Photoconductivity & photoelectron emission of $LiGaO_2$ crystal excited in intrinsic absorption range

T

A. Trukhin*, L. Trinkler

Institute of Solid State Physics, University of Latvia, LV-1063, Riga, Latvia

Vacuum ultraviolet

ABSTRACT

The photoelectric response spectra were studied in a $LiGaO_2$ crystal. The obtained spectra were interpreted as the release and diffusion of charge carriers, as well as external photoemission of electrons. The charge carrier release starts from excitation with a photon with energy greater than the optical gap of the $LiGaO_2$ crystal (~6 eV). The efficiency of generation of charge carriers exponentially increases up to 8 eV with saturation beginning from 9 eV. The nature of the photoelectric response is attributed to the Dember effect corresponding to the higher mobility of electrons compared to holes. The low yield of the internal photoelectron in the range of the intrinsic absorption band at 6 eV is associated with its exciton nature. Above 9.5–10 eV, an additional re-sponse was revealed that was interpreted as external photoelectron emission with a threshold of about E_{th} = 10.1 ± 0.2 eV. The relative emission yield of electrons increases as $(h\nu - E_{th})^3$, which corresponds to indirect transitions between the valence and conduction bands. The emission of photoelectrons for the direct band-to-band transitions increases linearly with the photon energy and the corresponding threshold is defined as 12.7 ± 0.2 eV.

1. Introduction

$LiGaO_2$ (LGO) crystal is a material belonging to class of crystals with high degree of bonds ionicity. Among them are e.g. Al_2O_3 and SiO_2 exhibiting electronic excitations and defects of small radius. Excitons are usually observed in this class of crystals and measurement of photoelectric properties is used for distinguishing of exciton. Some data on optical properties are obtained for nominally pure samples (see, for example [1]). This is a wide-band material (E_g around 6 eV) with yet insufficiently experimentally studied electronic structure. The electronic structure of other wide-band dielectric materials has been previously studied using a comparison of photoelectric effects and photoluminescence excited in the intrinsic absorption region (see e.g. Ref. [2]).

The spectrum of intrinsic absorption of LGO was estimated in Ref. [3] by the method of ellipsometry. The existence of a relatively sharp absorption band at 6 eV with position of maximum as a function of light polarization was obtained. The absorption level in this band reaches values of about 10^6 cm^{-1}. Such characteristic is typical to the exciton absorption band. Assignment of the 6 eV absorption band to an exciton requires verification with a direct measurement of the photoelectric conductivity.

When a dielectric is illuminated with light, two electrical effects may be observed - external photoelectron emission and photoconductivity. The first phenomenon involves the movement of the released charge carriers along the volume of the dielectric, followed by the escape from the sample into the vacuum (the volume external photoelectric effect or photoelectron emission), [4]. It is possible to determine the depth of the valence band relative to the vacuum level on the basis of the spectral dependence of the quantum yield of the photoelectron emission. For the volume photoelectron emission, the spectral dependence of the quantum yield near the threshold is determined by the formula [5]:

$$Y \sim (h\nu - E_{th})^n, \quad (1)$$

where E_{th} is the threshold energy; $h\nu$ is a photon energy; n is the exponential factor, usually equal to 1 for direct transitions and 3 for indirect ones.

Gudden and Pohl [6] (see also [7]) were pioneers in the study of photoconductivity in insulators. They have introduced the concept of primary and secondary currents. The primary current is connected with the charge carriers released by the light inside the sample, but the secondary current is a reaction to the primary current. Thus, contact between insulator and electrodes can occur [8] after charge carriers releasing. Then the injection of charge carriers from the electrodes can

E-

lead to a strong increase in the concentration carriers in the insulator. Injected charge carriers make the picture of the observed phenomena more complicated.

The main processes that determine the internal photoelectric effect are the diffusion of charge carriers and their capture on traps. If there is a difference in the diffusion coefficients of electrons and holes, there occurs their spatial separation, resulting in generation of an electric field in the volume of the dielectric (the Dember field [9]). Then it is possible detect electric response under photoexcitation without ex-ternal electric field. This effect is called a photoelectric polarization, [10].

The photoelectric properties of LGO have not yet been studied in detail. As previously for others materials [2] the obtained photoelectric properties of LGO were compared with corresponding photo-luminescence data [1].

