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Evidence for formation of self-trapped excitons in a β-Ga_2O_3 single crystal

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We have investigated photoluminescence (PL) and absorption properties of a β-Ga_2O_3 single crystal from the viewpoint of the stability of self-trapped excitons (STEs). A broad PL band with a large Stokes shift, which is conventionally assigned to the STE, was observed. To reveal the stability of the STE, we precisely measured the temperature dependence of the Urbach tails in absorption spectra. It was confirmed that the Urbach tails at all temperatures converge into a specific point, which verifies the validity of the treatment of the Urbach tail. We analysed the temperature dependence of the exponential slope, the so-called steepness constant, of the Urbach tail and evaluated the exciton-phonon coupling constant *g*, which defines the stability of the STE, to be $g = 5.4$. Based on a previously reported theory for exciton-phonon interactions, $g > 1$ generally results in that the STE is a stable state relative to a free exciton. Consequently, the above large *g* factor demonstrates that the STE formation is stable in β-Ga_2O_3.

1 Introduction Recently, one of the wide-gap group-III oxides, β-Ga_2O_3, the band-gap energy of which is 4.7 eV [1], has attracted much attention in applications for high-power field effect transistors [2] and optical functional materials in a deep ultraviolet region such as transparent conductive films and photodetectors [3-6]. The band-gap energy of β-Ga_2O_3 is considerably higher than those of conventional transparent conductive oxides such as In_2O_3, SnO_2, and ZnO, which is advantageous in optical applications. The crystal structure of β-Ga_2O_3 is base centred monoclinic [7]. The optical absorption of β-Ga_2O_3 has anisotropic polarization along the *b*- and *c*-axes [8-10]. It was reported that the photoluminescence (PL) spectrum of β-Ga_2O_3 exhibits a broad band with a large Stokes shift [10, 11]. Note that the broad band is phenomenologically attributed to self-trapped exciton (STE) consisting of self-trapped hole (STH) and a bound electron. STEs are usually observed in alkali halide crystals [12]. According to the theoretical results for β-Ga_2O_3 based on hybrid functional calculations [13], holes tend to form localized small polarons (STHs) with lattice distortions and STHs are localized mainly on a single O atom in the lattice with a shape characteristic of an O 2*p* orbital. However, there has been no clear experimental evidence for formation stability of the STE in β-Ga_2O_3.

According to the theory for exciton-phonon interactions reported by Schreiber and Toyozawa [14], the stability of the STE relative to a free exciton can be revealed from analysis of low-energy exponential tail of exciton absorption spectra, the so-called Urbach tail, in connection with an exciton-phonon coupling constant *g*. If *g* is larger than unity, the STE is generally a stable state. In this work, we systematically measured the temperature dependence of the Urbach tail in a β-Ga_2O_3 single crystal and analysed it on the basis of the theories reported in Refs. [14, 15] from the viewpoint of exciton-phonon interactions. The results of the analysis demonstrate the stability of the STE in β-Ga_2O_3.

2 Experimental details The sample used was a (010)-oriented undoped β-Ga_2O_3 single crystal with a thickness of 0.60 mm grown by an edge-defined film-fed growth method prepared in Tamura Corporation. Absorption spectra were measured using a double beam spectrometer with a resolution of 0.1 nm in the temperature range from 10 to 280 K with a step of 30 K. We did not use a polarizer; namely, the optical anisotropy was not analysed. We also measured PL and PL excitation (PLE) spectra. The excitation light sources for the PL and PLE spectra were the fifth harmonic generation light (213 nm) of a pulsed YAG laser and monochromatic light of a D_2 lamp dispersed by Carl Zeiss M4QIII monochromator, respectively. The PL spectrum was detected with a cooled charge coupled device attached to a single monochromator with a resolution of 1.5 nm. The PLE spectrum was analysed with a photon counting system with a resolution of 1.4 nm. The PL and PLE spectra were measured at 10 K. Sample temperatures were controlled using a closed cycle helium cryostat.

3 Results and discussion

Figure 1 shows the PL and PLE spectra at 10 K of the β-Ga_2O_3 single crystal, where the arrow indicates the detection energy for the PLE spectrum. We observe a broad PL band with a large Stokes shift of about 1.5 eV from the PLE peak energy. The peak structure of the PLE spectrum seems to be due to exciton absorption. In general, a PL band originating from the STE exhibits a large Stokes shift from the exciton absorption peak and a wide width because of strong lattice relaxation. As a result, the broad PL band is phenomenologically attributed to the STE [10, 11]. The previous theoretical study [13] on interactions between holes and phonons indicated that the STH is stable in β-Ga_2O_3. Thus, it is expected that the STE corresponding to a complex of the STH and a bound electron is also stable. It should be noted that the stability of the STE relative to the free exciton can be experimentally revealed from analysis of the Urbach tails of exciton absorption spectra, according to the theory for exciton-phonon interactions reported by Schreiber and Toyozawa [14]. Hereafter, we discuss the stability of the STE based on the theory in Ref. [14].

