

Short Communication

Structural destruction of cooperative luminescence – A new mechanism of fluorescence quenching

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ABSTRACT

The cooperative luminescence of Yb³⁺-trimers and Yb³⁺-dimers were observed in Yb³⁺-doped CaF₂ under excitation of near infrared (NIR) light at room temperature. With the increase of doped Al³⁺ or La³⁺ concentration, the cooperative luminescence from 3-Yb³⁺ trimers and 2-Yb²⁺ dimers decreased gradually and until to extinguished. In order to explain the phenomenon, in this paper, we propose a new fluorescence quenching mechanism, structure-destroyed fluorescence quenching. This new fluorescence quenching belongs to the static quenching.

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1. Introduction

Cooperative transitions, including cooperative luminescence (CL), cooperative absorption (CA), and cooperative energy transfer (CET), are closely relative to clustered lanthanide ions in solid hosts. CL generates from a frequency upconversion process in which two or more ions in the excited state decay simultaneously to the ground state and emit one photon with twice or more the energy of a single-ion transition. The CL originating from ytterbium ions was first observed in YbPO₄ by Nakazawa and Shionoya [1], since then numerous studies on cooperative upconversion luminescence have been carried out with Yb³⁺-Er³⁺, or Ho³⁺-Yb³⁺ doped systems [2–6]. On the other hand, CL is fundamentally fascinating from a purely theoretical perspective. A general theory based on electric multipole-multipole interactions between optically active 4f electrons in lanthanide systems was developed by Dexter [7] and Kushida [8]. Based on a generalization of the super exchange mechanism between dimers of lanthanide ions bridged by ligands, Mironov and Kaminskii proposed a different theoretical approach for CL [9]. In previous studies, we reported a triplet cooperative luminescence (TCL) at ~343 nm from three excited Yb³⁺ ions (Yb³⁺-trimer) in CaF₂, as shown in Fig. 1(a) [10]. In order to differentiate the CL of Yb³⁺-dimers from that of Yb³⁺-trimers (TCL), we named the CL of Yb³⁺-dimers as DCL. Furthermore, by considering the

electric multipole interactions between ions and using the coupled wave functions of a many-lanthanide-ion system, Qin et al. proposed the main cooperative transition mechanisms in the multi-ion system and calculated their transition probabilities [11]. Recently, we reported the upconversion luminescence from Cu²⁺ ions, in which three excited Yb³⁺ ions simultaneously transfer their energy to one Cu²⁺ ion [12]. Figs. 1(b) and 2 shows that the UC process was found to be dominated by the energy transfer process in which three excited Yb³⁺ ions simultaneously transfer their energy to one Cu²⁺ ion and lead to the excitation of Cu²⁺ ions. On the other hand, the UV emissions around 343 nm completely disappear when the doping concentration of Cu²⁺ ions reaches 1mol%, which strongly suggests that doped Cu²⁺ ions not only lead to the occurrence of cooperative energy transfer from Yb³⁺-trimers but also cause the structural destruction of Yb³⁺-trimers. In other words, the doped Cu²⁺ ions induce a new fluorescence quenching that comes from the destruction of Yb³⁺-trimer structures.

Fluorescence quenching usually means such a dynamic process in which an excited state is depopulated through a nonradiative transition. It can be classified as concentration quenching, temperature quenching, and impurity quenching. In this case, fluorescence quenching decreases the fluorescence intensity, lifetime, or quantum yield of luminescent species. On the other hand, chemists named another kind of fluorescence quenching—static quenching in that luminescence centers were changed [13–15]. Therefore, the fluorescence quenching caused by Cu²⁺ ions includes both of dynamic quenching and static quenching. When Cu²⁺ ions were doped in CaF₂:Yb³⁺ sample, the energy transfer

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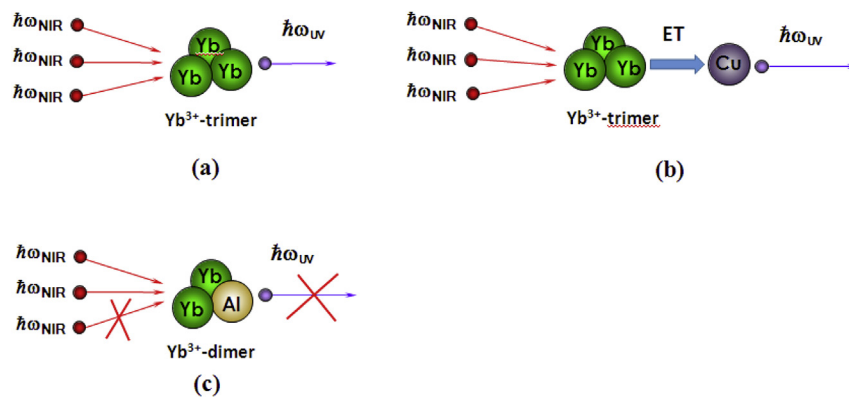


Fig. 1. The schematic diagram of (a) cooperative luminescence of Yb³⁺-trimers (b) The Cu²⁺ ions are excited by the sensitization of Yb³⁺-trimers. (c) The increase of Y³⁺ doping concentration, which indicates the structural destruction of Yb³⁺ clusters.

