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Temperature dependence of luminescence properties of praseodymium-doped perovskite $CaTiO_3$:Pr^{3+}

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ABSTRACT

A polycrystalline perovskite $CaTiO_3$:Pr^{3+} was synthesized and the temperature dependence of luminescence properties was investigated in the temperature range of 6–440 K. $CaTiO_3$:Pr^{3+} exhibits red emission ascribed to the *f*–*f* transition from the excited state $^1D_2$ to the ground state $^3H_4$ of Pr^{3+} upon the band gap photo-excitation between valence and conduction band, and upon the IVCT (inter valence charge transfer between Pr^{3+} and Ti^{4+}) photo-excitation. Below 330 K, the emission intensity upon the band gap excitation increased with temperature, while the temperature dependence of emission intensity upon the IVCT excitation is relatively small, indicating that the electron transfer process between Pr^{3+} and the host accompanied by the band gap excitation is thermally activated. Above 330 K, the thermal quenching of emission was observed upon both of the band gap and the IVCT excitation and the energy barrier for thermal quenching was estimated to be $\sim$5500 cm^{-1}.

1. Introduction

Pr^{3+} (electron configuration: $4f^2$) ion-doped phosphors usually exhibit the greenish-blue emission ascribed to the transition from the excited state $^3P_0$ state to the ground state $^3H_4$ ($^3P_0 \rightarrow {}^3H_4$) of Pr^{3+} and/or the red emission ascribed to that from the excited state $^1D_2$ to $^3H_4$ ($^1D_2 \rightarrow {}^3H_4$) of Pr^{3+} upon photo-excitation and electron-excitation [1]. Among them, Pr^{3+}-doped perovskite-type titanates ATiO$_3$ (A = Ca [2–13], Sr [7,8,11,13–17], Ba [7,11,18–20], (La, Li) [21], $Ln_{1/2}Na_{1/2}$(Ln = La [21–23], Gd, Lu, Y [22,23]), $La_{1/2}K_{1/2}$ [21]) have recently been considered attractive as red phosphor materials for a potential flat-panel display, field-emission display (FED) [2,14,15] and EL display [24], since intense red emission ($^1D_2 \rightarrow {}^3H_4$) dominates and greenish-blue emission ($^3P_0 \rightarrow {}^3H_4$) is quenched. Due to recent systematic studies with regard to Pr^{3+}-doped oxide phosphors with closed-shell cation, M^{n+} (electronic configuration d^0), such as perovskite titanates ATiO$_3$: Pr^{3+}, it was found that their luminescence originated from the *f*–*f* transition of Pr^{3+} ion occurs via the inter-valence charge transfer (IVCT) between Pr and M cation ($Pr^{3+} + M^{n+} \leftrightarrow Pr^{4+} + M^{(n-1)+}$) [9,10,23,25,26] and band-gap excitation processes[22]. The IVCT relaxation model can explain the quenching of the greenish-blue emission ascribed to $^3P_0 \rightarrow {}^3H_4$ above mentioned. The understanding with respect to the luminescence properties in Pr-doped titanates has become clearer owing to the previous studies. However, in order to elucidate the more detailed mechanism of luminescence, especially energy transfer process, further investigations are needed.

Since radiative and non-radiative transitions in phosphor materials often occur via thermally activated processes, the understanding of thermal processes is vital to elucidate the luminescence mechanism. In addition, the temperature dependence of emission intensity of phosphor materials is a crucial issue in utilizing as industrial products. We then measured the temperature dependence of luminescence properties of a Pr-doped perovskite-type oxide $CaTiO_3$:Pr^{3+} in the wide temperature range 6–440 K and discuss the luminescence mechanism in terms of thermal process.

2. Experimental procedure

Polycrystalline $CaTiO_3$ and its Pr^{3+}-doped compound, $Ca^{2+}{}_{1-3x/2}Pr^{3+}{}_xTiO_3$ (x = 0.002) (abbreviated as CTO and CTO:Pr, respectively) were synthesized by a conventional solid-state reaction at elevated temperature. The starting materials were $CaCO_3$ (Rare metallic Co., >99.9%), TiO_2 (rutile-type, Rare metallic Co., >99.9%), and $Pr(NO_3)_3$ solution. Pr nitrate solution was then prepared by dissolving Pr_6O_{11} (Rare metallic Co., >99.9%) using 3 M nitric acid. The metal contents of Pr_6O_{11} were determined by chelatometry with ethylenediaminetetraacetic acid (EDTA) because the commercial reagent of Pr_6O_{11} is non-stoichiometric. The appropriate mixture of powders and solution was dried and pressed into a pellet and calcined at 1273 K (1000 °C) for 12 h in

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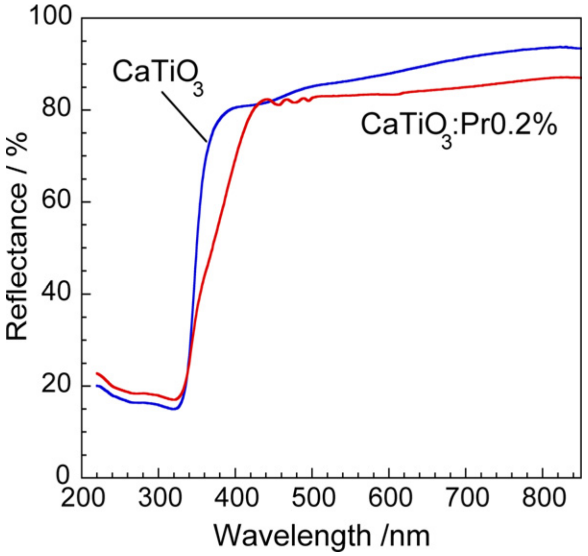

Fig. 1. Diffuse reflection spectra of pristine $CaTiO_3$ and $CaTiO_3$:Pr0.2% at room temperature.

air. The calcined powder was again pressed into pellets, heated at 1573 K (1300 °C) for 12 h in air and then furnace-cooled.

The phase identification for the samples was carried out by the powder X-ray diffraction method using a Rigaku RINT 2100 diffractometer (graphite-monochromatized CuKα).

The diffuse reflectance spectra were recorded using a JASCO V-550 ultraviolet and visible spectrophotometer. The emission and excitation spectra were measured using a JASCO FP-6500 spectrofluorometer. Light from a 150 W xenon lamp was used as an excitation source. The emission and excitation spectra were corrected with a standard lamp and the excitation spectrum of Rhodamine *B* in ethylene glycol (8 g/l) [27]. The temperature dependencies of emission and excitation spectra were measured using a cryostat equipped with a closed cycle helium refrigerator (SRDK-205 Cryocooler, Sumitomo Heavy Industries) in the temperature rang 6–300 K and using a home-made copper block cell equipped with a heater in the temperature range 300–440 K.

3. Results and discussion

3.1. Optical absorption and luminescent properties at room temperature of $CaTiO_3:Pr^{3+}$

The powder X-ray diffraction experiments revealed that CTO and CTO:Pr possess orthorhombic perovskite-type structure with a space group *Pnma* [28]. The diffuse reflection spectra of CTO and CTO:Pr at room temperature are shown in Fig. 1. For pristine CTO, the absorption edge was observed in the vicinity of a wavelength of 330 nm. This absorption energy corresponds to the band gap between the valence band and conduction band of CTO. The optical band gap energy, E_g is estimated to be 29,000 cm^{-1} (3.6 eV) from the optical absorption [22]. For CTO:Pr, the absorption peaks in the vicinity of 400–500 nm, and 610 nm were observed in addition to the absorption of band gap. These peaks correspond to the *f*–*f* transitions of Pr^{3+} from $^3H_4$ to $^3P_2$(450–460 nm), $^3P_1$ and $^1I_6$(475–485 nm), $^3P_0$(490–500 nm), and $^1D_2$(610–620 nm) [1]. In addition, for CTO: Pr the shoulder band beside the absorption edge was observed in the wavelength range of 350–410 nm. As seen in Fig. 1, the shoulder band was not observed in CTO, indicating that the shoulder band is related to Pr, but does not correspond to the *f*–*f* transition of Pr^{3+}. Boutinaud et al. [9,10,13,25,26] have firstly found this type of absorption in CTO:Pr, and proposed that this band is attributed to $Pr^{3+}/Ti^{4+} \leftrightarrow Pr^{4+}/Ti^{3+}$ inter-valence charge transfer state (IVCT). From the viewpoint of the relation between band structure of CTO and the energy levels of *f* state of Pr^{3+}, the shoulder absorption corresponds to the transition from the ground state of Pr^{3+}, $^3H_4$ to the bottom of conduction band (Fig. 2(a)). Using the wavelength of shoulder band (~375 nm) and the band gap energy, we can estimate that the ground state $^3H_4$ is located at higher energy level by approximately 2000 cm^{-1} (~0.3 eV) than that of the top of valence band. Since the bottom of conduction band is primarily originated from the anti-bonding contribution between Ti 3*d* t_{2g} and oxygen 2*p* atomic orbitals [29], the IVCT model of $Pr^{3+}/Ti^{4+} \leftrightarrow Pr^{4+}/Ti^{3+}$ is consistent with the scheme derived by the approach in terms of the electronic structure of CTO (Fig. 2).