2. Experimental

A method for studying the photoelectric properties of an insulator used was described previously for silica in Ref. [11]. In fact, we used a similar scheme to study the photoelectric properties of LGO. The sample was glued with silver dag to the holder. An electrode made of silver dag on the other surface of the sample is connected to an electrometer. The dynamic capacitor electrometer VA-J-52 was used for measurements of photoelectric response. The electrometer data were read by an Agilent voltmeter connected to a PC. As the source of excitation light there was used a deuterium discharge lamp with MgF_2 window (high-brightness light unit VUV Lighting unit Hamamatsu L10366 series with limited spectral range below ~10 eV) conjugated with interference filters or with a vacuum monochromator 0.5 m Seya-Namioka type, equipped with a spherical grating (2400 l/mm). Shutters were used to provide Π-shaped light pulses. Another light source was a duoplasmatron without windows with a discharge in hydrogen [12]. When using differential vacuum pumping in a monochromator, the system provides light up to 18 eV.

The studied LGO crystal was grown by Czochralski method.

Some experiments were carried out using an excimer laser ArF (6.4 eV or 193 nm).

3. Results

Several different experiments on photoelectric response measure-ments were done. Fig. 1 shows the pulses of the photoelectric response when the sample is excited with light through interference filters. The interference filters were chosen so that their transmission corresponds to excitation bands of luminescence in LGO (200, 225 and 250 nm for 280, 330 and 700 nm emission, correspondingly [1]). For 200 nm light,

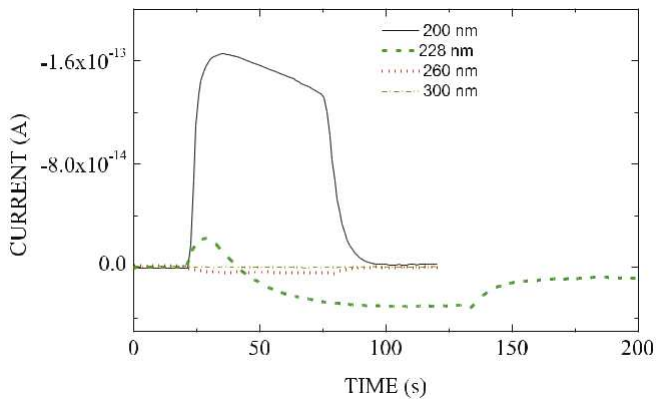

Fig. 1. Photoelectric response of LGO obtained for light pulses using a deu-terium lamp through interference filters. The excitation is performed through a window made of quartz glass. T = 293 K.

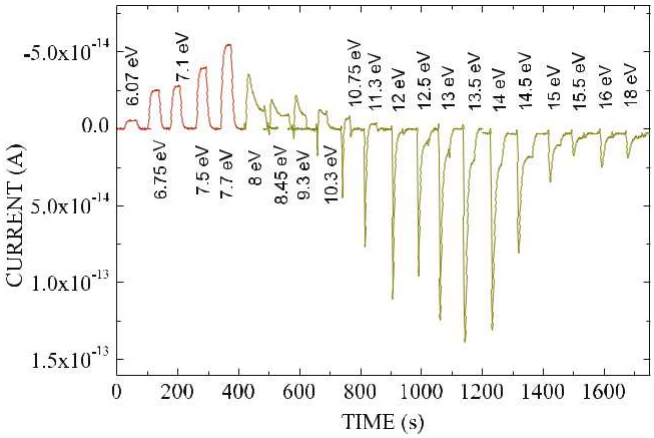

Fig. 2. The timing diagram of the photoelectric response pulses for different excitation photon energies. T = 293 K. Negative pulses in the range of 6–10.75 eV mainly correspond to the Dember effect with a higher electron mobility. Positive pulses in the range of 8.45–18 eV correspond to photoelec-tron emission, which provides positive charging of the sample. The shape of the pulses is determined by the space charge limited current and the unresolved mixture of signal intensities due to the Dember effect and photoelectron emission. The influence of the current limited by the space charge is insignif-icant in the case of the Dember effect, probably due to the high recombination rate of electrons and holes. The effect of current limiting space charge is large in the case of photoemission. The space charge in this case can be explained by the creation of a cloud of electrons near the surface, preventing the exit of the next electrons.

