VUV–UV Photoluminescence Spectra of Strontium Orthophosphate Doped with Rare Earth Ions

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The measurements of VUV–UV photoluminescence emission (PL) and photoluminescence excitation (PLE) spectra of rare earth ions activated strontium orthophosphate [$Sr_3(PO_4)_2$:RE, RE = Ce, Sm, Eu, Tb] are performed. Whenever the samples are excited by VUV or UV light, the typical emission of Ce^{3+}, Sm^{3+}, Eu^{3+}, Eu^{2+} and Tb^{3+} ions can be observed in PL spectra, respectively. The charge transfer bands (CTBs) of Sm^{3+} and Eu^{3+} are found, respectively, peaking at 206 and 230 nm. The absorption bands peaking in the region of 150–160 nm are assigned to the host lattice sensitization bands, i.e., the band-to-band transitions of PO_4^{3-} grouping in $Sr_3(PO_4)_2$. It is speculated that the first f–d transitions of Sm^{3+} (Eu^{3+}), and the CTB of Tb^{3+} are, respectively, located around 165 (1 4 3) and 167 nm by means of VUV–UV PLE spectra and relational empirical formula, these f–d transitions or CT bands are included in the bands with the maxima at 150-160 nm, respectively. The valence change of europium from trivalent to divalent in strontium orthophosphate prepared in air is observed by VUV–UV PL and PLE spectra. © 2002 Elsevier Science (USA)

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INTRODUCTION

The luminescence of alkali earth orthophosphates doped with rare earth ions has attracted much attention over the last decades. There was a large amount of spectra data on these hosts. Hoffman and Lagos reported on the UV-excited luminescence of $M_3(PO_4)_2$:Eu^{2+} (M = Sr, Mg, Zn) and $MM'_2(PO_4)_2$:Eu^{2+} (M = Mg, Ca, Sr, Ba; M' = Mg, Zn, Ba) prepared in H_2/N_2 reducing atmosphere (1−3). Tāle depicted the luminescent mechanisms of $Ba_3(PO_4)_2$:Eu^{2+} (4). The cathodoluminescence of $Sr_3(PO_4)_2$:Tb was presented by Bril (5). In 1986, Lammers published work on the

UV-excited luminescence of $M_3(PO_4)_2$:Ce,Tb (M = Sr, Ba) (6). The X-ray storage phosphor $Ba_3(PO_4)_2$:Eu^{2+},La^{3+} was described by Schipper in 1993 (7).

These phosphors exhibit satisfying luminescence whenever excited by UV light, cathode radiation or X ray. However, to our knowledge, no work has been published on the VUV-excited luminescence for rare earth ions activated strontium orthophosphate. In recent years, the spectral properties of rare earth ions in different hosts in the VUV range have been intensively reported. There are two reasons that compel the development for research on rare earth ions in this VUV region. The first reason is to study the high-energy states of rare earth ions in the VUV region. The second reason is to explore efficient VUV-excited luminescent materials that could be used in mercury-free fluorescent lamps or plasma display panels.

The primary interest of the present work is to study the possible reduction of Eu^{3+} in air. By the comparison of the structural characteristics of a series of matrices and dopant rare earth ions, some necessary conditions for reduction of trivalent rare earth in air have been proposed by our group (8). These conditions are: (1) there are no oxidizing ions in hosts; (2) the doped trivalent rare earth ions must substitute for the aliovalent (unequal valent) cations in host, such as divalent alkali earth ions; (3) rigid three-dimensional tetrahedral network structure of anions, such as BO_4 or PO_4 exist in the composite oxide matrices and (4) RE^{2+} have similar ionic radii to that of substituted cations. In such cases, Eu^{3+}, Sm^{3+}, Yb^{3+} and Tm^{3+} can be reduced to the corresponding divalent rare earth ions in hosts such as SrB_4O_7, SrB_6O_{10} and $SrBPO_5$ by solid-state reaction at high temperature even in air (9–11). The anion structure of alkali earth orthophosphates is tetrahedron PO_4^{3-}, so we could expect that Eu^{3+} is reduced in air also, and this reduction might be demonstrated by VUV–UV PL and PLE spectra.

