Pr$^{3+}$ $^1S_0 \rightarrow $Cr$^{3+}$ energy transfer and ESR investigation in Pr$^{3+}$ and Cr$^{3+}$ activated SrAl$_{12}$O$_{19}$ quantum cutting phosphor

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1. Introduction

Strontium aluminate SrAl$_{12}$O$_{19}$ (SAO) is a convenient host crystal for rare earth and transition-metal dopants [1]. Recently, much interest has been attracted to SAO:Pr$^{3+}$ 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 x 2.75 Å + 6 x 2.785 Å); as a result the dopants Pr$^{3+}$ occupy Sr$^{2+}$ sites and hence experience a weaker crystal field environment such that the 4f$^2$ $^1S_0$ state lies below the lowest 4f$^5$S state. Upon vacuum-UV excitation to the 4f$^5$S states of Pr$^{3+}$, QC through a cascade emission due to $^1S_0$–$^1I_{6,3}P_J$ about 402 nm followed by $^3P_0$–$^3H_4$ radiative transition around 485 nm could occur in this system. Then an internal quantum efficiency greater than 100% can be expected for SAO:Pr$^{3+}$.

By now, more than a dozen of such Pr$^{3+}$-based QC phosphors have been identified but found unsuitable for practical applications because the first step transition of Pr$^{3+}$, $^1S_0$–$^1I_{6,3}P_J$, 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 Sm$^{3+}$ [13,14], Eu$^{3+}$ [13–15], Gd$^{3+}$ [16], Dy$^{3+}$ [13,14], Er$^{3+}$ [13,14,17], Yb$^{3+}$ [13–15], Mn$^{2+}$ [13,14,18–23], Cr$^{3+}$ [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 Pr$^{3+}$ (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 Pr$^{3+}$ to Cr$^{3+}$ in SAO:Pr$^{3+}$, Cr$^{3+}$ systems. The results show that there is efficient ET from Pr$^{3+}$ $^1S_0$ to Cr$^{3+}$ in the co-doped samples, which converts the near-UV $^1S_0$–$^1I_{6,3}P_J$ emission of Pr$^{3+}$ into deep red emission (685 nm, $^2E$–$^4A_2$) of Cr$^{3+}$. In this work, mechanisms of ET from Pr$^{3+}$ $^1S_0$ to Cr$^{3+}$ have been discussed based on Dexter’s theory [27]. Electron spin resonance (ESR) spectra help us to investigate the localization of Cr$^{3+}$ ions in SAO. And then, a detailed discussion of probability of Pr$^{3+}$ $^1S_0$–Cr$^{3+}$ ET in SAO was presented. Finally, an overview is given about the research of the Pr$^{3+}$ $^1S_0$–codopants ET in their co-doped systems.

2. Experimental section

2.1. Sample preparation and characterizations

The samples of SAO:2% Pr$^{3+}$ (in mol), SAO:10% Pr$^{3+}$, SAO:x% Cr$^{3+}$ (x = 2, 5, 10), and SAO:5% Cr$^{3+}, 2$% Pr$^{3+}$ phosphors were synthesized by high-temperature solid-state reaction method...
using SrCO₃ (99.99%), γ-Al₂O₃ (99.99%), Pr₂O₃ (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: 1.4T, A-FC 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→³P₅₁/₂) and Cr³⁺ excitation spectra (⁴S₃/₂→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, \( P_{dd}^{SA} \), is firstly considered

\[
P_{dd}^{SA} = 3 \times 10^{12} \frac{f_d}{E} \frac{1}{\tau_{dd}} \int \frac{F_S(E)}{F_A(E)} dE
\]  

(1)

Here \( R \) is the distance between the sensitizer (S) and acceptor (A) (in Å), \( \tau_{dd} \) 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 \( S_0 = \int F_S(E) F_A(E) dE \) 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 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 \( P_{dd}^{SA} = 1 \) [31]. Therefore, critical distance for dd interaction, \( R_{dd}^{cr} \), can be written as

\[
(R_{dd}^{cr})^2 = 3 \times 10^{12} \frac{f_d}{E} \frac{1}{\tau_{dd}} \int \frac{F_S(E)}{F_A(E)} dE
\]  

