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Tuning of NIR-to-NIR luminescence from one photon to two photons anti-Stokes shift in $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$ via varying Cr^{3+} content

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Near-infrared (NIR) to NIR anti-Stokes luminescence from Cr^{3+}singly-doped $Ca_3Ga_2Ge_3O_{12}$ (CGGG) occurs under the excitation of 808 nm diode laser. The upconversion (UC) processes vary from one-photon to two-photon, depending on the Cr^{3+} content (*x*) in $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$. The results suggest that phonon-assisted anti-Stokes excitation and cooperative energy transfer are involved in the observed UC processes of CGGG: Cr^{3+}. The relevant Cr^{3+} doping concentration dependent NIR-to-NIR anti-Stokes luminescent mechanism, either one photon or two photons UC is investigated. Such an observation on modulating the UC process via varying the doping concentration, is helpful to broaden the understanding of the UC phenomena. © 2016 Optical Society of America

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Anti-Stokes shift based luminescence is allowed to obtain light-emission with higher photon energy than the absorbed photon energy. In general, upconversion (UC) materials contain the dopant ions of *d*-block and *f*-block elements. Examples of these ions are Ln^{3+}, Ti^{2+}, Ni^{2+}, Mo^{3+}, Re^{4+}, Os^{4+}, and so on [1-5]. For decades, UC luminescence has attracted great attention due to their promising applications, including bioimaging, solid-state laser diode, photovoltaic, lighting, etc. The conversion of near-infrared (NIR) spectra to visible (VIS) emission has been routinely found in a number of existing UC materials [6-9]. Until recently, NIR-to-NIR UC luminescent materials have become a research focus, particularly aiming at minimizing auto-fluorescence and achieving deeper penetration of biological tissue in bioimaging and sensing fields [10,11]. Specially, single-band NIR UC emission with high productivity is very promising for deep-in *vivo* imaging and cell-tracking [12,13].

It is noticeable that the electron configuration of Cr^{3+} ion is [Ar]$3d^3$. The unfilled $3d^3$ electronic shell of the Cr^{3+} ion has many low-lying energy levels, where optical transitions can arise generating photon emission. Luminescence due to Cr^{3+} can be observed from the far-red to NIR region. It is worth mentioning that the luminescence of Cr^{3+} in Al_2O_3 (ruby) has formed the basis for the first solid state laser in 1960 [14]. However, the report about UC of Cr^{3+} is generally through a NIR pumping of Yb^{3+} (~980 nm) in Cr^{3+}-Yb^{3+} co-doping or multiple-doping phosphors [15,16]. Recently, UC of Cr^{3+} was achieved in $Zn_3Ga_2GeO_8$: Cr^{3+} NIR persistent phosphor by phonon-assisted process under low-energy NIR (808 or 980 nm LD) excitation [17].

Doping concentration is a crucial factor to determine the UC brightness and emitting wavelength. Critical distance of donor-acceptor and radiative efficiency are concentration-dependent [18]. High dopant concentrations have been found to result in quenching of the luminescence due to cross-relaxation effect. Therefore, optimizing dopant concentration is frequently emphasized to avoid the quenching in most studies of activator-doped phosphors. Normally, it is common that the UC mechanism is not influenced by the excitation power, especially in rare-earth (RE) systems, when the excitation power is less than the saturation power [19] . However, the anti-Stokes shift is governed by either a one-photon excitation process with low-power excitation or one-photon excitation process with high-power excitation in $Zn_3Ga_2GeO_8$:Cr^{3+} phosphors [17, 20]. In this work, we have observed concentration-dependent NIR-to-NIR anti-Stokes luminescent in Cr^{3+} singly-doped $Ca_3Ga_2Ge_3O_{12}$ (CGGG) phosphors. Importantly, NIR-to-NIR anti-Stokes luminescence occurs via a linear one-photon and a two-photon UC processes by varying the Cr^{3+} content (*x*) from 0.005 to 0.10 in $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$ with laser diode (LD) at 808 nm as a pump source of fixed power range. The luminescent mechanisms are illustrated to explain the observation.

The $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$ (x = 0, 0.005, 0.01, 0.03, 0.05, 0.07, 0.10) samples were synthesized with the chemical formula of $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$ by conventional solid-state reaction technique. The raw materials contain 99.99% $CaCO_3$, 99.999% Ga_2O_3, GeO_2, and 99.95% Cr_2O_3. Appropriate amount of starting materials was thoroughly mixed and ground, and subsequently the mixture was prefired at 900 °C for 2 h. After slowly cooling down to room temperature, the samples were calcined at 1200 °C for 6 h in air atmosphere. Phase identification of the obtained products was analyzed by X-ray powder diffraction (XRD). Photoluminescence (PL) spectra were characterized using spectrofluorimeter equipped with various excitation sources. All the PL spectra were corrected for the wavelength-dependent response of the detector system. Appropriate optical filters were used to avoid stray light in all spectral measurements [21].

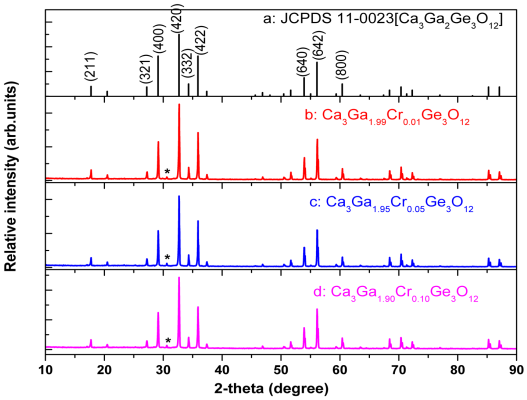

Fig.1 The XRD patterns of the CGGG standard card (JCPDS 11-0023) and the samples $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$ (x = 0.01, 0.05, 0.10). The symbol "*" represents $Ca_2Ga_2GeO_7$ impure phase.

Fig. 1 shows the XRD patterns of the CGGG standard card (JCPDS 11-0023) and the samples $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$ (x = 0.01, 0.05, 0.10) are labeled as curve a, b, c, and d, respectively. It can be observed that curve b, c, d are in good agreement with curve a except for a minor peak, as marked with the symbol "*". This minor peak locates at about 2θ = 30.5°, belonging to the small amount of impure phase of $Ca_2Ga_2GeO_7$, which should have little effect on the measured luminescence. The presented data suggest that the crystal structure of the material is not apparently modified when Cr^{3} ions substituting Ga^{3+} ions.

The UC emission spectra of a series of phosphors $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$ (x = 0.005, 0.01, 0.03, 0.05, 0.07, 0.10) upon 808 nm LD excitation with different power were measured, and similar spectral profiles were found . As an example, we first present the UC emission spectra of $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$ for x = 0.01 at room-temperature (RT) as shown in Fig.2.

As seen in Fig. 2, with the increase in irradiated power, only a broadband centered at around 730 nm is shown in the PL spectra, which is attributed to $^4T_2$-$^4A_2$ transition of Cr^{3+}. The optical properties of Cr^{3+} ion in crystals are analyzed by using the so-called Tanabe-Sugano diagrams as the standard reference data. In general, when Cr^{3+} lies in stronger crystal field site, the energy $^2E < {}^4T_2$, fluorescence spectra shows obvious sharp lines; on the contrary, when it is in weaker crystal field site, the energy $^2E > {}^4T_2$, only $^4T_2$ broadband emission spectra can be observed [22]. It is worth noting that only broadband emission spectra can be observed in all Cr^{3+}-doped samples at RT. Therefore, it is suggested that Cr^{3+} ions may occupy relatively weaker crystal field site in CGGG. The inset of Fig. 2 displays the pump power dependence of the overall UC emissions in the range of 650-750 nm. An approximate linear dependence (slope = 1.14) implies that a one-photon UC process dominates the observed UC PL.

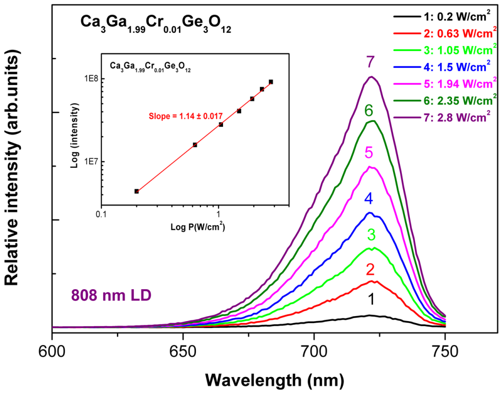

Fig.2 The UC emission spectra of $Ca_3Ga_{1.99}Cr_{0.01}Ge_3O_{12}$ upon 808 nm laser excitation with different power. The inset shows the log–log plots of emission intensity versus excitation power of 808 nm laser.

Interestingly, as shown in the Fig.3, when increasing Cr^{3+} concentrations from x = 0.005 to 0.10, the slope of the luminescence of P^n regularly increases and the value of n is varied from 0.93 to 2.07. Therefore, NIR-to-NIR anti-Stokes luminescent properties, either one photon or two photons UC depend on the Cr^{3+} doping concentration. Briefly, a linear one-photon UC process is dominated for lower Cr^{3+} doping concentration (e.g. x = 0.005 or 0.01), while two-photon UC process is obvious for higher Cr^{3+} doping concentration (e.g. x = 0.07 or 0.10).

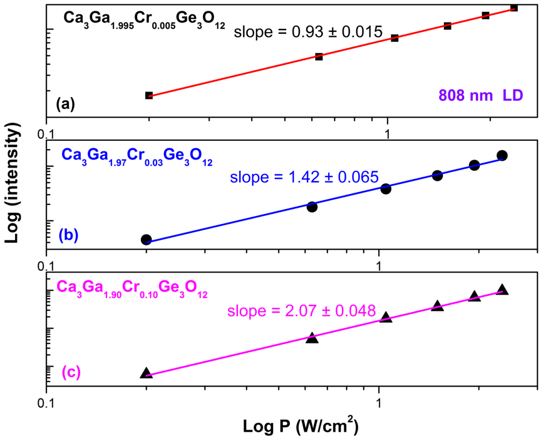

Fig.3 The log–log plots of emission intensity of a series of phosphors $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$ (x = 0.005, 0.03, 0.10) versus excitation power of 808 nm laser.

Generally speaking, the UC process can be implemented through the following three routes [23]. i) Excited-state absorption (ESA), which means sequential absorption of two photons to pump the ion into higher excited state via a real intermediary state intra single ion; ii) Energy transfer UC (ETU), which means two neighboring ions are excited to the intermediary states by ground-state absorption followed by non-radiative energy transfer between the two ions (identical or different), and finally one ion reaches to the excited state and the other one is back to the ground state; iii) The photon avalanche (PA), which means an unconventional process where the strong UC luminescence occurs without the resonance ground-state absorption when the excitation power exceeds a certain threshold. The pump wavelength is only resonant between a metastable state and a higher energy state.

From the results of Figs.2 and 3, the findings differing from the conventional UC mechanisms are listed as follows: i) Cr^{3+} anti-Stokes (UC) luminescence (~730 nm emission) occurs in the CGGG host under 808 nm LD excitation; ii) Concentration-dependent UC mechanisms are associated with one-photon or two-photon process. The two phenomena can be well explained by the following energy level diagram. Fig.4 illustrates the schematic electronic energy levels based on our above measured results for Cr^{3+} ions along with band gap and traps in the CGGG host.[19] According to our result and other group's report [21, 24, 25], Cr^{3+} activated CGGG phosphors possess NIR long-lasting phosphorescence (LLP) properties, ascribed to some traps in the host. In Fig.2, with suitable 808 nm excitation powder, a linear fit ($n \sim 1$) of the $I \sim P^n$ plot is obtained at a relatively low Cr^{3+} concentration (x = 0.005, 0.01), indicating that the anti-Stokes luminescence in CGGG:Cr with low-doping concentration is governed by a one-photon pump process [17]. That is, with the assistance of the phonon energy (PA), the CGGG:Cr system can be pumped to low-energy delocalized states (i.e., $^4T_2$) by absorbing a single 808 nm photon, followed by the filling of neighboring low-energy traps, as the schematic model shown in the left side of Fig. 4(denoted by ①) where, this process is named as a one-photon PAU charging process.

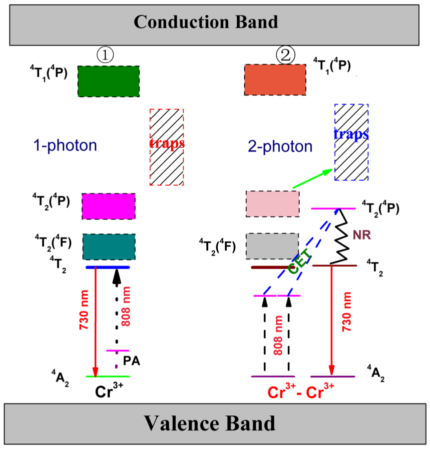

Fig.4 Energy level diagram for Cr^{3+} doped CGGG and possible upconversion mechanism related to PAU ① and CETU ②.

It is interesting that when pumping the CGGG at high Cr^{3+} doping concentration in the identical excitation power range, the $I - P$ dependence becomes $I \sim P^{2.07}$, indicating that two photons are involved in the process of trap filling. Considering the specific energy-level structure of Cr^{3+} in CGGG, two-photon cooperative energy transfer (CET) UC charging mechanism may be responsible for the $I \sim P^{2.07}$ relationship, as the schematic model shown in the right side of Fig. 4 (denoted by ②). The physical process can be explained as follows. At a higher Cr^{3+} doping concentration (e.g., x = 0.07, 0.10), the excitation powder nonlinearly pumps the system to high-energy states, e.g., the $^4T_2$ state, followed by the delocalization of the excited electrons to neighboring high energy traps. The Cr^{3+}: $^4T_2(^4P) \rightarrow {}^4A_2$ transition is located at approximately twice the photon energy of the 808 nm excitation. In the case of relatively high doping concentration of Cr^{3+}, the shorter the Cr^{3+}-Cr^{3+} distance, the higher energy transfer efficiency of Cr^{3+}-Cr^{3+}. The cooperative sensitization process could be a dominant relaxation process in this system. The concept of NIR-to-NIR two-photon UC through a CET from the CGGG: Cr system has been illustrated at higher doping concentration. The entire energy-transfer path is by the way of $Cr^{3+}\,(2 * 808\ \text{nm}) \xrightarrow{\text{CETU}} Cr^{3+}\,(460\ \text{nm}) \xrightarrow{\text{NR}} Cr^{3+}(730\ \text{nm})$.

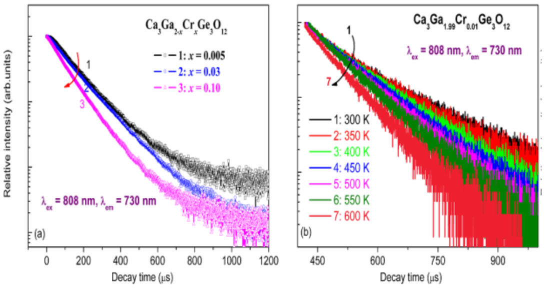

Fig.5 (a) The decay curves of the samples $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$ (x = 0.005, 0.03, 0.10) under λ_{ex} = 808 nm, λ_{em} = 730 nm at RT. (b) The decay curves of the sample $Ca_3Ga_{1.99}Cr_{0.01}Ge_3O_{12}$ under λ_{ex} = 808 nm, λ_{em} = 730 nm at different temperature.

At low doping concentration, almost no energy transfer occurs among Cr^{3+} ions, the mechanism of anti-Stokes luminescence shows a one-photon process, which will result in relatively slow decay. On the contrary, the efficient energy transfer occurs between Cr^{3+}-Cr^{3+} ion-pairs at high doping concentration, the mechanism of anti-Stokes luminescence shows a two-photon process, which will result in relatively fast decay. To verify the hypothesis, we have further measured the PL decay curves. As displayed in Fig.5 (a), with an increase in Cr^{3+} concentration from 0.005, 0.03 to 0.10, the lifetime (τ) of $^4T_2$ energy level becomes shorter from 135, 126 to 98μs, respectively.

In principle [25], fluorescence lifetime (τ) of rare-earth or transition metal ion-doped materials is the required time of the fluorescence decaying to the original light intensity 1/e . And also, fluorescence lifetime is also equal to the reciprocal of the rate of spontaneous emission of electrons in the excited state and the rate of non-radiative transitions. Thus, the following equation is taken:

$\tau(T)=\frac{1}{W_{ij}(T)+A_{ij}}$, where W_{ij}(T) is the rate of non-radiative transitions, A_{ij} is the rate of spontaneous radiation.

Fig.5 (b) shows the decay curves of the sample $Ca_3Ga_{1.99}Cr_{0.01}Ge_3O_{12}$ under λ_{ex} = 808 nm, λ_{em} = 730 nm at different temperature from 300 K to 600 K. Generally speaking, when the temperature of the samples increases, the host lattice possess more intense vibrations, resulting in larger probabilities of non-radiation transition. That is why the fluorescence decay lifetime shows a trend of decrease as seen in Fig. 5(b). On the other hand, when increasing the temperature, the efficiency of the energy transfer from activated ions to sensitized ions increases as well, leading to a reduced fluorescence lifetime. By considering the two effects, it is observed that the decay time decreases with the increase of temperature from Fig.5 (b). The values of the decay time are listed in Table 1, ranging from 109 μs at 300 K to 69 μs at 600 K by the mono-exponential function, matching with the theoretical model. The behaviors of temperature dependence of PL in CGGG: Cr^{3+} phosphors are potentially used in optical temperature sensing.

Table 1 The value of the decay from the Fig.5 (b) by mono-exponential equation

T(K)	300	350	400	450	500	550	600
τ(μs)	109	107	101	96	91	81	69

In conclusion, NIR (808 nm) to NIR (~730 nm) anti-Stokes luminescence from Cr^{3+} singly-doped $Ca_3Ga_2Ge_3O_{12}$ (CGGG) phosphors have been systematically investigated. A linear one-photon and a two-photon UC processes have been realized simply by varying the Cr^{3+} content (x) from 0.005 to 0.10 in $Ca_3Ga_{2-x}Cr_xGe_3O_{12}$ with 808 nm LD as a pump source of fixed power range. A linear one-photon process is observed in the samples with a relatively lower doping concentration of Cr^{3+} due to the assistance of the phonon energy named as PAU while a two-photon cooperative energy transfer (named as CETU) UC charging mechanism is explained for the measured results in the samples with a relatively higher doping concentration of Cr^{3+}. Moreover, the decay time of the CGGG: Cr^{3+} phosphors shows decreasing trend with the increase of the measured temperature. Our results provide an insight into better understanding UC luminescence.

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