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# Vacuum Referred Binding Energy of $3d$ Transition Metal Ions for Persistent and Photostimulated Luminescence Phosphors of Cerium-doped Garnet

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## ABSTRACT

The  $Y_3Al_{5-x}Ga_xO_{12}(YAGG):Ce^{3+}-Cr^{3+}$  persistent phosphor is one of the materials in which  $Cr^{3+}$  ions act as electron traps. The possibility of electron traps by other transition metal ions ( $TM^{3+}$ ,  $TM= Sc, Ti, V, Cr, Fe$ ) was investigated and those electron trap depth was compared with each other. In the TL glow curves, the  $YAGG:Ce^{3+}$  samples co-doped with different  $TM^{3+}$  ions show different TL glow peak temperatures (i.e. different electron trap depth). The estimated vacuum referred binding energy of  $TM^{2+}$  from the trap depth shows a zig-zag curve, which is found to be originated from the various  $3d$  electron energy affected by a number of  $d$  electron, nuclear charge and crystal field splitting. Utilizing the obtained  $TM^{2+}$  zig-zag curve, a new persistent phosphor of  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-Sc^{3+}$  and a photostimulated phosphor of  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-V^{3+}$  were successfully developed.

## 1. Introduction

Phosphors related carrier (electron or hole) trapping and detrapping processes, such as persistent phosphors, photostimulated phosphors, storage phosphors and photochromic materials, have been attracting a great deal of interest. These materials have been studied for a variety of applications, for example luminous paints[1], imaging plates for X-ray detection[2], dosimeter[3, 4] and photochromic materials[5, 6]. The fundamental principles driving each of these phenomena are very similar to each other. In each, carriers (mainly electrons) are trapped into some defects and de-trapped by either light or heat. To design the phosphors related with electron trapping and detrapping processes, it is important to understand the species of electron donors and acceptors, and its energy level location.

In 2013, we have developed novel persistent ceramic phosphors with a new combination of lanthanide luminescent centers and transition metal trap centers were developed in the  $Y_3Al_5-xGa_xO_{12}$  ( $x=2.5, 3, 3.5$ ) garnet (YAGG) doped with  $Ce^{3+}$  and  $Cr^{3+}$ . The phosphors show  $Ce^{3+}:5d-4f$  green persistent luminescence ( $\lambda_{em} = 510$  nm) for several hours after blue-light excitation[7]. In our following works, we demonstrated that  $Ce^{3+}$  ions are photo-oxidized and  $Cr^{3+}$  ions are photo-reduced by UV illumination from the thermoluminescence glow curves, vacuum referred binding energy diagram and the XANES measurement[7-11]. From these results, it is found that the  $Cr^{3+}$  ions can act as electron traps by changing their valence state to  $Cr^{2+}$  in YAGG host material. In many persistent phosphors developed after the  $SrAl_2O_4:Eu^{2+}-Dy^{3+}$ [1, 12, 13], the electron traps are usually formed by codoping with trivalent lanthanide ions ( $Ln^{3+}$ ). It is reported that the electron trap depth depends on the energy gap between  $Ln^{2+}$  (electron trap level) zig-zag curve and bottom of the conduction band (CB)[14-16]. Thus, the persistent luminescence properties can be controlled by co-dopant of  $Ln^{3+}$ . Similarly, we predicted that the vacuum

referred binding energy (VRBE) of an electron in  $TM^{2+}$  with different  $d$  electrons shows a zig-zag curve. For the analysis of  $TM^{2+}$  electron trap level, the  $Y_3Al_{5-x}Ga_xO_{12}:Ce^{3+}-TM^{3+}$  series were chosen because  $Ce^{3+}$  in  $Y_3Al_{5-x}Ga_xO_{12}$  is good electron donor materials by UV and blue excitation due to the suitable relative energy location of  $Ce^{3+}:5d_1$  excited state and the bottom of CB[9, 10] and photo-oxidized  $Ce^{3+}$  is a stable hole trapping center. In this study, the thermoluminescence (TL) glow curves of  $Y_3Al_{5-x}Ga_xO_{12}(YAGG):Ce^{3+}$  codoped with  $3d$  transition metal ions were analyzed, and the obtained trap depth was found to be changed in different  $TM^{3+}$  codopants. From the VRBE diagram constructed from the experimental TL data and first principle calculations, we concluded that the  $TM^{3+}$  acts as the electron traps and its VRBE of  $TM^{2+}$  are affected by the number of  $d$  electrons, effective nuclear charge and crystal field splitting.

## 2. Experimental procedure

Polycrystalline ceramics of  $Y_3Al_{5-x}Ga_xO_{12}(YAGG):Ce^{3+}$  codoped with transition metal ions were synthesized by solid state reaction. The compositions of the prepared samples are  $(Y_{0.995}Ce_{0.005})_3Al_{4.999-x}Ga_xTM_{0.001}O_{12}$  with  $x=0, 1, 2, 3, 4$  ( $TM=Sc, V, Cr$ ) and  $(Y_{0.995}Ce_{0.005})_3Al_{1.999-x}Ga_3TM_{0.001}O_{12}$  ( $TM=Ti, Fe$ ). For YAGG:Ce-TM (Sc, V, Cr), the chemicals  $Y_2O_3$  (99.99 %),  $Al_2O_3$  (99.99 %),  $Ga_2O_3$  (99.99 %),  $CeO_2$  (99.99 %),  $Sc_2O_3$  (99.99%),  $V_2O_5$  (99.9%),  $Cr_2O_3$  (99.9%) were used as starting materials. The powders were mixed by ball milling (Fritsch, Premium Line P-7) with ethanol and the obtained slurry was dried and pulverized. For YAGG:Ce-TM (Ti, Fe), the powders of  $Y_2O_3$  (99.99 %),  $Al_2O_3$  (99.99 %),  $Ga_2O_3$  (99.99 %),  $CeO_2$  (99.99 %) were mixed by ball milling (Fritsch, Premium Line P-7) with

