

# Characterizations of the nonlinear optical properties for (010) and ( $\overline{2}$ 01) beta-phase gallium oxide

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**Abstract:** We report, for the first time, the characterizations on optical nonlinearities of betaphase gallium oxide ( $\beta$ -Ga<sub>2</sub>O<sub>3</sub>), where both (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and ( $\overline{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> were examined for two-photon absorption coefficient, Kerr nonlinear refractive index, and their polarization dependence. The wavelength dependence of two-photo absorption coefficient and Kerr nonlinear refractive index were also estimated by a widely used analytical model.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> exhibits a two photon absorption (TPA) coefficient of 1.2 cm/GW for (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and 0.6 cm/GW for ( $\overline{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. The Kerr nonlinear refractive index is  $-2.1 \times 10^{-15}$ cm<sup>2</sup>/W for (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and  $-2.9 \times 10^{-15}$  cm<sup>2</sup>/W for ( $\overline{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. In addition,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> shows stronger in-plane nonlinear optical anisotropy on ( $\overline{2}$  01) plane than on (010) plane. Compared with GaN, TPA coefficient of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is 20 times smaller, and the Kerr nonlinear refractive index of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is also found to be 4–5 times smaller. These results indicate that  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> have the potential for ultra-low loss waveguides and ultra-stable resonators and integrated photonics, especially in UV and visible wavelength spectral range.

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**OCIS codes:** (160.4330) Nonlinear optical materials; (190.4180) Multiphoton processes; (160.1190) Anisotropic optical materials.

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#### 1. Introduction

As an emerging wide bandgap semiconductor material, beta-phase gallium oxide ( $\beta$ -Ga<sub>2</sub>O<sub>3</sub>) has attracted considerable attentions in catalysis [1,2], gas sensors [3], power electronics [4] and potential optical devices such as waveguides and resonators. Due to its wide bandgap (4.85 eV),  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> possesses a board transparent spectrum (>300 nm) from UV to visible wavelengths. Moreover,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is compatible with III-N material system [5]. This indicates  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> optical devices can integrate with III-nitride based visible light sources [6–8], detectors [9,10], and solar based applications [11,12]. Therefore,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is also a promising candidate for integrated photonics system, especially at UV and visible regime. In order to understand and improve the performances of various  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> devices, the comprehensive investigation on the material properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, previous researches mainly focused on the transmission [14], and refractive index [15,16]. However, the nonlinear optical properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> have not been investigated yet, not to mention in UV and visible regime.

In UV and visible spectral range, under high optical power density, the performance of optical waveguides and resonators are mainly degraded by two-photon absorption (TPA) process [18,19]. For resonators that operate by critical coupling from bus waveguides, the refractive index shifting is governed by Kerr nonlinear refractive index at high power density and decreases the coupling efficiency especially in ultra-high quality factor resonators [20]. Therefore, in order to demonstrate high performance  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based optical devices, it's critical to characterize the nonlinear optical properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> including TPA coefficient and Kerr nonlinear refractive index.

To investigate and evaluate the nonlinear optical properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> in visible spectral range, we performed a typical Z-scan characterization to study the TPA coefficient and Kerr nonlinear refractive index of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. It's found that  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has much smaller two photon absorption coefficient (20 times smaller) and Kerr nonlinear refractive index (4-5 times smaller) [18] than GaN, which is ideal for waveguides and resonators. Furthermore, due to the highly asymmetric crystalline structure of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, the optical nonlinearity is also highly anisotropic. Relative higher in-plane nonlinear optical anisotropy was observed on ( $\overline{2}$  01) plane than on (010) plane. These result can serve as references for the design of photonic devices based on  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.

This paper is organized as the following: In Section 2, we describe methods used in this work including experimental setup and theoretical models. In Section 3, we show our experimental results and make a discussion mainly on its significance in integrated photonics system. In section 4, we will draw the conclusion of this work.

# 2. Methods

The unintentionally doped (UID)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> samples were provided by Tamura Corporation with a carrier concentration on the order of ~10<sup>17</sup> cm<sup>-3</sup> and a thickness of ~500 µm. The backside of the samples was polished by hand-grinding method with diamond lapping film of 0.5 µm grade. The polishing process was carefully controlled so that the thickness of the samples after polishing was reduced by less than 100 µm.