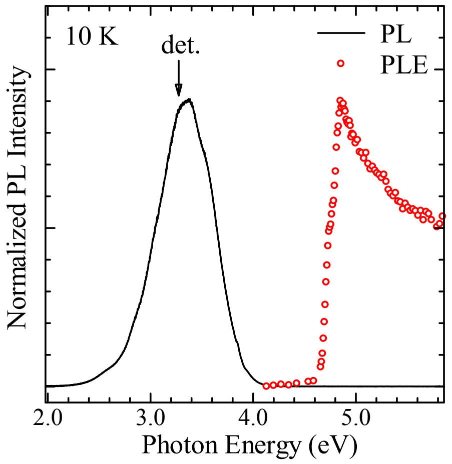

Figure 1 PL and PLE spectra depicted by the solid curve and open circles at 10 K in the β-Ga_2O_3 single crystal, respectively. The arrow indicates the detection energy for the PLE spectrum.

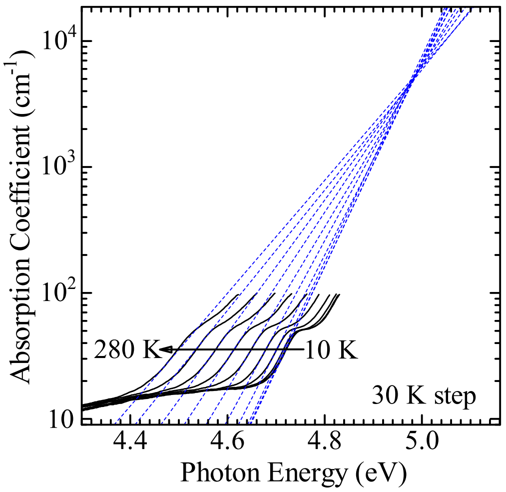

Figure 2 Temperature dependence of the low energy exponential tails (Urbach tails) of absorption spectra in the β-Ga_2O_3 single crystal at temperatures from 10 to 280 K with a step of 30 K, where the solid lines indicate the experimental data and the dashed lines are fitted results using Eq. (1) with $E_0 = 4.98$ eV and $\alpha_0 = 5.0\times10^3$ cm^{-1}.

Figure 2 shows the Urbach tails of absorption spectra at temperatures from 10 to 280 K with a step of 30 K, where the solid lines are experimental data. We clearly observe exponential absorption tails corresponding to the Urbach tails which are expressed as [14]

$$\alpha = \alpha_0 \exp\left(-\sigma(T)\frac{E_0 - E}{k_B T} \right), \tag{1}$$

where E_0, which determines a convergence energy of the Urbach tails, is near the absorption peak energy at the lowest temperature and $\sigma(T)$ is the dimensionless steepness constant which is temperature dependent. In Fig. 2, the absorption spectra exhibits shoulder structures. This is due to optical anisotropy peculiar to β-Ga_2O_3 [8, 9]. The difference in refractive indices due to the optical anisotropy is small, Δn = ~0.03 corresponding to ~1.5% [16]. Therefore, it is assumed that the small Δn results in the slight modulation of the Urbach tail as the step-like shape. In this analysis, we treated only the first exponential tails for simplicity. The dashed lines indicate the fitted results using Eq. (1). We can find that the dashed lines converge into a given point, where $E_0 = 4.98$ eV and $\alpha_0 = 5.0\times10^3$ cm^{-1}. The convergence energy E_0 is certainly close to the absorption peak energy observed in the PLE spectrum at 10 K.

Figure 3 shows the steepness constant $\sigma(T)$ (solid circles) obtained from the slope of the Urbach tail as a function of temperature. According to Ref. [15], the temperature dependence of the steepness constant is given by

$$\sigma(T) = \sigma_0 \frac{2k_B T}{E_{ph}} \tanh\left(\frac{E_{ph}}{2k_B T} \right), \tag{2}$$

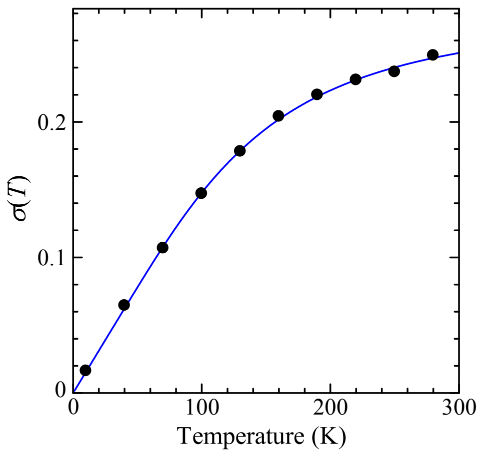

Figure 3 Temperature dependence of the steepness constant $\sigma(T)$, where the solid curve indicates the fitted result using Eq. (2) with $\sigma_0 = 0.28$, $E_{\mathrm{ph}} = 31$ meV.

where E_{ph} is the energy of a principal interacting phonon mode related to localization of excitons. The solid curve indicates the fitted results using Eq. (2). It is evident that the fitted curve well reproduces the experimental results.