In this paper, the VUV–UV PL and PLE spectra of rare earth ions activated strontium orthophosphate are reported. The reduction of Eu^{3+} in $Sr_3(PO_4)_2$ prepared in air is confirmed using the luminescence method also.

EXPERIMENTAL SECTION

Rare earth ions doped samples $Sr_3(PO_4)_2$:RE ($RE=$ Ce, Sm, Eu and Tb) and matrix $Sr_3(PO_4)_2$ were prepared by solid-state reactions at high temperatures. The starting materials were $SrCO_3$ (A.R., analytical reagent), $NH_4H_2PO_4$ (A.R.) and rare earth (CeO_2, Sm_2O_3, Eu_2O_3 and Tb_4O_7; 99.99%) oxides. Two firing steps were necessary for the synthesis of all samples. Stoichiometric amount of the starting materials were first thoroughly mixed and fired at 400°C for 2 h, and subsequently fired in air (for Sm- or Eu- doped samples) or CO reducing (for Ce- and Tb- doped samples) atmosphere at 1200°C for another 2 h. After these steps, the temperature was slowly lowered to room temperature. X-ray powder diffraction using $CuK\alpha_1$ radiation confirmed the synthesized samples to be of single phases.

UV excitation spectra and UV-excited luminescent spectra were recorded on a SPEX 2T2 spectrofluorometer equipped with 0.22 m SPEX 1680 double monochromators (resolution 0.1 nm) and a 450 W xenon lamp as excitation source.

The VUV PL and PLE spectra of the samples were measured at Beijing Synchrotron Radiation Facilities (BSRF) on beam 3B1B VUV spectral experimental station under normal operating conditions (2.2 GeV, 100 mA) at 293 K, respectively. An ARC-502 monochromator was used for excitation spectrum, an ARC-308 monochromator was used for emission spectrum and the signal was detected by an H7421-50 photomultiplier. The effect of the experimental setup response on the relative VUV PLE intensities of the samples were corrected by dividing the measured excitation intensities of the samples with the excitation intensities of sodium salicylate at the same excitation condition (12, 13).

RESULTS AND DISCUSSION

UV PL and PLE Spectra of $Sr_3(PO_4)_2$:Ce

Figure 1 shows the UV spectra of $Sr_{3(1-x)}Ce_{3x}(PO_4)_2$ ($x = 0.03$) at room temperature. The emission spectrum (excited under 293 nm) exhibits a broadband around 347 nm with a shoulder band at the short-wavelength side. This emission band can be deconvoluted into two sub-bands with maxima at 330 and 354 nm, respectively. These two sub-bands correspond to $5d^2$-F_J ($J=7/2$, 5/2) transitions in Ce^{3+}. The ^2F_J ($J=7/2$, 5/2) energy gap of Ce^{3+} in $Sr_3(PO_4)_2$ is 2054 cm^{-1}, which is close to the ^2F_J

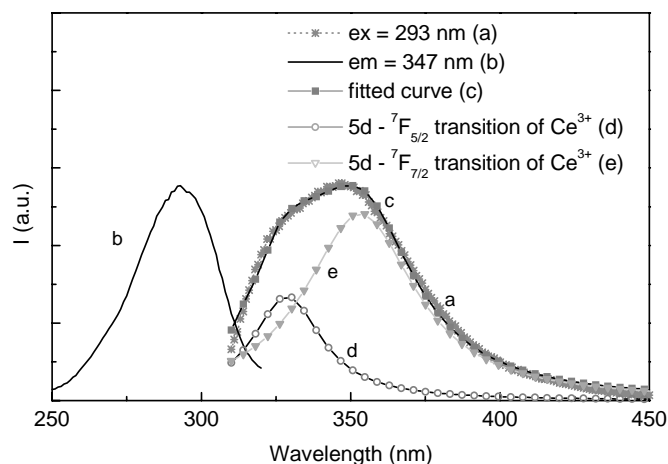**FIG. 1.** UV PL and PLE spectra of $Sr_3(PO_4)_2$:Ce at room temperature. (a) PL spectrum under the excitation at 293 nm; (b) PLE spectrum under the emission at 347 nm; (c) the fitted curve of curve (a); (d) and (e) the deconvoluted curves of curve (a).