Figure 1(a) schematically shows the experimental setup of the Z-scan measurement [19–22] used in this study. Figure 1(b) depicts the crystal structure of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, (010) and ( $\overline{2}$ 01) planes are also indicated. The light source was an ultrafast titanium-sapphire laser operating at 808 nm with 100 fs pulse width and 82 MHz repetition rate. A  $\chi^2$  crystal was used to generate second harmonic wave at the wavelength of 404 nm. The average power of input second harmonic beam was kept at 12 mW, which corresponds to ~7 × 10<sup>9</sup> W/cm<sup>3</sup> peak power density and ~0.7 mJ/cm<sup>3</sup> single pulse energy density. Due to the lack of reference, no

laser-induced damage threshold (LIDT) of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> was found. As investigated in Ref [23], the LIDTs of dielectric materials are correlated to bandgap energy. To roughly estimate LIDT of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, the LIDTs of two widely recorded materials, GaN (3.4 eV) and HfO<sub>2</sub> (5.2 eV), were checked. The threshold energy are ~5.4 J/cm<sup>3</sup> for GaN at 400 nm with 120 fs pulse width [24], and ranging from 0.5 J/cm<sup>3</sup> to 20 J/cm<sup>3</sup> for HfO<sub>2</sub> [25,26]. Those LIDTs are more than 500 times higher than the operation pulse energy density used in this work. Therefore, we neglected the laser-induced damage effects.

Half wavelength plate working on 404 nm was placed after  $\chi^2$  crystal for light polarization tuning. Beam was expanded by a set of lens before sending into optical objectives in order to fully utilize the numerical aperture. The samples were positioned between two optical objectives. An aperture was implemented in front of power meter to perform open and closed aperture testing.

To test the reliability of the setup, the beam size of the output light was used as an indicator. Based on Gaussian optics, with an incident beam diameter of 4 mm and a numerical aperture (NA) of 0.25, the calculated diameter of the output light is ~5 um (at  $1/e^2$ ) as shown in Fig. 1(c). This value is consistent with the beam diameter we extracted from open aperture Z-scan measurement in the next section.



Fig. 1. (a) Experimental setup used in this work. AT indicates the attenuator,  $\lambda/2$  the halfwavelength plate, PL the polarizer, OB the optical objective lens, A the aperture, PM the power meter. L1, L2, L3 are lenses. (b) Crystalline structure of  $\beta$ -Ga2O3 and planes that characterized in this study. (c) The field intensity at focal point estimated, which agree with our open aperture fitting.

The TPA coefficient and Kerr nonlinear refractive index can be obtained from open/closed aperture scanning based on Eqs. (1)–(3).

$$T \approx 1 - \frac{\alpha_{TPA} I_0 L_{eff}}{2\sqrt{2}} \times \frac{1}{1 + Z^2 / Z_0^2}$$
(1)

$$Z_0 = \frac{n\pi\omega_0^2}{\lambda} \tag{2}$$

$$n_{kerr} = \frac{\lambda \Delta \phi}{2\pi I_0 L_{eff}} \tag{3}$$

where T is the normalized transmission,  $I_0$  is the peak beam power density,  $L_{eff}$  is the effective sample length,  $Z_0$  is the Rayleigh range of the beam, n is the refractive index,  $\omega_0$  is the beam size at the focal plane, and  $\lambda$  is the wavelength in free space.  $L_{eff}$  is the sample thickness,  $\Delta \phi$  the nonlinear phase shift due to Kerr effect [21], S parameter defined in [21] was controlled to be 0.35 throughout the characterization. More information about these equations can be found in Ref [18,20,21,26–29]. It's should be noted that the samples were tested at 404 nm which is above half bandgap energy of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (506 nm). Therefore, three-photon absorption modification to Eq. (1) is not necessarily needed [30]. The wavelength-dependence of the TPA coefficients was also theoretically calculated using Eq. (4),

$$\alpha_{TPA}(\omega) = K \frac{\sqrt{E_p}}{n_0^2 E_g^3} F_2(\hbar \cdot \omega / E_g)$$
(4)

where  $E_g$  is the direct bandgap energy and  $E_p = 2|P_{vc}|^2 / m_0$ , obtained by the  $k \cdot p$  model [31], which is a material-independent parameter for direct bandgap semiconductors,  $n_0$  is the refractive index,  $\omega$  is the frequency, and K is a material-independent constant.  $F_2$  is a fitting function with the form  $F_2(x) = (2x-1)^{1.5} / (2x)^5$ . In our theoretical analysis, we did not consider phonon assisted TPA because it only contributes to optical nonlinearity at a narrow bandwidth near 506 nm wavelength.

#### 3. Experimental results and discussions

Figure 2 shows the open/closed aperture scanning results for (010) and ( $\overline{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. Fitting the experimental data with Eqs. (1)-(3) yielded the TPA coefficients and Kerr nonlinear refractive index, which was summarized in Table 1. (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> had a TPA coefficient  $\alpha_{TPA} = 1.2$  cm/GW and  $n_{kerr} = -2.1 \times 10^{-15}$  cm<sup>2</sup>/W when  $\vec{E} \perp$  [102], while  $\alpha_{TPA}$ of 0.6 cm/GW and  $n_{kerr}$  of  $-2.9 \times 10^{-15}$  cm<sup>2</sup>/W were obtained on ( $\overline{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> when  $\vec{E}$ [102]. The ( $\overline{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has smaller TPA coefficient than (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. This result indicates ( $\overline{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> waveguides and resonators will have less loss induced by TPA in visible spectral regime. On the other hand,  $(\overline{2} \ 01) \beta$ -Ga<sub>2</sub>O<sub>3</sub> has larger Kerr nonlinear refractive index. In addition, the output beam diameters were also obtained, which were in good agree with theoretical calculations based on Gaussian optics. It is worth noting that besides the transition from valance band (VB) to conduction band (CB),  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> exhibits up to three additional transition channels [1] that may contribute to the optical transition. Photon energies corresponding to the channels are: UV (3.2-3.6 eV), blue (2.8-3.0 eV), and green (2.4 eV). The green transition channel is mainly introduced by Be, Ge, and Sn dopants, therefore it is not a main factor in this work. The blue transition channel is originated from oxide vacancies and correlated to the n-type conductivity of sample. Those intermediate states may enhance the TPA process and introduce saturable one photon absorption [32]. But this process should have minimum effect in this study as the sample used in this work is UID bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> with high crystalline quality. The UV transition channel is resulted from recombination between free electrons and self-trapped holes. The electrons deep inside VB are required to be excited in order to contribute to the absorption process, which is relatively less efficient than transition from VB to oxide vacancy states.

From Fig. 2, it can be clearly observed that closed aperture measurement exhibits more intense noise comparing with open aperture curve. This can be mainly attributed to two reasons: firstly, the testing wavelength was located at 404 nm which is the second harmonic beam from Ti:S laser. Therefore, comparing with our previous work [19], the laser power was ~80 times lower. It is the low power that makes the noise from beam nonidealities more significant, which results in the "bump" and "dip" features in Figs. 2(c) and 2(d) at Z~0.2 mm. Secondly, according to Ref [31], n<sub>kerr</sub> is supposed to be zero near ~0.7Eg photon energy, which corresponds to 3.4 eV for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. Since the testing photon energy at 404 nm is ~3.1 eV, the n<sub>kerr</sub> is supposed to be in a relative small magnitude. This also increase testing difficulties throughout the experiment. To verify the closed aperture data, relation Z<sub>pv</sub> ≈ 1.7Z<sub>0</sub> was implemented [21], the Z<sub>pv</sub> represents peak-valley distance in closed aperture scan and Z<sub>0</sub> was obtained from Eqs. (1) and (2). Fitting of Figs. 2(a) and 2(b) yielded Z<sub>0</sub> of 0.15 mm and 0.13 mm, corresponding to Z<sub>pv</sub> of 0.25 mm and 0.22 mm, respectively. These are consistent with the measured (0.22 mm and 0.23 mm) Z<sub>pv</sub> shown in Figs. 2(c) and 2(d).