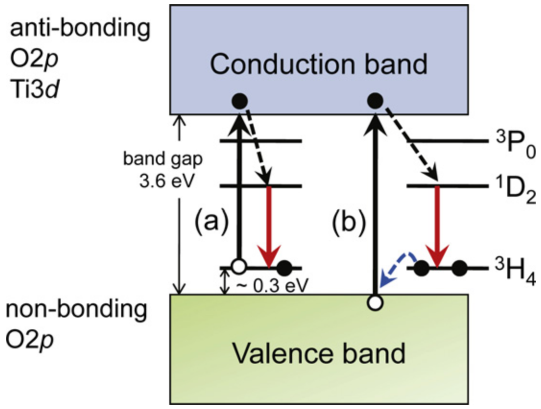

Fig. 2. Schematics of the relation between the band structure and the energy levels of 4*f* state of Pr^{3+} in CTO:Pr, emission upon (a) the IVCT excitation and (b) the band gap excitation.

Fig. 3 shows the emission, excitation, and diffuse reflectance spectra of CTO:Pr at room temperature. Upon a photo-excitation with a wavelength of 333 nm corresponding to the absorption edge of CTO, *i.e.* the band gap excitation, CTO:Pr exhibits intense red emission in the vicinity of 615 nm ascribed to the transition from a excited state $^1D_2$ to the ground state $^3H_4$ of Pr^{3+}($^1D_2 \rightarrow {}^3H_4$) and weak emission at the longer wavelengths in the vicinity of 700 nm ascribed to $^1D_2 \rightarrow {}^3H_5$ of Pr^{3+}. The excitation spectrum was monitored at 615 nm corresponding to the red emission ascribed to $^1D_2 \rightarrow {}^3H_4$ of Pr^{3+}. As shown in Fig. 3, the main excitation peak corresponds to the absorption edge. Furthermore, as seen in the

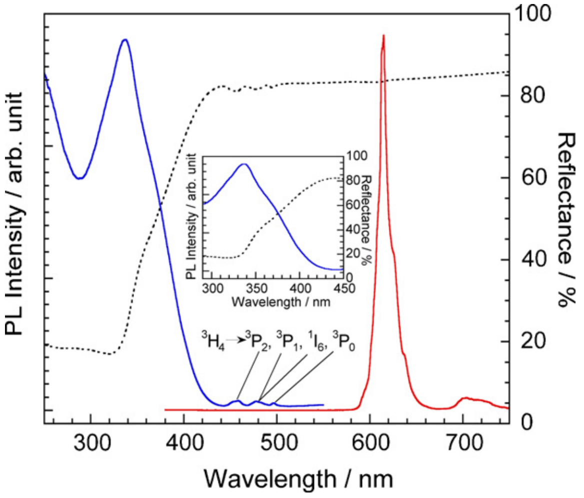

Fig. 3. Excitation and emission spectra of $CaTiO_3:Pr^{3+}$ 0.2%. Dotted line indicates diffuse reflectance spectrum. The inset shows the enlarged excitation and diffuse reflection spectra.

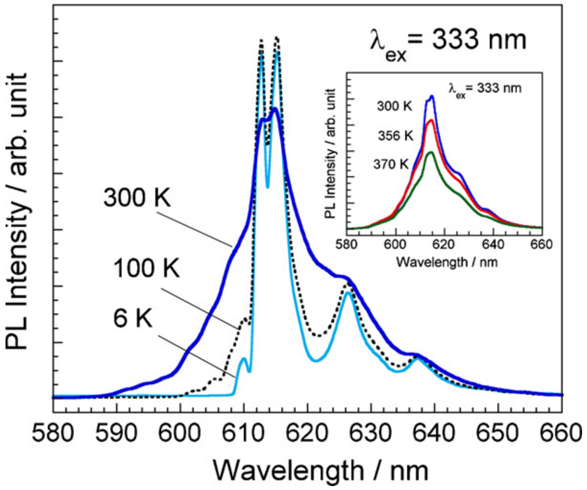

Fig. 4. Emission spectra upon photo-excitation with a wavelength of 333 nm at various temperatures, 6 K, 100 K, and 300 K for $CaTiO_3$:Pr^{3+} 0.2%. The inset shows the emission spectra at 300 K, 356 K, and 370 K.