(2)

As shown in Fig. 2, the absorption band of Cr³⁺ arises from the interconfiguration parity-forbidden and spin-allowed transition of \(^{4}S_{3/2} \rightarrow ^{4}T_{1}(F)\), in which typical oscillator strength, \( f_d \), is in the order of \( 1 \times 10^{-4} \) [32–34]. The overlap integral in Eq. (2) can be calculated...
Sr (2d) D₃h CaO₁₂-cuboctahedron – –

Al₁ (2a) D₃d AlO₆-regular octahedron 1.876 6.890

Al₂ (2b) D₃h AlO₃-trigonal bipyramid 1.954 4.155

Al₃ (4f) Cᵥ AlO₄-tetrahedron 1.802 5.544

Al₄ (4f) Cᵥ AlO₄-antiprism (octahedron) 1.920 2.932

Al₅ (12k) Cs AlO₆-dirsorted octahedron 1.909 4.172

Note: All Al–O and Al–Sr distances are evaluated from the data presented in Ref. [29].

Table 1

<table>
<thead>
<tr>
<th>Ion (site)</th>
<th>Symmetry</th>
<th>Coordination polyhedron</th>
<th>Mean Al–O distance (Å)</th>
<th>Mean Al–Sr distance (Å)</th>
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<tr>
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<td>4.172</td>
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</table>

Some characteristics of the different cations sites available for Al³⁺ in the SAO unit cell with magnetoplumbite crystal structure (split atom model, cell dimensions: a = 5.5666 Å, c = 22.0018 Å [29]).

For $dq$ mechanism, the transfer probability is given as

$$P_{SA}^{dq} = 3 \times 10^{12} \frac{F_{S}^{2}}{R_{0}^{6}} \frac{1}{V} \int F_{S}(E)F_{A}(E)\text{d}E$$

(3)

Here $f_{S}$ is the electric-quadrupole oscillator strengths of the optical absorption transition of $A$ species. $\lambda_{D}$ is the wavelength position of the donor emission. Typically, electric-quadrupole oscillator strength is roughly three or four orders of magnitude smaller than that of electric dipole transition [35,36]. Thus, the $f_{S}$ of the Cr³⁺ ion is considered of order $10^{-8}$-$10^{-7}$. According to $P_{SATd} = 1$, the critical distance for $dq$ interaction, $R_{dq}^{c}$ can be written as

$$(R_{d}^{c})^{8} = 3 \times 10^{12} \frac{F_{S}^{2}}{R_{0}^{6}} \frac{1}{V} \int F_{S}(E)F_{A}(E)\text{d}E$$

(4)

Using $\lambda_{S} = 4020$ Å, we found that $R_{dq}^{c} = 14.4$–19.2 Å.

If the ex interaction is taken into consideration, it is hard even impossible to calculate the exact critical distance, $R_{dd}^{c}$, due to its strong dependence on the tails of the wave functions. In most cases the critical distance is less than 5 Å and the possibility of ET is of exponentially dependence on the interionic distance [37].

Fig. 3. ESR spectra at room temperature of (a) SAO:2% Cr³⁺, (b) SAO:10% Cr³⁺, (c) SAO:5% Cr³⁺, 2% Pr³⁺ and (d) SAO:2% Pr³⁺.

The theoretic critical distances for $dd$ and $dq$ interactions have been given above. According to Van Uitert formula [38], in SAO:Pr³⁺, Cr³⁺, assuming a random distribution of Pr³⁺ and Cr³⁺ ions, the experimental critical distance of Pr³⁺ and Cr³⁺ is given by

$$R_{0} = (3V/4\pi C_{0})^{1/3}$$

(5)

where $R_{0}$ is the experimental critical distance, $V$ is the volume of the unit cell of SAO and $C_{0}$ is the critical concentration of acceptor, at which the emission intensity of the donor is half of that without it. By taking the experimental and analytic values of $C_{0}$ and $V$, about 3% for the transfer form Pr³⁺ 1S₀ to Cr³⁺ [24] and 681.77 Å³ [29], respectively, into the formula, $R_{0}$ is found to be about 17.6 Å, which is larger than $R_{dd}^{c}$ but within the region of $R_{dq}^{c}$. In addition, $R_{0}$ is also larger than the typical critical distance for ex interaction (< 5 Å) [37]. It indicates that the ex interaction is not a dominate mechanism in the ET process. Finally, we can then conclude that the electric $dq$ interaction mechanism is predominantly responsible for the ET from Pr³⁺ 1S₀ to Cr³⁺ in SAO:Pr³⁺, Cr³⁺ samples.