($J = 7/2$, 5/2) energy gap of Ce^{3+} (2000 cm^{-1}) in most Ce^{3+} activated phosphors (14). The lowest f–d transition excitation band of Ce^{3+} in $Sr_3(PO_4)_2$ can be observed with a peak at 293 nm (viz., 34,134 cm^{-1}) as shown in Fig. 1, when the emission at 347 nm is monitored. Lammers et al. have reported the optical spectra of this phosphor, they found that Ce^{3+} showed an emission with a maximum at 325 nm and a shoulder at 350 nm, the excitation band of Ce^{3+} has its maximum at about 290 nm (i.e., 34,483 cm^{-1}) (6). The results that we observed are close to that of Lammers et al.

It is known that from the lowest 5d level energy of Ce^{3+} in a specific compound, the 5d energies of other rare earth ions in that compound can be predicted fairly well (15–17). Dorenbos gathered and analyzed the $4f$–$5d$ transition energies of triply ionized lanthanides in various compounds and proposed that the crystal field depression D (Ln, A) of the energy of lowest $4f^{n-1}5d$ levels of a lanthanide ion in compound A relative to the level energies in the free ion, i.e.,

$$D(\text{Ln}, \ A) = E(\text{Ln, free}) - E(\text{Ln}, \ A) \qquad [1]$$

is almost independent of the type of lanthanide ion (15–17). The main purpose of our work on the UV spectra of $Sr_3(PO_4)_2$:Ce is to investigate the crystal field depression D(Ln, A) value of $Sr_3(PO_4)_2$. The f–d excitation transition of Ce^{3+}, E(Ce, A) we found was at 293 nm (i.e., 34,130 cm^{-1}), the reported d level energy of free Ce^{3+} is 49,340 cm^{-1} (15). So we can calculate that the f–d transition energy of Ce^{3+} in $Sr_3(PO_4)_2$ is depressed by 15210 cm^{-1}, compared to that of free Ce^{3+} ions. It implies that the $D[Ce^{3+}, Sr_3(PO_4)_2]$ is 15,210 cm^{-1}. Accordingly, the $D[Ce^{3+}, Sr_3(PO_4)_2]$ value 14,857 cm^{-1} could be

calculated from Lammers reported spectra data, and the $D[Ce^{3+}, Sr_3(PO_4)_2]$ value collected by Dorenbos was $15,687\,cm^{-1}$ (17). The D value we obtained is located in the midst of the ones reported by Dorenbos and Lammers. By combining both values, the mean $D[Ce^{3+}, Sr_3(PO_4)_2]$ can be calculated as around $15,251 \pm 394\,cm^{-1}$.

VUV–UV PL and PLE Spectra of $Sr_3(PO_4)_2$:Sm

As shown in Fig. 2, the VUV–UV PL spectra of $Sr_{3(1-x)}Sm_{3x}(PO_4)_2$ ($x = 0.03$) were obtained when the sample was excited under the $^6H_{5/2}$–$^4K_{11/2}$ transition of Sm^{3+} at 401 nm or VUV light at 147 nm, respectively, at room temperature. The spectrum is composed of typical $^4G_{5/2}$–^6H_J (J 5/2, 7/2, 9/2) transitions of Sm^{3+}, and the main emission line is the $^4G_{5/2}$–$^6H_{7/2}$ transition at 596 nm. The VUV–UV PLE spectra are recorded by monitoring the emission at 596 nm. The main excitation line in UV spectrum is $^6H_{5/2}$–$^4K_{11/2}$ transition of Sm^{3+} at 401 nm.

