



Pr³⁺ ¹S₀ → Cr³⁺ energy transfer and ESR investigation in Pr³⁺ and Cr³⁺ activated SrAl₁₂O₁₉ quantum cutting phosphor

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ABSTRACT

With the help of the Dexter's theory, the energy transfer mechanism from Pr³⁺ ¹S₀ to Cr³⁺ is investigated theoretically in SrAl₁₂O₁₉:Pr³⁺, Cr³⁺ quantum cutting phosphors. The electron spin resonance (ESR) spectra of Pr³⁺ and Cr³⁺-doped SrAl₁₂O₁₉ with magnetoplumbite structure have been studied. The Cr³⁺ ion is found to enter the Al4(4f) site, which is very close to the Sr(2d) site replaced by the Pr³⁺ ions in the host. The theoretical results indicate that the efficient Pr³⁺ ¹S₀ → Cr³⁺ energy transfer can only take place in the intermediate mirror planes, in which for the nearest and next-nearest Pr³⁺–Cr³⁺ pairs, both dipole–dipole and dipole–quadrupole interactions can play their parts in the transfer. Finally, an overview is given about the research on the energy transfer from Pr³⁺ ¹S₀ to codopants in their co-doped materials.

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1. Introduction

Strontium aluminate SrAl₁₂O₁₉ (SAO) is a convenient host crystal for rare earth and transition-metal dopants [1]. Recently, much interest has been attracted to SAO:Pr³⁺ quantum cutting (QC) phosphor for its potential applications in such as plasma displays and mercury-free fluorescent tubes [2–9]. Strontium in this crystal has a large coordination number (12) and large distances to nearest-neighbour oxygen ions (6 × 2.75 Å + 6 × 2.785 Å); as a result the dopants Pr³⁺ occupy Sr²⁺ sites and hence experience a weaker crystal field environment such that the 4f² ¹S₀ state lies below the lowest 4f5d state. Upon vacuum-UV excitation to the 4f5d states of Pr³⁺, QC through a cascade emission due to ¹S₀–¹I₆, ³P_J about 402 nm followed by ³P₀–³H₄ radiative transition around 485 nm could occur in this system. Then an internal quantum efficiency greater than 100% can be expected for SAO:Pr³⁺.

By now, more than a dozen of such Pr³⁺-based QC phosphors have been identified but found unsuitable for practical applications because the first step transition of Pr³⁺, ¹S₀–¹I₆, ³P_J, is near the UV region, unsuitable for practical applications [10–12]. An appropriate codopant which can convert this first step photon to proper visible photon through energy transfer (ET) could be a solution for this situation. Many codopants, such as Sm³⁺ [13,14], Eu³⁺ [13–15], Gd³⁺ [16], Dy³⁺ [13,14], Er³⁺ [13,14,17], Yb³⁺ [13–15],

Mn²⁺ [13,14,18–23], Cr³⁺ [24,25], etc, have been tried in various matrixes, in which the absorption of codopants have sufficient spectral overlaps with the near-UV emission of Pr³⁺ (the prerequisite of the occurrence of ET [26]). However, in most co-doped materials, efficient ET cannot be observed. A detailed investigation has to be carried out, why ET is that less efficient and how the problem of converting the 402 nm photon to visible light can be solved.

In the earlier work [24], we have reported the evidences for the ET from Pr³⁺ to Cr³⁺ in SAO:Pr³⁺, Cr³⁺ systems. The results show that there is efficient ET from Pr³⁺ ¹S₀ to Cr³⁺ in the co-doped samples, which converts the near-UV ¹S₀–¹I₆, ³P_J emission of Pr³⁺ into deep red emission (685 nm, ²E–⁴A₂) of Cr³⁺. In this work, mechanisms of ET from Pr³⁺ ¹S₀ to Cr³⁺ have been discussed based on Dexter's theory [27]. Electron spin resonance (ESR) spectra help us to investigate the localization of Cr³⁺ ions in SAO. And then, a detailed discussion of probability of Pr³⁺ ¹S₀ → Cr³⁺ ET in SAO was presented. Finally, an overview is given about the research of the Pr³⁺ ¹S₀ → codopants ET in their co-doped systems.

