Characterization and optical properties of \((\text{Gd}_{1-x}, \text{Pr}_x)_2\text{O}_2\text{S}\) nano-phosphors synthesized using a novel co-precipitation method

Jingbao Lian\(^a,\)\(^b\), Xudong Sun\(^a,\)\(^*\), Ji-Guang Li\(^a\), Bing Xiao\(^c\), Kai Duan\(^d\)

\(^a\) Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), School of Materials and Metallurgy, Northeastern University, Shenyang 110004, PR China
\(^b\) School of Chemical Engineering, Liaoning Shihua University, Fushun 113001, PR China
\(^c\) School of Materials Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, PR China
\(^d\) Faculty of Science, Engineering and Health, CQ University, Gladstone, QLD 4680, Australia

**A R T I C L E  H I S T O R Y**

Received 13 April 2009
Received in revised form 23 January 2010
Accepted 4 March 2010

**Keywords:**
Oxysulfide
Co-precipitation
Optical properties
First principles calculation

**A B S T R A C T**

A novel co-precipitation method for synthesizing \((\text{Gd}_{1-x}, \text{Pr}_x)_2\text{O}_2\text{S}\) nano-phosphors was developed, using the commercially available \(\text{Gd}_2\text{O}_3\), \(\text{Pr}_6\text{O}_{11}\), \(\text{H}_2\text{SO}_4\) and \(\text{NaOH}\) as the starting materials. This method has the advantage of controllable phosphor particle size and shape, simplicity in processing, low cost, and not involving toxic carbon disulfide or hydrogen sulfide. It was found that the as-synthesized precursor is mainly composed of \((\text{Gd}_{1-x}, \text{Pr}_x)_2(\text{OH})_4\text{SO}_4\cdot n\text{H}_2\text{O}\). By calcining the \((\text{Gd}_{1-x}, \text{Pr}_x)_2(\text{OH})_4\text{SO}_4\cdot n\text{H}_2\text{O}\) precursor at a temperature higher than 700 °C for 1 h in flowing hydrogen, pure quasi-spherical shaped \((\text{Gd}_{1-x}, \text{Pr}_x)_2\text{O}_2\text{S}\) particles can be synthesized. The \((\text{Gd}_{1-x}, \text{Pr}_x)_2\text{O}_2\text{S}\) particles have a narrow size distribution with a mean grain size of about 20–30 nm. UV–vis spectra indicates that the absorption edge of the samples has a blue shift with increasing calcination temperature, while PL spectra of \((\text{Gd}_{1-x}, \text{Pr}_x)_2\text{O}_2\text{S}\) under 301 nm excitation show a green emission at 511 nm as the most prominent peak, which corresponds to the \(^{3}\text{P}_0 \rightarrow ^{3}\text{H}_4\) transition of \(\text{Pr}^{3+}\) ions. The optimal \(x\) value is 0.01 for the highest luminescent emission intensity.

© 2010 Elsevier B.V. All rights reserved.

**1. Introduction**

Rare earth oxysulfides are wide-gap (4.6–4.8 eV) semiconductors, and often exhibit favorable properties such as excellent chemical stability, insolubility in water, high melting point, innocuity and high luminescence efficiency\([1,2]\). Therefore, they have been widely utilized as catalysts\([3,4]\) and laser materials\([5]\). They are also efficient phosphorescent host materials for a variety of applications, e.g., high efficiency \(Y_2\text{O}_2\text{S}:\text{Eu}^{3+}\) red phosphors in the phosphor screen of display devices\([6]\), X-ray imaging systems for medical diagnosis\([7]\), and up-conversion phosphors\([8]\). Among these oxysulfides, \(\text{Gd}_2\text{O}_2\text{S}\) is a promising host for scintillation material, because of its high density (7.34 g cm\(^{-3}\)) and high atomic number \((Z)\) of \(\text{Gd}\) (64), which leads to a high stopping power for X-ray radiation. Particularly, \(\text{Gd}_2\text{O}_2\text{S}\) doped with trivalent praseodymium provides an advantageous high intrinsic X-ray to light conversion efficiency, short decay time and low afterglow for ultra fast X-ray imaging application\([9]\).