Two obvious absorption bands appeared in region 130–250 nm in the VUV PLE spectrum. About the VUV PLE spectra of rare earth ions activated luminescent materials, five physical processes have been reported: (1) f–f transition of the rare earth ions: a direct photon absorption promotes one f-electron from the ground state to $4f$ excited levels within the $4f^n$ ground state configuration. Recently, Meijerink *et al.* have studied the rare earth ions activated fluorides and extend the Dieke diagram up to energies of about $68,000\,cm^{-1}$ (18, 19). As f–f transitions of the rare earth ions are electric dipolar transitions which are forbidden by the parity selection rules but forced by the crystal field configuration mixing due to the odd terms of

the crystal field Hamiltonian development, we think that although this sharp line transition do exist in the VUV region in $Sr_3(PO_4)_2$:Sm, however, it is hard to be observed because the f–f intra-configuration transition of Sm^{3+} in this range are weak and hidden by other stronger broadband transitions. (2) f–d transition of the rare earth ions (20). The $4f$–$5d$ dipolar electric transitions, between these two configurations of opposite parity, are allowed by the Laporte parity selection rule and consequently they give rise to intense and broad absorption. Because the outer $5d$ orbits are involved, and the $5d$-electrons strongly interact with the neighboring anion ligands in the compound, the positions of the $4f^{n-1}5d$ levels are much more influenced by the crystal field interaction than the $4f^n$ levels are. Though the f–d transitions of some rare earth ions have been reported in several fluoride hosts, the experimental data of this transition for Sm^{3+} or Eu^{3+} in composite oxide hosts are scarce. (3) Charge transfer band (CTB) from coordination anions to the rare earth ions (21). (4) The absorption of the host lattice (22–25). (5) $4f$–$6s$ transition of rare earth ions (26). We believe that the two bands observed in the VUV range in $Sr_3(PO_4)_2$:Sm are related to the following processes.

(a) It is no doubt that the band with a maximum at 206 nm is the charge transfer band of Sm^{3+} in $Sr_3(PO_4)_2$.

(b) The band from 130 to 180 nm, with a maximum around 157 nm is the dominant one in the VUV PLE spectrum of $Sr_3(PO_4)_2$:Sm. Comparing the VUV PLE spectra of $Sr_3(PO_4)_2$:Sm with Eu^{3+}- or Tb^{3+}-doped samples, we can find that all VUV PLE spectra exhibit a band around this wavelength. Because the appearance of this band is independent of the nature of rare earth ions, we consider that this band is resulting from the absorption of the host lattice, namely, the band-to-band transition of PO_4^{3-} anion grouping in $Sr_3(PO_4)_2$. The absorptions of some phosphates host lattice have already been reported. Nakazawa *et al.* considered that the absorption of rare earth orthophosphates host $REPO_4$ ($RE = $ Y, La, Gd and Lu) are at about 152, 159, 160 and 145 nm, respectively (27). Kim and co-authors considered that the host sensitization bands of $Tb_xY_{1-x}PO_4$, $K_3Tb(PO_4)_2$ and polyphosphates $KTbP_4O_{12}$, TbP_5O_{14} are in regions 130–160 nm (23). Using the extended Hückel method, Saito *et al.* calculated the energy levels of tetrahedral PO_4^{3-} molecule (28), according to their results the lowest intramolecular transition of $2t_2 \rightarrow 2a, 3t_2$ was found to exist at 7–10 eV (124–177 nm). The host sensitization band we observed is close to the reported energies and the calculated results.

