Luminescence upconversion under hydrostatic pressure in the 3*d*-metal systems Ti²⁺:NaCl and Ni²⁺:CsCdCl₃

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We present a study of upconversion materials and processes under external hydrostatic pressure. The nearinfrared to visible photon upconversion properties of Ti^{2+} -doped NaCl and Ni^{2+} -doped CsCdCl₃ 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-ofmagnitude enhancement of the overall upconversion efficiency of this material. For Ni^{2+} :CsCdCl₃ 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.⁴ 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 Ti²⁺ and Ni²⁺ 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% Ti²⁺:NaCl and 5% Ni²⁺:CsCdCl₃. We show that in 0.8% Ti²⁺: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

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overall UC efficiency of this system. The example of Ni^{2+} :CsCdCl₃ 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.⁸ Figure 1(a) shows the relevant energy levels for octahedrally coordinated d^2 ions as a function of the crystal field strength.⁹ 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 15 500 cm⁻¹ are observed, and according to Fig. 1(a) they are assigned to the spin-allowed ${}^{3}T_{1g} \rightarrow {}^{3}T_{2g}$ and ${}^{3}T_{1g} \rightarrow {}^{3}T_{1g}$ transitions, respectively.⁸ Due to their weakness, no spin-forbidden transitions.



FIG. 1. (a) Tanabe-Sugano energy level diagram for octahedrally coordinated d^2 ions. The vertical dashed line represents the ligand field strength in Ti²⁺:NaCl. The 15 K ambient pressure absorption and luminescence spectra (excited at 15 454 cm⁻¹) are shown in (b) and (c). (d) shows the pressure dependence of the ${}^{3}T_{1g}(t_{2g}e_{g}) \rightarrow {}^{3}T_{1g}(t_{2g}^{2})$ (VIS, circles) and ${}^{3}T_{2g}(t_{2g}e_{g})$ $\rightarrow {}^{3}T_{1g}(t_{2g}^{2})$ (NIR, squares) luminescence band maxima. The latter data points were shifted to higher energy by 7300 cm⁻¹. The straight lines are linear regression fits to the experimental data with slopes of 9 cm⁻¹/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 15454 cm⁻¹. Two broad luminescence bands centered at 5460 and 12850 cm⁻¹ with 15 K lifetimes of 1.5 ms and $\approx 20 \ \mu s$, 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.¹⁰ Figure 1(d) dis-plays the energy of the ${}^{3}T_{1g} \rightarrow {}^{3}T_{1g}$ (circles) and ${}^{3}T_{2g} \rightarrow {}^{3}T_{1g}$ (squares) luminescence band maxima at 15 K as a function of external hydrostatic pressure.¹¹⁻¹³ The ${}^{3}T_{2g}$ \rightarrow $^{3}T_{1g}$ 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 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 Ti²⁺: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 ${}^{3}T_{1\varrho}$ 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).¹⁰ At 34 kbar [Fig. 2(d)] there is a rise preceding the decay, which is typical for an UC mechanism involving nonradiative processes that proceed after the excitation pulse.¹⁰ This so-called energy transfer UC (ETU) process is illustrated in Fig. 3(b). Two nearby ${}^{3}T_{2g}$ excited Ti²⁺ ions combine their energy to yield one ion in the ${}^{3}T_{1g}(t_{2g}e_{g})$ higher excited state and one



FIG. 3. Energy level schemes for Ti²⁺:NaCl illustrating the dominant UC mechanisms at (a) ambient pressure and (b) 34 kbar. Solid arrows represent the radiative processes of GSA, ESA, and luminescence; dashed arrows represent a nonradiative ETU process, and the wavy arrows represent multiphonon relaxation.

ion in the ${}^{3}T_{1g}(t_{2g}^{2})$ ground state (dashed arrows). This process requires a spectral overlap of ${}^{3}T_{2g} \rightarrow {}^{3}T_{1g}(t_{2g}^{2})$ emission with ${}^{3}T_{2g} \rightarrow {}^{3}T_{1g}(t_{2g}e_{g})$ ESA, which, from simple energetic considerations, is zero at ambient pressure and 15 K.⁸ However, with increasing pressure, the ${}^{3}T_{2g} \rightarrow {}^{3}T_{1g}(t_{2g}^{2})$ emission is blueshifted, whereas the ${}^{3}T_{2g} \rightarrow {}^{3}T_{1g}(t_{2g}e_{g})$ 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 mechanism in Ti²⁺:NaCl.

The GSA/ESA UC rate $R_{\rm ESA}$ is dependent on the ground state and excited state absorption cross sections σ at the laser excitation wavelength $\lambda_{\rm exc}$ (9394 cm⁻¹):¹⁰

$$R_{\rm ESA} \propto \sigma_{\rm GSA} \sigma_{\rm ESA} N_{\rm GS}, \qquad (1)$$

where N_{GS} is the ground state population density. Similarly, for the UC rate in case of a GSA/ETU mechanism, Eq. (2) is valid:¹⁰

$$R_{\rm ETU} \propto \omega_{\rm ETU} \sigma_{\rm GSA}^2 N_{\rm GS}^2, \qquad (2)$$

where ω_{ETU} is the power-independent ETU parameter governing the ETU process. As discussed above, the ESA step is pressure independent, i.e., σ_{ESA} stays constant. Based on the GSA spectrum in Fig. 2(b) and the ${}^{3}T_{2g}$ shift rate of 9 cm⁻¹/kbar, we estimate that at $\lambda_{\text{exc}}=9394 \text{ cm}^{-1} \sigma_{\text{GSA}}$ increases by a factor of 2 between 1 bar and 34 kbar. Consequently, in this pressure range and for 9394 cm⁻¹ excitation, the efficiency of the GSA/ESA mechanism is expected to double. Inspection of Fig. 2(d) shows that at t=0 the ${}^{3}T_{1g}(t_{2g}e_g)$ population is roughly 10% of its maximum value at $t=17 \ \mu$ s. Thus, at 34 kbar, GSA/ETU is about 10 times more efficient than GSA/ESA,¹⁰ and this is because ω_{ETU} has increased from zero to a finite value. The overall upconversion efficiency of 0.8% Ti²⁺:NaCl at 15 K has thus increased by about a factor of 20 between ambient pressure and 34 kbar.

