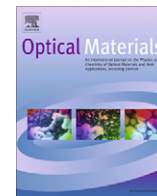


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The electron beam induced short lived absorption in PLZT optical ceramics

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ABSTRACT

The short lived absorption induced by a pulsed electron beam in the lead–lanthanum–zirconate–titanate (PLZT) optical ceramics was studied. The measured absorption spectrum covers 1.1–2.9 eV energy range and consists of several strongly overlapping peaks. The rise of the absorption is delayed with respect to the excitation pulse, due to charge carrier migration before trapping at centers responsible for the absorption. The formation rate of absorption centers and decay rate of absorption depend on the photon energy. The kinetics of short lived absorption varies over spectrum and can be approximated with a stretched exponent. The stretched exponent parameters indicate that the local disorder of a matrix is similar around all absorption centers.

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1. Introduction

The quality of optical ceramics strongly depends on defect concentration since the defects are responsible for optical properties including additional absorption as well as light scattering by aggregates of point defects. The progress in optical ceramic production could be illustrated e.g. by yttrium–aluminum garnet optical ceramics which were produced of a very high quality, with the optical losses close to those known for single crystals, so that these ceramics are useable for active media for lasers [1]. The lanthanum modified lead zirconate–titanate (PLZT) optical ceramics is known as the material for electro-optical modulators, as well as for electrically driven light switches and other applications [2–4].

Therefore, the optical properties of this material are of interest and a number of papers were devoted to the study of electro-optical effect as well as optical absorption dependence on material synthesis and treatment parameters [5–7]. The well resolved absorption bands were observed for doped PLZT ceramics [8,9]. The irradiation of material by electron beam causes the change of charge density distribution. This change is responsible for a number of effects including appearance of induced absorption, enhancement of efficiency of second harmonic generation [10] and other.

The absorption changes induced by a pulsed electron beam in PLZT ceramics was described [11], it was found that the gradually growing absorption tail covers a wide range of the optical spectrum, with several overlapping absorption bands.

However, there were no atomistic studies of point defects in PLZT ceramics and the information on the optical absorption change due to recharging of pre-existing point defects is missing.

Therefore, we performed here the study of electron beam induced short lived absorption in PLZT optical ceramics.

2. Experimental

The PLZT 8/65/35 ($\text{Pb}_{0.92}\text{La}_{0.08}\text{Zr}_{0.65}\text{Ti}_{0.35}\text{O}_3$) optical ceramics were produced using a hot pressing method described elsewhere [12]. The rectangular shape samples $3 \times 6 \times 10$ mm were cut off from a large ceramic boule and the samples were polished to obtain optical grade surfaces. The conventional absorption spectrum was recorded at room temperature using LABOMED UVS-2800 spectrophotometer. The equipment for a short lived absorption registration consists of a pulsed electron beam source for excitation, a xenon flash for probing light, a grating monochromator MDR-2, a photomultiplier tube (PMT) at exit slit of monochromator and a digital storage oscilloscope TEKTRONIX TDS 5052B for PMT output signal display. The pulsed electron beam source operated at 270 kV accelerating voltage, pulse length (the full width at half-maxima) was 7 ns, an electron flux 10^{12} el/cm². Probing light pulse from a xenon flash has flat top within 10 μs which was used for a short lived absorption measurements. The probing light enters into a sample from one side, was totally reflected from the irradiated surface of a sample and come out from sample other side (Fig. 1). This measurement arrangement is necessary since the penetration depth of electrons in the sample is only ~ 0.2 mm and therefore the optical path of light is small in the normal direction to the irradiated surface. The configuration used allows us a longer optical path of probing light through the sample and therefore the more sensitive registration of absorption changes.

The probing light which passes the sample was collected on the entrance slit of monochromator and detected by PMT. The output signal from PMT was displayed on a digital storage oscilloscope.

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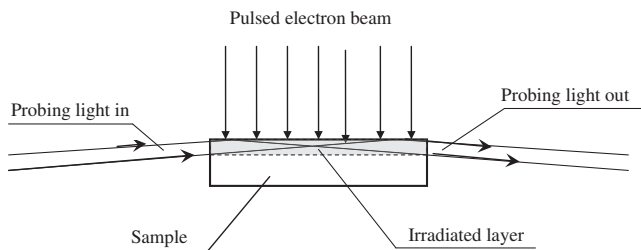


Fig. 1. Schematics of induced absorption registration.

The electron beam pulse hits the sample at the moment when an initial part of the probing light pulse flat top passes a sample. The registration of light intensity changes during the irradiation pulse as well as after it was performed and these data were used for optical density changes calculation (Fig. 2) at the fixed wavelength selected by monochromator, as the result we obtain the absorption kinetics at the fixed wavelength.

The set of absorption kinetics obtained for a number of fixed wavelengths was used for constructing the absorption spectra at different delay times with respect to the beginning of the electron beam pulse. The measurements were performed at room temperature (RT).

3. Results and discussion

The conventional absorption spectrum (Fig. 3) does not show any bands within the 1.1–3.0 eV energy range, consequently, there exist no well separated defects (absorption centers) responsible for absorption in this range. However, the gradual decrease of the absorption coefficient below 2.9 eV might be due to defects contribution, since the band-gap in PLZT is estimated to be ~ 3.35 eV [2,13].

The conventional absorption data show that the pulsed electron beam induced absorption changes could be studied below 2.9 eV. The short lived absorption spectra measured at RT at different delay relative to the electron pulse are shown in Fig. 4.

The spectrum with 30 ns delay reveals at least three poorly resolved bands peaking at ~ 1.3 ; 1.7 and 2.1 eV. However, a number of overlapping absorption bands might be larger. The spectrum at 90 ns delay reveals the main peak at ~ 2.3 eV and a shoulder at ~ 2.5 eV. The optical density within ~ 2.3 –2.7 eV region at 90 ns de-

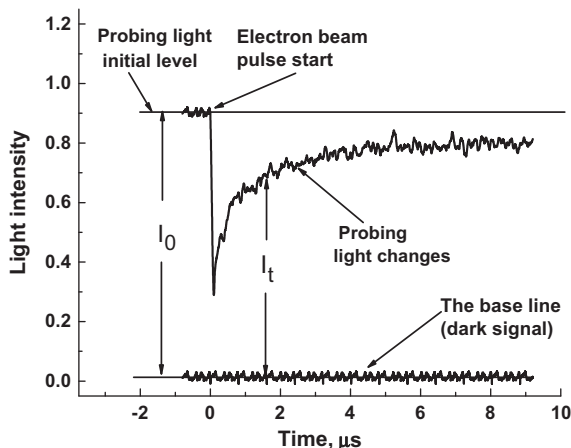


Fig. 2. The scheme explaining data processing: I_0 – the average intensity of probing light at flat top of pulse; I_t – the probing light intensity at time t ; The optical density D_t was calculated as $D_t = \log(I_0/I_t)$ and used as the characteristics of induced absorption.

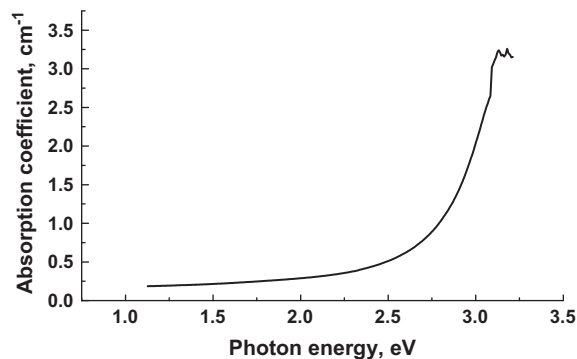


Fig. 3. Conventional absorption spectrum of PLZT optical ceramics.

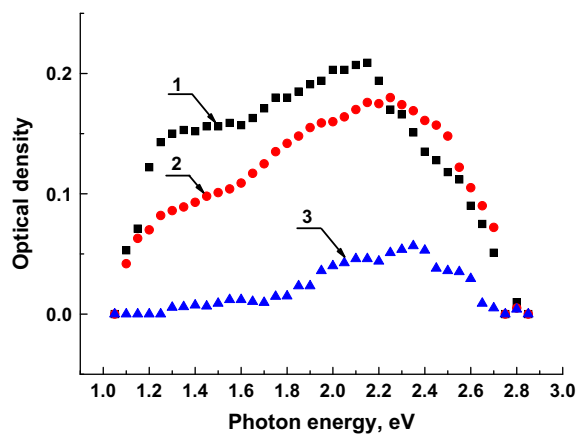


Fig. 4. Short lived absorption spectra of PLZT optical ceramics; 1 – at 30 ns delay; 2 – at 90 ns delay; 3 – at 8 μ s delay.

lay exceeds that at 30 ns delay (Fig. 4); therefore, rise of the absorption continues after excitation pulse. The shape of spectrum at 8 μ s delay seems close to that at 90 ns delay, however, the optical density at 8 μ s delay is low and thus the spectrum shape was not well defined. The comparison of spectra at 30 ns and 8 μ s delays shows that at 1.3 eV during 8 μ s decays close to 96% from the absorption initial level whereas at 2.35 eV it is close to 63% decay. The appearance of a shoulder at 2.5 eV in delayed spectrum as well as different decay rates over the spectrum clearly indicate that more than three absorption bands are overlapping.

There are several reasons for short lived absorption under electron beam excitation: (I) electron transition from the electronically excited states to higher excited levels; (II) a creation of new defects; (III) recharging of pre-existing defects; (IV) formation of intrinsic polarons.

Usually luminescence arises due to a radiative decay of excited states. The luminescence of PLZT was described in a number of papers [9,14–17]; however, this luminescence mainly is observed for doped PLZT ceramics. The luminescence of undoped PLZT ceramics is strongly quenched at RT. The luminescence in our experiments also was not observed within the 1.1–3.0 eV range. Therefore, the electron transition from some excited state to higher state cannot be responsible for the short lived absorption observed.

There are two mechanisms of new lattice defects creation: a knock-on mechanism and a sub-threshold mechanism. In the present study, the energy of electrons was 270 keV. The lightest element in PLZT ceramics is oxygen, therefore, the oxygen displacement is more probable in the knock-on process. However, for most oxides the threshold energy of electrons for oxygen displacement is well above 270 keV. For instance, the study of magne-

sium oxide [18,19] showed that the threshold energy of electrons for oxygen atom is close to 480 keV and the electron transfer only ~ 64 eV to oxygen atom during direct collision. The calculations for SrTiO₃ suggest the energy for oxygen atom displacement from a lattice site to be 50 eV [20] with the relevant energy of electrons above 350 keV. The estimate of possible new defects concentration created by an electron beam in our experiments showed that it cannot exceed $5 \times 10^{13} \text{ cm}^{-3}$ and this concentration is several orders of magnitude below our equipment sensitivity. Therefore, the possibility of new defect creation by knock-on mechanism was excluded.

The sub-threshold mechanism is based on the idea that nonradiative decay of electronic excitations can result in creation of the Frenkel defects pair in crystalline lattice [21]. A number of experimental results strongly confirm that this mechanism is responsible for defects creation in alkali halides [22] and, possibly, in some silver halides [23]. The lattice defect creation via the sub-threshold mechanism is very fast – the halide interstitial atom and anion vacancy were formed in a sub-nanosecond range [22]. Therefore, the creation of defects and appearance of corresponding absorption in our experiments can be completed within electron beam pulse without any delay. Since the observed absorption rise continues in our experiments after the end of the electron beam pulse (Fig. 4), the sub-threshold mechanism of defects creation was also excluded.

The possibility that recharging of existing defects takes place is the most realistic, since in any ceramic materials defect concentrations are rather large. These defects, as a rule, are responsible for distortion of the fundamental absorption edge – the extended tail to the long wave side appears without well resolved individual bands. The absorption tail in PLZT ceramics extends at least from 1.2 eV until 2.9 eV (Fig. 3). Therefore, it was concluded that the short lived absorption could arise due to recharging of pre-existing defects. Another possible origin of the short lived absorption is a polaron formation. The intrinsic (free) polarons are formed when an ion in the regular lattice site traps an electron or hole, e.g., in LiNbO₃ the Nb⁵⁺ traps an electron and Nb⁴⁺ is created [24,25]. The free electron polarons are known in other crystals [26–29] also, besides free polarons, the *bound* polarons were observed. The free polaron formation is a very fast process, since the charge (say, an electron) from the conduction band was trapped at the regular lattice site, however the bound polaron formation could be slower due to the migration of free polaron to the some distorted lattice site. On the other hand, in some materials the formation of bound polaron was observed in sub nanosecond range [24]. The electron polaron in PLZT ceramics could be represented as Ti³⁺ as well as Zr³⁺, both ions could be detected by the electron spin resonance (ESR) experiments. However, the ESR signal from Ti³⁺ was not observed [25], even in a doped PLZT, in which Ti³⁺ could be formed as a charge compensator. Therefore, the responsibility of electron polarons for short lived absorption in PLZT ceramic seems doubtful, however, we have no strong arguments for exclusion the contribution from bound polarons in the short lived absorption observed in our experiments.

The analysis of rise front kinetics shows its variation over the energy spectrum – at the long wave side the fast absorption rise is followed by its immediate decay, whereas at short wavelength side the more complicated absorption rise was observed. Therefore, the absorption kinetics increases for several wavelengths were compared (Fig. 5). The rise fronts of the short lived absorption starts simultaneously with the electron beam pulse, however, the absorption rise continues after the end of electron beam pulse. It was found that over a whole spectrum the induced absorption rise is delayed with respect to the excitation pulse. The absorption kinetics at spectrum short wave side consists of a fast initial rise followed by a slow decay. This could be interpreted as a result of

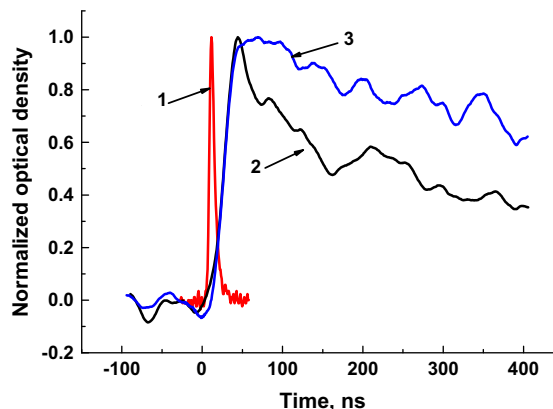


Fig. 5. Rise of absorption continues after end of excitation pulse; 1 – excitation pulse, 7 ns at half maxima, no more that 25 ns at the bottom; 2 – absorption kinetics at 1.45 eV; 3 – absorption kinetics at 2.25 eV.

charge carrier (or possibly, polaron) migration and multifold trapping at shallow traps before final localization at energetically more favorable position. The optical absorption due to these shallow traps could lie in the infrared region of spectrum and therefore was not detected in the present experiments.

Note that under electron beam irradiation electrons and holes were created and both carriers are trapped at defects and could be responsible for induced short lived absorption observed. However, the mobility of electrons and holes as well as possible traps depth for them could be quite different. The estimated time between the induced absorption rise beginning and moment at which the absorption reaches its maximum is not the same over a whole spectrum (Fig. 6). This dependence is step like: within 1.25–2.05 eV the rises of all kinetics are very close to each other, whereas within 2.05–2.25 eV significant longer rise times take place. Therefore, the relative fast rise of absorption at long wave side might be due to a migration and trapping of one kind charge (e.g. electrons) whereas a slow rise at short wave side – due to migration and trapping of other kind charge (e.g. holes).

The absorption decay kinetics was analyzed for several spectrum points. The kinetics shape was different over the spectrum, see Fig. 7. The same conclusion follows from spectra evolution also.

The absorption at 1.45 eV decays almost completely during $\sim 6 \mu\text{s}$, whereas that at 2.45 eV does not. The absorption decay at 1.45 eV cannot be approximated by a single exponent or single hyperbolic law. The approximation with a sum of the two expo-

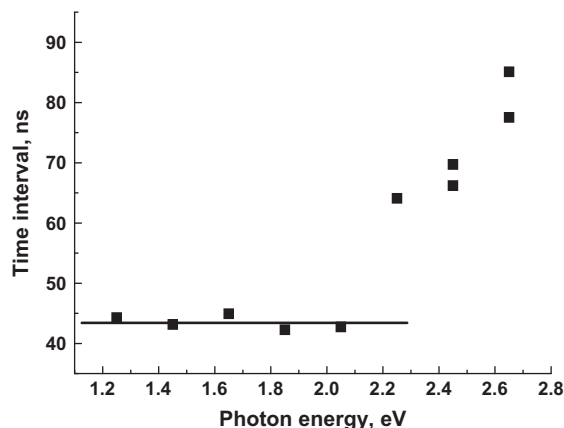


Fig. 6. Induced absorption rise – the time interval between absorption rise start and maximum position. Within 1.25–2.05 eV this time interval is close to 44 ns.

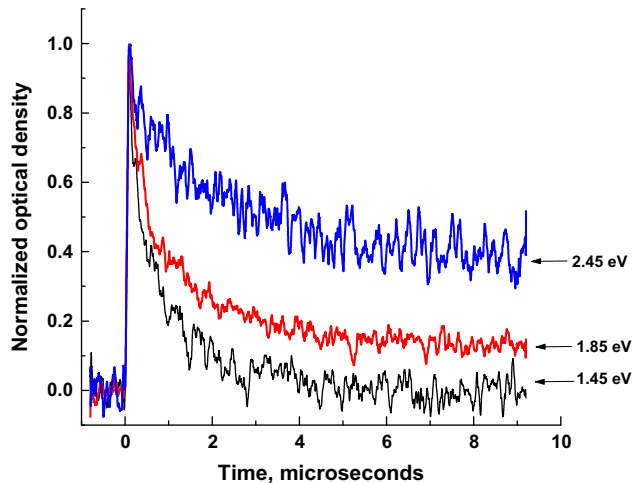


Fig. 7. Short lived absorption decay kinetics at three positions.

nents fails also. It is well known that ceramics, including PLZT, are disordered materials. The centers responsible for luminescence in disordered materials have certain distribution of the excited state lifetimes and luminescence decay can be well approximated by stretched exponent [30]. We suggested that a similar approximation could hold also for centers responsible for a short lived absorption in disordered materials. Thus, the stretched exponent model was used for absorption decay in PLZT ceramics:

$$D = D_0 \exp\{-(t/\tau)^\beta\}, \quad (1)$$

where D is optical density at time t , D_0 the optical density at $t = 0$, and β is stretching constant.

The first step was determination of β . The experimental results were plotted in the coordinates $\ln(\ln D_0/D)$ and $\ln(t)$. The decay kinetics in these coordinates can be approximated by the straight line from which the β estimated. The data within 0.05–8.5 μs for absorption kinetics at 1.45 eV were used. Since the absorption decay approximation was carried out, the D_0 was set close to the maximal value of absorption and in accordance with Eq. (1) the time corresponding D_0 is $t = 0$. The corresponding results are shown in Fig. 8. The straight line fitting seems good; hence the short lived absorption decay could be analyzed using the stretched exponent model.

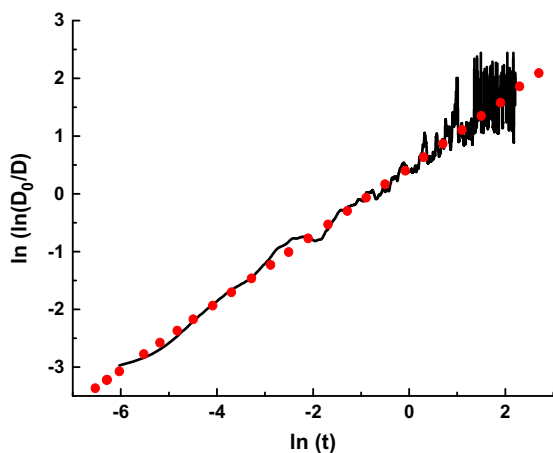


Fig. 8. Short lived absorption decay at 1.45 eV, experiment – the line, the approximation – symbols representing a straight line. The relevant parameter $\beta = 0.59$ was obtained.

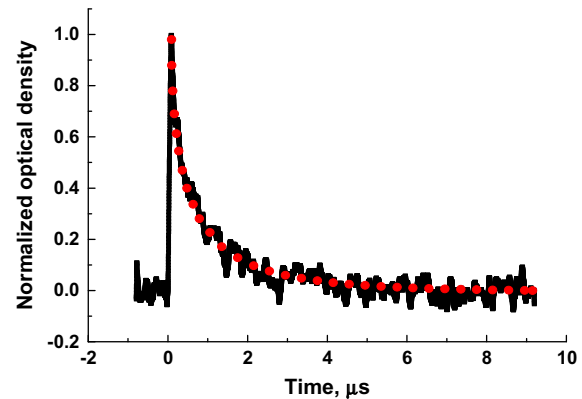


Fig. 9. The 1.45 eV absorption decay approximation with stretched exponent. The line – experimental results, the symbols – approximation with stretched exponent.

The parameter $\beta = 0.59$ was estimated in Fig. 8, another estimate gave parameter $\tau = 0.48 \mu\text{s}$. These parameters were used for a comparison of the model and experimental data in Fig. 9. The model fits experimental data good, therefore, one can conclude that the centers responsible for the short lived absorption at 1.45 eV have not well defined surrounding and this is a reason for complicated decay kinetics. The approximation of the decay part of absorption kinetics at 1.85 and 2.45 eV with stretched exponents also gave good results.

However, some constant background additional to the stretched exponent was necessary for these kinetics approximations:

$$D = D_0 \exp\{-(t/\tau)^\beta\} + D_{\text{background}} \quad (2)$$

This background indicates additional slow process. Unfortunately, the technical limitations of our equipment did not allow us to measure the longer kinetics and to study the details of slow absorption decay. However, the good approximation of absorption decay at 2.45 eV with the stretched exponent (containing the time independent background) could indicate possible presence of stable recharged defects in PLZT optical ceramics.

The calculated parameter β is similar for all kinetics, unlike the mean decay time τ . The parameter β characterizes the distribution function of the decay time τ . The close value of β indicates that this distribution functions is similar or even the same for all short lived absorption centers. The distribution function of τ depends on the structure disorder around centers. Hence, the disordering could be similar around all centers responsible for short lived absorption observed. Moreover, the specific value $\beta = 0.6$ was suggested in the specific case of the short range disordering [31].

4. Conclusions

The short lived absorption due to recharging of pre-existing defects was induced in PLZT ceramics by a pulsed electron beam. Several overlapping absorption bands cover the energy range 1.1–2.8 eV.

The rise of the induced absorption is delayed with respect to the end of the excitation pulse, indicating at a possible migration of charge carriers before trapping. The observed difference in the delay of absorption rise over an energy spectrum was probably due to mobility differences for electrons and holes.

The decay rate of short live absorption also differs over the spectrum and can be approximated by the stretched exponent. The stretched exponent parameters indicated that the local disordering is similar around centers responsible for short lived absorption.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.optmat.2012.12.029>.

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