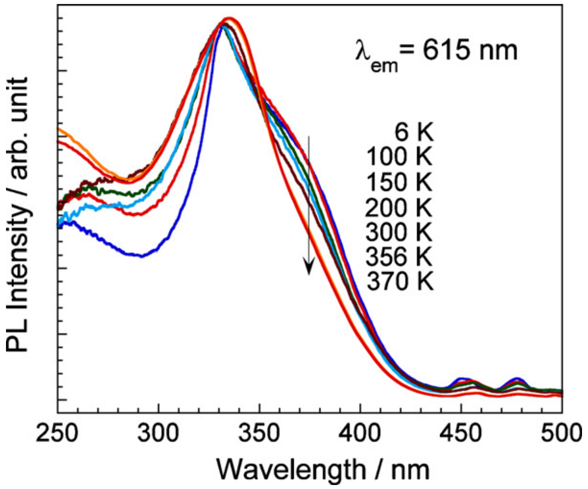

Fig. 5. Excitation spectra monitored at 615 nm at various temperatures, 6 K, 125 K, 150 K, 200 K, 250 K, 300 K, 356 K, and 370 K for $CaTiO_3$:Pr^{3+} 0.2%. The excitation spectra are normalized by the peak intensity at 330 nm.

inset of Fig. 3, on the longer wavelength side of excitation peak, the shoulder band was also observed in the wavelength range of 360–380 nm, which is the same wavelength range as the shoulder band observed in the diffuse reflectance spectrum (Fig. 1). The finding supports that the shoulder band is attributed to the IVCT excitation. Upon the irradiation with a wavelength of 375 nm corresponding to the IVCT excitation, the emission profiles were the same as those upon the band gap excitation, *i.e.* only the red emission was observed and the greenish-blue emission was quenched. The intensity of excitation peak ascribed to the *f*–*f* transitions of Pr^{3+} from $^3H_4$ to $^3P_2$ $^3P_1$, $^1I_6$ and $^3P_0$, are relatively weak. These behaviors are consistent with the results reported by Jia et al. [8], Boutinaud et al. [9,10,13] and Kyômen et al. [11]. Consequently, in CTO:Pr, there are primarily two different excitation processes, the IVCT excitation and the band gap excitation (Fig. 2). In the following section, we focus on the temperature dependence of luminescence properties, especially emissions upon these two excitation process.

3.2. Temperature dependence of luminescence properties of $CaTiO_3$:Pr^{3+}

Fig. 4 shows the emission spectra upon the photo-excitation with a wavelength of 333 nm at 6, 100, 300, 356, and 370 K. Though the stark splitting was clearer with decreasing temperature, the similar emission profiles were observed. The finding is consistent with the fact that CTO undergoes no phase transition in the measuring temperature range [30]. As seen in the inset of Fig. 4 above 330 K the emission intensity evidently decreased with increasing temperature, *i.e.* a thermal quenching occurred.

Fig. 5 shows the excitation spectra monitored at 615 nm at various temperatures. Here, the excitation spectra are normalized by the peak intensity at 330 nm. The relative intensity of the shoulder band in the vicinity of 375 nm to the excitation peak decreased with increasing temperature. The similar tendency was also observed in the comparison between excitation spectra at 77 K and 300 K reported by Boutinaud et al. [13]. In order to compare the temperature dependences of emission intensity upon the band gap excitation and the IVCT excitation, the temperature dependence of emission intensities ascribed to $^1D_2 \rightarrow {}^3H_4$ of Pr^{3+} upon the photo-excitation with wavelengths of 333 nm and 375 nm are shown in Fig. 6. Here, the emission intensities are the integral ones of red emission in the wavelength range of 575–675 nm. Below 330 K, the emission intensity upon the photo-excitation with a wavelength of 333 nm increased with increasing temperature, while the temperature dependence of emission intensity upon the photo-excitation with a wavelength of 375 nm is relatively small. This indicates that the electron transfer process accompanied by band gap excitation is thermally activated. The possible explanations for this phenomenon are as follows. As shown in Fig. 2(b), upon the band gap excitation [22], the electron in the valence band is photo-excited into the conduction band and then the electron of Pr^{3+} is resonantly transferred to the valence band, *i.e.* the generated hole accompanied by the excitation of electron is transferred to the Pr^{3+}. The excited electron in the conduction band relaxes to the excited state of Pr^{3+}, $^1D_2$ (this relaxation process may be via the IVCT state), and then returns to the ground state of Pr^{3+}, which is accompanied by the red emission. Therefore, if the electron transfer process from the ground state of Pr^{3+} ion, $^3H_4$, to the valence band is thermally activated, the emission upon band gap excitation would be promoted with increasing temperature.