Simultaneously, we consider that the band appearing around 157 nm in the sample $Sr_3(PO_4)_2$:Sm includes f–d transition of Sm^{3+} also. Just as mentioned above, according to Dorenbos concept of D, the calculated $D[Ce^{3+}, Sr_3(PO_4)_2]$ of Ce^{3+} in $Sr_3(PO_4)_2$ is $15,251 \pm 394\,cm^{-1}$. As this value is independent of the
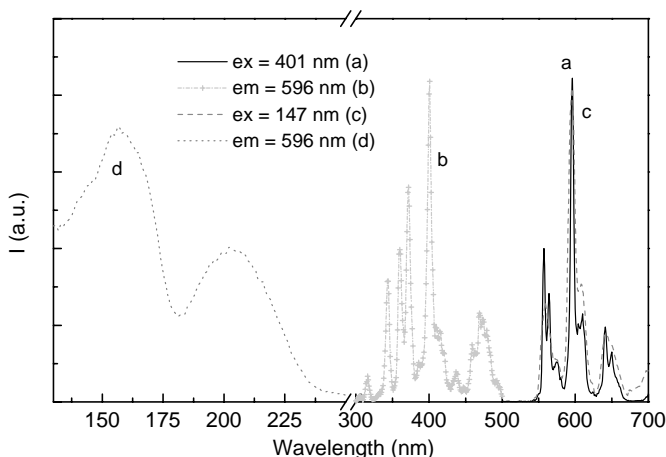

FIG. 2. VUV–UV PL and PLE spectra of $Sr_3(PO_4)_2$:Sm at room temperature. (a) UV PL spectrum under the excitation at 401 nm; (b) UV PLE spectrum under the emission at 596 nm; (c) VUV PL spectrum under the excitation at 147 nm; (d) VUV PLE spectrum under the emission at 596 nm.

nature of the rare earth ions and only related to the host lattice $Sr_3(PO_4)_2$, the $D[Sm^{3+}, Sr_3(PO_4)_2]$ value can be expected to be $15,251 \pm 394 \, cm^{-1}$ also. It is reported that the f–d transition energy of free Sm^{3+} ions is $75,840 \, cm^{-1}$ (15−17). Using expression [1], we can calculate that the lowest f–d transition energy of Sm^{3+} in $Sr_3(PO_4)_2$ is $60,589 \pm 394 \, cm^{-1}$, viz., the lowest f–d transition of Sm^{3+} in $Sr_3(PO_4)_2$ is about 165 nm

VUV–UV PL and PLE Spectra of $Sr_3(PO_4)_2$:Eu

The VUV–UV PL and PLE spectra of $Sr_{3(1-x)}Eu_{3x}(PO_4)_2$ ($x = 0.03$) prepared in air are shown in Fig. 3a and 3b. The emission of Eu^{2+} and Eu^{3+} could be observed whenever the sample was excited by VUV at 147 nm or UV at 394 nm, and the emission band (or lines) position of Eu^{2+} (or Eu^{3+}) excited under VUV light is consistent with
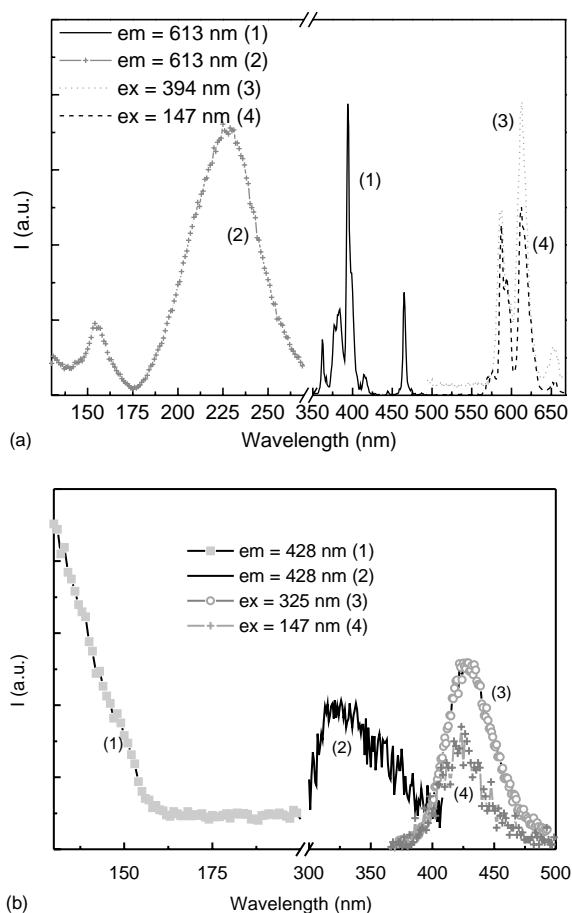

