( \text{Ni}^{2+}:\text{CsCdCl}_3 \) demonstrates that UC luminescence excitation spectroscopy can be used to study the pressure-, and thus ligand field-dependent energy shifts of ESA transitions.

This pressure study of upconversion processes and materials demonstrates that pressure is an important variable for tuning the upconversion properties, in particular for increasing the efficiency of the process. On the other hand, our study demonstrates that upconversion can be used for a fundamental study and understanding of excited state absorption processes, which are otherwise not experimentally accessible.

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The crystals were grown by the Bridgman technique. Absorption spectra were measured on a Cary 5e instrument. Luminescence spectra were excited with a Kr$^+$ laser (Coherent CR500K). For UC luminescence and excitation spectra either a cw Ti$^3^+$: sapphire laser (Spectra Physics 3900S, typical power 150 mW) or a pulsed Nd$^3^+$:YAG laser (Quanta Ray DCR-3, 1064 nm, 20 Hz, pulse width 10 ns) was used. Wavelength dispersion occurred in a 0.75 m monochromator (Spex 1402) and a photomultiplier tube (RCA C31034) was used for detection. Luminescence spectra were recorded using a SR400 photon counting system and transients were recorded on a SR430 multichannel scaler. Pressure dependent luminescence spectra were obtained from samples enclosed in a homebuilt gasketed (Beryllco) sapphire anvil cell as described in Ref. 11. Merck spectroscopic paraffin oil served as pressure transmitting medium. Pressure calibration occurred with the ruby $R$-line luminescence method from Ref. 12. Up to 46 kbar, the width of the Ruby $R1$ line increases by less than 10%, indicating that nonhydrostatic effects play a minor role in our experiment. In using Eq. (3) as it stands, $C=4B$ is assumed. Consequently, these are ground state quantities which are not directly applicable to ESA transitions. We use these values to illustrate our point on a qualitative basis.