Above 330 K, apparent thermal quenching of emission was detected. The emission intensity, $I(T)$ was fitted to the following

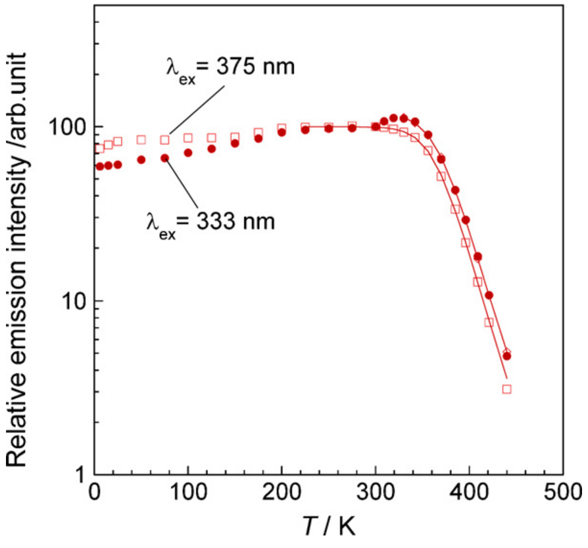

Fig. 6. Temperature dependence of red emission intensity upon photo-excitation at 333 nm (solid circle) and 375 nm (open square) for $CaTiO_3$:Pr^{3+} 0.2%. The solid lines denote the fitting ones.

equation based on the model by Struck and Fonger [31–33],

$$\frac{I(T)}{I_0} = \left[1 + \frac{s}{A}\exp\left(-\frac{E}{k_B T}\right)\right]^{-1} \quad (1)$$

where A is the radiative decay rate of the $^1D_2$ state of Pr^{3+}, s is the attempt rate for thermal quenching, k_B is Boltzmann's constant, and E is the energy barrier for thermal quenching. When using the data in the temperature range of 330–440 K for the emission upon a photo-excitation of 333 nm, we obtained the values, $s/A = (1.1 \pm 0.8) \times 10^9$, $E = (541 \pm 20) \times 10^1\ \mathrm{cm}^{-1}$. Here, E is considered to correspond to the energy gap from $^1D_2$ state to the cross-over point with the quenching state. On the other hand, when we fitted the data in the temperature range of 225–440 K for the emission upon a photo-excitation of 375 nm, we obtained the values, $s/A = (1.8 \pm 0.6) \times 10^9$, $E = (551 \pm 9) \times 10^1\ \mathrm{cm}^{-1}$. These values are in accord with those upon the excitation of 333 nm within the errors. This indicates that the relaxation process including the electron transfer from the conduction band to the excited state $^1D_2$ of Pr^{3+} are the same for the band gap excitation and the IVCT excitation (Fig. 2). The estimated energy of 5400–5500 cm^{-1} (0.7 eV) is greater than that reported by Boutinaud et al. [13], $E = 4000\ \mathrm{cm}^{-1}$ (0.5 eV) for CTO:Pr, which implies that the temperature dependence of luminescence properties depend on samples of CTO:Pr and there is a possibility to control the temperature dependence of emission intensity, *e.g.* by changing the synthetic condition or ion-doping. Further investigations are necessary to clarify the physical meaning of the energy barrier estimated from the temperature dependence of emission intensity.

4. Conclusion

The temperature dependence of luminescence properties for CTO:Pr was examined in the temperature range 6–440 K. CTO: Pr exhibits intense red emission ascribed to $^1D_2 \rightarrow {}^3H_4$ of Pr^{3+} upon the band gap and the IVCT (inter-valence charge transfer) photo-excitation. Below 330 K, the emission intensity upon the band gap excitation increases with increasing temperature. This implies that the electron transfer process accompanied by the band gap excitation in CTO:Pr is promoted with increasing temperature. Above 330 K, the thermal quenching of red emission was then observed. The effects of the promotion of the process related to band gap excitation and the thermal quenching with increasing temperature on the emission intensity are competitive. At lower temperature the former effect is dominant, while at higher temperature the latter effect is dominant. The energy barrier for thermal quenching estimated from the temperature dependence of emission intensity, 5400–5500 cm^{-1} is rather larger than that reported by Boutinaud et al. The finding indicates that the estimated activation energy is dependent of samples of CTO:Pr. Further investigations are necessary to clarify the physical meaning of the activation energy, which would provide us the important information to control the temperature dependence of emission intensity.

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