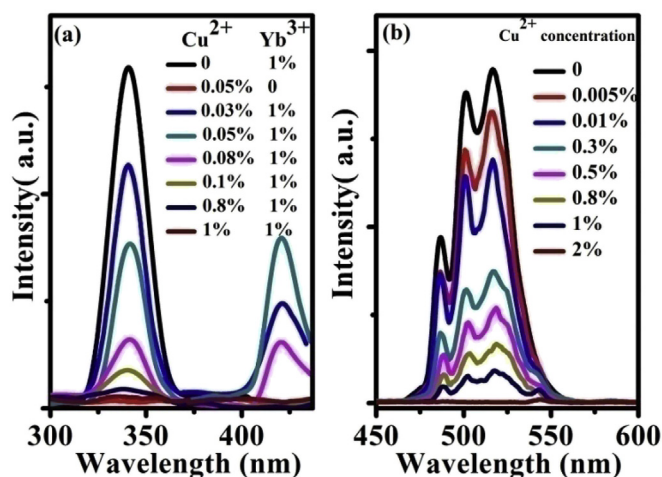


Fig. 2. (a) Emission spectra (300–450 nm) of CaF₂: x%Yb³⁺, y%Cu²⁺ (x = 0, 1; y = 0.03, 0.05, 0.08, 0.1, 0.8, 1) upon 978 nm excitation at room temperature. (b) Emission spectra (450–600 nm) of CaF₂:1%Yb³⁺, y%Cu²⁺ (y = 0, 0.005, 0.01, 0.3, 0.5, 0.8, 1, 2) with various Cu²⁺ doping upon 978 nm excitation at room temperature.

from Yb³⁺-trimers to Cu²⁺ ions quenched the fluorescence of Yb³⁺ ions and induced the fluorescence of Cu²⁺ ions, which formed dynamic quenching; on the other hand, the doped Cu²⁺ ions substituted Yb³⁺ ions of Yb³⁺-clusters in CaF₂ and destroyed the Yb³⁺-trimers that emitted UV CL and transferred their energy to Cu²⁺ ions, which formed static quenching.

In order to study the static quenching of DCL and TCL further, in this work, we chose trivalent Al³⁺ and La³⁺ ions as the destroyers due to that they could not participate the dynamic quenching of Yb³⁺-clusters. Fig. 1(c) shows that Al³⁺ ions (or La³⁺ ions) with the same valence state of Yb³⁺ ions can easily substitute Yb³⁺ ions and lead to the structural destruction of Yb³⁺ clusters. We named this new quenching process “structure-destroyed fluorescence quenching.” It belongs to the static quenching.

2. Experimental

CaF₂:Yb³⁺ and CaF₂:Yb³⁺, Al³⁺ (or Y³⁺/La³⁺) samples with various doping concentrations were prepared by solid-state reactions, respectively. CaF₂ (99.99%, Aladdin), YbF₃ (99.99%, Aladdin), YF₃ (99.99%, Aladdin), LaF₃ (99.99%, Aladdin) and AlF₃ (99.99%, Aladdin) were mixed with the specified stoichiometric ratios for each samples. Then these fluoride mixtures were ground

and calcined at 1180 °C for 2 h under argon atmosphere, then cooled to room temperature naturally. The luminescence spectra were recorded with a one meter monochromator (SPEX 1000M; HORIBA JobinYvon Inc., Edison, NJ, USA) equipped with an 1800 lines mm⁻¹ grating. The excitation light source was a power adjustable continuous wave laser diode (978 nm, 10 W; BWT Beijing Ltd, Beijing, China). The mean power of this excitation light source is 10 W, and the NIR laser was focused on the sample by a lens. A digital oscilloscope (DPO4104B, bandwidth 1 GHz, sampling rate 5 GS s⁻¹; Tektronix, Shanghai, China), a power adjustable continuous wave laser diode (CW978 nm, 10 W), and a chopper were used to record decay curves.

3. Results and discussion

Under the excitation of a 978 nm NIR laser, the CaF₂:Yb³⁺ sample showed 343 nm UC emissions spectra, which has been previously reported [10]. Our previous works has demonstrated that the 343 nm UC fluorescence is the TCL of Yb³⁺-trimers. With the increase of doped Yb³⁺ concentration, the ultraviolet (UV) emission peaked at 343 nm first increases and then decreases, as shown in Fig. 3. The maximum UC emission intensity of Yb³⁺-trimers is obtained at the concentration of Yb³⁺ reaches 1 mol%.

In order to investigate the structural destruction of Yb³⁺-trimers

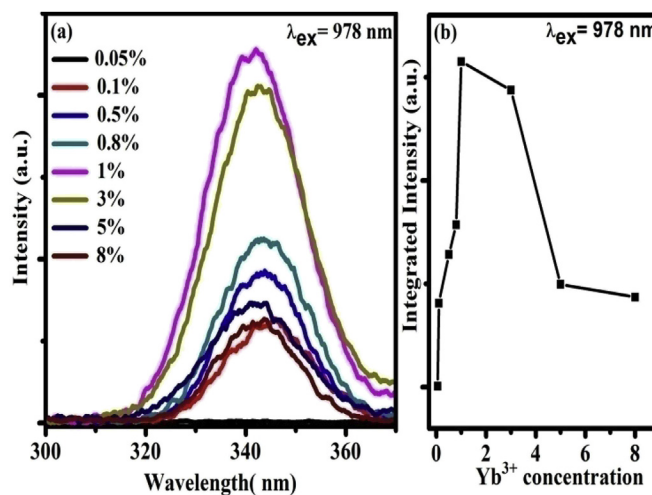


Fig. 3. (a) Emission spectra (300–380 nm) of CaF₂: x%Yb³⁺ (x = 0.05, 0.1, 0.5, 0.8, 1, 3, 5, 8) upon 978 nm excitation at room temperature. (b) Integrated intensity dependence of 343 nm UC emissions on the doping concentration of Yb³⁺.

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