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Letter

Upconversion luminescence of Nd^{3+}–Pr^{3+} codoped CsCl modified Ge–Ga–S glasses and the relevant energy transfer mechanism

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ABSTRACT

The visible upconversion luminescence properties of Pr^{3+}/Nd^{3+} co-doped CsCl modified Ge–Ga–S glasses are investigated. Enhanced emissions from Pr^{3+} ions via energy transfer from Nd^{3+} ions are observed at 488, 678 and 729 nm. The possible mechanisms accounting for the enhanced Pr^{3+} emissions and upconversion emissions of Nd^{3+}, i.e. energy transfer upconversion (ETU) are discussed. The results show that the CsCl modified Ge–Ga–S glasses are promising luminescent materials for solid state lasers and displays, etc.

1. Introduction

Rare-earth (RE) ion upconversion (UC) luminescence has many fascinating applications, such as diode-laser-pumped, all-solid-state UC lasers [1]; luminescent bioassays [2]; next-generation lightings [3]; and silicon solar cell near-infrared response [4]. Increasing interest has been given to the studies of UC luminescence of single-ion-doped or multi-ion co-doped glasses. Co-doping with two or more RE ion species usually improves upconversion efficiency [5]. Nd^{3+} can be a good sensitizer because the lifetime of the $^4F_{3/2}$ level in glasses is long enough to enable efficient energy transfer (ET) to other REs. For example, visible emissions from Pr^{3+} ions via ET from Nd^{3+} ions have been realized in Pr^{3+}/Nd^{3+} co-doped fluorozirconate and tellurite glasses upon 796 nm or 800 nm laser excitation [6,7]. But in order to obtain UC luminescent materials with even higher quantum efficiency, hosts with lower phonon energies are required. In this respect, fluoride and sulfide glasses are among the best candidates. The advantage of sulfide glass over fluoride counterpart is the still lower phonon energy [8] (less than 400 cm^{-1}) [9]. By incorporating the metal halides, e.g. K(Br, I), Cs(Cl, I), etc., into the sulfide glasses forming the so-called chalcohalide glasses, as it turned out, increases the bandgap and transparency in the visible light region, which helps to reduce the absorption loss associated with the host materials and thus increases the efficiency of UC luminescence. The RE doped halide-modified chalcogenide glasses also demonstrated the improved fiber-drawing and optical properties [10]. Very recently, Heo and co-workers reported on the effect of CsBr/Ga ratio on the blue UC emission from the Pr^{3+}–Nd^{3+} co-doped CsBr modified Ge–Ga–S glasses [11]. In this paper, we also observed the red UC emission from the Pr^{3+}–Nd^{3+} co-doped but CsCl modified Ge–Ga–S glasses. Especially, the Pr^{3+}/Nd^{3+} co-doping ratio has been adjusted to understand and distinguish the most possible ET routes. The CsCl modified chalcogenide glasses also show increased transparency in the visible light region as compared to CsBr modified ones.

2. Experiment

The chalcohalide glasses were prepared from high-purity (5 N) germanium and gallium ingots and sulfur chips, and cesium chloride (3 N). The elements were batched into a silica ampoule, which was vacuumed to 10^{-4} Torr. Finally, the ampoule was sealed using an oxyacetylene torch.

Once sealed, the ampoule was protected with a grille and placed in a rocking furnace. Samples were heated to the reaction temperature at a very slow heating rate, typically 3 °C min^{-1}, to avoid explosion. Halide-modified glasses were found to react more vigorously than pure sulfide compounds which usually require a low heating rate about 1.0 °C min^{-1}.

