Photo-electronic properties and persistent luminescence in Pr³⁺ doped (Ca, Sr)TiO₃ ceramics

Yumiko Katayama^{1,3}, Jumpei Ueda¹, Setsuhisa Tanabe^{1,2}

¹ Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-Nihonmatsu, Sakyo, Kyoto 606-8501, Japan

² Japan Science and Technology Agency Precursory Research for Embryonic Science and Technology (JST-PRESTO), Chiyoda, Tokyo 102-0075, Japan

³ E-mail: katayama.yumiko.48a@st.kyoto-u.ac.jp,

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Abstract. We obtained direct evidence of intervalence charge transfer (IVCT) in Ca_{1-x}Sr_xTiO₃:Pr³⁺ (x=0, 0.3, 0.5, 0.8, 1) by a photocurrent excitation (PCE) measurement, and propose a mechanism of the persistent luminescence based on the results of the PCE and persistent luminescence measurements. The PCE spectra in all samples showed two bands in UV range due to the band-to-band and IVCT transitions. With increasing Sr content, x, the host bandgap energy decreased monotonically from 3.59 to 3.23 eV, and the IVCT energy increased from 3.20 to 3.38 eV. PCE bands of the Pr³⁺:³H₄→³P_J transitions in blue region were observed only in the samples with x=0, 0.3, 0.5 and the relative intensity decreased with increasing Sr content, x. Based on temperature dependence of the PCE results in the sample with x=0, a thermally assisted photoionization process was indicated under the ³H₄→³P_J excitation. Red persistent luminescence was observed in the samples with x=0, 0.3 and 0.5, showing trap depth in the range of 0.48 to 0.35 eV, which was estimated from the thermoluminescence measurement. The afterglow process by the electron moving through the conduction band was evidenced by the similar quenching behavior of the ³H₄→³P_J band both in the PCE and afterglow excitation spectra. The difference in the processes of persistent luminescence between the band-to-band, IVCT and ³H₄→³P_J excitations was discussed.

1. Introduction

Rare-earth-doped inorganic crystals have long been of interests for materials science and engineering. Many important modern applications, e.g. fluorescent lamps, white light emitting diodes, were built up mainly due to developments of some excellent rare-earth-doped phosphors. Generally, reasonable design of a phosphor requires clear understanding of the energy level structure as well as knowledge on electron dynamic processes in solids.

The Pr³⁺-doped CaTiO₃ is a well-known red phosphor with a perovskite structure. This phosphor has been widely studied for applications in field-emission displays and electroluminescence displays because of its highly monochromatic red luminescence, which peaks at 613 nm due to the 4f-4f transition (¹D₂→³H₄) of the Pr³⁺ ion [1, 2]. In the CaTiO₃:Pr³⁺ phosphor, the luminescence bands from the Pr³⁺:³P_J (J=0, 1, 2) levels are completely quenched, and only the sensitized luminescence bands from the ¹D₂ level are observed. In order to explain the luminescence quenching from the ³P_J levels, Boutinaud et al. proposed an intervalence charge-transfer (IVCT) state, denoted as (Pr³⁺/Ti⁴⁺)↔(Pr⁴⁺/Ti³⁺), which offers a route for relaxation of the ³P_J levels to the ¹D₂ level [3-8]. In their model, the IVCT transition is an electron transition from the ³P₀ state of Pr³⁺ to Ti⁴⁺ ions, the 3d orbital of which consists of the bottom of the conduction band (CB) of the host CaTiO₃ [3-9]. The proposed model has widely been used to predict the location of the levels of all trivalent lanthanides relative to the top of the valence band and the bottom of conduction band as well as to explain the ³P_J luminescence quenching [10]. However, this model is considered as conjecture before direct and clear experiment proof is found.