It also worth noting that below 3.4 eV photon energy, using the widely implemented fitting model [31] developed by Sheik-Bahae *et al.* the  $n_{kerr}$  is supposed to be positive, while the  $n_{kerr}$  obtained in this work is negative. Such negative  $n_{kerr}$  value has profound physics behind. As suggested in [31], the  $n_{kerr}$  is contributed from TPA effect, Raman effect, linear stark effect, and quadratic stark effect. For  $n_{kerr}$  obtained at relative long wavelength, fitting model implementing only TPA effect is sufficient. However, at short wavelength (~0.7 Eg photon energy), contribution from TPA effect is approaching zero and quadratic stark effect contributes significant negative phase change which in turn gives  $n_{kerr}$ . This explains why negative  $n_{kerr}$  was obtained in this work.



Fig. 2. Typical open aperture scanning curve obtained in this work. (a) Scan curve for (010) sample, (b) for  $(\overline{2}01)$  sample. (c) and (d), closed aperture Z-scan measurement of (010) and  $(\overline{2}01)$  samples, respectively.

| (010), $\vec{E} \perp$ [102] |                                        |       | $(\overline{2}01), \vec{E} \parallel [102]$ |                                        |       |
|------------------------------|----------------------------------------|-------|---------------------------------------------|----------------------------------------|-------|
| α <sub>TPA</sub> (cm/GW)     | n <sub>kerr</sub> (cm <sup>2</sup> /W) | R(µm) | $\alpha_{TPA}(cm/GW)$                       | n <sub>kerr</sub> (cm <sup>2</sup> /W) | R(µm) |
| 1.2                          | $-2.1 \times 10^{-15}$                 | 5.8   | 0.6                                         | $-2.9\times10^{-15}$                   | 5.7   |

Table 1. TPA coefficient, Kerr nonlinear refractive index obtained in this work for (010) and  $(\overline{2}01)$  samples. Beam diameter from fitting parameter is also shown.

There are several physical models that can be implemented to understand the higher optical nonlinearity at (010) plane [33–38]. Quantum mechanical approach [33,34] calculates third order susceptibility accurately but requires intensive computing resources. Therefore it is only utilized in simple crystal structures [34]. A simplified bond-orbital model developed in [35–38] successfully explained the optical nonlinearities for various kind of materials including metal-oxide crystals [38]. We employed this model in this work to qualitatively understand the anisotropic nonlinearity of (010) and  $(\overline{2} 01) \beta$ -Ga<sub>2</sub>O<sub>3</sub>. From bond orbital model, optical anisotropy of crystal is mainly contributed from bonding electrons between adjacent atoms [35]. While for other electrons that screening around individual atoms, the contribution to the optical anisotropy is less significant. As investigated comprehensively in [39],  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is constructed by two types of gallium ions and three types of oxygen ions shown in Figs. 3(a) and 3(b). Type I gallium ion Ga(1) is surrounded by a distorted tetrahedron of oxygen ions with atom distance from 1.80 A to 1.85 A (1.83 A in average), type II gallium ion Ga<sub>(II)</sub> is surrounded by a distorted octahedron with atom distance from 1.95 A to 2.08 A (2.00 A in average). On (010) plane of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, the bonds are not orderly orientated and therefore electrical field in (010) plane are more likely to interact with most of the bonds. However, on (201) plane, bonds between  $Ga_{(1)}$  and  $O_{(11)}$  are highly oriented along (010) direction. Such bonds have relative weak interaction with electric field polarized in (201)plane. The consequence is that the optical nonlinearity on  $(\overline{2}01)$  is relatively weaker than that on (010) plane.



Fig. 3. Schematic view for the arrangement of ions inside  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, different types of ions are marked out by numbers. (a) Schematic view for (010) sample, (b) for ( $\overline{2}$  01) sample.

We previously estimated TPA coefficients and Kerr nonlinear refractive index for GaN [19] at same wavelength. The TPA coefficient of (010) and ( $\overline{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> are ~10 and ~20 times smaller than that of GaN at 404 nm, respectively. Since the bandgap energy of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

and GaN are different, we compare their nonlinear optical coefficient at same relative photon energy which is defined as  $E_p/E_g$  (0.63 for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> tested at 404 nm). At  $E_p/E_g = 0.63$  relative photon energy, TPA coefficient of (010) and ( $\overline{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> samples are ~15 and ~30 times smaller than that of GaN. The high TPA coefficient observed in GaN might due to its exciton effects [22]. This result implies that  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> material is more capable to handle high optical power density applications in visible wavelength spectral range. Furthermore, Kerr nonlinear refractive index of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> are also 4–5 times smaller at 404 nm and 5–7 times smaller at same relative photon energy than that of GaN. For optical applications that requires critical coupling, e.g. coupling from bus waveguide to ring or disk resonators, Kerr effect modifies the coupling efficiency at high optical power density, especially in those high resonance quality factor resonators [20]. Therefore,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based resonators will exhibit extreme coupling stability under high power operation comparing with GaN based resonators.

Figure 4 represents the polarization dependences of transmission minimum of (010) and ( $\overline{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> during open aperture testing. Since  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has a monoclinic crystal structure (Fig. 1), 41 independent nonzero elements are required to fully describe its third order nonlinearity  $d_{il}$ . Therefore, it is very difficult and inconvenient to find explicit expression for  $d_{eff}$  using polarization angle and individual nonlinear component  $d_{il}$  [21,22,27,28]. To describe the in-plane anisotropic nonlinearity clearly, we use  $\Delta T_{max}/\Delta T_{min}$  in this work. Relative higher in-plane nonlinear optical anisotropy was found on ( $\overline{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> with  $\Delta T_{max}/\Delta T_{min}$  of 1.93 while (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> had a  $\Delta T_{max}/\Delta T_{min}$  of 1.29.



Fig. 4. Polarization dependence of minimum transmittance obtained in this work. (a) Polarization dependence for (010) sample, (b) for  $(\overline{2}01)$  sample.

Figure 5 shows the wavelength dependence of TPA coefficient using Eq. (4) for (010) and  $(\overline{2}01) \beta$ -Ga<sub>2</sub>O<sub>3</sub>. For (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>,  $E \perp$  has larger TPA coefficient that  $E \parallel$ . For  $(\overline{2}01) \beta$ -Ga<sub>2</sub>O<sub>3</sub>,  $E \perp$  has smaller TPA coefficient that  $E \parallel$ . Highest TPA absorption coefficient is observed in (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> when electric field is perpendicular to [102] direction, while lowest TPA coefficient is obtained on  $(\overline{2}01) \beta$ -Ga<sub>2</sub>O<sub>3</sub> when electric field is parallel to [102] direction. For each plane, the polarization dependence of TPA coefficient is a function of multiple physical parameters [38] such as bond iconicity, covalent radii, etc. It is extremely difficult to give a quantitative explanation and out of the scope of this work. Future experimental and theoretical studies are undergoing to clarify its polarization dependence. For both samples, the maximum TPA absorption occurs at ~360 nm wavelength. For wavelength above 360 nm, TPA coefficient decreases as wavelength increases. It can be attributed to the decreased excitation energy with increasing wavelength. While for wavelength below 360



nm, the TPA coefficient increase with increasing wavelength as the transition approaches its resonance wavelength.



Fig. 5. The estimated wavelength dependence of TPA coefficient for (010) and ( $\overline{2}$ 01) samples. " $E \perp$ " indicates that the electrical field intensity is perpendicular to [102] direction, while " $E \parallel$ " indicates that field intensity is parallel to [102] direction

# 4. Conclusions

We characterized the TPA coefficient and Kerr nonlinear refractive index of both (010) and  $(\overline{2} \ 01) \beta$ -Ga<sub>2</sub>O<sub>3</sub>. TPA coefficient of Ga<sub>2</sub>O<sub>3</sub> was found to be 10 to 20 times smaller than that of GaN at 404 nm. The Kerr nonlinear refractive index of Ga<sub>2</sub>O<sub>3</sub> was 4 to 5 times lower than that of GaN. Therefore, due to its ultra-low TPA coefficient and its small Kerr nonlinear refractive index,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has the potential to serve as a more efficient platform for integrated photonic applications in UV and visible spectral range. Furthermore, the optical nonlinearities of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is highly anisotropic due to the asymmetric crystal structure of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. These results can serve as guidelines for designing  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based integrated photonics system.

# 5. Acknowledgement

The authors thank Dr. Michael Gerhold of US Army Research Office for the helpful discussion. This work is supported by the Bisgrove Scholar Program from Science Foundation Arizona. We gratefully acknowledge the use of facilities within the LeRoy Eyring Center for Solid State Science and CLAS Ultra Fast Laser Facility at Arizona State University.