Once the reaction temperature was reached, start the rocking for at least 10 h. The reaction temperature was 900 °C. The temperature of the furnace was then reduced to 850 °C and the oven was held in vertical position for several hours before quenching. This step allows the glass to settle, minimizing bubbles and composition microinhomogeneities. Finally, the samples were quenched in water and annealed at

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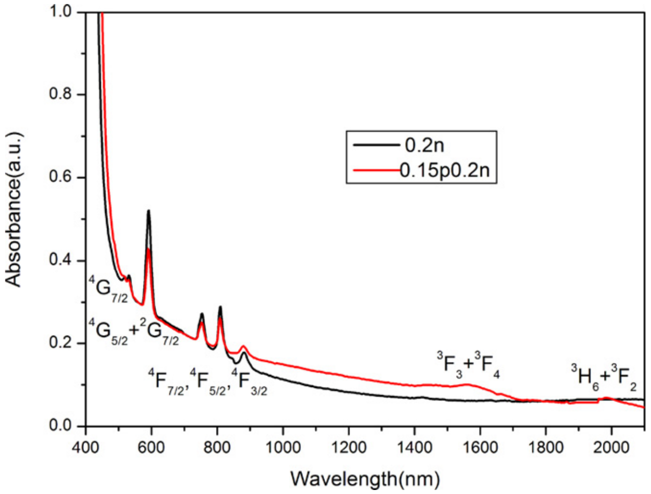

Fig. 1. VIS–NIR absorption spectra of singly Nd^{3+} doped and doubly Nd^{3+}–Pr^{3+} co-doped samples (the letter p represent Pr^{3+} and n represent Nd^{3+}, the number are followed by the unit mol%).

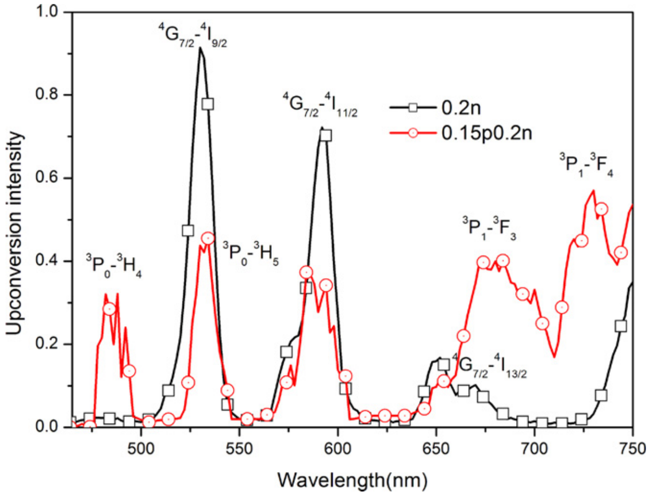

Fig. 2. UC luminescence spectra of singly Nd^{3+} doped and doubly Nd^{3+}–Pr^{3+} co-doped samples (the letter p represent Pr^{3+} and n represent Nd^{3+}, the number are followed by the unit mol%).

the glass-transition temperature for 2 h. The composition $60GeS_2$–$20Ga_2S_3$–20CsCl was found thermally stable studied in this work.

Samples with a size of Ø 10 mm × 2 mm were well polished. Conventional absorption spectra were performed using a Jasco V-570 spectrophotometer (JASCO Ltd., Great Dunmow, U.K.). The VIS emission spectra were recorded using a Zolix SBP300 spectrofluorometer (Zolix Corp., Beijing, China) with a multiplier phototube as the detector in 400–750 nm. The excitation laser is semiconductor laser of 808 nm. The resolution of the detector was ±1 nm. All optical measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the measured absorption spectra of 0.2 mol% Nd doped (0.2n) and 0.15 mol% Pr and 0.2 mol% Nd co-doped (0.15p0.2n) glasses. Each absorption spectrum consists of several absorption bands marked at the bottom of the curves corresponding to the absorptions from the ground state $^4I_{9/2}$ to the excited states $^4G_{7/2}$, $^4G_{5/2}+^2G_{7/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$ of Nd^{3+} and another two absorption bands indicated on the top of the curves due to electron transitions from the ground state $^3H_4$ to the excited states $^3F_3+^3F_4$, $^3H_6+^3F_2$ of Pr^{3+}. The band positions are similar to that reported in Ge–Ga–Sb–Se chalcogenide glasses [12]. Three Judd–Ofelt intensity parameters Ω_2, Ω_4, Ω_6 can be determined from the measured absorption spectra. The parameters for Nd^{3+} are compared with their values for other glass hosts in Table 1. Of the three parameters, Ω_2 correlated with the degree of covalence is the most sensitive to local structure and host composition. Ω_2 is larger than others in chalcohalide glass due to the covalent nature of chemical bonding around the RE ion.

UC emissions from Nd^{3+} ion were observed when an 808 nm pump laser was used as shown in Fig. 2. It can be seen that Nd^{3+}-doped sample exhibits three emissions at 532, 592 and 668 nm originating from the electronic transitions of $^4G_{7/2}$–$^4I_{9/2}$, $^4G_{7/2}$–$^4I_{11/2}$ and $^4G_{7/2}$–$^4I_{13/2}$ [13], respectively. With Pr^{3+} co-doping, intensities of Nd^{3+} emissions decrease greatly, on the other hand, three new emissions appear at 488, 678 and 729 nm due to the transitions of $^3P_0$–$^3H_4$, $^3P_1$–$^3F_3$ and $^3P_1$–$^3F_4$ from Pr^{3+} ions [7]. As Pr^{3+} ion itself lacks the energy level that responds directly to the 808 nm laser excitation, Pr^{3+} emissions in Nd^{3+}–Pr^{3+} co-doped samples can be attributed to the energy transferring from Nd^{3+} ions which will be discussed later.

Table 1
Comparison of Judd–Ofelt intensity parameters (Ω_2, Ω_4, $\Omega_6 \times 10^{20}$ cm^2) for Nd^{3+} in different hosts.

Glass	Ω_2	Ω_4	Ω_6
Chalcohalide (present work)	5.02	1.67	5.22
Chlorophosphate [12]	4.38	1.86	4.15
35ZnO·65TeO$_2$ [13]	2.59	7.26	5.45
ZBLAN [14]	0.84	4.79	9.13

To investigate the effects of Pr^{3+} or Nd^{3+} concentration on UC emissions, we prepare a series of samples with different Pr^{3+} or Nd^{3+} contents. Fig. 3 shows UC emission spectra of co-doped glasses with 0.2 mol% Nd^{3+} and different amount of Pr^{3+} ions. The intensities of all emissions show a maximum at 0.1 mol% Pr^{3+}. By fixing the optimum Pr^{3+} concentration at 0.1 mol% and increasing Nd^{3+} concentration, emissions from Nd^{3+} and Pr^{3+} ions are enhanced simultaneously as shown in Fig. 4. In particular, intensities of two red emissions from Pr^{3+} increase dramatically compared with their blue counterpart. These observations indeed demonstrate that there exists energy transfer (ET) process between Nd^{3+} and Pr^{3+}.

The energy level diagrams of Nd^{3+} and Pr^{3+} ions are shown in Fig. 5. In Nd^{3+}-doped sample, there is a possible mechanism for population of the high energy $^4G_{7/2}$ level: energy transfer UC (ETU). In the processes, one Nd^{3+} ion in the ground state is excited to the

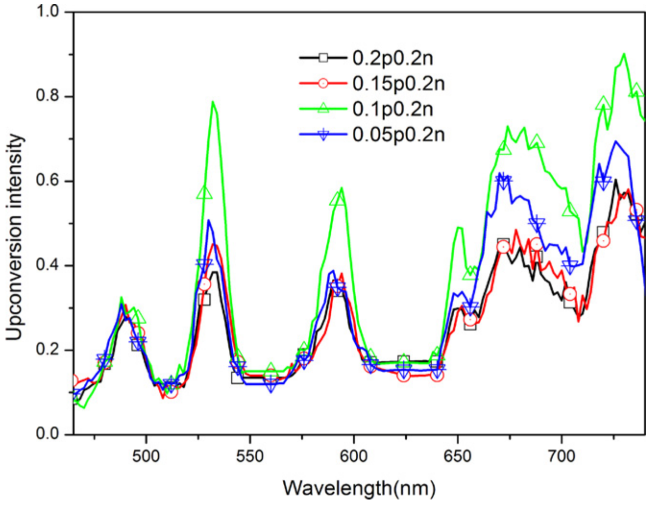

Fig. 3. UC luminescence spectra of glasses as a function of Pr^{3+} concentration with fixed Nd^{3+} concentration (the letter p represent Pr^{3+} and n represent Nd^{3+}, the number are followed by the unit mol%).

