

A pulsed optical absorption spectroscopy study of wide band-gap optical materials

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ABSTRACT

The paper presents the results of a study on the formation and evolution of short-lived radiation-induced defects in wide band-gap optical materials with the mobile cations. The spectra and decay kinetics of transient optical absorption (TOA) of radiation defects in crystals of potassium and ammonium dihydro phosphates (KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$) were studied by means of the method of pulsed optical absorption spectroscopy with the nanosecond time resolution under excitation with an electron-beam (250 keV, 10 ns). A model of electron tunneling between the electron and hole centers under conditions of the thermally stimulated mobility of one of the recombination process partners was developed. The model describes all the features of the induced optical density relaxation kinetics observed in nonlinear optical crystals KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ in a broad decay-time range of 10 ns–10 s after the pulse of radiation exposure. The paper discusses the origin of radiation defects that determine the TOA, as well as the dependence of the decay kinetics of the TOA on the temperature, excitation power and other experimental conditions.

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1. Introduction

Crystals of lithium borates (LiB_3O_5 (LBO), $\text{Li}_2\text{B}_4\text{O}_7$ (LTB), $\text{Li}_6\text{Gd}(\text{BO}_3)_3$ (LGBO)) and dihydro phosphates of potassium and ammonium (KH_2PO_4 (KDP), $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP)) are wide bandgap optical materials containing mobile cations. These compounds are studied intensively in recent years, both in terms of fundamental properties, and in terms of their practical applications as optical materials operating in a broad spectral range from the visible to the vacuum ultraviolet region. These materials are widely used in nonlinear and integrated optics, in laser technology, as well as they are used as detectors and transformers of ionizing radiation. Despite the differences in chemical compositions, these materials are combined a number of common properties. They have low symmetry of the crystal lattices and complex elementary cells. All these compounds contain the boron–oxygen or dihydrogen phosphate anionic groups. A distinctive feature of these compounds is the sharp contrast between the strong covalent bonds inside the anionic groups and the relatively weak ionic bonds between cations and the anionic group.

The presence of a weakly bound sublattice of cations in combination with the rigid anionic framework should seriously affect on the electronic excitations dynamics and the peculiarities of radiation defects creation. This problem is acute for the case of

the lightweight mobile cations of small radius in crystals of lithium borates, potassium and ammonium dihydro phosphates. However, despite the obvious importance of this phenomenon, a systematic study of the formation and evolution of short-living radiation-induced defects in these crystals was not carried out before our research. Especially it concerns the nanosecond time-range. Only few works were known in this field. Davis et al. have found that irradiation of the KDP crystal by the powerful (GW cm^{-2}) 266 nm laser pulse at room temperature results in formation of a broad band of transient optical absorption (TOA), which overlaps a large portion of the visible and the near ultraviolet region [1]. Marshall et al. have performed a semi-quantitative measurement of the TOA decay kinetics in the KDP crystal and they estimated also the effect of TOA on generation of the fourth-harmonics in this crystal [2]. Pirogova et al. have measured the TOA of the KDP crystal under excitation by an electron beam of microsecond duration [3]. We have previously investigated the TOA of crystals with a sublattice of mobile lithium (LTB [4], LBO [5], LGBO [6,7]) and hydrogen (ADP and KDP [8]) cations. For these crystals it has been experimentally revealed that the TOA decay kinetics in the time-range from 10 ns to 10 s was controlled by the electron tunneling under conditions of the thermally stimulated cation mobility. However, a detailed quantitative study of the electron tunneling decay kinetics under conditions of cations mobility in these crystals has not yet been carried out.

The main goal of this work is a study of the electron tunneling decay kinetics in terms of cations mobility. In this paper we will concentrate on the mathematical modeling in comparison with

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experimental results on TOA of crystals ADP and KDP in the visible and ultraviolet regions of the spectrum under excitation by an electron beam of nanosecond duration.

2. Experimental details: technique and results

In the present work, we have examined the KDP and ADP crystals of high optical quality grown at the Issyk-Kul State University (Karakol, Kyrgyzstan) [9]. The samples were plane-parallel transparent plates measuring $6 \times 5 \times 1 \text{ mm}^3$.

The experimental setup and the main characteristics of the luminescence and absorption spectroscopy with a nanosecond-scale time-resolution employed are described in considerable details in Ref. [10]. The electron-beam accelerator had the following parameters: average electron energy was 0.25 MeV; pulse duration, which is adjustable in the range of 3–15 ns, was 10 ns; current density in the pulse was 1000 A cm^{-2} , and the maximum energy density of a pulse was 160 mJ cm^{-2} . The pulse energy density used for excitation was usually either 23% or 12% of the maximum level.

Registration system recorded the temporal behavior of the optical density $D(t)$ after exposure of a crystal to a radiation pulse at the time moment $t=0$. The optical density was expressed by $D(t) = \log_{10}(I_0/I(t))$ where I_0 is the intensity of a probe light transmitted through the crystal before irradiation, and $I(t)$ is the temporal behavior of the probe light intensity after exposure to a radiation pulse. After each pulse, we checked the relaxation of the optical density until the initial level, to ensure no permanent damage to the crystal.