2. Experimental section

2.1. Sample preparation and characterizations

The samples of SAO:2% Pr³⁺ (in mol), SAO:10% Pr³⁺, SAO:x% Cr³⁺ (x = 2, 5, 10), and SAO:5% Cr³⁺, 2% Pr³⁺ phosphors were synthesized by high-temperature solid-state reaction method

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using SrCO₃ (99.99%), γ-Al₂O₃ (99.999%), Pr₆O₁₁ (99.99%) and Cr₂O₃ (99.99%) (all from Beijing Fine Chemical Company) as raw materials. The microcrystalline samples were verified to be in single phase by X-ray diffraction. All the measurements were performed at room temperature. ESR experiments were carried out using an ESR JES-TE 300 spectrophotometer (magnetic field: 1.4 T, AFC stability: 1 × 10⁻⁶, output power: 12 kW). Fluorescence and excitation spectra with a resolution of 0.2 nm were recorded using a Hitachi F-4500 spectrophotometer equipped with a continuous 150 W Xe-arc lamp (PMT voltage 700 V).

2.2. Crystal structure of SAO hexa-aluminate

SAO adopts a hexagonal magnetoplumbite (M.P.) structure, crystallizing in space group P63/mmc [28]. A projection of the unit cell on the [110] plane is shown in Fig. 1. It consists of two spinel-like blocks containing Al³⁺ cations separated by intermediate mirror planes containing Al³⁺ and Sr²⁺ cations. Some characteristics of the different cations sites available for Al³⁺ in the SAO unit cell (split atom model) are gathered in Table 1. The average Al–O and Al–Sr distances are calculated from the data in Ref. [29]. Due to charge neutrality and ion size of Cr³⁺, the trivalent Cr ions (75.5 pm, 6-coord.; all radii taken from Ref. [30]) replace trivalent Al ions (67.5 pm, 6-coord.) instead of the divalent and considerably large Sr ions (~132 pm) in the host [25].

3. Results and discussion

3.1. Critical distance of Pr³⁺ ¹S₀ → Cr³⁺ energy transfer

Fig. 2 explicitly shows the spectral overlap between the Pr³⁺ emissions (¹S₀–¹I₆, ³P_J) and Cr³⁺ excitation spectra (⁴A₂–⁴T₁(F)) in the region of interest (~402 nm). The spectral overlaps between other Pr³⁺ ¹S₀ emission lines and Cr³⁺ absorptions will not be discussed in this report. According to Dexter's theory [27], ET from Pr³⁺ ¹S₀ to Cr³⁺ should therefore in principle be possible. Under these resonant conditions, radiative and nonradiative transfer could both be involved in the ET process.

Firstly, to inspect whether the radiative and re-absorption process prevails or not, 50% SAO:10% Pr³⁺ and 50% SAO:5% Cr³⁺ powder materials were mixed together and then were pressed into pellets. The mixture sample does not show any emission of Cr³⁺ under excitation of Pr³⁺ 4f5d band at 205 nm, where the absorption of Cr³⁺ is very weak and can be ignored. The results indicate that the radiative transfer is not responsible for this ET process.

Nonradiative ET from one center to another may occur via electric multipole–multipole interaction or via exchange (*ex*) interaction. For multipole–multipole interaction, we assume the interaction is of the electric dipole–dipole (*dd*) or electric dipole–quadrupole (*dq*) type. For a quantitative analysis the expression derived by Dexter for the ET probability of *dd* interaction, P_{SA}^{dd} , is firstly considered

$$P_{SA}^{dd} = 3 \times 10^{12} \frac{f_d}{R^6 \tau_S E^4} \int_E F_S(E) F_A(E) dE \quad (1)$$

Here R is the distance between the sensitizer (*S*) and acceptor (*A*) (in Å), τ_D is the radiative decay rate of the donor transition (in seconds), f_d is the electric dipole oscillator strength of the optical absorption transition of *A* ion, E stands for the energy of maximum spectral overlap (in eV) and $SO = \int F_S(E) F_A(E) dE$ defines the spectral overlap between the normalized shape of the the emission band of *S* and the absorption band of *A* (in eV⁻¹). To evaluate if ET rate can compete with radiative decay, the critical distance, R_c , for the transfer from *S* to *A* should be determined. The