at which the sample is not transparent, the electrical response pulse shows a negative charge of the sample with a certain rise time, then some decrease during the light pulse. After ceasing of the light pulse, a current decay appears with time parameters similar to the initial rise. Thus, under irradiation with Π-shaped light pulses, the photoelectric response produces slightly distorted pulses of the Π-form. At 228 nm light irradiation the sample becomes more transparent, and the pulse of the electrical response starts from the negative sign, and then comes to a positive sign. The beginning and the cut of the light pulse are both with some delay of photoelectric response. At 260 nm irradiation the response changes to a positive sign, but the response intensity drops strongly and disappears at 300 nm irradiation.

Fig. 2 shows the photoelectric response pulses of an LGO crystal measured using two different light sources. In the case of irradiation by the deuterium lamp with MgF_2 window, the photoelectric response has a shape of slightly distorted by Π-shaped pulses, as in the case of an interference filter. Under irradiation with the windowless light source, the pulse shape strongly deviates from the Π-shape and has a more pronounced damped part of the pulse. At energies above 10 eV, an additional component of the reaction appears. Its sign is opposite, which means positive charging of the sample. Its intensity increases with increasing photon energy. As a result, a complex shape of the re-sponse pulse is formed. One part is the same as for the lower energies and another part is an additional positive pulse. For high-energy pho-tons above 12 eV, a part of the pulse having a negative sign is sup-pressed by a positive pulse. We interpret the positive pulse as a phe-nomenon of external photoelectrons emission. Photoelectrons leave the sample and make it charged positively. A sharp form of external pho-toemission pulses appears due to generation of a space charge by a cloud of electrons on the illuminated surface of the sample. The un-distorted Π-shape of pulses of the internal photoelectric response at energies lower than 7.7 eV (Fig. 2) indicates that there is no effective generation of a space charge inside the sample. That is, we did not observe the effects of limited current with space charge, and therefore in the LGO crystal we have an effective recombination of the released charge in the bulk, whereas for photoelectron emission, a cloud of

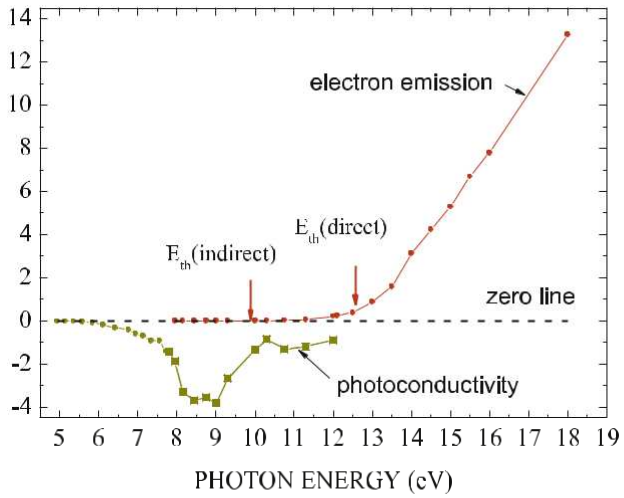

Fig. 3. The photoelectric response spectra of a $LiGaO_2$ crystal. The amplitudes corresponding to photoconductivity were assumed to be the amplitudes of ne-gative pulses, and the amplitudes of positive pulses shown in Fig. 2, as relative values of the quantum yield of electron emission. Then these intensities were normalized according to the intensity of the exciting light.

electrons near the surface provides the effect of a current limited by a space charge.

The intensities of the pulses of the photoelectric response normal-ized to the intensities of the exciting light versus photon energy are shown in Figs. 3 and 4. The spectrum of a positive signal was inter-preted as the external photoelectron emission corresponding to ex-pression (1), allowing determining the position of the threshold. The low-energy part of the curve can be well approximated by expression

(1) with n = 3, and therefore the corresponding threshold (10.1 ± 0.2 eV) has the character of indirect transitions. For n = 1, the threshold of direct transitions is obtained (12.7 ± 0.2 eV, Fig. 4). The spectrum of internal release of charge carriers, that is the negative part in Fig. 3, corresponds to the Dember effect, when electrons are more

