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Synthesis and spectral properties of $Ce[Ag(CN)_2]_3$

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Abstract

Cerium ion luminescence in crystalline hosts forms the basis of many blue phosphor and scintillator technologies. We report the synthesis of luminescent single crystals of cerium dicyanoargentate. The luminescence properties are characterized using both steady-state and time-resolved spectroscopy. The broad, overlapping dicyanoargentate and Ce^{3+} emissions are decomposed into three Gaussians, revealing the characteristic dicyanoargentate emission at 350 nm while the Ce^{3+} 5d–4f transitions are observed at 359 nm and 391 nm. Excitation measurements show that the 4f–5d Ce^{3+} absorption overlaps the 320 nm emission of the dicyanoargentate ions, leading to a strong coupling between the dicyanoargentate energy donors and Ce^{3+} acceptors. We conclude that the cerium is excited through an energy transfer process from the dicyanoargentate species, resulting in strong room temperature luminescence.

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1. Introduction

Single crystals of $R[Ag(CN)_2]_3$ (R = La, Tb, Eu, Dy) have been studied extensively due to their interesting photoluminescence properties [1–5]. Dicyanoargentate crystals are particularly interesting because their emission bands result from the formation of excimers and exciplexes, excited state Ag–Ag interactions. These emission bands can be tuned by site-selective excitation [6,7].

Energy transfer between the dicyanoargentate donor and the parity forbidden 4f–4f optical transitions of the rare earth acceptor has been well characterized for $Eu[Ag(CN)_2]_3$ [1], $Dy[Ag(CN)_2]_3$ [2], and $Tb[Ag(CN)_2]_3$ [5]. In all cases, the luminescence intensity of the rare earth dopant was found to increase with increasing temperature over the range 77 K to room temperature, with a concomitant temperature quenching of the dicyanoargentate luminescence.

The crystal structures of many rare earth doped dicyanoargentates have been reported previously and all have been found to belong to the hexagonal crystal system [8–10]. Crystals form in a layered structure with layers of linear dicyanoargentate ions alternating with layers of rare earth ions coordinated with water molecules. Within the dicyanoargentate layer, the silver atoms are found to be very closely spaced (3.344 Å apart in $Eu[Ag(CN)_2]_3$, for example), while the rare earth ions and cyanide ligands are also very closely coordinated (2.539 Å in $Eu[Ag(CN)_2]_3$) [10]. This leads to efficient energy transfer by the exchange mechanism between the metal dicyanide donor and the rare earth acceptor when there is a suitable spectral overlap between the donor emission and acceptor absorption.

Cerium is a particularly interesting candidate for energy transfer studies because the electronic transitions in the visible region are parity allowed 4f–5d transitions. The sensitivity of the 5d levels to the local environment of the impurity ion results in a broad absorption in the region of the silver emission. This broad absorption is in direct contrast with the narrow band absorptions of the other

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trivalent rare earths previously used in energy transfer in these systems. In addition, because it is a parity allowed transition the lifetime is short, generally less than 50 ns [11–13] which is several orders of magnitude faster than the parity forbidden f–f transition in other trivalent lanthanides. The short lifetime eliminates the bottleneck created when further energy transfer from the dicyanoargentate donors is restricted because of saturation of the excited states of the acceptors, as evidenced by lifetime and time-resolved work performed on $Tb_xLa_{1-x}[Ag(CN)_2]_3$, which showed a decrease in the rate of energy transfer with increasing x [14].

In this work, we show that luminescence in this novel crystal is due to both dicyanoargentate donors (350 nm) and cerium impurities (359 nm and 391 nm) and that cerium excitation is through fast energy transfer (<50 ns) from the dicyanoargentate donors under 266 nm excitation.

2. Experimental

For all measurements between 77 K and room temperature, the sample was mounted in a Janis model ST100 cryostat controlled by a LakeShore 331 temperature controller.

2.1. Sample preparation

Crystals were prepared using a gel moderated slow-diffusion method. A 1wt.% agar solution was allowed to gel in the bottom of a standard U-shaped drying tube. Stoichiometric aqueous solutions of $KAg(CN)_2$ and $Ce(NO_3)_3$ were then layered one in each arm of the tube. The ions from the solutions diffused through the gel and clear, hexagonal shaped crystals approximately 2 mm × 2 mm × 0.4 mm formed near the center of the gel. Crystals were harvested after two weeks.

2.2. Steady-state photoluminescence

Steady-state photoexcitation and emission spectra were obtained using a deuterium lamp as the excitation source. An Oriel CornerStone 1/4 m monochromator was used for wavelength selection. The emission was detected with an Oriel CornerStone 1/4 m monochromator fitted with a photomultiplier tube. The output from the photomultiplier tube was recorded by an Oriel Multifunction Optical Power Meter (model 70310) interfaced with a personal computer. The emission and excitation spectra for $La[Ag(CN)_2]_3$ were obtained using an experimental set-up whose details have been reported previously [14,15]. All excitation spectra have been corrected using a rhodamine B quantum counter method [16].

2.3. Time resolved photoluminescence

Lifetime measurements were obtained using a 266 nm pulsed laser (JDS Uniphase) for excitation and an Oriel CornerStone 1/4 m monochromator fitted with a photomultiplier tube. The output from the photomultiplier tube is recorded with a LeCroy Waverunner LT262 1 gigahertz oscilloscope. All decays were averaged over 1000 laser pulses. Lifetime values were obtained by fitting the natural log of the averaged data to a line using a MATLAB curve fitting routine. Time resolved spectra were obtained by integrating the decay curves at each wavelength value. The delay time after the laser pulse and gate width (Δt for the integration) are selected on the oscilloscope prior to the integration.

3. Results and discussion

Fig. 1 shows the steady state excitation and emission spectra for $Ce[Ag(CN)_2]_3$ at both 78 K and 240 K. The emission spectrum is characterized by a broad emission in the near ultraviolet to blue region, centered around 390 nm. The excitation spectrum shows several peaks in the ultraviolet.

The photoluminescence properties of $La[Ag(CN)_2]_3$ have been reported elsewhere [15]. We can understand the properties of the $Ag(CN)_2^-$ emission by considering this sample because the La^{3+} ions have no optically active energy levels in the visible spectrum. When excited at 266 nm, the $Ag(CN)_2^-$ species has two emission bands, at approximately 320 nm (31,250 cm^{-1}) and 350 nm (28,500 cm^{-1}) (Fig. 2, top), assigned as $^*[Ag(CN)_2]_3$ localized exciplexes of different geometries. Consistent with the literature, we will label these bands B-1 and B-2 [7]. As the temperature is increased from 78 K, the dicyanoargentate emission decreases in intensity and is barely detectable above 200 K where nonradiative decay mechanisms dominate.

We notice two striking differences between the undoped and doped crystals. First, we note the absence of the 320 nm band that was present in the undoped crystal. Sec-

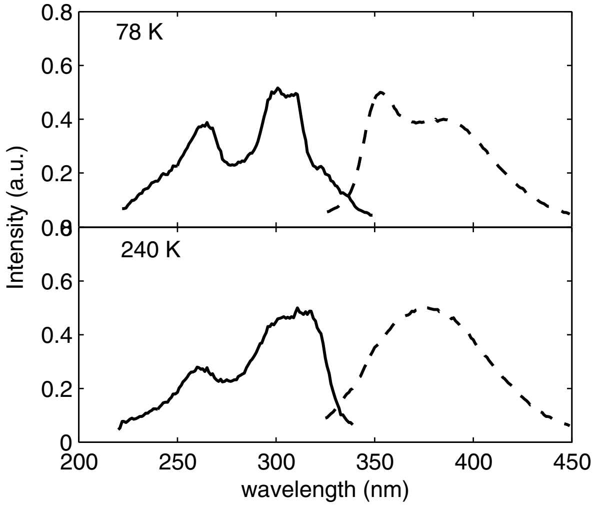

Fig. 1. Excitation (solid line) and emission (dashed line) spectra at 78 K (top) and 240 K (bottom) for $Ce[Ag(CN)_2]_3$. For excitation the emission was monitored at the cerium emission (390 nm) and for emission the excitation wavelength was 266 nm (steady-state). The spectra have been normalized to facilitate comparison.