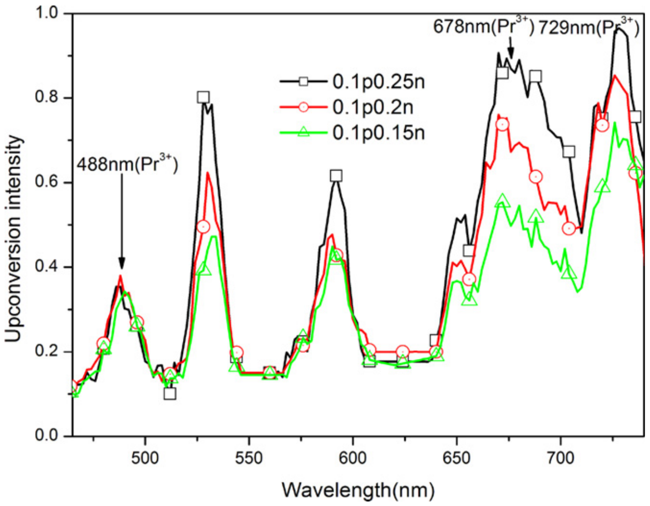

Fig. 4. UC emission spectra of glasses as a function of Nd^{3+} concentration with fixed Pr^{3+} concentration (the letter p represent Pr^{3+} and n represent Nd^{3+}, the number are followed by the unit mol%). Emissions of Pr^{3+} are marked.

$^4F_{5/2}$ state by absorbing one infrared (IR) photon. The excited Nd^{3+} ion then decayed non-radiatively to the lower lying long-lived $^4F_{3/2}$ level [14]. When two Nd^{3+} ions are excited to the $^4F_{3/2}$ state, one ion goes to $^4I_{11/2}$ state by transferring energy to another which goes to $^2D_{3/2}$ state can decay non-radiatively to $^4G_{7/2}$ state; also one ion goes to $^4I_{13/2}$ level by transferring energy to another which goes directly to $^4G_{7/2}$ level. These two coexisting processes contribute to the excitation of Nd^{3+} ions into the higher $^4G_{7/2}$ level where the excited ion/ions relax radiatively to generate the recorded visible emission signals as indicated in the energy-level diagram in Fig. 5.

According to the Miyakawa–Dexter theory [15], the probability of phonon-assisted energy transfer is obtained from

$$W_{ET} = W_{ET}(0)\exp(-\beta\Delta E) \quad (1)$$

where ΔE is an energy gap between the energy level of an energy donor and that of an energy acceptor, $W_{ET}(0)$ is the transfer rate when $\Delta E = 0$, and β is a function of effective phonon energy and electron-phonon coupling strength. Equation (1) implies that the smaller the energy gap is, the faster the energy transfer occurs. In Pr^{3+}–Nd^{3+} co-doped glasses, the energy gap between the Nd^{3+}: $^2D_{3/2} \to {}^4I_{9/2}$ transition and the Pr^{3+}: $^3H_4 \to {}^3P_1$ transitions is quite small, the energy transfer $^2D_{3/2}(Nd) + {}^3H_4(Pr) \to {}^4I_{9/2}(Nd) + {}^3P_1(Pr)$ (A) can be considered to occur between Nd^{3+} ions and Pr^{3+} ions with high quantum efficiency. And the red emissions of Pr^{3+} around 678 and 729 nm are originating from the $^3P_1 \to {}^3F_3$ and $^3P_1 \to {}^3F_4$ transitions. It is inevitable that Pr^{3+} ions relax non-radiatively through multiphonon relaxation from the $^3P_1$ level to $^3P_0$ level from where the intense emission at around 488 nm is obtained as shown in Fig. 5. With the increase of Pr^{3+} concentration from 0.05 to 0.1%, the UC emissions from Nd^{3+} and Pr^{3+} ions enhanced simultaneously as shown in Fig. 3. Moreover, as the $^3P_0$ energy level of Pr^{3+} ion is slightly higher than the $^4G_{7/2}$ level of Nd^{3+} ions, it may offer a channel of energy back transfer from Pr^{3+} to Nd^{3+} ions (B). The likely presence of ET channel B also explains well the phenomenon that the Pr^{3+} blue emission is not sensitive to the Nd^{3+} ions concentration (refer to Fig. 4), because ET channel B counter balances the ET effect coming from the increased Nd^{3+} ions.