Therefore, the primary purpose of our research is to obtain direct evidence of the IVCT by a photocurrent excitation (PCE) spectra measurement, which gives information about a relationship between the excited energy levels of a dopant and the CB of host material [11-13]. In this report, (Ca,Sr)TiO₃:Pr³⁺ phosphors were chosen for the investigation because both bandgap and IVCT energies vary with the compositional modification in this solid solution [9, 14, 15].

In addition, we discuss the mechanism of persistent luminescence in the (Ca,Sr)TiO₃:Pr³⁺ phosphors. It is known that the CaTiO₃:Pr³⁺ shows red persistent luminescence and its intensity and the duration time are de-

creased by a substitution of Sr to Ca site [14, 16, 17]. Although the mechanism of persistent luminescence in the (Ca,Sr)TiO₃:Pr³⁺ phosphors has also been discussed in several papers, it is not fully understood especially about the process under different excitations. Therefore, we performed afterglow excitation (AGE) and thermoluminescence (TL) measurements. Comparing the PCE result with the afterglow properties, we propose a new scheme which explains the process of persistent luminescence in the (Ca,Sr)TiO₃:Pr³⁺.

2. Experiment

Polycrystalline ceramics of (Ca_xSr_{1-x})_{0.997}Pr_{0.002}TiO₃ (x=0, 0.3, 0.5, 0.8, 1) were synthesized by solid state reaction. As 0.2 mol% of the trivalent Pr ions were incorporated into the samples by substitution for divalent Ca/Sr, charge compensation was achieved at compositions deficient in calcium/strontium by 0.1 mol%. Commercial powders of CaCO₃(99.99%), SrCO₃(99.99%), Pr₆O₁₁(99.99%) and, TiO₂ (99.99%) were used as starting materials. Batches of the starting powders were mixed in the presence of ethanol. After drying, the mixture was calcined at 1200 °C for 2 h in air, cooled, crushed, pressed into pellets with 13 mm in diameter and sintered at 1300 °C for 5 h. The grinding and sintering processes were performed twice to ensure complete reactions. For reference, non-doped polycrystalline ceramics with compositions of Ca_{1-x}Sr_xTiO₃ (x: same as Pr³⁺-doped sample) were also synthesized by the same method.

The crystalline phases of the sintered samples were identified by X-ray diffraction (XRD) (Rigaku, UltimaIV). Diffuse reflectance spectra were measured using a scanning-type spectrophotometer (Shimadzu, UV3600) with a BaSO₄-based integrating sphere. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra, afterglow decay curves and afterglow excitation (AGE) spectra were measured using a fluorescence spectrophotometer (Shimadzu, RF-5000). Photocurrent excitation (PCE) spectra and thermoluminescence (TL) measurements were performed in a cryostat (Advanced Research Systems, Helitran LT3). For the PCE spectra, monochromatic light excitation was obtained by the combination of a 300-W Xe lamp (Asahi spectra Co., Ltd, MAX-302) and a monochromator (Nikon, G250). Gold electrodes spaced 1 mm apart were deposited on each sample. Each sample was connected by nickel mesh wires and mounted into the cryostat. A DC voltage of 20-40 V was applied to each sample, and the photocurrent was measured with a digital elec-

trometer (ADVANTEST, 8240). PCE was measured at room temperature and 100 K. For the TL measurement, the samples were irradiated for 5 min at 100 K by UV light over the wavelength range of 250 nm to 400 nm, which was obtained by a 300-W Xe lamp with a cold mirror(Asahi spectra Co., Ltd, MAX-302). The heating rate used to obtain the TL curves was 10 K/min.

3. Results

3.1. Crystal structures

Fig. 1 shows the XRD patterns of the (Ca,Sr)TiO₃:Pr³⁺ samples. All of the samples show the diffraction peaks characteristic of a perovskite structure. The diffraction peaks shifted to lower angles (upper of Fig. 1) with increasing Sr content, x. This shift indicates the lattice expansion by substitutions of larger Sr ions for Ca sites. The crystalline phases were orthorhombic for the sample with x=0, 0.3, 0.5, tetragonal for x=0.8 and cubic for the x=1. The compositional dependence of the crystalline systems was consistent with the binary phase diagram of CaTiO₃ and SrTiO₃[18].