(a)

(b)

FIG. 3. VUV–UV PL and PLE spectra of $Sr_3(PO_4)_2$:Eu prepared in air at room temperature. (a) Spectra of Eu^{3+}: (1) UV PLE spectrum and (2) VUV PLE spectrum under the emission at 613 nm; (3) UV PL spectrum under the excitation at 394 nm; (4) VUV PL spectrum under the excitation at 147 nm. (b) Spectra of Eu^{2+}: (1) VUV PLE spectrum and (2) UV PLE spectrum under the emission at 428 nm; (3) VUV PL spectrum under the excitation at 147 nm; (4) UV PL spectrum under the excitation at 325 nm.

that excited under UV light. The f–d transition emission of Eu^{2+} was located around 428 nm as shown in Fig. 3b. The emission lines of Eu^{3+} are composed of a group of typical $^5D_0$–^7F_J ($J = 1, 2, 3, 4$) transitions and the main line is $^5D_0$–$^7F_2$ transition at 613 nm as shown in Fig. 3a. From the VUV–UV PL spectra, one can observe that a small quantity of Eu^{3+} might be reduced in $Sr_3(PO_4)_2$:Eu prepared by solid-state reaction at high temperature in air.

The VUV–UV PLE spectra were obtained by monitoring the emission of Eu^{2+} at 428 nm and the emission of Eu^{3+} at 613 nm, respectively.

The faint excitation band of Eu^{2+} was the lowest $4f$–$5d$ transition peaking at about 325 nm, the intra-configuration $4f$ emission lines of Eu^{3+} was composed of transitions from the ground $^7F_0$ state to the excited $^5I_{5, 6}$, $^5L_{9, 10}$, $^5L_6$, $^5D_3$ and $^5D_2$ levels, and the predominant emission line is $^7F_0$–$^5L_6$ transition at 394 nm as shown in Fig. 3a. Both the excitation and the emission spectra imply that the trivalent europium could be partially reduced in $Sr_3(PO_4)_2$:Eu prepared in air.

There was no other obvious absorption band in the VUV PLE spectrum of Eu^{2+}, except for the absorption band of the matrix. Two excitation peaks appeared in VUV PLE spectrum of Eu^{3+}. (a) The dominan excitation band with a maximum at 230 nm was the charge transfer band (CTB) of Eu^{3+} in $Sr_3(PO_4)_2$. On comparing the position of this band with that of CTB of Sm^{3+} in $Sr_3(PO_4)_2$, it could be found that the CTB of Eu^{3+} is redshifted. This phenomenon demonstrated the electronic transfer capability from O^{2-} to RE^{3+} in RE–O (RE = Sm, Eu). (b) The band from 140 to 175 nm, with a maximum around 154 nm was due to the absorption of the host lattice. At the same time, we thought that this band includes the f–d transition of Eu^{3+} also. It is known that the D value of Ce^{3+} in $Sr_3(PO_4)_2$ is $15,251 \pm 394 \, cm^{-1}$, and the f–d transition energy of free Eu^{3+} ions is $85,300 \, cm^{-1}$ (15–17). So the f–d transition of Eu^{3+} in $Sr_3(PO_4)_2$ could be speculated as $70,049 \pm 394 \, cm^{-1}$, viz., the lowest f–d transition of Eu^{3+} in $Sr_3(PO_4)_2$ is about 143 nm using expression [1]. Krupa et al. already measured the f–d transitions of Eu^{3+} in some fluorides. The lowest f–d transitions of Eu^{3+} in oxygen contaminated REF_3 (RE = La, Y) were at about 125 nm (9.9 eV, RE = La) and 140 nm (8.8 eV, RE = Y) (29), respectively. It is consistent with the fact that the position of the lowest f–d transitions in fluorides is usually located at a higher energy than that in oxides.

Ordinarily, for reduction of the trivalent rare earth ions by solid-state reaction at high temperature, reducing atmospheres, such as H_2/N_2, activated carbon or CO, NH_3 are needed. The abnormal reduction of Eu^{3+} in $Sr_3(PO_4)_2$ can be achieved in air atmosphere, which are related to the following reasons.

(a) The doped Eu^{3+} would substitute Sr^{2+} in the host lattice in general. In order to keep the electroneutrality of

the compound, two Eu^{3+} ions would substitute for three Sr^{2+} ions. Therefore, two positive defects of $[Eu_{Sr}]$ and one negative Sr^{2+} vacancy of $[V_{Sr}]$ would be created (30). By thermally stimulated movement, the electrons on the vacancies $[V_{Sr}]$ would be transferred to the doped Eu^{3+} ions in the Sr-sites $[Eu_{Sr}]$ and the ions $[Eu_{Sr}]$ are reduced into divalent state $[Eu_{Sr}]^{\times}$ by these free electrons.

(b) The rigid tetrahedral PO_4 anions are favorable to the stabilization of Eu^{2+} ions. This point is supported by the fact that rare earth ions can be reduced in the matrices such as SrB_4O_7, SrB_6O_{10} and BaB_8O_{13}. In host SrB_4O_7, all borate anions existed in the form of tetrahedron BO_4, the Eu^{3+} can be reduced in air (8, 31). While in host BaB_8O_{13}, the borate anions are composed of triangular structure BO_3 and tetrahedron BO_4, the Eu^{3+} can also be reduced in air, whereas fewer Eu^{3+} ions can be reduced in BaB_8O_{13}:Eu than in SrB_4O_7:Eu (32). But in $Sr_3B_2O_6$, $Sr_2B_2O_5$ and SrB_2O_4, they contain only triangular BO_3 group, Eu^{3+} ion cannot be reduced in air by aliovalent substitution (8).

(c) Eu^{2+} ions have similar ionic radii with Sr^{2+} ions. We think that this factor is suitable to stabilize the Eu^{2+} ions. When Eu^{2+} ions occupy the substituted lattice sites of Sr^{2+} ions, the replacement cannot lead to obvious distortion for tetrahedral anion PO_4^{3-}. The rigid tetrahedral PO_4^{3-} groups can efficiently surround the produced Eu^{2+} ion and protect the inserted Eu^{2+} from the reaction with the oxygen in air, so the reduced state is easy to be stabilized.

VUV–UV PL and PLE Spectra of $Sr_3(PO_4)_2$:Tb

The VUV–UV PL and PLE spectra of $Sr_{3(1-x)}Tb_{3x}(PO_4)_2$ ($x = 0.03$) are shown in Fig. 4. The emission spectra of the sample excited by VUV or UV are similar. The luminescence of Tb^{3+} was composed of typical $^5D_4$–^7F_J ($J = 3, 4, 5, 6$) transitions, and the main emission line was $^5D_4$–$^7F_5$ transition at 542 nm. Two obvious bands appeared in VUV PLE spectrum, as shown in Fig. 4. The dominant band was the f–d transition of Tb^{3+}, which located at about 229 nm. The observed f–d transition position of Tb^{3+} in $Sr_3(PO_4)_2$ is close to the calculated value by using Eq. [1] and the Dorenbos D value of Ce^{3+} in $Sr_3(PO_4)_2$, which is in the wavelength range 212–243 nm for allowed and forbidden f–d transitions. The band around 159 nm probably related to the host absorption and the charge transfer between Tb^{3+} and O^{2-}.

The position of the charge transfer band (CTB) of Tb^{3+} ions can be calculated with the help of an empirical formula given by Jørgensen (33, 34):

$$E_{CT} = [(X) - (M)] \times 30,000 \text{ cm}^{-1}. \qquad [2]$$

Here E_{CT} gives the position of the CTB in cm^{-1}, (X) the optical electronegativity of the anion, and (M) that of central metal ion. Using (O) = 3.2 (33), (Tb) = 0.95 (35), the CTB of Tb^{3+} in oxides can be calculated as $67,500 \text{ cm}^{-1}$,
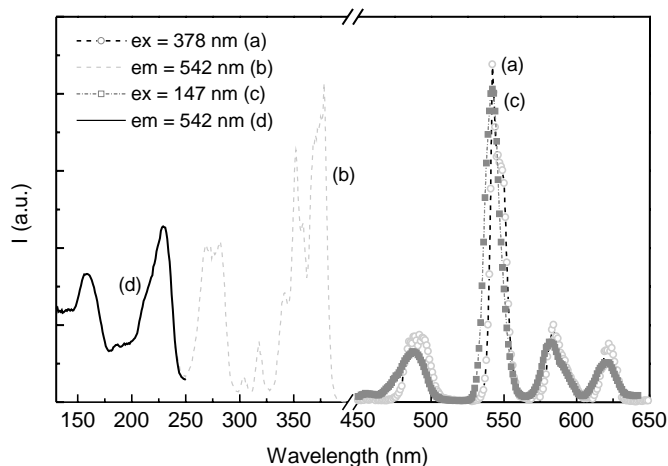

FIG. 4. VUV–UV PL and PLE spectra of $Sr_3(PO_4)_2$:Tb at room temperature. (a) UV PL spectrum under the excitation at 378 nm; (b) UV PLE spectrum under the emission at 542 nm; (c) VUV PL spectrum under the excitation at 147 nm; (d) VUV PLE spectrum under the emission at 542 nm.

namely, the CTBs of Tb^{3+} in oxides was around 167 nm. The results are close to the O^{2-}-Tb^{3+} CT bands $68,100 \text{ cm}^{-1}$ ($RE = Y$) and $63,500 \text{ cm}^{-1}$ ($RE = La$) reported in oxygen blurred REF_3 ($RE = La, Y$) (36).

CONCLUSIONS

The measurements of VUV–UV PL and PLE spectra of rare earth ions activated strontium orthophosphate were achieved and the following conclusions could be suggested.

(1) The band-to-band transition of P–O in $Sr_3(PO_4)_2$ was in the region of 150–160 nm.

(2) The band around 154 nm in VUV PLE spectra of $Sr_3(PO_4)_2$:Eu^{3+} included the f–d transition of Eu^{3+} also. In the f–d transition absorption of Eu^{3+} in $Sr_3(PO_4)_2$ deduced from the Dorenbos empirical formula, the energy was speculated as 143 nm. The CTB of Eu^{3+} was located at 230 nm.

(3) The band around 157 nm in VUV PLE spectra of $Sr_3(PO_4)_2$:Sm^{3+} is related to the absorption of the host lattices and the f–d transition of Sm^{3+}. The CTB of Sm^{3+} was located at 206 nm.

(4) The band around 159 nm in the VUV PLE spectra of $Sr_3(PO_4)_2$:Tb^{3+} is associated with the absorption of the host lattice and the CTB of Tb^{3+}. The f–d transition of Tb^{3+} was located at 229 nm.

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