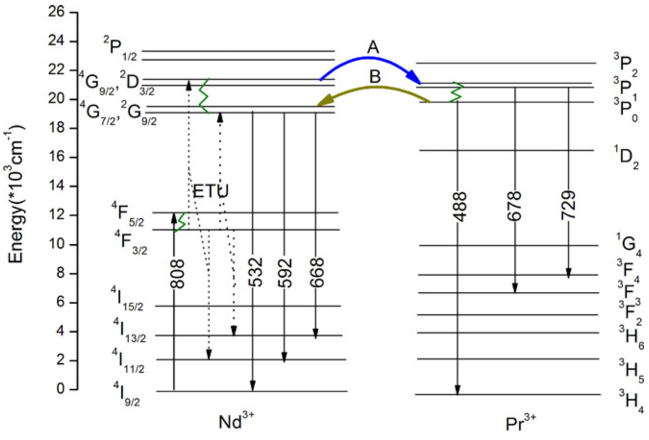

Fig. 5. The energy level diagram of Nd^{3+}–Pr^{3+} ions.

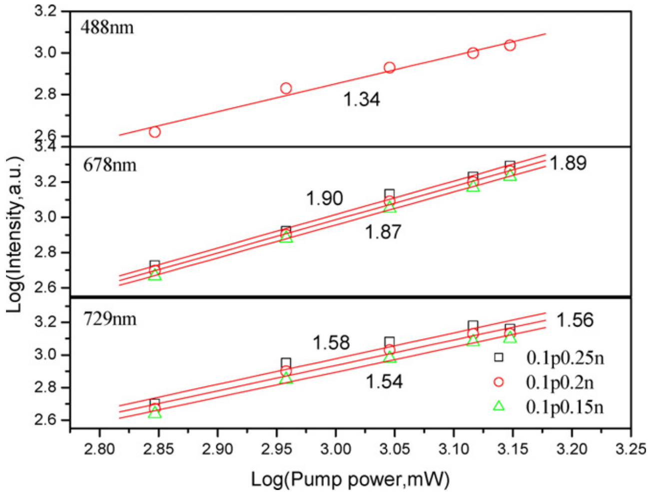

Fig. 6. Log–log plots of UC luminescence intensities for Pr^{3+} as a function of the 808 nm laser excitation power.

The 808 nm laser pumping power dependence of three emission bands of Pr^{3+}/Nd^{3+} co-doped chalcohalide glasses was investigated according to the formula $I \propto P^n$, where I is the integrated intensity of UC luminescence, P is the power of the pumping laser, and n is the corresponding photon number involved in the multiphoton absorption process. As shown in Fig. 6, the absorbed photon numbers for 678 and 729 nm emissions increase with the Nd^{3+} addition whereas for the 488 nm one it changes little. The n values are close to two for the 678 and 729 nm ones, thus it is proposed that two photons may take part in the blue and red upconversion processes via Nd^{3+} ions.

4. Conclusions

Pr^{3+}–Nd^{3+} co-doped CsCl modified Ge–Ga–S glasses have been prepared and their UC luminescence properties are characterized. Strong blue and red UC emissions from Pr^{3+} are observed upon 808 nm laser excitation. The emissions are due to ET from Nd^{3+}. The possible mechanisms involved in the UC process include ETU for Nd^{3+} and a different ET channel for both Nd^{3+} and Pr^{3+}. These observations may be helpful in searching solid state lasers and displays with the specified color demands.

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