3.2. Photoluminescence property

Fig. 2 shows the PL (λ_{EX} =460 nm) and PLE (λ_{EM} =613 nm) spectra of the (Ca,Sr)TiO₃:Pr³⁺ samples. The sample with x=0 showed a strong red luminescence band peaked at 613 nm due to the Pr³⁺:¹D₂→³H₄ transition. For the other samples, luminescence bands from the Pr³⁺:³P₀ level peaked at 500 nm, 600 nm and 650 nm were observed and the intensity increased as the Sr content, x, increased.

In the PLE spectra, two broad bands between 250 and 400 nm and sharp lines between 450 and 500 nm were observed, which can be attributed to the band-to-band and IVCT transitions (350 nm) and the ³H₄→³P_J transitions (450 to 500 nm), respectively. With increasing x, the peak of the UV band due to the band-to-band and IVCT transitions shifted from 336 to 364 nm. Although the band-to-band and IVCT transitions were overlapped, tails of the IVCT band were observed at approximately 380 nm in the samples with x=0 and x=0.3.

Fig. 1. X-ray diffraction patterns of $(\text{Ca,Sr})\text{TiO}_3:\text{Pr}^{3+}$ samples.

3.3. Photocurrent excitation spectra

In Fig. 3, the diffuse reflectance spectra of the non-doped samples and, the PCE spectra of the non-doped and Pr^{3+} -doped $(\text{Ca,Sr})\text{TiO}_3$ samples are depicted. For the sample with $x=0$, the PCE of the non-doped sample showed a band-to-band transition at 340 nm, which is consistent with the absorption edge of the diffuse reflectance spectrum. For the Pr^{3+} -doped sample, in addition to the band at 340 nm, an IVCT peak at 390 nm and $^3\text{H}_4 \rightarrow ^3\text{P}_J$ bands in the range of 450 to 500 nm were observed. The UV bands of the band-to-band transitions in the non-doped samples shifted from 340 to 380 nm when the Sr content, x , increased. This tendency is consistent with the shift of absorption edge. On the other hand, the

Fig. 2. Photoluminescence (PL) spectra (460 nm excitation) and photoluminescence excitation (PLE) spectra (monitored at 613 nm) of $(\text{Ca,Sr})\text{TiO}_3:\text{Pr}^{3+}$.

Fig. 3. Diffuse reflectance spectra (top) and PCE spectra of the non-doped (middle) and Pr^{3+} -doped $(\text{Ca,Sr})\text{TiO}_3$ (bottom) samples at room temperature and PCE of the Pr^{3+} -doped sample with $x=0$ at 100 K (dotted lines in the bottom figure).

Pr^{3+} -doped samples showed additional peaks due to the IVCT and $^3\text{H}_4 \rightarrow ^3\text{P}_J$ transitions. The IVCT peaks showed a blue shift with increasing x . The $^3\text{H}_4 \rightarrow ^3\text{P}_J$ bands were observed only in the samples with small x , and the relative intensity decreased with increasing x . The PCE spectrum of the sample with $x=0$ at 100 K is shown as a dotted line in the bottom panel of Fig. 3. At 100 K, the PCE bands of the band-to-band and IVCT transitions were observed whereas that of the $^3\text{H}_4 \rightarrow ^3\text{P}_J$ transition disappeared.

Fig. 4 shows the compositional variation of the bandgap and IVCT energies, which were estimated by deconvolution fitting. The bandgap energy decreased linearly from 3.59 to 3.23 eV, whereas the IVCT energy increased nonlinearly from 3.20 to 3.38 eV with increasing x .

Fig. 4. Compositional dependence of bandgap and IVCT energies estimated by PCE result and the reference values of bandgap and IVCT[14, 15, 17].