3.2. ESR study of Cr³⁺ and Pr³⁺-doped SAO powder

Fig. 3 displays the room temperature ESR spectra of Pr³⁺ and Cr³⁺-doped SAO powders. As shown in Fig. 3a and b, the spectra of Cr³⁺-doped SAO consist of a single line at $B = 345$ mT flanked by some weak satellites on its two wings. Similar ESR result was also observed in other Cr³⁺-doped host crystals with M.P. structure [33]. The weak lines in the 198 mT region could be assigned to Cr³⁺ forbidden transitions ($\Delta M_s = 2$) [39]. When the Cr³⁺ content increases, there is a broadening of the central ESR line and an
increase of the satellites. This broadening phenomenon is due to the dipolar interactions between neighboring Cr³⁺ ions.

Firstly, there are no other ESR lines up to 1000 mT in the spectra, which indicates the zero field splitting, D, of the chromium ions in this site is large. Diagonalization of the spin Hamiltonian of the Cr³⁺ ions allows us to deduce the value of the axial zero field parameter. From the portion of the central ESR line, we get g = 1.934 and assuming \( g_z = g \), the position of the perpendicular line gives D = 0.95 cm⁻¹ [40]. From these results one can propose a localization for the Cr³⁺ ions, recalling that the larger crystal field stabilization of Cr³⁺ in octahedral symmetry precludes its localization in the two tetrahedral sites, Al2(2b) and Al3(4f) (see Table 1), of the M.P. unit cell. Besides the ESR spectra, according to ligand field theory [41], the spectral properties of the energy states of Cr³⁺ in SAO also indicate that the Cr³⁺ ions enter Al³⁺ sites with octahedral symmetry [25]. Anyway, two tetrahedral sites of the M.P. unit cell should be excluded first. Although there are three possible octahedral Al³⁺ sites in the host lattice, only one site of Cr³⁺ emission is observed [25]. Among the three sixfold-coordinated Al sites, the Al1(2a) site (regular octahedron) must be discarded because it is too regular to be accountable for the high Cr³⁺ D value [40]. In addition, as plotted in Fig. 3a and b, there are some additional weak satellites flanked almost symmetrically on the wings of the central ESR line of Cr³⁺. Similar phenomenon was found in other Cr³⁺-doped M.P. structures [33]. It was found that this result arise from the occurrence of (4f)Cr³⁺–(4f)Cr³⁺ pairs, which have their inter-nuclear axis parallel to c in M.P. structure as displayed in Fig. 1, even at low doping levels. This is exactly the situation corresponding to Cr³⁺ in two neighboring Al4(4f) antiprism sites, which cling to the mirror plane and are close enough (~2.62 Å) in SAO to develop interactions between each other. The nearest Al5(12k) sites, however, are screened to some extent by some intermediary oxygen ions and the distance between them is so large (~6.23 Å) that is almost impossible to develop this kind of direct interaction.

In addition, after adding 2% Pr³⁺ into SAO:5% Cr³⁺, besides the weak satellites of Cr³⁺, we observed new weak lines flanking the central ESR line, as shown in Fig. 3c, which indicates that dopant Pr³⁺ gives a new action to Cr³⁺ in SAO. It has been recognized that Pr³⁺ (~126 pm) replaces the big Sr²⁺ (~132 pm) ions in the host [4]. The distance between Sr(2d) and Al4(4f) sites is so short (~2.932 Å) that it is enough for Pr³⁺ and Cr³⁺ to achieve interactions between them. The new satellites may arise from the Pr³⁺–Cr³⁺ pairs. Thus, this result can be a further evidence for Cr³⁺ substituting Al4(4f) site in SAO. Indeed, as depicted in Fig. 1, relative to Al5(12k), the shorter distance of the nearest Al4(4f) and Sr²⁺(2d) sites is more suitable to explain the new-interaction phenomenon. Additional remark supports this attribution. The antiprism Al4(4f) site presents the largest mean Al–O distance of the unit cell, as listed in Table 1. Because of the relative radius of Al³⁺ and Cr³⁺ ions, 67.5 pm and 75.5 Å, respectively, size effects favor chromium localization in this site.