The fitting parameters were obtained to be $\sigma_0 = 0.28$ and $E_{\mathrm{ph}} = 31$ meV.

According to the theory reported by Schreiber and Toyozawa [14], the stability of STEs is characterized using the exciton-phonon coupling constant g, which is defined as

$$g = \frac{E_{\mathrm{LR}}}{B}, \tag{3}$$

where E_{LR} is the lattice relaxation energy and B is a half width of an exciton band, which are schematically shown in Fig. 4. When g is larger than unity, the STE is generally a stable state relative to the free exciton. Furthermore, g is proportional to the reciprocal of σ_0 given by Eq. (2) [14]:

$$g = \frac{s}{\sigma_0}. \tag{4}$$

The dimensionless constant s is called the steepness index which depends on the dimensionality of a crystal. The typical value of s is 1.5 in three dimensions [14]. Note that $s = 1.5$ is strictly correct in a simple cubic crystal. However, $s = 1.5$ has been empirically used in various non-cubic crystals including molecular crystals [12]. In β-Ga_2O_3, the value $\sigma_0 = 0.28$, which was obtained from analysis of the Urbach tails using Eq. (2), along with assumed $s = 1.5$ in this noncubic material, results in $g = 5.4$. This g value is sufficiently larger than unity. Consequently, the above analysis demonstrates that the STE is stable in β-Ga_2O_3. In other word, the broad PL band shown in Fig. 1 can be assigned to the STE emission.

According to the STE model (Fig. 4) reported by Toyozawa [17], E_0, which corresponds to the convergence energy of the Urbach tails as shown in Fig. 2, is given by $E_0 = E_a – B$, and the PL band of the STE appears at $E_a – 2E_{\mathrm{LR}}$, where E_a is the centre of energy in the exciton band. Therefore, the Stokes shift E_S is written as

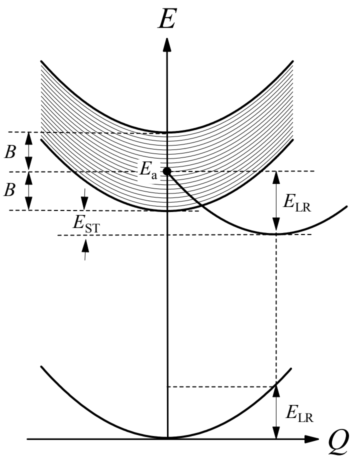

Figure 4 Schematic diagram of the exciton and STE energy states as a function of configuration coodinate Q.

$$E_S = 2E_{\mathrm{LR}} - B. \tag{5}$$

As mentioned above, the Stokes shift was estimated to be 1.5 eV from Fig. 1. Using $g = 5.4$ and $E_s = 1.5$ eV, Eqs. (3) and (5) give the lattice relaxation energy E_{LR}=0.83 eV and the half width of the exciton band B=0.15 eV.

Finally, we discuss the stability energy of the STE. According to Ref. [17], the stability energy E_{ST} is schematically shown in Fig. 4. Thus, E_{ST} is simply given by

$$E_{\mathrm{ST}} = E_{\mathrm{LR}} - B. \tag{6}$$

The value of E_{ST} is obtained to be 0.68 eV using Eq. (6). In Ref. [13], the stability energy of the STH in β-Ga_2O_3 was theoretically calculated to be 0.53 eV. The stability energy of the STE is dominantly determined by that of STH because the STH is the formation centre for the STE. In alkali halide crystals, the STH is called a V_k centre [12]. Consequently, the fact that the value of E_{ST} obtained in the present work is almost consistent with the theoretical value of the STH suggests the validity of the present analysis for the stability of the STE.

4 Conclusions We have investigated the stability of the STE in a β-Ga_2O_3 single crystal. Based on the theory for exciton-phonon interactions reported by Schreiber and Toyozawa [14], we analysed the temperature dependence of the exponential low energy tails, Urbach tails, of absorption spectra. It was found that the exciton-phonon coupling constant is $g = 5.4$. Note that the STE is generally stable relative to the free exciton when $g > 1$. Consequently, it is concluded that the STE is a stable state; therefore, the broad PL band is attributed to STE emission. Furthermore, we estimated the stability energy of the STE to be 0.68 eV. This value is almost in agreement with the theoretical value of STH that is 0.53 eV [13].

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