Fig. 5. Afterglow decay curves of $(\text{Ca}, \text{Sr})\text{TiO}_3:\text{Pr}^{3+}$ by band-to-band excitation.

Fig. 6. Thermoluminescence of $(\text{Ca}, \text{Sr})\text{TiO}_3:\text{Pr}^{3+}$, after excitation for 5 minutes by UV light source and monitored red thermoluminescence.

Fig. 7. PCE and AGE spectra of $(\text{Ca}, \text{Sr})\text{TiO}_3:\text{Pr}^{3+}$ samples ($x=0, 0.3, 0.5$).

3.4. Afterglow characteristics

Fig. 5 shows the afterglow decay curves of the $(\text{Ca}, \text{Sr})\text{TiO}_3:\text{Pr}^{3+}$ samples under the band-to-band excitations. The samples with larger x showed shorter afterglow decay time. The TL glow curves are shown in Fig. 6. In the sample with $x=0$, the main peak at the highest temperature of 250 K was observed. The glow peaks shifted to lower temperature with increasing x .

The PCE and AGE spectra of the samples with $x=0, 0.3, 0.5$ are compared in Fig. 7. The persistent luminescence intensities 30 s after shutting off the excitation light are plotted as red dots. The samples showed AGE bands of the band-to-band, IVCT and $^3\text{H}_4 \rightarrow ^3\text{P}_j$ transitions. The samples with smaller x showed the $^3\text{H}_4 \rightarrow ^3\text{P}_j$ bands with a relatively weaker intensity. This tendency is the same as that observed in the compositional variation of the PCE spectra. The relative intensities of the IVCT and $^3\text{H}_4 \rightarrow ^3\text{P}_j$ bands in the AGE spectra were stronger than that in the PCE spectra.

4. Discussion

4.1. Photoluminescence properties and IVCT energy

In this section, compositional dependence of quenching of ³P_J levels and IVCT energy was discussed based on the configuration coordinate model. When an activation energy ΔE is defined as the energy difference from the bottom of the ³P₀ parabola to the cross-point with the IVCT parabola, luminescence quenching from the ³P₀ level in a sample with $x=0$ is due to a small ΔE . In PL spectra by 460 nm excitation, higher relative intensity of ³P₀ luminescence was observed in the samples with larger x . This phenomenon can be explained by the shift of the IVCT parabola to upper or right direction. This shift results in larger ΔE , and lower the relaxation probability through the IVCT state. This explanation is also consistent with the increase in the IVCT energy with increasing Sr content, x , which was observed in the PLE and PCE results (Fig. 2 and Fig. 3).

4.2. Compositional variation in the bandgap and the IVCT energies

As shown in Fig. 4, the bandgap energies of the end compositions, CaTiO₃ and SrTiO₃, are consistent with values reported in the literature [15, 17] whereas the IVCT energies are approximately 0.1 to 0.2 eV lower than the values estimated by Boutinaud et al [14]. We detected the photocurrent under the IVCT excitations in the Pr³⁺-doped (Ca,Sr)TiO₃ samples (Fig. 3). This result is important evidence of photoionization of Pr³⁺, i.e., electron transfer from Pr³⁺ ion to the CB of the (Ca,Sr)TiO₃ host materials under the IVCT excitation. Both in CaTiO₃ and SrTiO₃, the bottom of the CB consists of a vacant titanium 3d orbital [9, 19]. Therefore, from the PCE measurement, the occurrence of the IVCT between Pr³⁺ and Ti⁴⁺ (3d⁰) was confirmed.

As shown in Fig. 3, under ³H₄→³P_J excitations, the photocurrent was observed in the samples with smaller x at room temperature. In particular, for the sample with $x=0$, the ³H₄→³P_J bands, observed at room temperature were diminished as the sample was cooled to 100 K. This result strongly suggests that photoionization is a thermally assisted process through the ³P_J excited levels. Because the relative intensity of the ³H₄→³P_J bands decreased as the Sr content x increased, the activation energy of the thermally assisted photoionization increased with increasing x . Based on these results, we propose a schematic energy diagram as shown in Fig.

8. The ground state, Pr³⁺:³H₄, is defined as zero. The energy locations of the 4f energy levels of the Pr³⁺

ion and the host band edges were shown in Fig. 8. In this case, the energy of the bottom of the CB, E_{CB} is equal to the IVCT energy, E_{IVCT} . The relative energy location of the top of the valence band (VB), E_{VB} , was obtained by

$$E_{VB} = E_{IVCT} - E_g = E_{CB} - E_g \quad (1)$$

In the CaTiO₃ host ($x=0$), the 4f ground state, Pr³⁺:³H₄, is located 0.39 eV above the top of the VB ($E_{VB}=-0.39$ eV) and the ³P_J excited states are located close to the bottom of the CB, leading to the thermally assisted photoionization under the blue excitation of the ³H₄→³P_J transitions. With increasing Sr content, x , the energy difference between the ground state of the Pr³⁺ and the top of the VB decreases and the ground state is within the VB in the sample with x greater than 0.8. On the other hand, the energy gap between the ³P_J excited states and the bottom of the CB increases, as evidenced by the quenching of the ³H₄→³P_J band in the PCE spectra (Fig. 3).

4.3. Possible mechanism of persistent luminescence in (Ca,Sr)TiO₃:Pr³⁺

It was reported that the glow curves of the Pr³⁺-doped CaTiO₃ showed peaks at approximately 150 K, 250 K and 330 K [14, 16] and that the peak at 150 K showed the highest thermoluminescence intensity; however, our sample exhibited the main peak at 250 K, as shown in Fig. 6. The difference between our samples and those reported in the literature is ascribed to the difference in composition of the materials. In our samples, charge imbalance due to the doping of trivalent Pr³⁺ ion into divalent Ca²⁺ (and Sr²⁺) sites was compensated by Ca (Sr) vacancies to preserve electrical neutrality. Therefore, two defect sites, $V''_{Ca/Sr}$ and $Pr^{\bullet}_{Ca/Sr}$ may exist and act as hole trapping centers as follows.

Considering the nature of Pr³⁺ which is easily oxidized to tetravalent state, Pr⁴⁺, a hole trapped defect, $Pr^{\bullet\bullet}_{Ca/Sr}$ in Eq.2 is possible. Based on the compositional difference between our material and that of the reported data, the traps which showed the largest TL glow peaks in our samples are probably due to defects

related to Ca (Sr) vacancies. Therefore, an associated defect, i.e. $[\text{Pr}_{\text{Ca/Sr}}^{\bullet} - V_{\text{Ca/Sr}}'']'$ can be created and works as a hole trapping center. The trap depth can be roughly estimated from the peak temperature of glow curves using the following simple equation [20],

$$E_T = T_m/500, \quad (4)$$

where E_T is the trap depth and T_m is the peak temperature of the TL glow curve. The trap depth was approximately 0.48 eV for the sample with $x=0$, 0.42 eV for $x=0.3$ and 0.35 eV for $x=0.5$. The sample with smaller x has the smaller trap depth. Given that the glow peaks are derived from the same kind of defects among the different compositions, the trap centers can probably be the hole trapping centers such as $V_{\text{Ca/Sr}}''$, $\text{Pr}_{\text{Ca/Sr}}^{\bullet} (\text{Pr}^{3+})$ and $[\text{Pr}_{\text{Ca/Sr}}^{\bullet} - V_{\text{Ca/Sr}}'']'$. The trap levels are illustrated as hole trapping centers in Fig. 8 with some distribution. As shown in Fig. 8, the location of the trap levels are close to the ground state of Pr^{3+} ion, and both levels get close to the VB with increasing Sr content, x .