As for Pr³⁺ in the crystal field, the \(^3H_2\) ground state of Pr³⁺ is split into three Kramers doublets separated by a few hundreds of cm⁻¹ [37]. Hence, there are low-lying excited states above the lowest energy Kramers doublet. It follows that Orbach spin lattice relaxation process is very efficient and the time is very short. As plotted in Fig. 3d, the ESR spectra of SAO:Pr³⁺ are undetectable at room temperature because of the lifetime broadening, similar to other trivalent lanthanide ions (except Gd³⁺) [40,42].

### 3.3. Probability of Pr³⁺ → Cr³⁺ energy transfer

The shortest distance between Pr³⁺ and Cr³⁺ in SAO is about 2.932 Å (see Table 1), which is so short that dd, dq and ex interactions may all play a role in the ET from Pr³⁺ \(^1S_0\) to Cr³⁺ [27].

The lifetime of the \(^1S_0\) state in SAO:2% Pr³⁺ is about 600 ns [5,8], and then the radiative rate is \(1.67 \times 10^9\) s⁻¹. Based on Eq. (1), the ET probability at the shortest distance via dd interaction can be calculated to be about \(2.95 \times 10^5\) s⁻¹. And from Eqs. (1) and (3), at the same distance, the ratio of \(P_{SA}^{dd}\) and \(P_{SA}^{dd}\) is given by

\[
\frac{P_{SA}^{dd}}{P_{SA}^{dd}} \approx \left( \frac{g_{dd}}{g_{ex}} \right) \frac{E_{dd}}{E_{ex}}
\]

If we take \(E_{dd} = 1.88 \times 10^2\) and \(E_{ex} = 1.93 \times 10^2\), then we get \(P_{SA}^{dd} \approx 5.55 \times 10^{-1}\) s⁻¹ and \(P_{SA}^{dd} \approx 2.95 \times 10^5\) s⁻¹, respectively. The ET probability via dq interaction is much larger than that via dd interaction, which is in accord with the results in Section 3.1, and they are both much larger than the radiative rate of Pr³⁺ \(^1S_0\).

The probability of ET by ex interaction, \(P_{exch}\), is difficult to estimate. Dexter estimated \(P_{exch}\) to be \(10^{10} – 10^1\) s⁻¹ for ions at distance of about 4 Å [27]. In SAO, the shortest Pr³⁺–Cr³⁺ distance of about 2.932 Å is not prohibitive at all for ex interaction, but the Pr³⁺–Cr³⁺ configuration seems to be very unfavorable, both for the direct exchange and superexchange. Screening by more or less intermediary oxygen ions will be disadvantageous for the direct exchange. In fact, the critical distance deduced from multipole-multipole interaction above is in accord with the experimental results. This can be regarded as an evidence for the inefficiency of ex interaction. Nevertheless, this is not a sufficient argument for completely excluding exchange as a possible transfer mechanism. For superexchange [43], Blasse has argued that this mechanism is unlikely to occur in cases where the angle between the luminescence centers and the intermediary ion (e.g. Pr–O–Cr angle) strongly deviates from 180°, in other words, in cases where the overlap of the wavefunctions is low. In SAO, the Pr and Cr ions have an about 90° Pr–O–Cr configuration, so that the probability of transfer by superexchange interaction will be very low.

Because the Cr³⁺ ions are very close to the mirror plane, we assume they are in the intermediate layer. The distance from Pr³⁺ to the nearest Cr³⁺ in the adjacent layer is about 9.69 Å, which is about equal to the critical distance of ET via dd interaction, but smaller than that via dq interaction. Thus, dq interaction should play a main role in the ET between different layers. The ratio of the transfer probabilities based on dq interaction between nearest neighbors in adjacent layers and that in the same layers can be given by

\[
\frac{\alpha_{SA}^{dq}(\text{different layer})}{\alpha_{SA}^{dq}(\text{same layers})} = \left( \frac{2.93}{9.69} \right)^8 = 6.99 \times 10^{-5}
\]

Following this result, the ET rate between Pr³⁺ and Cr³⁺ positioned in the same intermediate layer is much more effective than that in different layers across the rather formidable obstacle, i.e. a spinel-like block, as shown in Fig. 1, that the latter can be ignored.

Assuming a random distribution of Pr³⁺ and Cr³⁺ ions, the experimental mean critical distance of Pr³⁺ and Cr³⁺ in SAO is in accordance with the theoretical one. However, the ET is in fact can only occur approximately in a two-dimensional plane. Thus the reasonable critical distance should be given by

\[
R_0 = \left( \frac{S_{\text{plane}}}{\pi C_0} \right)^{1/2}
\]

Here, \(S_{\text{plane}}\) is the area of mirror plane containing large cations. By taking the experimental and analytic values of \(C_0\) and \(S_{\text{plane}}\), 3%
and 30.99 Å² [29], respectively, into the formula, $R_0$ is found to be about 18.1 Å, which is still within the range of the critical distance via $dq$ interactions.

3.4. Overview of energy transfer from Pr$^{3+}$ $^1S_0$ to codopants

The reason why it is difficult to find a suitable transfer partner should firstly be ascribed to the relatively short lifetime of the Pr$^{3+}$ $^1S_0$ state. Theoretically, the amount of the opposite parity 5d components mixed into 4f states is affected critically by their energetic separation. Thus, the $^1S_0$ state, which is quite close to the lowest 4f5d band in QC phosphors, usually shows some unique properties which are different from those of other low-lying 4f states [5,7]. One of the distinguishing characteristics is that the lifetime of $^1S_0$ is very short, usually in the magnitude of nanosecond, while those of other low-lying 4f states in microsecond or millisecond. The shorter lifetime results in a larger radiative rate, thus based on $P_{qtO} = 1$, a larger ET rate at critical distance is needed to compete with the radiative one.

Secondly, the oscillator strength of the transitions, which are in resonance to the $^5S_{0–}^5I_{6,3P_j}$ transitions of Pr$^{3+}$, of most codopants are usually very low. For the transitions in 4f$^n$ configurations of rare-earth ions and the parity and spin forbidden ones of transition-metal ions, their oscillator strengths are usually in the range $10^{-6}$–$10^{-8}$ [35,36]. Let us look at the parameters in Eq. (2). The spectral integral, SO, differs empirically only one order of magnitude between different investigated $S$ and $A$ with sufficient spectral overlaps. Actually, the critical distance is not sensitive to SO for the reason that ($R_0^{dd}$)/SO in addition, the radiative transitions of Pr$^{3+}$ $^1S_0$ are within the 4f shell, which is shielded from the energetic positions of Pr$^{3+}$ $^1S_0$ emissions are not sensitive to the crystal environment, that is, the parameter $E$ is roughly a fixed value. Finally, only the oscillator strength can change in several orders of magnitude between different transitions and different ions. And further, the ET rate via electric multipole interaction is proportional to the oscillator strength of the relative transitions. Thus, the magnitude of the oscillator strength has a decisive effect on estimating whether the ET can occur or not between Pr$^{3+}$ $^1S_0$ and acceptors if sufficient spectral overlap is fulfilled. In fact, the efficient ET from Pr$^{3+}$ $^1S_0$ to Cr$^{3+}$ in this work profits very much from the relatively large oscillator strength, typically in the order of $10^{-4}$ for the spin-allowed $^4A_2–^4T_1(F)$ transition of Cr$^{3+}$. Now we assume the value of the spectral integral between the emission of $^5D_0–^5I_{9}$ and the excitation of the codopants is 1, the oscillator strength of the resonant transitions is in $10^{-6}$–$10^{-8}$ and the host matrix used is SAO. Then, from Eq. (2), we get the critical distance is in $2.63–5.68$ Å. If we fix the concentration of Pr$^{3+}$ at 1%, following Eq. (5), a concentration value between 89% and 895% is needed for the codopants. Practical dopant concentration is usually much smaller than this value. This is the reason why the efficient ET is difficult to be observed.

