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Control of electron transfer between Ce^{3+} and Cr^{3+} in $Y_3Al_{5-x}Ga_xO_{12}$ host by conduction band engineering

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Supplementary Information

Heating rate method

The heating rate method is an effective method to determine precise trap depths because the parameters of TL peak temperature, T_m, and heating rate, β, can be obtained with high accuracy [1]. The method, however, is based on first-order kinetics and a single trap depth. Here, we like to show the validity of the heating rate method in the case of materials with a trap depth distribution. The effectiveness of heating rate method was investigated by simulation using a first-order Randall–Wilkins glow curve without and with trap depth distribution as shown in Eq.(S1). [2-5]

$$I(T) = -\frac{1dn}{\beta dt} = \int_0^\infty N(E_T) f_0(E_T) \frac{s}{\beta} exp\left(-\frac{E}{kT}\right) \times exp\left[-\frac{s}{\beta}\int_{T_0}^{T} e\right. \qquad \text{(S1)}$$

In these equations, β is the heating rate, s is the frequency factor, E is the trap depth, k is the Boltzmann constant, T is the temperature, $N(E_T)$ is the number of available traps with trap depth E_T, $f_0(E_T)$ describes which fraction of the traps is filled at $t = 0$[5].

Fig. S1 shows a first-order TL glow curves using frequency factor (1×10^{11}) from the traps with a single trap depth and traps with a Gaussian trap depth distribution (Gaussian parameters: xc=1.0 eV, w=0.087 eV). The TL glow curves of the traps with a Gaussian trap depth distribution becomes much broader compared with that with a single trap depth, and the shape of the TL glow curve in the case with trap distribution becomes more symmetric. From these simulation data, we plot Ln (T_m^2/β) vs $1/kT_m$ according to the below Eq. (S2) as shown in Fig. S2.

$$\frac{\beta E}{k{T_m}^2} = s\ exp\left(-\frac{E}{kT_m}\right) \qquad \text{(S2)}$$

From the heating rate plot, the obtained trap depth in the case of the single trap and the Gaussian trap distribution are 1.00 and 0.99 eV, respectively. The error is only within 0.01 eV. Therefore, the effectiveness of heating rate plot is valid even for the situation with a trap depth distribution.

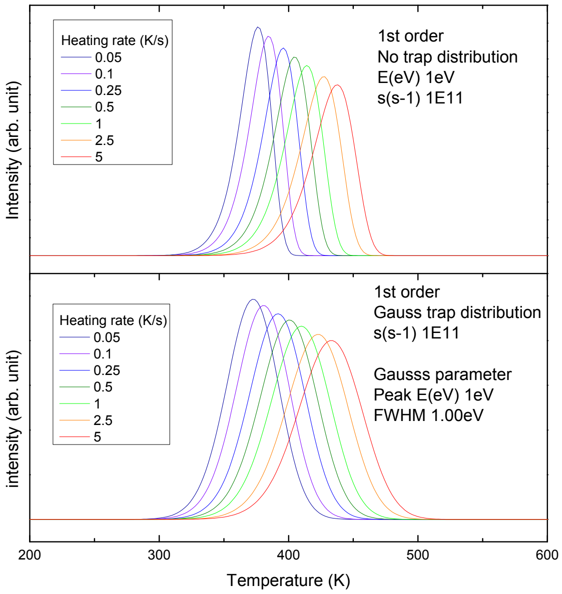

Fig. S1. Effect of the heating rate on the shape and the position of a first-order Randall–Wilkins glow peak of traps with single trap depth (above figure) and traps with a trap depth distribution (bottom figure).

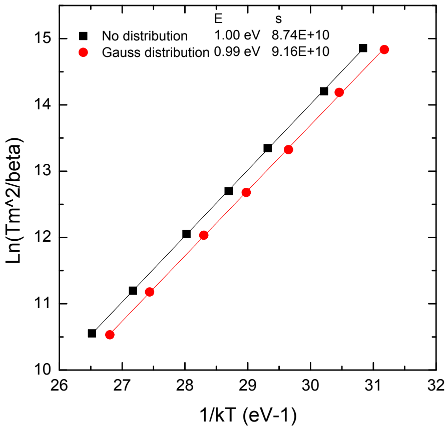

Fig. S2. Heating rate plot of T_m and β obtained from simulation.

As an example, the change of the glow curves with heating rate of the YAGG:Ce-Cr(x=0) sample is shown in Fig. S3. A clear shift of the TL glow peak maximum was observed with increasing heating rate.

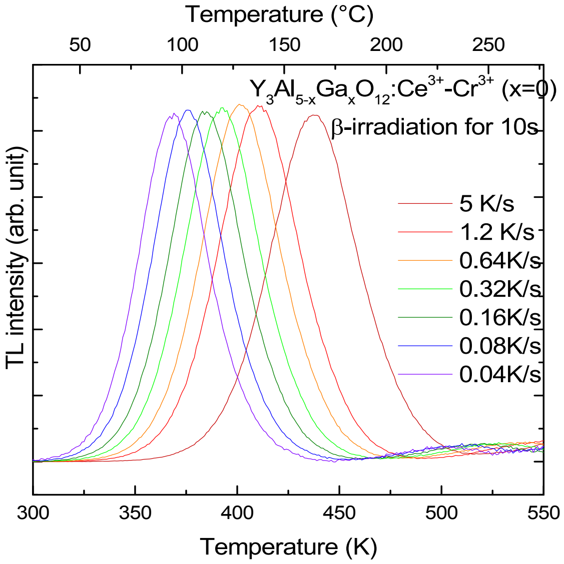

Fig. S3. TL glow curves of YAGG:Ce-Cr (x=0) sample at different heating rates.