In the previous section, we concluded that the activation energy of thermally assisted photoionization under $^3\text{H}_4 \rightarrow ^3\text{P}_J$ excitations increased with increasing x . Because the AGE results also indicate the same compositional dependence as was observed for the PCE results, it is concluded that electron transfer occurs through CB even under $^3\text{H}_4 \rightarrow ^3\text{P}_J$ excitations.

From the PCE results, we obtained information about the electron-transfer process under different photo-excitations. On the other hand, the AGE results provide us information of carrier trapping and recombination process of persistent luminescence as well as the electron-transfer process. As shown in Fig. 7, the samples with smaller x showed high AGE intensities under the IVCT and $^3\text{H}_4 \rightarrow ^3\text{P}_J$ excitations despite the low intensity of the corresponding bands in the PCE spectra. This result is probably due to the difference in the carrier trapping and recombination process between band-to-band excitation and IVCT and $^3\text{H}_4 \rightarrow ^3\text{P}_J$ excitations.

An electron-hole pair is generated under the band-to-band excitation (the left part of Fig. 8). The hole generated by the band-to-band excitation (①) is captured by hole trapping centers such as $V_{\text{Ca/Sr}}''$, $\text{Pr}_{\text{Ca/Sr}}^{\bullet} (\text{Pr}^{3+})$ and $[\text{Pr}_{\text{Ca/Sr}}^{\bullet} - V_{\text{Ca/Sr}}'']'$ (②) as mentioned above. The red persistent luminescence of

$\text{Pr}^{3+}:^1\text{D}_2 \rightarrow ^3\text{H}_4$ is observed when the thermally released (③) hole recombined with the Pr^{3+} centers (④).

On the other hand, electron and Pr^{4+} are temporarily generated when the IVCT ($\text{Pr}^{3+} + \text{Ti}^{4+} \rightarrow \text{Pr}^{4+} + \text{Ti}^{3+} \rightarrow \text{Pr}^{4+} + \text{Ti}^{4+} + e^-$) and $^3\text{H}_4 \rightarrow ^3\text{P}_J$ ($\text{Pr}^{3+} \rightarrow \text{Pr}^{3+*} (^3\text{P}_J \text{ excited state}) \rightarrow \text{Pr}^{4+} + e^-$) transitions occur (⑤). In this case, the generated electron captured by some electron traps (⑥) is transferred through the CB, and the hole remains at Pr as Pr^{4+} ($\text{Pr}_{\text{Ca/Sr}}^{\bullet\bullet}$) (Eq.2 and Fig. 8). The red persistent luminescence of $\text{Pr}^{3+}:^1\text{D}_2 \rightarrow ^3\text{H}_4$ is observed when the electron recombines with Pr^{4+} ($\text{Pr}_{\text{Ca/Sr}}^{\bullet\bullet}$) (⑧). The origin of the electron traps is still unknown.

The observation of persistent luminescence in the samples with $x=0, 0.3, 0.5$ under blue light excitation ($^3\text{H}_4 \rightarrow ^3\text{P}_J$ transitions) indicates the potential application of these materials as persistent phosphors under the illumination of blue LED lighting by the introduction of appropriate electron traps, unlike most persistent phosphors, which operate only under Hg-based fluorescent tubes.

Fig. 8. Energy level diagram of $(\text{Ca}, \text{Sr})\text{TiO}_3:\text{Pr}^{3+}$. The energy of the ground state of the Pr^{3+} is defined as zero. Both the bottom of CB and top of VB increased with increasing Sr content, x . With increasing the bottom of CB, the thermal ionization and relaxation probabilities from the $^3\text{P}_J$ excited levels decreased. The persistent luminescence mechanism under band-to-band excitation (①) depicted in the left part as the hole tapping process (②) and the mechanism under IVCT and $^3\text{H}_4 \rightarrow ^3\text{P}_J$ excitations (⑤) is depicted as hole remaining (trapping) process at Pr^{3+} as Pr^{4+} .

5. Conclusions

The photoluminescence, persistent luminescence, thermoluminescence and photocurrent properties of the $(\text{Ca}_{1-x}\text{Sr}_x)\text{TiO}_3:\text{Pr}^{3+}$ ($x=0, 0.3, 0.5, 0.8, 1$) phosphors were investigated. By the PCE measurements, the IVCT

band was observed with the PCE band of band-to-band transition, which is the direct evidence supporting IVCT model. In the samples with smaller x (x=0, 0.3, 0.5), thermally assisted photoionization under $^3\text{P}_j$ transition was also observed. Based on TL results, energy of trap depth decreased with increasing Sr content, x. Comparing the AGE spectra with the PCE results, the afterglow process induced by electron moving through CB was evidenced, where Pr^{3+} works as hole trapping center.

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Figure captions

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References

- [1] H. Takashima, K. Shimada, N. Miura, T. Katsumata, Y. Inaguma, K. Ueda and M. Itoh, *Adv. Mater. (Weinheim, Ger.)* 21 (2009) 3699-3702.
- [2] P. T. Diallo, P. Boutinaud, R. Mahiou and J. C. Cousseins, *physica status solidi (a)* 160 (1997) 255-263.
- [3] P. Boutinaud, R. Mahiou, E. Cavalli and M. Bettinelli, *J. Appl. Phys.* 96 (2004) 4923-4929.
- [4] E. Pinel, P. Boutinaud and R. Mahiou, *J. Alloys Compd.* 380 (2004) 225-229.
- [5] P. Boutinaud, R. Mahiou, E. Cavalli and M. Bettinelli, *J. Lumin.* 122-123 (2007) 430-433.
- [6] P. Boutinaud, E. Pinel, M. Dubois, A. P. Vink and R. Mahiou, *J. Lumin.* 111 (2005) 69-80.
- [7] P. Boutinaud, E. Cavalli and M. Bettinelli, *J. Phys.: Condens. Matter* 19 (2007) 386230-386241.
- [8] P. Boutinaud, E. Pinel, M. Oubaha, R. Mahiou, E. Cavalli and M. Bettinelli, *Opt. Mater.* 28 (2006) 9-13.
- [9] K. Ueda, H. Yanagi, H. Hosono and H. Kawazoe, *Journal of physics Condens Matter* 11 (1999) 3535-3545.
- [10] P. Dorenbos, A. Krumpel and E. V. d. Kolk, *Opt. Mater.* 32 (2010) 1681-1685.
- [11] J. Ueda, S. Tanabe and T. Nakanishi, *J. Appl. Phys.* 110 (2011) 53102-531026.
- [12] W. M. Yen, M. Raukas, S. A. Basun, W. v. Schaik and U. Happek, *J. Lumin.* 69 (1996) 287-294.
- [13] U. Happek, A. A. Basun, J. Choi, J. K. Krebs and M. Raukas, *J. Alloys Compd.* 303-304 (2000) 198-206.
- [14] P. Boutinaud, L. Sarakha, E. Cavalli, M. Bettinelli, P. Dorenbos and R. Mahiou, *J. Phys. D: Appl. Phys.* 42 (2009) 045106-045113.
- [15] Y. Yamada and Y. Kanemitsu, *Phys. Rev. B* 82 (2010) 1-4.
- [16] W. Jia, D. Jia, T. Rodriguez, D. R. Evans, R. S. Meltzer and W. M. Yen, *J. Lumin.* 119-120 (2006) 13-18.
- [17] Y. Pan, Q. Su, H. Xu, T. Chen, W. Ge, C. Yang and M. Wu, *J. Solid State Chem.* 174 (2003) 69-73.
- [18] M. A. Carpenter, C. J. Howard, K. S. Knight and Z. Zhang, *J. Phys.: Condens. Matter* 18 (2006) 10725-10749.
- [19] M. Cardona, *Phys. Rev.* 140 (1965) A651-A655.
- [20] K. Van Den Eeckhout, P. F. Smet and D. Poelman, *Mater.* 3 (2010) 2536-2566.