Fig. 1 presents the time-resolved TOA spectra of ADP and KDP measured immediately after the termination of the excitation pulse and $10 \mu\text{s}$ later. The spectra of both crystals have a similar structure and consist of partially overlapping bands of Gaussian shape in the energy region of 1.5–5.5 eV. All the parts in the time-resolved TOA spectra decay homogeneously over the examined spectral region, reproducing the original shape of the spectra. The TOA decay kinetics will be discussed in Section 4, here we only note that within about 100 s after each pulse of radiation, we ob-

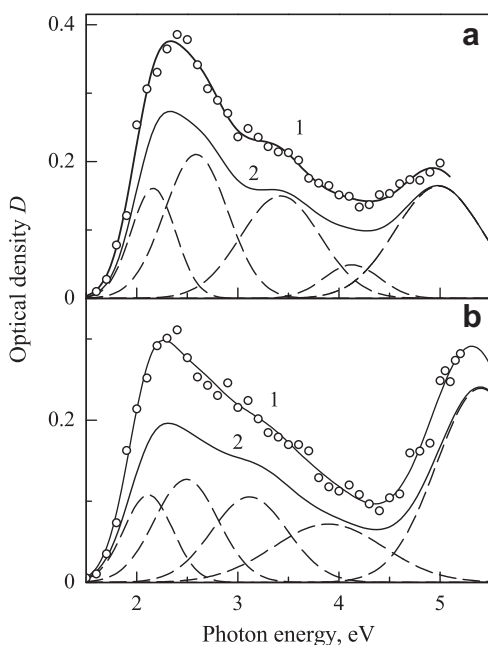


Fig. 1. TOA spectra of ADP – (a) and KDP – (b) measured at 290 K immediately after the end of the excitation pulse – (1) and $10 \mu\text{s}$ thereafter – (2). Circles are experimental data and solid lines are fitting by a sum of Gaussians.

served a complete recovery of the initial optical density of the crystal. This indicates a lack of permanent damage to the crystal during the spectroscopic measurements. In fact, the spectroscopic measurements require only 10–100 pulses of radiation, whereas the permanent damage to the crystal occurs at a much larger number of radiation pulses, see e.g. [11].

3. Theory and modeling

Let us consider a system consisting of two types of defects. The first group (*A*-type defects) consists of the trapped hole centers in the form of a cation vacancy captured an additional hole. The second group (*B*-type defects) includes the trapped electron centers in the form of a mobile interstitial cation captured an electron. Tunneling electron transfer between *B* and *A* defects leads to their disappearance as a result of recharging. It is known [12] that in general case the kinetics of the electron tunneling in a system of mobile reagents can be described by the kinetic Eq. (1) for the correlation function of dissimilar defects $Y(r, t)$. In the linear approximation to describe the recombination process dynamics for two types of defects $A + B \rightarrow 0$ it is possible to consider only the macroscopic concentrations of these defects (n_A, n_B) and the correlation functions of dissimilar defects $Y(r, t)$.

$$\frac{\partial Y(r, t)}{\partial t} = \nabla D_{AB} \nabla Y(r, t) - W(r) Y(r, t), \quad (1)$$

where D_{AB} is the relative diffusion coefficient, m^2/s ; r is interdefect distance, m ; t is decay time, s ; W is probability of the defect disappearance in recombination process, s^{-1} . For distant reactions in particular electron tunneling, we have the equation

$$W(r) = W_0 \exp(-r/a_B), \quad (2)$$

where a_B is half the Bohr radius of the wavefunction of the electron center and W_0 is a constant. For contact reactions the alternative mechanism of defect disappearance has the probability

$$W(r) = W_0 \Theta(r - r_0), \quad (3)$$

where Θ is the Heaviside step function and r_0 is the annihilation radius.

The initial and boundary conditions for this equation: $Y(r_0, t) = 0$; $Y(\infty, t) = 1$; $Y(r, 0) = 1 + f(r)/n_0$, where n_0 is the initial concentration of defects; $f(r) = (1/b) \exp(-r/b)$ is the spatial distribution within the pairs of defects as the exponential function of the relative distance, r ; b is half the mean distance between defects. The $f(r)$ function should be normalized:

$$\int_0^\infty f(r) dr = 1. \quad (4)$$

The time-dependent reaction rate constant is governed by the equation:

$$K(t) = \int_V W(r) Y(r, t) dV. \quad (5)$$

Bimolecular stage of interaction of defects, i.e. recombination between different pairs of defects, can be described by the kinetic Eq. (6) for the macroscopic concentrations

$$\frac{dn_A(t)}{dt} = -K(t) n_A(t) n_B(t). \quad (6)$$

The solutions of Eqs. (1) and (6) were performed numerically using the Crank–Nicholson finite-difference scheme in a spherical coordinate system. This finite-difference scheme has a better convergence, but each step requires the solution of three-point finite-difference equations. In the present work the equations were solved numerically using the software [13].

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