When Ni^{2+} is doped into CsCdCl₃ it enters a site of trigonally distorted octahedral Cl⁻ coordination.¹⁴ A schematic energy level diagram for Ni^{2+} in a hexachloro environment



FIG. 4. (a) Energy level diagram for Ni²⁺ in octahedral Cl⁻ coordination illustrating the Ni²⁺ UC mechanism. The solid upward arrows represent ground state and excited state absorption, respectively, and the solid downward arrow represents luminescence. The wavy arrow stands for nonradiative multiphonon relaxation. (b) 15 K ${}^{1}T_{2g} \rightarrow {}^{3}A_{2g}$ upconversion luminescence of Ni²⁺:CsCdCl₃ excited around 12 400 cm⁻¹ at 1 bar, 29 kbar, and 41 kbar.

is displayed in Fig. 4(a). The ${}^{3}T_{2g}$ and ${}^{1}T_{2g}$ excited states are metastable and emit light in a wide variety of Ni²⁺-doped inorganic hosts.^{14,15} Figure 4(b) shows the 15 K ${}^{1}T_{2g} \rightarrow {}^{3}A_{2g}$ UC luminescence spectra of Ni²⁺:CsCdCl₃ at ambient pressure, 29 and 41 kbar. The luminescence band maximum blueshifts with 19 cm⁻¹/kbar. As indicated in Fig. 4(a), the ${}^{3}A_{2g}$ and ${}^{1}T_{2g}$ states derive from the $(t_{2g}^{6}e_{g}^{2})$ and $(t_{2g}^{5}e_{g}^{3})$ electron configurations, respectively. Consequently, an increase in the octahedral ligand field parameter 10 Dq can account for the above blue-shift with pressure, quite analogous to the case of the Ti²⁺:NaCl luminescence band maxima shifts. Thus, the UC luminescence changes color from red at 1 bar to yellow at 34 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 Ni²⁺:CsCdCl₃ has demonstrated that in this system UC occurs via a GSA/ESA mechanism as illustrated in Fig. 4(a).¹⁴ ${}^{3}A_{2g} \rightarrow {}^{1}E_{g}$ GSA is followed by rapid nonradiative (multiphonon) relaxation to ${}^{3}T_{2g}$ (wavy arrow) and ${}^{3}T_{2g} \rightarrow {}^{1}T_{2g}$ ESA. As Eq. (1) indicates for this mechanism, the UC excitation spectrum is given by the product of the GSA and ESA spectra.¹⁶ The sharp feature on the low-energy side in the top spectrum of Fig. 5(a) has been assigned to ${}^{3}T_{2g} \rightarrow {}^{1}T_{2g}$ ESA by means of two-color experiments.¹⁴ With increasing pressure, this band undergoes a redshift with 4 cm⁻¹/kbar. As indicated in Fig. 4(a) both the ${}^{1}T_{2g}$ and the ${}^{3}T_{2g}$ excited states derive from the $(t_{2g}^{5}e_{g}^{3})$ electron configuration. Their energy difference $\Delta E = E({}^{1}T_{2g}) - E({}^{3}T_{2g})$ is given by Eq. (3):^{9,17}

$$\Delta E = \frac{33}{2}B + \frac{1}{2}10Dq - \frac{1}{2}\sqrt{49 \ B^2 + 2 \ 10DqB + (10Dq)^2},$$
(3)

where B is the so-called Racah interelectron repulsion parameter, which is a measure for the covalency of metal-



FIG. 5. (a) Excitation spectra of the three upconversion luminescence bands in Fig. 4(b). (b) Dependence of the ${}^{3}T_{2g} \rightarrow {}^{1}T_{2g}$ ESA transition energy on 10Dq for $B = 830 \text{ cm}^{-1}$. (c) Dependence of the same ESA transition energy on *B* for $10Dq = 6210 \text{ cm}^{-1}$, see Eq. (3). $10Dq = 6210 \text{ cm}^{-1}$ and $B = 830 \text{ cm}^{-1}$ are the ground state ligand field parameters obtained from the 15 K GSA spectrum of Ni²⁺:CsCdCl₃ (data not shown) (Ref. 18).

ligand interactions. Figure 5(b) shows that ΔE increases as a function of 10Dq for constant *B* and can thus not explain the observed redshift with pressure.¹⁷ Only a simultaneous pressure-induced reduction of *B* can account for the observed behavior. This is illustrated by Fig. 5(c), which plots ΔE for decreasing *B* values at constant 10Dq.¹⁸ Thus, for this ESA transition the decrease in *B* has a greater impact than the increase in 10Dq. Pressure increases the covalency of the Ni²⁺-CI⁻ bond, resulting in the observed redshift of the ${}^{3}T_{2g} \rightarrow {}^{1}T_{2g}$ ESA transition.¹⁹ 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 Ti^{2+} :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 Ti^{2+} UC efficiency. The example of Ni^{2+} :CsCdCl₃ demonstrates that UC luminescence excitation spectroscopy can be used to study the pressure-, and thus ligand fielddependent energy shifts of ESA transitions.¹⁹

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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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 (Berylco) 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 *R*1 line increases by less than 10%, indicating that nonhydrostatic effects play a minor role in our experiment.

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