A number of synthesis routes have been developed for processing \(\text{Re}_2\text{O}_2\text{S}\) (\(\text{Re} = \text{rare earth}\)) phosphors, including solid-state reaction (SSR) method\([10]\), combustion synthesis method\([11]\), reduction method\([12]\), emulsion liquid membrane (ELM) method\([13]\), gas sulfuration method\([14]\) and decomposition method\([15]\). Among these synthesis methods, the SSR method is the most typical and common one because of its high reliability, low cost, and high product luminescent properties. However, the SSR method has the disadvantage of unable to achieve nanosized phosphor and difficult to control the particle morphology. Thus, the SSR method is not easily to meet the requirements for increasing high resolution of display due to the coarser particle. In contrast, combustion synthesis is an efficient method to synthesize nano-phosphor due to the direct crystallization of fine grains, low processing temperature and short processing time. However, this method is a high cost synthesis route due to the use of expensive dithiooxamide or other organic solvent as fuels. The other methods also have some disadvantages, e.g., the reduction method is not suitable for producing nanosized oxysulfides, the ELM method is a complicated and time-consuming preparation process, and the gas sulfuration and the decomposition methods normally involve the use of hydrogen sulfide (\(\text{H}_2\text{S}\)), carbon disulfide (\(\text{CS}_2\)) or sulfur vapor which are harmful to the environment.

In this work, a novel co-precipitation method that uses commercially available \(\text{Gd}_2\text{O}_3\), \(\text{Pr}_6\text{O}_{11}\), \(\text{H}_2\text{SO}_4\) and \(\text{NaOH}\) as the starting materials was developed for the synthesis of \((\text{Gd}_{1-x}, \text{Pr}_x)_2\text{O}_2\text{S}\) nano-phosphors. This method has the advantage of controllable phosphor particle size and shape, simplicity in processing, low cost,
and not involving toxic carbon disulfide or hydrogen sulfide. Optical properties of the (Gd_{1-x}, Pr_x)_{2}O_{2}S nano-phosphors were studied in details.

2. Experimental procedure

2.1. Synthesis of (Gd_{1-x}, Pr_x)_{2}O_{2}S

Gd_{2}O_{3} powder (99.99% purity, Shanghai New Materials Yuelong Co., Ltd., Shanghai, China), Pr_{2}O_{3} powder (99.99%, Nanfang Rare Earth High Technology Co., Ltd., Ganzhou, China), H_{2}SO_{4} (GR, Shenyang Xinhua Reagent Factory, Shenyang, China) and NaOH (AR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used as the starting materials. (Gd_{1-x}, Pr_x)_{2}O_{2}S solutions (0.01 mol\(^{-1}\)) with x varying from 0.02 to 0.04 were prepared by dissolving a stoichiometric amount of Gd_{2}O_{3} and Pr_{2}O_{3} powders in dilute H_{2}SO_{4} solution. NaOH solution (0.2 mol\(^{-1}\)) was obtained by dissolving sodium hydroxide in deionized water and was used as the precipitant. The co-precipitation process involves the addition of the precipitant solution at a speed of 0.1 ml min\(^{-1}\) to vigorously stirred (Gd_{1-x}, Pr_x)_{2}O_{2}S solution. In our previous paper [16], we found that the optimal molar ratio \([m]\) of NaOH to Gd_{2}O_{3} is 4. On this basis, Pr\(^{3+}\) doped (Gd_{1-x}, Pr_x)_{2}O_{2}S nH\(_2\)O precursors were synthesized according to the procedure described by Ref. [16]. Then, the (Gd_{1-x}, Pr_x)_{2}O_{2}S nH\(_2\)O precursor was calcined at 600, 700, 800 and 900 \(^\circ\)C respectively for 1 h in a flowing hydrogen atmosphere to produce the (Gd_{1-x}, Pr_x)_{2}O_{2}S phosphors. For the convenience of further discussion, these nano-phosphors obtained at 600, 700, 800 and 900 \(^\circ\)C are marked as P600, P700, P800 and P900 for \(x = 0\), respectively.

2.2. Characterization

Fourier transform infrared spectra (FT-IR) were recorded in the region of 4000–400 cm\(^{-1}\) using a Perkin-Elmer FT-IR spectrophotometer with KBr pellets. The surface composition was analyzed by X-ray photoelectron spectroscopy (ESCALAB250, Thermo VG) using Al K\(_\alpha\) (1486.6 eV) X-ray source with a power of 150 W. Its background pressure was <10\(^{-7}\) MPa. The sputtering was performed for 30 s in an ultra high vacuum (UHV) analysis chamber with a 2 keV Ar\(^{+}\) ion beam. The detector work function was calibrated using the C1s peak at 284.5 eV for a highly oriented pyrolytic graphite (HOPG) sample. The background was subtracted by the Tougaard method, and the peaks were deconvoluted by fitting the Gaussian–Lorentzian line shapes. Thermal analysis, i.e. thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) were performed using a simultaneous differential thermal and thermo-gravimetric analyzer (SDT 2960) with a heating rate of 10 \(^\circ\)C/min in flowing hydrogen atmosphere.

3. Results and discussion

3.1. FT-IR and XPS analysis

FT-IR analysis was performed to gain more insight into structure and composition of the synthesized phosphors. Fig. 1 shows FT-IR spectra of the precursor, and the P600, P700, P800 and P900 samples, respectively. The two absorption peaks centered at about 1510 and 1415 cm\(^{-1}\) in all samples can be assigned to the characteristic asymmetrical split stretching of CO\(_3^{2-}\), and shows the presence of CO\(_2^{2-}\) on the surface of the samples, which originates from absorbed H\(_2\)O and CO\(_2\) from ambient atmosphere [1.19]. The spectrum for the precursor shows the absorption peaks of absorbed water and hydroxyl group [20] (near 3430 cm\(^{-1}\)), the SO\(_4^{2-}\) anion (near 1120, 985, and 610 cm\(^{-1}\)), and crystal water (near 1630 cm\(^{-1}\)). This particular spectrum confirms that the precursor is mostly composed of gadolinium hydroxyl and sulfate groups with some crystal water. On the basis of the stoichiometric amounts of (Gd\(_{1-x}, \) Pr\(_x\))\(_2\)O\(_2\)S and NaOH (1:4), it can be concluded that the precursor is mainly composed of (Gd\(_{1-x}, \) Pr\(_x\))\(_2\)O\(_2\)S nH\(_2\)O. After calcinating at 600 \(^\circ\)C, the broad SO\(_4^{2-}\) absorption peaks split, and the strong broad absorption band centered at 3430 cm\(^{-1}\) becomes weak and the peak centered at 1630 cm\(^{-1}\) becomes negligible, suggesting the removal of hydroxyl water and crystal water from the precursor. Two new absorption peaks centered at about 315 and 430 cm\(^{-1}\) appear, which correspond to the characteristic vibration peaks of Gd–O bond in the synthesized phosphor. This shows that the precursor has been gradually transformed into (Gd\(_{1-x}, \) Pr\(_x\))\(_2\)O\(_2\)S phosphor. With increasing calcination temperature from 700 to 900 \(^\circ\)C, two broad SO\(_4^{2-}\) absorption peaks centered at about 1120 and 610 cm\(^{-1}\) fade away gradually, suggesting the transformation of SO\(_4^{2-}\) anion to S\(_2^{2-}\) anion. While the peaks centered at 1510 and 1415 cm\(^{-1}\) remain, two new weak peaks located at 950 and 850 cm\(^{-1}\) arise, which are associated with the out-of-plane bending of CO\(_3^{2-}\) [21]. This further confirms the presence of CO\(_3^{2-}\). A weak peak at 1125 cm\(^{-1}\) may arise due to the absorption of small amount of residual SO\(_4^{2-}\). Moreover, a new absorption peak centered about...
515 cm$^{-1}$ appears, corresponding to the characteristic vibration peak of Gd–O bond in all calcined phosphors, and the vibration peak of Gd–S bond is not observed in the present frequency range due to its lower vibrational frequency ($<300$ cm$^{-1}$) [22], indicating that (Gd$_{1-x}$Pr$_x$)$_2$O$_2$S can be synthesized by calcination of the precursor at higher than 700 °C for 1 h in flowing hydrogen atmosphere. These results are also consistent with those obtained using the DTA–TG–DTG and XRD techniques. The surface composition of P900 sample was further analyzed by XPS measurements. Fig. 2 gives wide scan and narrow scans for C1s and O1s XPS spectra of the P900 sample. As demonstrated in Fig. 2a, the elements of Gd, O, S and C can be detected. The carbon on the surface of P900 sample is ascribed to the adsorbed CO$_2$ from the ambient environment and the adventitious hydrocarbon from the XPS instrument itself. The narrow scans for C1s and O1s spectra before and after Ar$^+$ sputtering were also measured. The fitting results imply the presence of the two peaks at binding energies of 284.16 and 287.85 eV for C1s and three peaks at 528.68, 530.65 and 531.67 eV for O1s before Ar$^+$ sputtering. The peaks centered at 287.85 eV for C1s and 531.67 eV for O1s are tentatively assigned to the spectrum of CO$_3^{2−}$ [23], which result from the surface water and CO$_2$ adsorbed from the ambient environment. The peaks centered at 528.68 and 530.65 eV for O1s correspond to structural oxygen and adsorbed oxygen [24], respectively. It is known that rare earth oxysulfides are easily hygroscopic when they are exposed to atmospheric conditions. The peaks of C1s centered at 287.85 eV and O1s centered at 531.67 eV disappeared after Ar$^+$ sputtering, implying that the CO$_3^{2−}$ is only absorbed on the surface of P900 sample (in a range of 5–10 nm) and can be removed.

Fig. 2. Wide scan (a) and narrow scans for C1s (b and c) and O1s (d and e) XPS spectra of the P900 sample.
3.2. Thermal analysis

To understand the formation mechanism of Gd$_2$O$_2$S and find out the optimal calcination temperature for the precursor, DTA–TG–DTG of the precursor was carried out from room temperature to 800 °C, as shown in Fig. 3. The TG curve shows a continuous weight loss between room temperature and 800 °C, with an overall weight loss of approximately 38.8% by mass. The total weight loss mainly consists of four distinct steps in temperature ranges of 200–500, 500–650 and 650–800 °C, respectively, as seen from the DTG curve. The weight loss in the temperature range of room temperature–200 °C is resulted from the removal of physically absorbed water from the precursor. This weight loss corresponds to a weak endothermic peak at around 55 °C in the DTA curve, and a broad peak at about 110 °C in the DTG curve. The second step weight loss, which occurs between about 200 and 500 °C, is associated with the complete elimination of crystal water. This weight loss corresponds to a weak peak at around 300 °C in the DTG curve, and a weak endothermic peak near 360 °C in the DTG curve. The third step weight loss between 500 and 650 °C is about 8.0% by mass, which proceeds according to the following reaction:

$$\text{Gd}_2(\text{OH})_4\text{SO}_4 = \text{Gd}_2\text{O}_2\text{SO}_4 + 2\text{H}_2\text{O} \uparrow$$  \hspace{1cm} (1)$$

The weight loss is associated with the complete dehydroxylation of the precursor with DTG maxima at 590 °C and DTA maxima at 618 °C. The fourth step weight loss (14.7%) starting at about 650 °C with DTG maxima at 683 °C is attributed to the reduction of Gd$_2$O$_2$SO$_4$. This weight loss follows the reaction:

$$\text{Gd}_2\text{O}_2\text{SO}_4 + 4\text{H}_2 = \text{Gd}_2\text{O}_2\text{S} + 4\text{H}_2\text{O} \uparrow$$  \hspace{1cm} (2)$$

A weak exothermic peak centered at about 735 °C in the DTA indicates that the above process is an exothermic reaction, which can be attributed to crystallization of Gd$_2$O$_2$S.

3.3. XRD patterns and structure determination

Fig. 4 shows the XRD patterns of the precursor, P600, P700, P800 and P900, respectively. As shown in Fig. 4, the precursor is amorphous in structure with essentially no diffraction peaks. When the precursor was calcined at 600 °C, the XRD pattern shows that most of the XRD peaks observed were well indexed into Gd$_2$O$_2$SO$_4$ phase (ICDD card Nos. 00-041-0683 and 00-029-0613), indicating that the precursor has gradually crystallized and can be converted into the stable intermediate phase, Gd$_2$O$_2$SO$_4$. With increasing calcination temperature to 700 °C, the diffraction peaks of single phase Gd$_2$O$_2$S begin to appear in the XRD patterns and the obtained diffraction patterns are well consistent with the data reported in ICDD card No. 00-026-1422. Further increase in the calcination temperature to 900 °C leads to the enhanced Gd$_2$O$_2$S diffraction peak intensity and reduction in the full width at half maximum (FWHM) because of the improvement of crystallinity and grain growth. Moreover, on the basis of XRD patterns, the mean crystalline sizes of the calcined phosphors were also calculated. The mean crystalline sizes \(d\) of the Gd$_2$O$_2$S nano-phosphor can be estimated using Scherrer’s formula:

$$d = \frac{0.89\lambda}{B\cos \theta}$$  \hspace{1cm} (3)$$

where \(\lambda\) is the wavelength of Cu k\(\alpha\) radiation, \(B\) is the corrected FWHM of the diffraction peak, and \(\theta\) is the diffraction angle. The estimated mean crystalline sizes for P700, P800 and P900 were 21, 23 and 29 nm, respectively. It is noted that, the increase in grain size is not obvious. It will be found in a later section on PL spectra that the intensity of photoluminescence improves markedly with increasing calcination temperature. Furthermore, the crystal structure of P900 was determined by Powder index, Powder solve and Rietveld refinement using Reflex module. The refinements...
Table 1

The crystal structural data of Gd$_2$O$_2$S.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Hexagonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P6_3M1</td>
</tr>
<tr>
<td>Lattice parameter</td>
<td></td>
</tr>
<tr>
<td>$a$ ($\text{Å}$)</td>
<td>3.85252 ± 0.00077</td>
</tr>
<tr>
<td>$b$ ($\text{Å}$)</td>
<td>3.85252 ± 0.00077</td>
</tr>
<tr>
<td>$c$ ($\text{Å}$)</td>
<td>6.66490 ± 0.00137</td>
</tr>
<tr>
<td>Atomic position</td>
<td></td>
</tr>
<tr>
<td>Atom</td>
<td>x</td>
</tr>
<tr>
<td>Gd</td>
<td>1/3</td>
</tr>
<tr>
<td>O</td>
<td>2/3</td>
</tr>
<tr>
<td>S</td>
<td>0</td>
</tr>
</tbody>
</table>

yielded $R$ factor, i.e. $R_{wp} = 7.74\%$. The results of the final refinement indicate that the lattice parameters are $a = b = 3.85252 ± 0.00077 \text{Å}$, $c = 6.66490 ± 0.00137 \text{Å}$ and all the diffraction peaks can be indexed into a hexagonal structure. The result of refinement is shown in Fig. 5. The final crystal structural data of Gd$_2$O$_2$S are summarized in Table 1.

3.4. FE-SEM and TEM images

Fig. 6 shows FE-SEM and TEM images along with selected area electron diffraction (SAED) patterns of the precursor, P700, P800 and P900, respectively. It can be seen that all samples are mainly composed of quasi-spherical shaped particles, which distribute in a narrow size range of 20–30 nm. The observed particle sizes do not show obvious variation with calcination temperature, and are consistent with the mean crystalline size estimated using Scherrer’s formula. It is evident, however, that the degrees of crystallization increase with rising calcination temperature, as revealed by SAED. The inserted SAED in Fig. 6a indicates that the precursor is amorphous, which is consistent with the result of XRD. The SAED of in Fig. 6b seems quite sparse compared with that of Fig. 6c and d due to the lower degree of crystallization. The SAED of the P900 sample indicates complete crystallization due to the higher calcination temperature.

3.5. First principles calculation

In this section, the band structure, density of states (DOS), and the polycrystalline absorption spectra for Gd$_2$O$_2$S and (Gd$_{0.75}$Pr$_{0.25}$)$_2$O$_2$S were estimated, and the calculated results were com-

![Fig. 6. FE-SEM, TEM images and SAED patterns of the precursor, P700, P800 and P900 samples.](image-url)
pared with those observed. The band structure of Gd$_2$O$_2$S along high symmetrical points of the first Brillouin zone is shown in Fig. 7a, and the band structure of (Gd$_{0.75}$, Pr$_{0.25}$)$_2$O$_2$S around Fermi level (−5 to 10 eV) is shown in Fig. 7b. The zero energy is arbitrarily taken at the Fermi level (dashed line). As shown in Fig. 7a, the top of the valence band lies at the A point and the bottom of the conduction band is at the K point. Thus Gd$_2$O$_2$S is an indirect-gap semiconductor, and the difference between the A and K points gives the indirect band gap energy of 2.85 eV, which is lower than 4.6 eV, as given in the literature [25]. It is well known that DFT calculations within GGA underestimate the band gap. In the present study, the scissors operator is not considered when calculating band structure and DOS, although a scissors operator has been applied to fit the optical absorption band edge in estimating the absorption spectra. To assign these bands, total and partial density of states (TDOS and PDOS) of (Gd$_{0.75}$, Pr$_{0.25}$)$_2$O$_2$S are shown in Fig. 8. According to Fig. 8, the lowest bands around −45 eV consist of 5s states of Gd. The 5p states of Gd are located at around −21 eV. The bands around −16 and −11 eV are derived from the 2s states of O and the 3s states of S, respectively. The narrow and dense bands around −6 eV can be assigned as the 4f states of Gd. The 4f states have a sharp peak due to its strong localization character. The valence bands (VBs) between −4 and 0 eV mainly originate from the hybrid states of O2p and S3p with very small mixings of the 5d states of Gd. The conduction bands (CBs) are formed by the 5d and 6s states of Gd, with a small contribution of the states of O2p and S3p. According to Figs. 7b and 8, the top VBs and the CBs ranging from 1 to 1.5 eV can be assigned as the 4f states of Pr with the very strong but narrow double peaks, representing the localized character of the Pr 4f states. The position of the Pr 4f states observed in the present system is basically consistent with that of praseodymium monophosphate [26].
where \( E_g \) indicates that Gd band gap for semiconductor, e.g., a direct band gap for light frequency, and band gap, respectively. In this case, the absorption edge of Gd be seen that the absorption band around 4 eV gradually become weaker. The absorption edge of Gd samples after a Kubelka–Munk transformation, where it can be seen that the absorption band around 4 eV for P900 sample can be attributed to the reduction in crystal defects and its good crystallinity due to higher calcination temperature, as confirmed by the SAED results.

3.6. Optical properties

3.6.1. UV–vis absorption spectra

For a semiconductor, the absorbance in the vicinity of the onset due to the electronic transition follows the equation below:

\[
A(hv) = C(hv - E_g)^n
\]

where \( A \), \( h \), \( v \), and \( E_g \) are absorption coefficient, Planck constant, light frequency, and band gap, respectively. \( C \) is a constant. \( n \) is a parameter that decides the characteristics of the transition in a semiconductor, e.g., a direct band gap for \( n = 1/2 \) and an indirect band gap for \( n = 2 \). The band structure estimated in the previous section indicates that Gd\(_2\)O\(_2\)S is an indirect band gap semiconductor. In this case, \( n \) is equal to 2 for this indirect allowed transition. Fig. 10a shows the plots of \((A(hv))^{1/2} \) versus \( h_v \) of P700, P800 and P900 samples after a Kubelka–Munk transformation, where it can be seen that the absorption band around 4 eV gradually become weaker. The absorption edge of Gd\(_2\)O\(_2\)S shows a gradual blue shift as calcination temperature increases. In the previous section, it has been shown in Fig. 6 that the particle sizes increase slowly from 21 to 30 nm, which corresponds to the increases in calcination temperature from 700 to 900 °C, as confirmed by the XRD and FE-SEM results. It can be concluded that the blue shift after calcination depends primarily on crystal defect and crystal status, and is almost independent of the particle size. The disappearance of the absorption band around 4 eV for P900 sample can be attributed to the reduction in crystal defects and its good crystallinity due to higher calcination temperature, as confirmed by the SAED results.

Furthermore, the band gap of P900 sample was determined by extrapolations of the linear regions of the plots to zero absorption. The band gap is originated from the transitions of electrons from the states of S3p and O2p to the states of Gd5d based on first principles calculation, as found in the figure is 4.6 eV, which is consistent with the value observed in bulk materials. The plots of \((A(hv))^{1/2} \) versus \( h_v \) of P900 and 1.0 mol\% Pr doped P900 samples after a Kubelka–Munk transformation are shown in Fig. 10b. For 1.0 mol\% Pr doped P900 sample, an absorption band centered at about 4 eV is observed, which is attributed to the 4f \( \rightarrow \) 5d transitions of Pr\(^{3+} \) ions. In addition, these absorption peaks in the range of 2–3 eV (inset in Fig. 10b) are attributed to the 4f intra-transitions of Pr\(^{3+} \) ions, which correspond to the \( ^3H_4 \rightarrow ^1D_2 \), the \( ^3H_4 \rightarrow ^3P_0 \), the \( ^3H_4 \rightarrow ^3P_1 \), the \( ^3H_4 \rightarrow ^1J_6 \) and the \( ^3H_4 \rightarrow ^3P_2 \) transitions, respectively [9,27]. The differences between P900 and 1.0 mol\% Pr doped P900 samples show that the formation of Pr impurity level above valence band in 1.0 mol\% Pr doped P900 sample leads to the red shift of the absorption edge. This is in agreement with first principles calculation, and indicates that the Pr doping leads to reduced band gap energy.

3.6.2. PL spectra

Fig. 11 shows the excitation and emission spectra of 1.0 mol\% Pr doped P700, P800 and P900 samples, where it can be seen that all the calcined phosphors exhibit similar excitation and emission spectra. The typical excitation and emission spectra consist of two broad excitation bands in the excitation spectrum and a prominent peak at 511 nm in the emission spectrum, and the relative intensity of the composed bands depends strongly on the calcination temperatures. The excitation band near 301 nm in Fig. 11 can be related to the 4f \( \rightarrow \) 5d transition of Pr\(^{3+} \) ions, which is consistent with the result obtained from UV–vis absorbance spectrum, while the weaker excitation band located at 270 nm is attributed to the band gap absorption of Gd\(_2\)O\(_2\)S host lattice (\( E_g = 4.6 \) eV). With increasing calcination temperature from 700 to 900 °C, the intensities of the two broad excitation bands increase markedly. As shown in Fig. 11, the emission spectra under 301 nm UV excitation exhibit green emission at 511 nm as the most prominent peak, which corresponds to the \( ^3P_0 \rightarrow ^3H_4 \) transition of Pr\(^{3+} \) ions. The peak around 500 nm with a shoulder is attributed to the \( ^3P_1 \rightarrow ^3H_5 \) transition of Pr\(^{3+} \) ions, and the weak peak located at 545 nm corresponds to the \( ^3P_1 \rightarrow ^3H_3 \) transition of Pr\(^{3+} \) ions [9]. Moreover, as the calcination temperature is raised from 700 to 900 °C, the photoluminescence intensity increases significantly because of the increase in particle size, the improvement of crystallinity and the elimination of defects. This is because the defects associated with low crystallization and/or grain boundaries often serve as centers of non-radiative
the strongest emission peak is located at 511 nm under 301 nm UV excitation for the (Gd\(_{1-x}\), Pr\(_x\))\(_2\)O\(_2\)S calcined at 900 °C. The optimal x value is 0.01 for the highest luminescent emission intensity. The co-precipitation method is simple and convenient for preparing pure (Gd\(_{1-x}\), Pr\(_x\))\(_2\)O\(_2\)S nano-phosphors.

Acknowledgements

This work is supported by Program for Changjiang Scholars and Innovative Research Team in University (IRT0713), the National Natural Science Foundation of China (50672014) and the National Science Fund for Distinguished Young Scholars (50425413).

References