So far, efficient ET from Pr$^{3+}$ $^1S_0$ to rare-earth ions has not been reported [13–17]. The interests of researchers have shifted to transition-metal ions [18–25]. The great drawback of SAO:Pr$^{3+}$, Cr$^{3+}$ QC phosphor is that the emission of Cr$^{3+}$ is near the infrared region ($\sim$685 nm), which color-rendering is still very low. Usually, the requirements for the transfer partners of Pr$^{3+}$ are in principle the following: (1) it should have a strong transition around 400 nm, i.e., in resonance to the $^5S_{0–}^5I_{6,3P_j}$ transitions of Pr$^{3+}$; (2) it should emit predominantly in the visible range with high sensitivity of the human eye; and (3) the whole energy level scheme may not have any energy levels interfering with those of the Pr$^{3+}$ in a way, that the cascade emission is affected or even prevented. The three conditions above are only the fundamental ones, however. As discussed in the introduction, many rare-earth and transition-metal ions fulfill the above-stated requirements; however, ET was not observed. From the analysis in this report, we add at least one more requirement, which may really give rise to the occurrence of ET: (i) the resonant transition of the codopants should have large oscillator strength. Since 4f–5d transitions of rare earth are allowed electric dipole transitions, in which oscillator strengths are usually in the order of $10^{-8}$, ET from Pr$^{3+}$ $^1S_0$ to the ions with resonant 4f–5d transitions may takes place efficiently; or (ii) the co-doped ions can form some clusters with Pr$^{3+}$ in the host. Then even at a low concentration, the mean $S–A$ distance can be smaller than the critical distance of ET due to the limit of clusters. This is not necessarily impossible. For example, the oscillator strength of the transitions of Mn$^{2+}$, $^6A_{1g}$–$^4E_g$, $^6A_{2g}$, which are usually in resonance to the $^5S_{0–}^5I_{6,3P_j}$ transitions of Pr$^{3+}$, are very low, typically in $10^{-6}$–$10^{-8}$. Thus, ET between Pr$^{3+}$ and Mn$^{2+}$ cannot be observed in most cases [16–19]. However, efficient ET was reported in LaMgB$_2$O$_{10}$:Pr$^{3+}$, Mn$^{2+}$ [20,21] and SrB$_4$O$_7$:Pr$^{3+}$, Mn$^{2+}$ [22,23]. Fu et al. [23] investigated LaMgB$_2$O$_{10}$:Pr$^{3+}$, Mn$^{2+}$ systems and suggested that, due to $R_0 \gg R_{np}$ and $R_{np} < R_{mn}$, it is likely that some near neighboring sites of La$^{3+}$ and Mg$^{2+}$ are substituted by Pr$^{3+}$–Mn$^{2+}$ cluster to maintain the balance of the lattice.

4. Conclusions

The ET mechanism from Pr$^{3+}$ $^1S_0$ to Cr$^{3+}$ was investigated theoretically. The $dq$ interaction plays a dominate role in the ET process from Pr$^{3+}$ $^1S_0$ state to Cr$^{3+}$ in SAO. With the help of ESR investigation, we find that the Cr$^{3+}$ ions enter the Al(4f) site in the host. Efficient ET can take place only in the intermediate mirror planes, in which for the nearest and next-nearest Pr$^{3+}$–Cr$^{3+}$ pair, both $dd$ and $dq$ interactions can play their parts in the ET from Pr$^{3+}$ $^1S_0$ state to Cr$^{3+}$, and in this case the exchange mechanism cannot be excluded. The efficient ET profits from the relatively large oscillator strength of the spin-allowed resonant transition of Cr$^{3+}$, $^4A_{2}–^4T_{1}(F)$.

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References