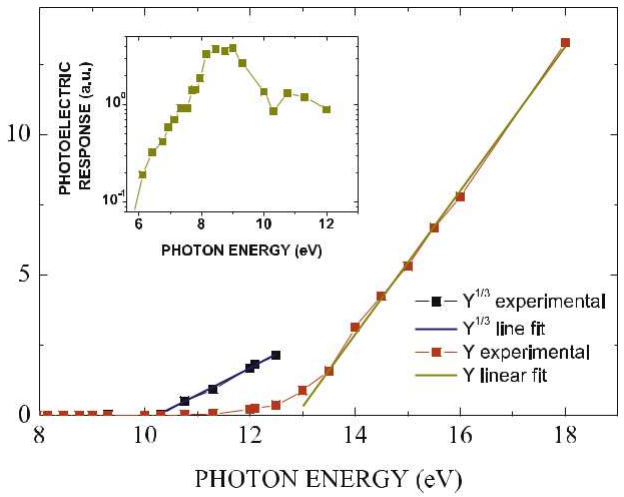

Fig. 4. External photoelectron emission spectra approximation with expression (1). Spectrum with straight part corresponds to emission due to direct transi-tions. Crossing of this line with abscissa gives value of threshold for direct transitions equal 12.7 ± 0.2 eV. Part of spectra straitened with $Y^{1/3}$ corre-sponds to indirect threshold of photoelectron emission with value 10.1 ± 0.2 eV. Inset provide photoconductivity spectrum taken from negative part of Fig. 3. It was multiplied with −1 and presented in semilog scale. Such presentation shows exponential growth of photoconductivity in the part of spectra 6–7.5 eV.

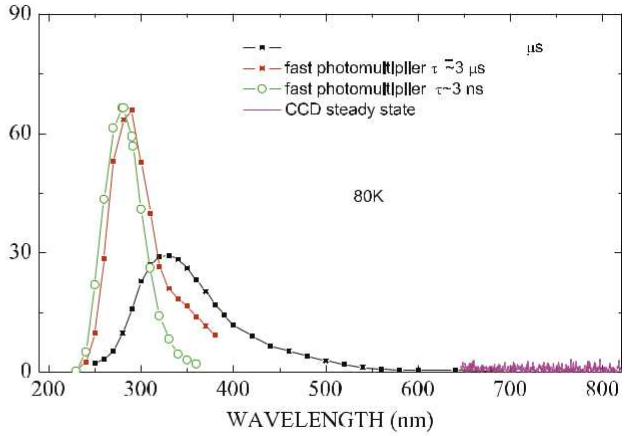

Fig. 5. Time resolved luminescence spectra of $LiGaO_2$ crystal excited with an ArF laser (measurements at 80 K).

mobile than holes. The efficiency of charge release increases ex-ponentially with increasing photon energy, starting with the optical gap at about 6 eV, Fig. 3 and inset of Fig. 4.

The photoluminescence data were published earlier [1,13] and are now presented for comparison with photoelectric data. The photo-luminescence spectra of the LGO crystal under excitation with an ArF laser (193 nm or 6.4 eV) are shown in Fig. 5. The spectrum in steady-state mode shows the main band at 280 nm. Time-resolved spectra show a band with a maximum at 275 nm (4.5 eV) for decay time in the ns time interval; 280 nm (4.4 eV) for the decay time in a time interval of μs and 330 nm (3.75 eV) in a time interval of about 80 μs. In addition to detecting the fast decay of the photoluminescence shown in Fig. 5, a long duration afterglow (tens of seconds) was observed for various excitation energies. The spectrum of the afterglow creation is shown in Fig. 6 with large filled squares. The excitation spectra of the photo-luminescence are shown in Fig. 6, measured in steady state using a vacuum monochromator for selecting excitation light and interference filters for selecting the PL band. Fig. 6 also shows the measured pho-toconductivity spectrum from Fig. 3, multiplied by −1 and normalized to 1.