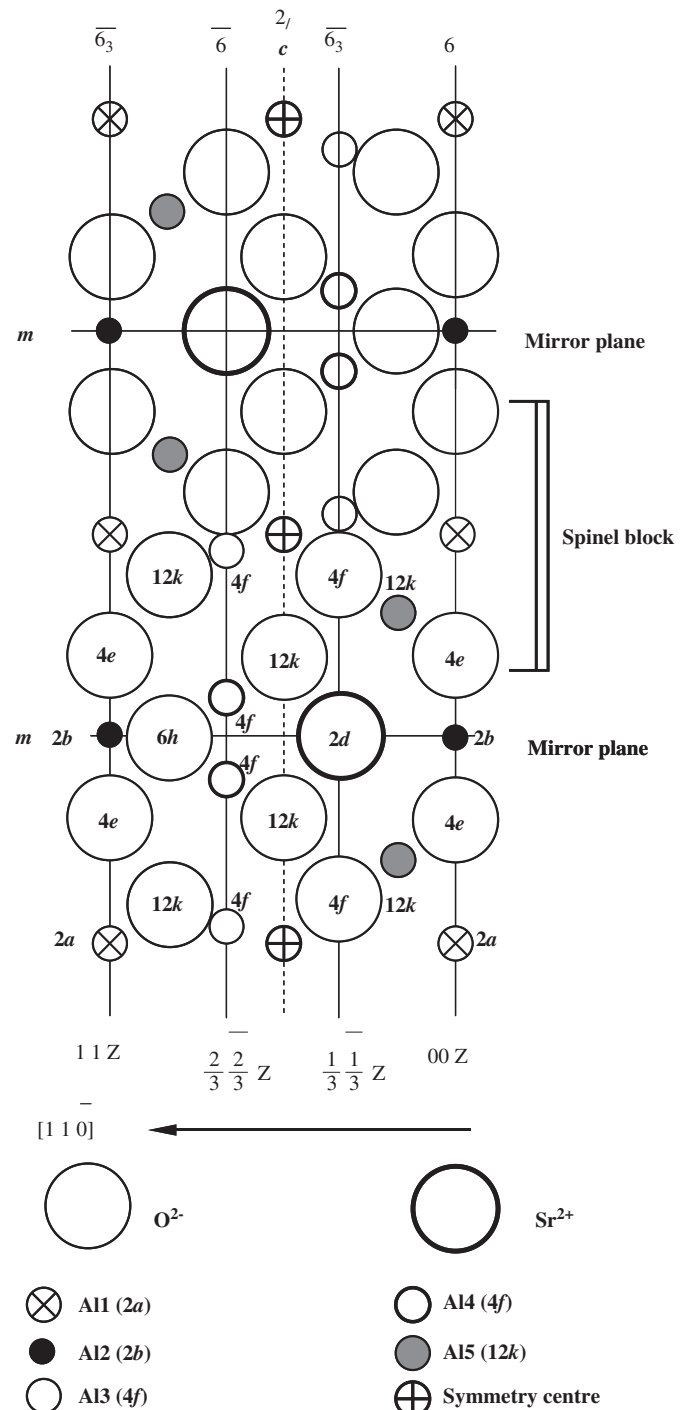


Fig. 1. Projection on the [110] plane of SAO unit cell of magnetoplumbite crystal structure.

critical distance is defined as the distance for which the probability of transfer equals to that of radiative emission of *S* or that for which $P_{SA} \tau_D = 1$ [31]. Therefore, critical distance for *dd* interaction, R_c^{dd} can be written as

$$(R_c^{dd})^6 = 3 \times 10^{12} \frac{f_d}{E^4} \int_E F_S(E) F_A(E) dE \quad (2)$$

As shown in Fig. 2, the absorption band of Cr³⁺ arises from the interconfiguration parity-forbidden and spin-allowed transition of ⁴A₂–⁴T₁(F), in which typical oscillator strength, f_d , is in the order of 1 × 10⁻⁴ [32–34]. The overlap integral in Eq. (2) can be calculated

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