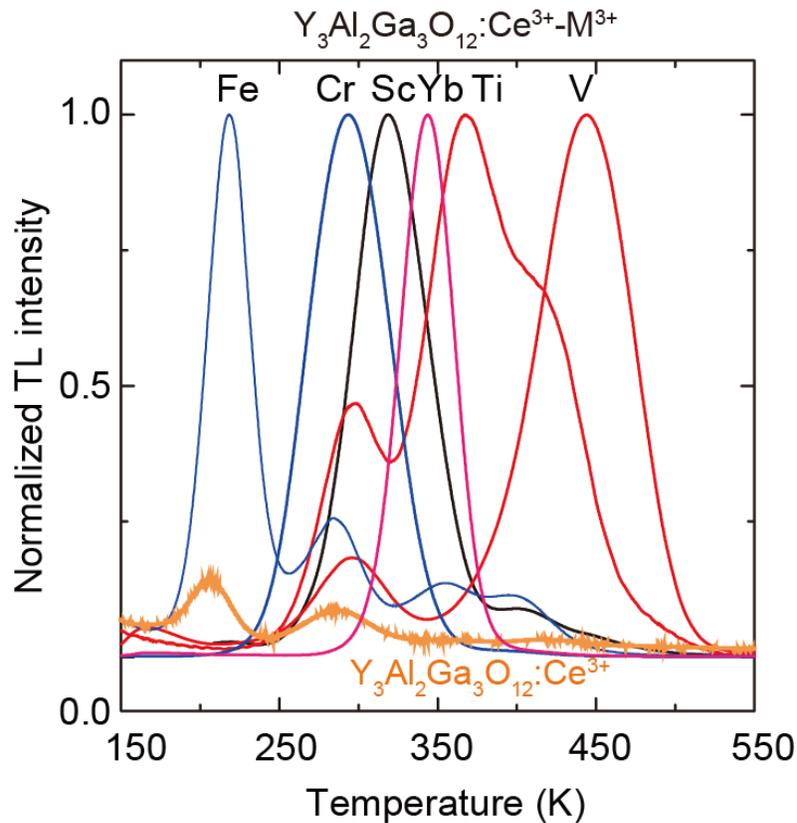
ethanol. The obtained slurry was dried and pulverized, and then  $\text{TiCl}_3$  (99.9%),  $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  solution was added and mixed well. The dried powders were pressed at 50 MPa into pellets sized 10 mm- $\phi$  x 2 mm thick. The pellets were sintered at 1600 °C for 24 h in air.

TL glow curves were measured using a PMT (Hamamatsu Photonics, R3896) with a 475 nm short-cut filter and a 600nm long cut filter for detecting only  $\text{Ce}^{3+}$  luminescence. The samples were mounted on a cryostat (Advanced Research Systems, Helitran LT3) in order to control the temperature. The samples were excited by UV excitation (250 nm ~ 400 nm) from a 300W Xe-lamp at 100K for 10 min and started to be heated with 10K/min. heating rate to 600K 10 min after stopping the excitation light. PersL decay curves were measured by the PMT with 475-600 nm transparent window by the filters after excitation of the Xe lamp with a 460 nm bandpass filter. Photostimulated luminescence was detected by a multi-channel monochromator (Ocean Optics, QE65PRO) with 980 nm infra-red (IR) laser stimulation after and before charging by UV excitation (250nm~400nm). The charge transfer energy from  $\text{O}^{2-}$  to  $\text{TM}^{3+}$  in  $\text{Y}_3\text{Al}_5\text{O}_{12}$  was calculated by the discrete variational multielectron (DVME) method developed by Ogasawara[17] using  $\text{TMO}_6^{9-}$  cluster with lattice relaxation correction. The effective Madelung potential was produced by surrounding the cluster with point charges at external atomic sites. The configuration dependent correction (CDC) between the  $3d^n$  and  $3d^{n+1}L^{-1}$  was taken into account, where  $L^{-1}$  denotes a ligand hole.

### 3. Results

#### 3.1. TL glow curves

Figure 1 shows the normalized TL glow curves of  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-TM^{3+}$  (TM=Sc, Ti, V, Cr, Fe). As a reference data, TL glow curves of  $Ce^{3+}$ -singly-doped  $Y_3Al_2Ga_3O_{12}$ [11] and  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-Yb^{3+}$  are also shown. Main TL peak of  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-TM^{3+}$  (TM=Sc, Ti, V, Cr, Fe) was observed at 319 K, 367 K, 444 K, 294 K and 218 K. The Ga content dependence of TL glow curve in  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-TM^{3+}$  (TM=Sc, V) are shown in Figure 2 and 3, respectively. The main TL peak is shifted to a higher temperature up to x=1 sample, and then to lower temperature with increasing Ga content. The TL peak temperatures for  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-TM^{3+}$  (TM=Sc, V, Cr) are listed in Table 1.



**Figure 1. Normalized TL glow curves recorded with 10K/min heating rate of  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-TM^{3+}$  (TM=Sc, Ti, V, Cr, Fe),  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-Yb^{3+}$  and  $Y_3Al_2Ga_3O_{12}:Ce^{3+}$  after UV charging at 100 K.**

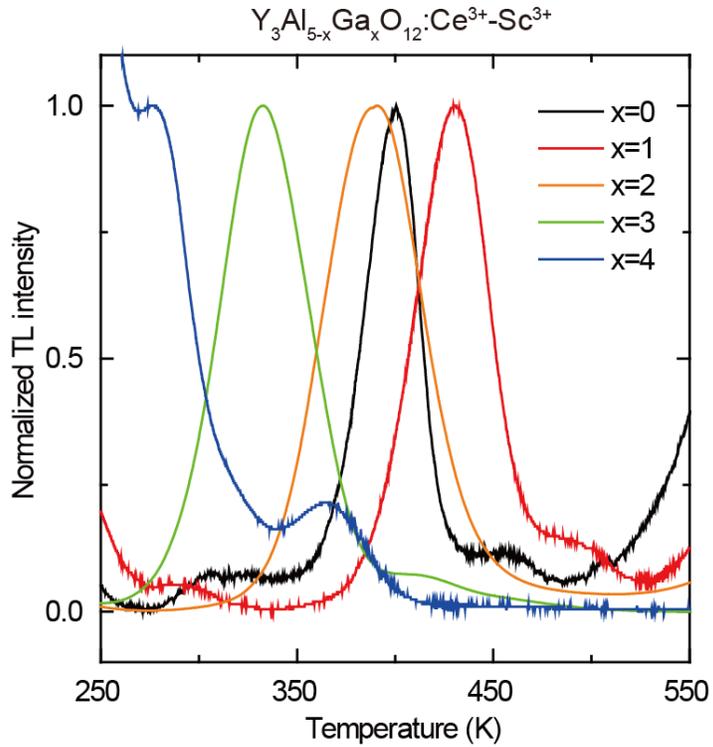


Figure 2. Normalized TL glow curves recorded at 10K/min heating rate of  $Y_3Al_{5-x}Ga_xO_{12}:Ce^{3+}-Sc^{3+}$  with different Ga content  $x$  after UV charging at 100 K.

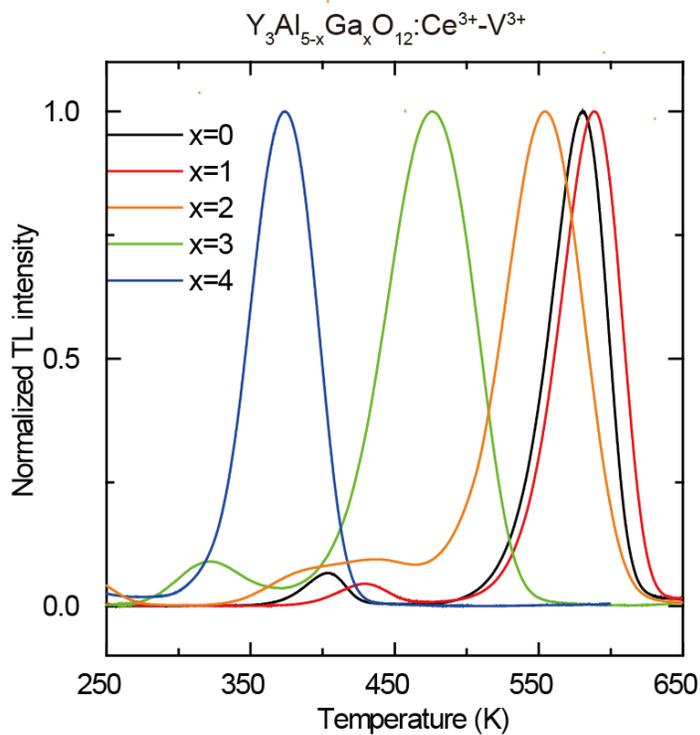


Figure 3. Normalized TL glow curves recorded at 10K/min heating rate of  $Y_3Al_{5-x}Ga_xO_{12}:Ce^{3+}-V^{3+}$  with different Ga content  $x$  after UV charging at 100 K.

From the obtained TL glow peak temperature, the trap depth was estimated assuming first order kinetics and using Eq.(1) below[18, 19].

$$\frac{\beta E^{trap}}{kT_m^2} = s \exp\left(-\frac{E^{trap}}{kT_m}\right) \quad (1).$$

Here,  $\beta$  is the heating rate (K/s),  $E^{trap}$  is trap depth,  $k$  is Boltzmann constant,  $T_m$  is a maximum temperature of TL glow peak,  $s$  is frequency factor. We already reported the frequency factor,  $s$ , in the  $Y_3Al_{5-x}Ga_xO_{12}:Ce^{3+}-Cr^{3+}$  with different Ga content  $x$  by the heating rate analysis of TL glow curves[9]. Because the frequency factor usually depends on the host materials, the frequency factors in the  $Y_3Al_{5-x}Ga_xO_{12}:Ce^{3+}-Cr^{3+}$  were used for the calculation of trap depth in  $Y_3Al_{5-x}Ga_xO_{12}:Ce^{3+}$  samples with different codopants. The trap depth of the main TL glow peak in  $Y_3Al_2Ga_3O_{12}:Ce^{3+}$  codoped with  $Sc^{3+}$ ,  $Ti^{3+}$ ,  $V^{3+}$ ,  $Cr^{3+}$ , and  $Fe^{3+}$  is estimated to be 0.87, 0.96, 1.26, 0.81 and 0.56 eV, respectively. For the  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-Yb^{3+}$  as a reference, the observed TL peak temperature is 344 K, which corresponds to the 0.91 eV of trap depth. The TL peak temperature and the trap depth of the main TL glow peak in  $Y_3Al_{5-x}Ga_xO_{12}:Ce^{3+}-TM^{3+}$  (TM=Sc, V, Cr) with different Ga content are shown in Table 1. The decline tendency of the trap depth for Ga content was observed.

**Table 1. Temperature maximum,  $T_m$ , of TL glow curves recorded at 10 K min<sup>-1</sup> heating rate, the trap depth,  $E^{trap}$ , and VRBE of  $Sc^{2+}$ ,  $V^{2+}$  and  $Cr^{2+}$  ( $E_{Sc^{2+}}$ ,  $E_{V^{2+}}$  and  $E_{Cr^{2+}}$ )**

	$T_m$ (K)			$E^{trap}$ (eV)			$E_{Sc^{2+}}$ (eV)	$E_{V^{2+}}$ (eV)	$E_{Cr^{2+}}$ (eV)
	Sc	V	Cr	Sc	V	Cr			
x=0	401	580	384	1.23	1.80	1.02	-2.94	-3.51	-2.73
x=1	430	589	396	1.27	1.75	1.08	-2.91	-3.39	-2.72
x=2	391	554	343	1.14	1.64	1.02	-2.89	-3.39	-2.77
x=3	360	476	279	0.87	1.26	0.81	-2.86	-3.25	-2.80
x=4	(276)	374	214	0.69	0.95	0.56	-2.82	-3.08	-2.69

## 4. Discussion

### 4.1 VRBE of $\text{TM}^{2+}$

As shown in Figure 1, the TL peak temperature is dramatically changed by varying the codopant  $3d$  transition metal ions. Also, it is entirely different from the small TL glow curve of  $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}^{3+}$ , which is possibly caused by the intrinsic defects. These results strongly suggest that the carrier trap is formed by  $3d$  transition metal ion. Our previous results of XANES spectrum in  $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}^{3+}-\text{Cr}^{3+}$  supports that the photoionized electron from  $\text{Ce}^{3+}$  moves to the  $\text{Cr}^{3+}$  after charging. Considering these results, other  $3d^n$  transition metal ions are also likely to act as the electron traps and itself changes to  $3d^{n+1}$  electron configuration.

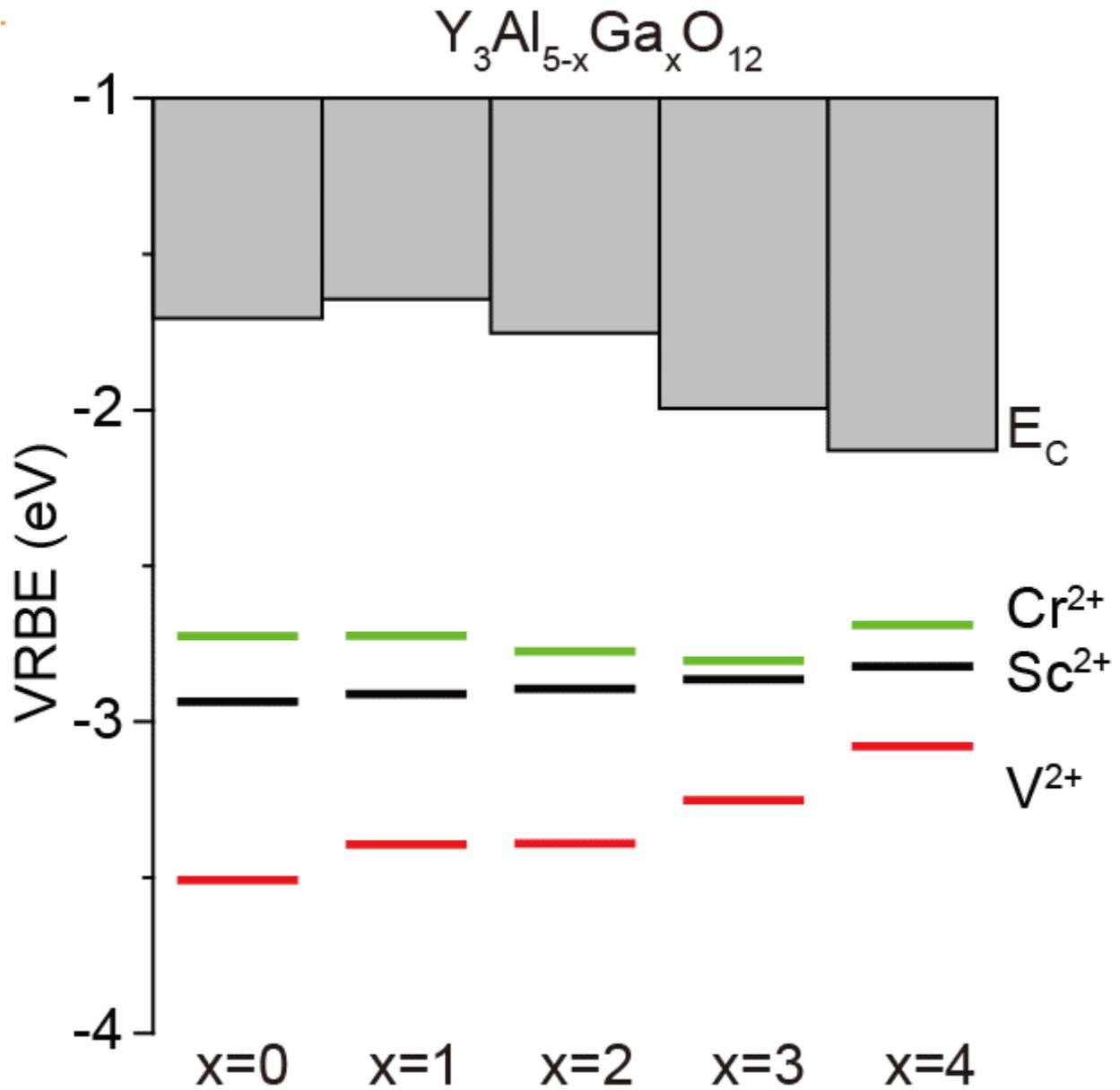
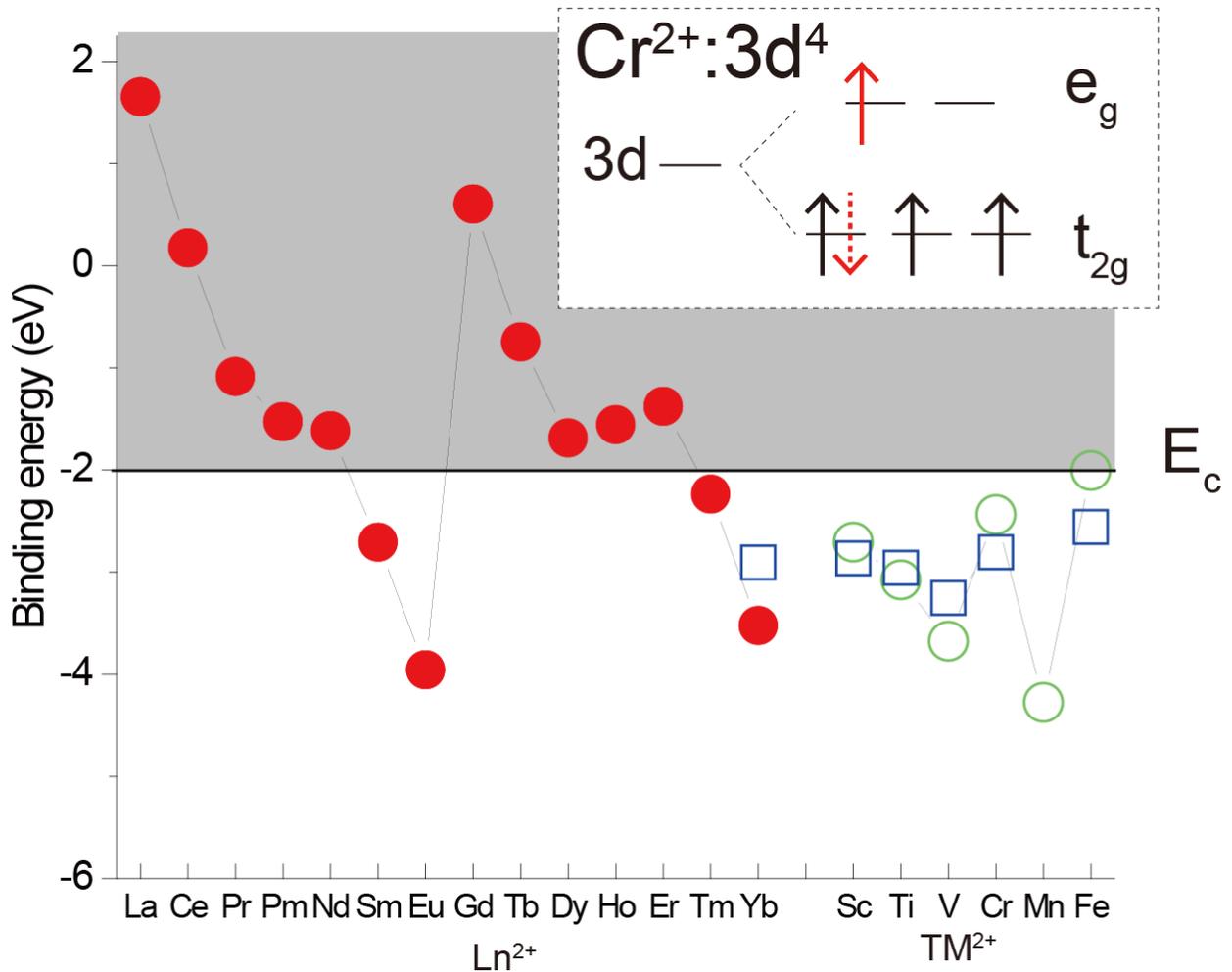


Figure 4. Stacked VRBE diagrams of  $Y_3Al_{5-x}Ga_xO_{12}$  for  $TM^{2+}$  (TM=Sc, V, Cr).

Figure 4 shows the stacked vacuum referred binding energy of  $Y_3Al_{5-x}Ga_xO_{12}$ , which is constructed mainly using the parameter in our previous paper[9]. The VRBE of  $Sc^{2+}$ ,  $V^{2+}$  and  $Cr^{2+}$  ( $E_{Sc^{2+}}$ ,  $E_{V^{2+}}$ ,  $E_{Cr^{2+}}$ ) level is plotted by subtracting the corresponding trap depth from the energy of the bottom of CB ( $E_C$ ). As reported in previous our paper,  $E_{Cr^{2+}}$  in YAGG always

appears near  $-2.75 \text{ eV} \pm 0.06 \text{ eV}$ [9].  $E_{V^{2+}}$  and  $E_{Sc^{2+}}$  in YAGG were spread near  $-3.30 \pm 0.22 \text{ eV}$  and  $-2.88 \pm 0.06 \text{ eV}$ , respectively. The VRBE of the single electron in the lowest energy  $3d$ ,  $4d$ , and  $5d$  levels in group IIIa, IVa, Va and VIa transition metal (TM) and lanthanide (Ln) ions spread  $\pm 1 \text{ eV}$  around a mean value [20-23]. Therefore, it is regarded that the VRBE of each  $TM^{2+}$  in  $Y_3Al_{5-x}Ga_xO_{12}$  has the reasonable range. The VRBE of  $TM^{2+}$  (TM=Sc, V) slightly increases with increasing Ga content. This is probably because the crystal field splitting of  $3d$  transition metal ions becomes much weaker and the  $t_{2g}$  state of  $TM^{2+}$  shifts higher energy. Also, from the charge transfer energy of  $6.67 \text{ eV}$  in  $Y_3Al_5O_{12}:Sc^{3+}$ [24],  $E_{Sc^{2+}}$  was reported to be  $-2.71 \text{ eV}$  by Dorenbos, which is the very similar value with the obtained  $E_{Sc^{2+}}$  of  $-2.94 \text{ eV}$  from the trap depth. This coincidence also supports that these electron trap levels are due to  $TM^{2+}$ .



**Figure 5.** VRBE diagram of Ln<sup>2+</sup> and TM<sup>2+</sup> in Y<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>, blue square is estimated from the experimental data of TL, red circle is estimated from the Dorenbos model, green circle is estimated from the DMVE calculation in this work.

Here, the VRBE of TM<sup>2+</sup> is discussed from the viewpoint of the number of *d* electron, effective nuclear charge and crystal field splitting. Figure 5 shows the VRBE diagram of Ln<sup>2+</sup> and TM<sup>2+</sup> in the Y<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub> host. The VRBE of Ln<sup>2+</sup> (red circles in Figure 5) is referred from the paper by Dorenbos[25, 26], and for the Ln<sup>2+</sup>, the typical zig-zag curve can be seen. The values of VRBE of TM<sup>2+</sup> were estimated from two methods: One is from the trap depth, which is calculated by the peak temperature of measured TL glow curve (blue squares in Figure 5 and

$E_{\text{TM}^{2+}_{\text{exp}}}$  in Table 2). Another value is estimated by using DVME calculation as discussed later (green circle in Figure 5 and  $E_{\text{TM}^{2+}_{\text{cal}}}$  in Table 2). The absolute energy of CT energy can be discussed because the calculated energy shows good agreement with the experimental result; for example, the experimental and calculated charge transfer energies from and 6.49 eV, respectively.

For the VRBE of  $\text{TM}^{2+}$  from the experimental data ( $E_{\text{TM}^{2+}_{\text{exp}}}$ ), when 3d electron increases, it does not follow the monotonic increase (or decrease) tendency, but like a zig-zag curve. Although some  $E_{\text{TM}^{2+}_{\text{exp}}}$  are lacking due to the limitation of material synthesis and thermoluminescence investigation,  $E_{\text{TM}^{2+}_{\text{exp}}}$  of  $3d^1$  ( $\text{Sc}^{2+}$ ),  $3d^2$  ( $\text{Ti}^{2+}$ ),  $3d^3$  ( $\text{V}^{2+}$ ),  $3d^4$  ( $\text{Cr}^{2+}$ ) with the continuous number of 3d electrons can be discussed reasonably. The  $E_{\text{TM}^{2+}_{\text{exp}}}$  decreases with increasing 3d electron from  $\text{Sc}^{2+}$  to  $\text{V}^{2+}$  and increases at  $\text{Cr}^{2+}$ . If we consider only the number of 3d electrons and effective nuclear charge in free ions, VRBE of  $\text{TM}^{2+}$  should monotonically decrease from  $3d^1$  to  $3d^4$ . This is because the effective nuclear charge increases in the order of  ${}_{21}\text{Sc}$ ,  ${}_{22}\text{Ti}$ ,  ${}_{23}\text{V}$ ,  ${}_{24}\text{Cr}$ , which attract electrons strongly with increasing atomic number, and there is no strong electron repulsion due to the less 3d electrons than the electrons for the semi-closed shell. To discuss the non-monotonic tendency, we should consider the effect by the crystal field splitting for  $E_{\text{TM}^{2+}_{\text{exp}}}$  in compounds. The trivalent 3d transition metal from  $\text{Sc}^{3+}$  to  $\text{Cr}^{3+}$  can occupy the octahedral site in the garnet crystal rather than the tetrahedral site due to the relatively large ionic radius. The electron traps by trivalent 3d transition metal (i.e.  $E_{\text{TM}^{2+}}$ ) is also located at the octahedral site. In the octahedral site, the 3d energy level splits to  $t_{2g}$  ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{yz}$ ) and  $e_g$  ( $d_{z^2}$ ,  $d_{x^2-y^2}$ ) as shown in Figure 5 inset. If the 3d electrons are less than 4, all 3d electrons occupy the  $t_{2g}$  level by the Hund rules. On the other hand, for the  $3d^4$  electron configuration of  $\text{Cr}^{2+}$ , the fourth electron can occupy the  $e_g$  level as high spin state or the  $t_{2g}$  level as low spin state

as shown in red dot lines in Figure 5 inset. Both the high and low spin state of  $\text{Cr}^{2+}$  could have the higher energy compared with  $\text{V}^{2+}$  even if the increase of effective nuclear charge is taken into account. This is because for the high spin state the  $e_g$  level accommodating the fourth electron is located at higher energy compared with  $t_{2g}$  level and for the low spin state the fourth electron at  $t_{2g}$  level is affected by strong Coulomb repulsion due to the occupation of two electrons into the same  $3d$  orbit.

**Table 2. Calculated charge transfer energy of  $3d$  transition metal from DVME,  $E_{\text{cal}}^{\text{CT}}$ , the calibrated charge transfer energy,  $E_{\text{cal\_calib}}^{\text{CT}}$ , the estimated VRBE from the DVME calculation in  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ,  $E_{\text{TM}^{2+}\_{\text{cal}}}$ , and the VRBE estimated from TL experimental data in  $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ ,  $E_{\text{TM}^{2+}\_{\text{exp}}}$ .**

	$E_{\text{cal}}^{\text{CT}}$	$E_{\text{cal\_calib}}^{\text{CT}}$	$E_{\text{TM}^{2+}\_{\text{cal}}}$	$E_{\text{TM}^{2+}\_{\text{exp}}}$
Sc	8.40	6.67	-2.71	-2.86
Ti	8.03	6.30	-3.07	-2.96
V	7.43	5.70	-3.67	-3.25
Cr	8.67	6.94	-2.43	-2.80
Mn	6.83	5.10	-4.27	-
Fe	9.10	7.37	-2.00	-2.56

To discuss this hypothesis, the charge transfer energies of  $\text{TM}^{3+}$  ( $\text{O}^{2-} - \text{TM}^{3+} \rightarrow \text{O}^- - \text{TM}^{2+}$ ) in the  $\text{Y}_3\text{Al}_5\text{O}_{12}$  were estimated using Ab initio calculation. The second column of Table 2 is the

charge transfer energy,  $E_{\text{cal}}^{\text{CT}}$ , estimated by DVME calculation with lattice relaxation correction. Since there is a systematic overestimation of the theoretical CT energy, the values are shifted by -1.86 eV, which is estimated from the CT energy (6.67eV) from  $\text{O}^{2-}$  to  $\text{Sc}^{3+}$  in  $\text{Y}_3\text{Al}_5\text{O}_{12}$ <sup>[24]</sup>, as shown in the third column of Table 2. Then, the VRBE of  $\text{TM}^{2+}$  was estimated by adding the calculated  $E^{\text{CT}}$  to the top of VB in  $\text{Y}_3\text{Al}_5\text{O}_{12}$  which was reported previously[9]. The VRBE of  $\text{TM}^{2+}$  in  $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$  estimated from the trap depth obtained in TL glow curves as shown in Figure 1. From the calculation, it is found that the high spin state of  $\text{Cr}^{2+}$  is much more stable than the low spin state in the garnet crystal. The estimated VRBE from the calculation,  $E_{\text{TM}^{2+}\text{,cal}}$ , in  $\text{Y}_3\text{Al}_5\text{O}_{12}$  can be compared with the  $E_{\text{TM}^{2+}\text{,exp}}$  in  $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$  because the VRBE of 3d transition metal ions in  $\text{Y}_3\text{Al}_{5-x}\text{Ga}_x\text{O}_{12}$  spread in the narrow region as discussed in Figure 4. As shown in column 4 and 5 of Table 2, the calculated  $E_{\text{TM}^{2+}\text{,cal}}$  is in line with the  $E_{\text{TM}^{2+}\text{,exp}}$  from Sc to Cr. Therefore, the increase of  $E_{\text{TM}^{2+}}$  at  $\text{Cr}^{2+}:3d^4$  is confirmed to be caused by the crystal field splitting. The  $E_{\text{TM}^{2+}\text{,cal}}$  of  $\text{Mn}^{2+}$  decreases significantly because of the semi-closed shell, and the  $E_{\text{TM}^{2+}\text{,cal}}$  of  $\text{Fe}^{2+}$  increases due to strong Coulomb repulsion of two electrons on the same 3d orbit.

## 4.2. Design of electron (de)trapping phosphors

From the obtained zig-zag curve of  $\text{TM}^{2+}$ , we can design a new electron trapping materials such as persistent phosphors, photostimulated phosphors and storage phosphors. Figure 6 shows the persistent luminescence decay curves of  $\text{Ce}^{3+}$  luminescence after 460 nm charging for 5 min in  $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}^{3+}$  and  $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}^{3+}\text{-TM}^{3+}$  (TM=Sc, V, Cr). The detrapping rate is determined by  $s \times \exp(-E_{\text{trap}}/kT)$ , so that the persistent decay profile can be controlled by changing the transition metal codopants. In the order of  $\text{Cr}^{2+}$ ,  $\text{Sc}^{2+}$ ,  $\text{V}^{2+}$ , the trap depth becomes

much deeper as shown in Figure 1. Consequently, the persistent luminescence intensity at ambient temperature is much weaker at beginning, but the persistent luminescence decay slope becomes much gentle as shown in Figure 6. For  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-V^{3+}$ , the trap depth of 1.26 eV is too deep for the persistent luminescence at ambient temperature. However, the deeper trap is suitable for the photostimulated phosphor. Figure 7 shows the luminescence spectrum stimulated by the 980 nm IR laser before and after UV charging in  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-V^{3+}$ . Before charging, there is no luminescence while after charging  $Ce^{3+}:5d_1-4f$  luminescence was observed by IR-stimulation, which is so-called as photostimulated luminescence. This result clearly shows that  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-V^{3+}$  with the deeper traps is suitable for photostimulated phosphors. We can successfully demonstrate that  $TM^{3+}$  codopant ions also act as suitable electron traps like co-dopants of trivalent lanthanide ions in persistent phosphors, and open up a new cation combination material group for phosphors related carrier trapping.

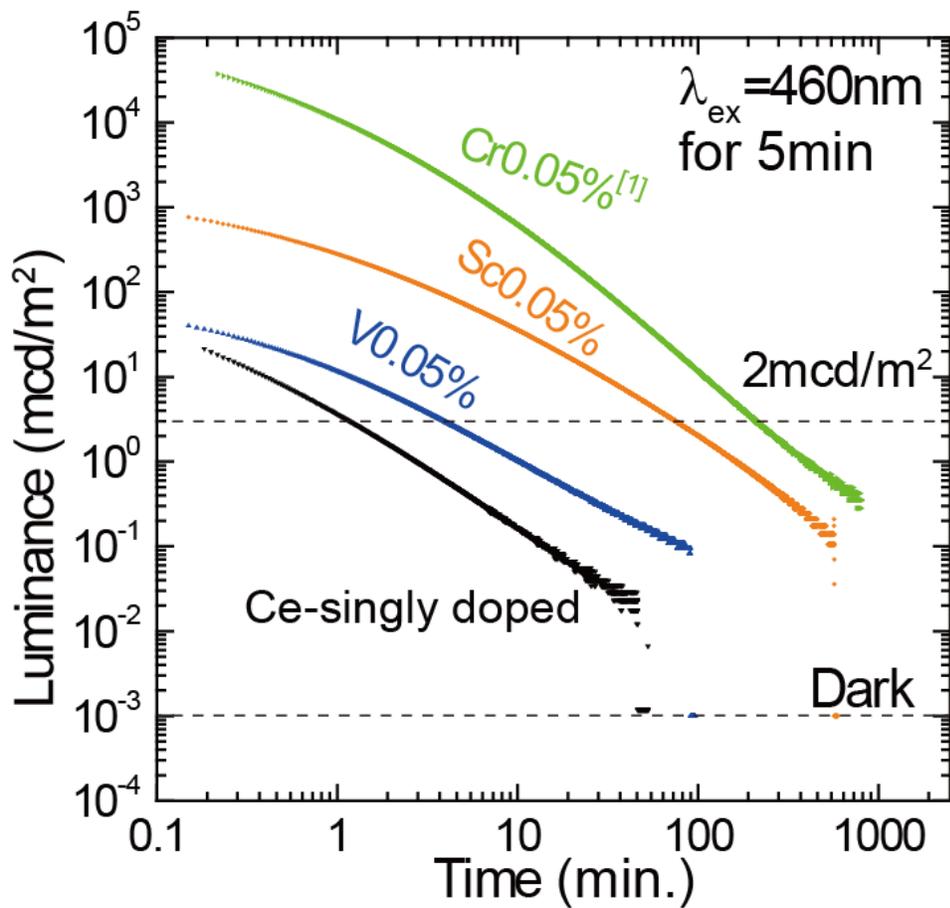


Figure 6. Ce<sup>3+</sup>:5d<sub>1</sub>-4f Persistent luminescence decay curves in Y<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>:Ce<sup>3+</sup>-TM<sup>3+</sup> (TM=Sc, V, Cr) and Y<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>:Ce<sup>3+</sup>.

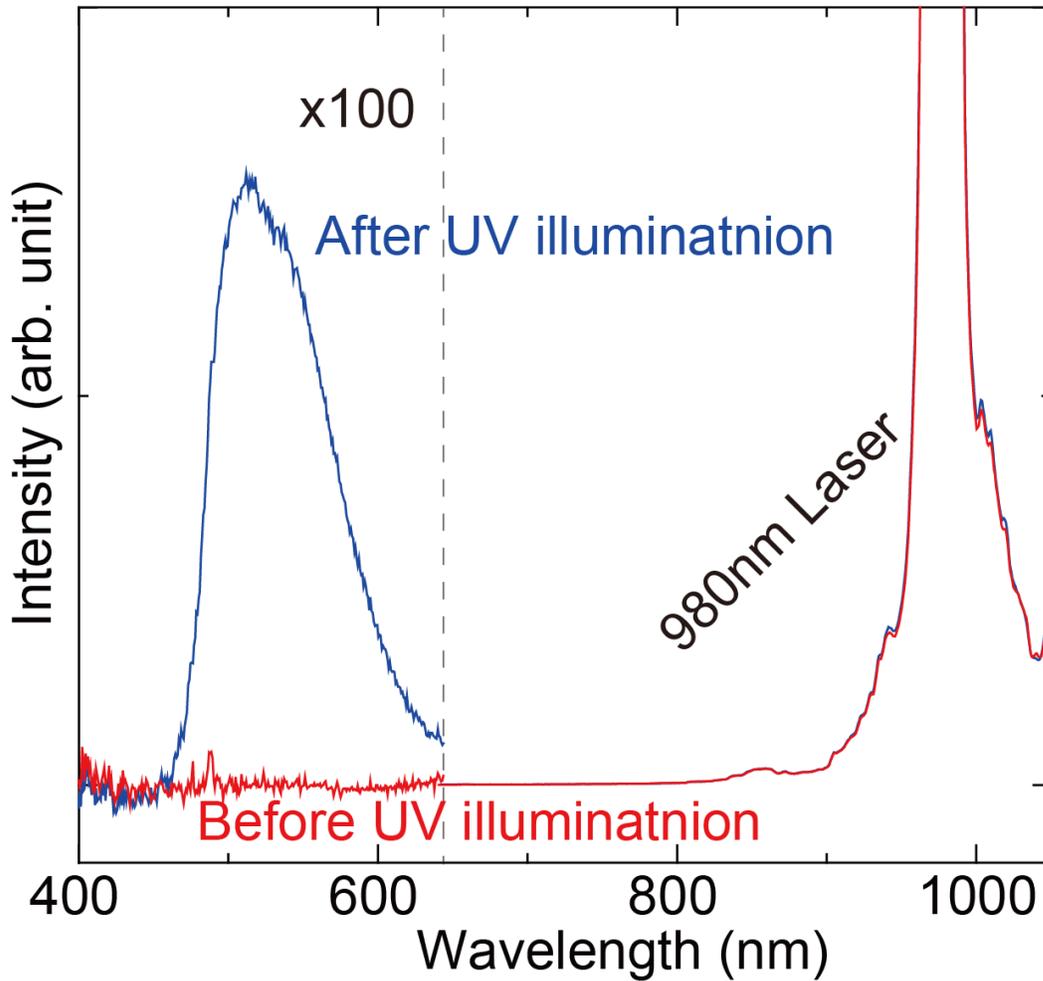


Figure 7. Photostimulated luminescence spectrum by 980 nm before UV charging and after UV charging.

## 5. Conclusions

Thermoluminescence glow curves in  $Y_3Al_{5-x}Ga_xO_{12}:Ce^{3+}$  codoped with  $3d$  transition metal ions ( $TM^{3+}$ ) were investigated. The TL peak temperature is dramatically changed by varying  $TM^{3+}$  ion. The electron trap depth in the samples with different  $3d$  transition metal ions is totally different from each other. This is because electron trap is formed by  $3d$  transition metal ions.

The estimated vacuum referred binding energy of  $\text{TM}^{2+}$  from trap depth shows a zig-zag curve, which is found to be affected by the number of d electron, nuclear charge and crystal field splitting according to the results by the first-principle calculation. Utilizing the obtained  $\text{TM}^{2+}$  zig-zag curve, new persistent phosphors of  $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}^{3+}-\text{Sc}^{3+}$  and photostimulated phosphors of  $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}^{3+}-\text{V}^{3+}$  were successfully developed.

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## Figure captions

Figure 1. Normalized TL glow curves recorded with 10K/min heating rate of  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-TM^{3+}$  (TM=Sc, Ti, V, Cr, Fe),  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-Yb^{3+}$  and  $Y_3Al_2Ga_3O_{12}:Ce^{3+}$  after UV charging at 100 K.

Figure 2. Normalized TL glow curves recorded at 10K/min heating rate of  $Y_3Al_{5-x}Ga_xO_{12}:Ce^{3+}-Sc^{3+}$  with different Ga content x after UV charging at 100 K.

Figure 3. Normalized TL glow curves recorded at 10K/min heating rate of  $Y_3Al_{5-x}Ga_xO_{12}:Ce^{3+}-V^{3+}$  with different Ga content x after UV charging at 100 K.

Figure 4. Stacked VRBE diagrams of  $Y_3Al_{5-x}Ga_xO_{12}$  for  $TM^{2+}$  (TM=Sc, V, Cr).

Figure 5. VRBE diagram of  $Ln^{2+}$  and  $TM^{2+}$  in  $Y_3Al_2Ga_3O_{12}$ , blue square is estimated from the experimental data of TL, red circle is estimated from the Dorenbos model, green circle is estimated from the DMVE calculation in this work.

Figure 6.  $Ce^{3+}:5d_1-4f$  Persistent luminescence decay curves in  $Y_3Al_2Ga_3O_{12}:Ce^{3+}-TM^{3+}$  (TM=Sc, V, Cr) and  $Y_3Al_2Ga_3O_{12}:Ce^{3+}$ .

Figure 7. Photostimulated luminescence spectrum by 980 nm before UV charging and after UV charging.

## Table captions

Table 1. Temperature maximum,  $T_m$ , of TL glow curves recorded at  $10 \text{ K min}^{-1}$  heating rate, the trap depth,  $E^{\text{trap}}$ , and VRBE of  $\text{Sc}^{2+}$ ,  $\text{V}^{2+}$  and  $\text{Cr}^{2+}$  ( $E_{\text{Sc}^{2+}}$ ,  $E_{\text{V}^{2+}}$  and  $E_{\text{Cr}^{2+}}$ )

Table 2. Calculated charge transfer energy of 3d transition metal from DVME,  $E^{\text{CT}}_{\text{cal}}$ , the calibrated charge transfer energy,  $E^{\text{CT}}_{\text{cal\_calib}}$ , the estimated VRBE from the DVME calculation in  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ,  $E_{\text{TM}^{2+}\text{-cal}}$ , and the VRBE estimated from TL experimental data in  $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ ,  $E_{\text{TM}^{2+}\text{-exp}}$ .