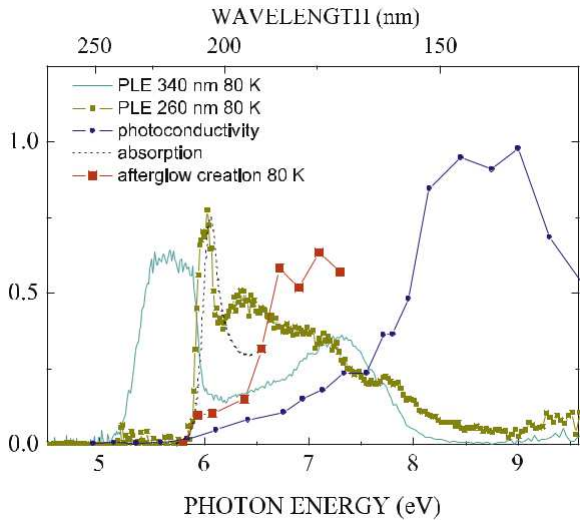

Fig. 6. Comparison of the obtained photoconductivity spectrum with the ab-sorption spectrum [3] and the excitation spectra (PLE) of the photo-luminescence [13] PLE bands of 280 nm and 340 nm (obtained using inter-ference filters), as well as with the afterglow creation spectrum. Good agreement is observed between the photoconductivity spectra and the after-glow creation spectra.

4. Discussion

Fig. 6 compares the main data associated with the LGO crystal. It is seen that in the area of the intrinsic absorption band at 6.06 eV (this band absorption coefficient is calculated from the measurements of n and k performed in Ref. [3], where details of this band property could be found). The absorption coefficient reaches values of about 10^6 cm^{-1} at band maximum [13]. The measurements in Ref. [3] were carried out in a narrow photon energy range, and the absorption spectrum for higher energies is not yet known. In the region of this band, the photoconductivity level is low. Therefore, this band can be attributed to the creation of an exciton. In addition, the pure re-combination process, determined from the luminescence afterglow, shows minimal efficiency in the band at 6.06 eV, see Fig. 6, a curve with large closed squares. This also indicates the creation of an exciton at 6 eV. Presumably, the spectral region with an exponential increase in photoconductivity (inset in Fig. 4) corresponds to a charge release, also associated with the formation of excitons at a higher energy and sub-sequent dissociation of excitons. Accordingly, the entire region with an exponential increase in photoconductivity corresponds to the formation of excitons. The situation is similar to the creation of many different excitons and the observation of the exponential growth of photo-conductivity in a wide photon energy range in crystalline quartz [2,11]. In the case of quartz, many different excitons were resolved in a wide spectral region. In the case of LGO, a similar situation is possible, al-though there is not enough data. As the next step, an absorption spectrum is required for a wider photon energy range. In the measured photoconductivity spectra, all excitation photons are absorbed. In the case of purely band-to-band transitions, the number of released carriers should be proportional to the number of absorbed photon, and photo-conductivity should be independent of energy. In practice, we observe an exponential increase in photoconductivity. Consequently, there is no case of purely band-to-band transitions. In LGO, we have a similar case observed for crystalline quartz [2,11], where various excitons with different dissociation efficiencies provide an exponential increase in photoconductivity, measured in the primary current mode [7].

The definition of the energy distance between the top of the valence band and the bottom of the conduction band in such a situation the exponential growth of photoconductivity is not clearly defined. Only estimates are possible. The lower limit that coincides with the optical transmission threshold is not the width of the band gap. The observed recombination processes can be associated with the dissociation of excitons on defects and in phonon-assistant process. The value of the upper limit of the band gap can be defined as energy of the sharp in-crease in photoconductivity at 7.5 eV, Figs. 3 and 4. The region of band-to-band transitions begins above $E_g \sim$ 7.5 eV, since the photo-conductivity starts an increase with saturation at about 8 eV. Thus, we could roughly estimate the difference in the energy bands by this amount. In this case, from the value of the indirect transition for the external photoemission E_{th} (indirect) = 10.1 eV, we could estimate the affinity of electrons to be equal to 2.6 eV for LGO crystal (E_{th} (indirect)-E_g). This value is reasonable compared with other insulators. The electron affinity is high for semiconductors (for Si it is about 4.5 eV) and small for dielectrics [14]. Therefore, it supports our estimate of the energy gap for a LGO crystal.