Simulation of TL glow curve

Fig. S4 shows the simulation of TL glow curves by a first-order Randall–Wilkins glow curve [2-4] using the obtained trap depth (E) and frequency factor (s) from the heating rate method as shown in Table 2 of the paper. The FWHM of a TL glow curve should become much narrower with decreasing trap depth

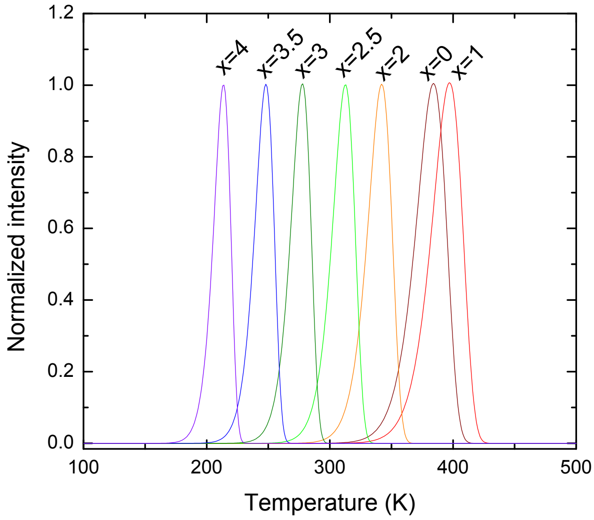

Fig. S4. Simulation of 1st order TL glow curves with the trapping parameters according Table 2 of the paper (heating rate = 10 K/min).

Pre-heating method of TL glow curve

Pre-heating method is effective to analyse the trap depth distribution. Recently, Van den Eeckhout et al summarize the analysis of the electron trap distribution and show the electron trap distribution in persistent phosphors.[5] The pre-heating method itself has been known from 1960's. [6, 7] In this method, before measuring TL glow curves, the samples were pre-heated to partially deplete the-trapped electrons. From the TL glow curve of the pre-heated sample, we can get information only from the un-detrapped trapping centre with a deeper trap depth. The corresponding trap depth is estimated by initial-rise plot of the TL glow curves according to Eq.(S3), (S4). [8]

$$I(T) = C * exp(-\frac{E}{kT}) \qquad \text{(S3)}$$

This equation can be written as

$$Ln(I(T)) =- \frac{E}{kT} + \ln C \qquad \text{(S4)}$$

The Initial Rise method can be applied under condition that only a small fraction of the electron has been released. The method is not only valid for 1st-order kinetics but also for, 2nd and general order kinetics, Fig. S5 shows the TL glow curves of the YAGG:Ce-Cr(x=0) sample for various pre-heating temperatures. The TL glow peak shifts to higher temperature. This result indicates the existence of a trap depth distribution. The intensity of TL glow curve decreases with increasing pre-heating temperature. From this result, the trap filling was estimated at each temperature range. In order to investigate the trap depth by initial rise method, we plot the TL intensity with log e scale as a function of 1/T as shown in Fig. S6 and estimated trap depth from the slope. From the estimated relative trap filling and trap depth, the trap depth distribution was constructed.

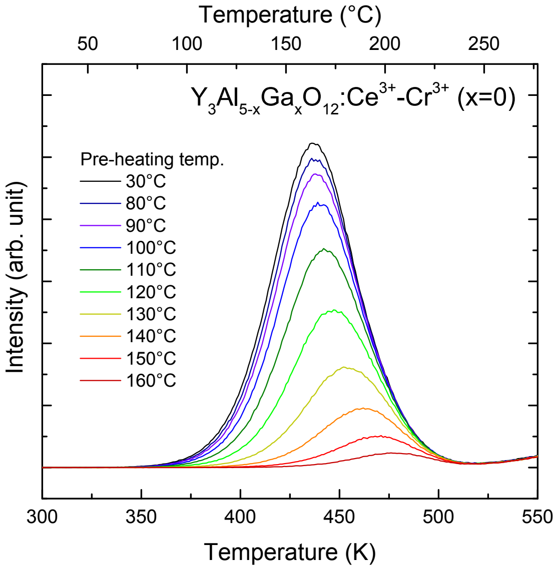

Fig. S5. TL glow curves (5 K/s) of the YAGG:Ce-Cr (x=0) sample after □-irradiation for various pre-heating temperatures.

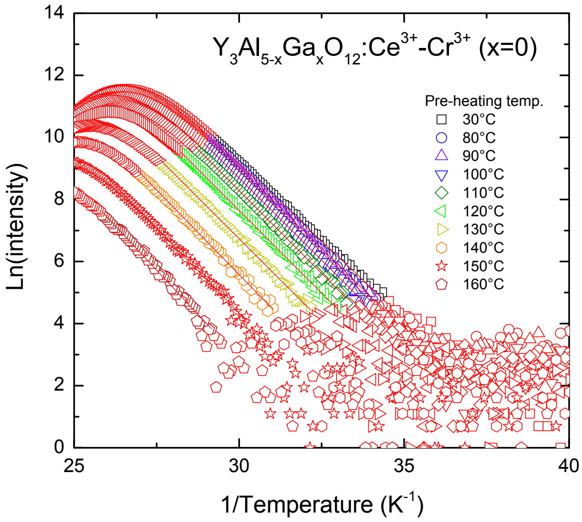

Fig. S6. Initial-rise plots of TL glow curves of YAGG:Ce-Cr (x=0) sample for various pre-heating temperatures.

References

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