The luminescence band at 280 nm is excited only in the intrinsic absorption region (Fig. 5). Earlier, the nature of this band was attrib-uted to the recombination of donor – acceptor pairs belonging to host material [1,13]. The maximum of this excitation band is close to in-trinsic absorption band at 6.06 eV (Fig. 6), which we associated with the creation of an exciton. The PL band at 280 nm can be assigned to a self-trapped exciton (STE). At the same time, the observation of the luminescence band at 280 nm in the afterglow and the TSL [13] below 60 K indicates self-trapping of charge carriers. Self-trapped electrons and holes can be considered as donor-acceptor pairs, previously de-scribed in Ref. [13]. It was assumed that this luminescence band is due to tunneling recombination of donor – acceptor pairs (Ga with a trapped electron and O with a trapped hole) with a random separation distance. Very close pairs are identical with STE. Role of lithium states in conduction band was presumed [15] small. Self-trapped excitons, which are identical to the nearest donor – acceptor pairs, mainly con-tribute to the luminescence band at 280 nm.

Another band at 330 nm, which is excited in the region of optical transparency (Fig. 6), was attributed to recombination luminescence with the participation of intrinsic defects, presumably, a lithium ion in the interstitial position Li_i^0 [13].

5. Conclusions

The photoelectric response was observed for a $LiGaO_2$ crystal. This response consists of two effects: the internal release of charge or pho-toconductivity and the photoelectron emission from the crystal into vacuum. The photoconductivity threshold begins with the onset of in-trinsic absorption (~6 eV), but its efficiency increases exponentially with the photon energy. The relative level of charge release in the range of the intense absorption band (~10^6 cm^{-1}) at ~6 eV is low, and this character of the band is explained by the creation of an exciton by light. The upper limit of the band gap is estimated about 7.5 eV. The external photoelectron emission with a threshold for an indirect transition is E = 10.1 ± 0.2 eV. The threshold of the photoelectron emission of direct transitions is determined as 12.7 ± 0.2 eV. The affinity of elec-trons is estimated by 2.6 eV.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influ-ence the work reported in this paper.

Acknowledgement

This research is funded by the Latvian Council of Science, project “Research of luminescence mechanisms and dosimeter properties in prospective nitrides and oxides using TL and OSL methods], project No. lzp-2018/0361.

References

[1] L. Trinkler, A. Trukhin, B. Berzina, V. Korsaks, P.S. Cajev, R. Nedzinskas, S. Tumenas, M.M.C. Chou, L. Chang, C.-A. Li, Opt. Mater. 69 (2017) 449–459.
[2] A. Trukhin, J. Non-Crys. Sol. 149 (1992) 32–45.
[3] S. Tumenas, P. Mackoni, R. Nedzinskas, L. Trinkler, B. Berzina, L. Chang, M.M.C. Chou, Appl. Surf. Sci. 424 (2017) 837–842.
[4] W.E. Spicer, Photoemission and band structure, Survey of Phenomena in Ionized Glasses. Vienna, 1968, pp. 271–289.
[5] G.W. Gobeli, F.G. Allen, Phys. Rev. 127 (1962) 141–151.
[6] B. Gudden, R. Pohl, Uber lichtelektrische leitffafigkeit von Diamanten, Zeit. f. Phys. 3 (1920) 123–124.
[7] N. Mott, R. Gurney, Electronic Processes in Ionic Crystals, Oxford, (1958).
[8] M. Lampert, P. Mark, Current Injection in Solids, Academic press N.-Y and London, 1970.
[9] H. Dember, Phys. Z. 32 (1931) 554–556.
[10] I. Vitol, I. Tale, Institute of Physics and Astronomy of the Academy of Science of Estonian SSR, , Nr10 (1959) 220-238..
[11] A. Trukhin, Phys. Solid State 86 (1978) 67–75.
[12] J.A.R. Samson, Techniques of Vacuum Ultraviolet Spectroscopy, John Wiley & Sons, Inc., New York, London • Sydney, 1967.
[13] L. Trinkler, A. Trukhin, Mitch M.C. Chou, Latv. J. Phys. Tech. Sci. N 6 (2018) 4–12.
[14] P. Dorenbos, Phys. Rev. B 87 (2013) 035118-8.
[15] N.W. Johnson, J.A. McLeod, A. Moewes, J. Phys. Condens. Matter 23 (2011) 445501 (6pp).

Institute of Solid State Physics, University of Latvia as the Center of Excellence has received funding from the European Union’s Horizon 2020 Framework Programme H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART²