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Radiation effects in $Li_2B_4O_7$ oxide crystals

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Abstract

The lithium tetraborate single crystal has been irradiated by neutrons and the optical properties of these crystals are studied. Irradiation induces optical absorption bands at 42 000, 33 000, and 20 000 cm^{-1}. The intensities of these bands depend on the energy of the neutrons, on the irradiation temperature, and on the presence of an external electric field. An applied electric field induces the displacement of charged particles, creating the micrononhomogeneous regions in the crystal leading to a decrease of the intensities of the absorption bands. It has been established that the irradiation damages not only the surface of the crystal but also the deeper layers.

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Keywords: Lithium tetraborate; Radiation effect; Absorption spectra; Neutron irradiation; Displacement defects

1. Introduction

It is known that polycrystals and glass of lithium tetraborate, doped with rare-earth and manganese ions are used as thermoluminescence dosemeters [1,2]. In particular, a dosemeter of $Li_2B_4O_7$:Tm glass allows to determine γ-irradiation in the dose interval of 10^{-4}–10^4 Gy due to the linear dependence of the thermoluminescence on the dose. Natural single-phase unidirectional transducers (NSPUD) [3] have attracted much attention for implementing low-loss surface acoustic wave devices. Previously, new NSPUDT orientations on lithium tetraborate ($Li_2B_4O_7$) substrate were reported in [4]. $Li_2B_4O_7$ is an attractive piezoelectric substrate because of its moderately large piezoelectric coupling and zero temperature coefficient of delay [5,6].

Single crystals of $Li_2B_4O_7$ belong to the space group $I4_1cd$ with unit-cell parameter $a = b = 0.9477$ nm and $c = 1.0286$ nm [7]. The density is $\rho = 2.46$ g/cm^3, Mohs' hardness – 6, microhardness H = 920 kg/mm^2 perpendicular to the [001] direction and H = 820 kg/mm^2 parallel to the [001] direction. The borate anion consists of two three-dimensional interlocking networks, extending throughout the crystal. The basic unit of the networks is a group consisting of two boron atoms tetrahedrally coordinated by oxygen. The atoms in the group are arranged as a twisted double ring.

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In comparison to other oxide crystals the physical properties of lithium tetraborate are reflected in a limited number of reports [8–15].

The lithium tetraborate single crystals have been irradiated with neutrons and the optical properties of these crystals are studied.

2. Experimental

The lithium tetraborate single crystals are grown by Czochralski method in air, the *z*-cut plates were used for experiments. The sample thickness was in the range of 0.5–1 mm.

The neutron irradiation was performed in Latvian 5 MW water – water research reactor. The fluence of fast neutrons with an energy > 0.1 MeV was in the range of 10^{14}–10^{17} cm^{-2}, and the fluence of thermal neutron was in the range of 10^{14}–2.5×10^{17} cm^{-2}. Accompanied γ-irradiation with average energy 1.1 MeV gave an absorption dose of 0.33 Gy. The irradiation temperatures are 300–700 K. A cadmium filter was used for thermal neutron absorption. The samples were put between two plates of nickel electrodes like a sandwich and located in the resistance furnace that allowed to change the temperature during irradiation up to 700 K. The electric fields used were 10 kV/m. The electric field direction coincided with neutron flux and was perpendicular to the plates plane. The standard technique for absorption spectra measurement was based on a "Specord M-40" two-beam spectrophotometer operating in the 50 000–11 000 cm^{-1} (200–900 nm) range. For surface investigation we used image automatic analyzer "MORPHOQUANT" with television camera and additional computer equipment. Optical measurements before and after irradiation were made at room temperature.

3. Results

As-grown crystals exhibit no optical absorption bands. Absorption spectra of neutron-irradiated crystals contain additional bands [12] at 42 000 cm^{-1} (238 nm), 33 000 cm^{-1} (303 nm) and 20 000 cm^{-1} (500 nm). To separate the effects of irradiation with thermal neutrons and annealing during irradiation, the lithium tetraborate crystals were irradiated with and without cadmium filter at two different temperatures. The curves in Fig. 1 illustrate the optical absorption for samples irradiated with and without cadmium filter at temperatures of 300 and 444 K. The temperature increase during irradiation leads to a decrease of absorption spectra intensity in the whole spectral region, and the intensity is smaller for samples irradiated with cadmium filter. Fig. 2 shows optical absorption spectra for lithium tetraborate irradiated with and without electrical field. The intensity of additional absorption band 33 000 cm^{-1} (303 nm) for irradiation in electrical field is several times smaller than that irradiated without field. Before irradiation the crystals have undamaged surfaces and no heterogeneity in the bulk. For lithium tetraborate irradiated with thermal neutrons the surface is damaged. A typical structure is shown in Fig. 3. The neutron fluence increasing up to 4×10^{16} cm^{-2} damages not only the surface, but also the bulk as well. Such radiation damages are heavier for

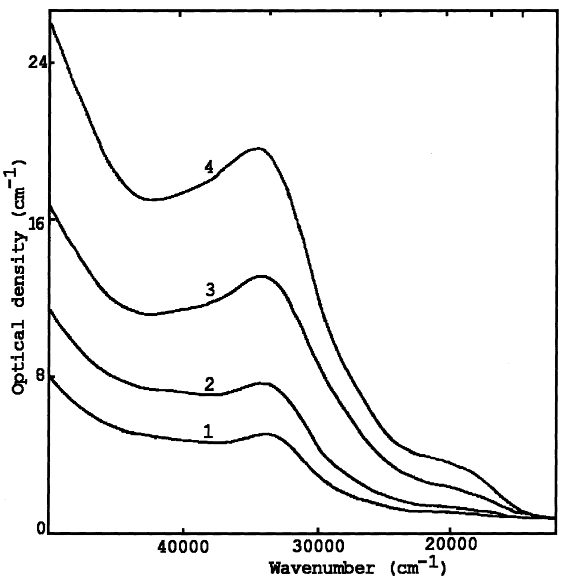

Fig. 1. The optical absorption spectra of neutron irradiated of fluence 5×10^{16} cm^{-2} lithium tetraborate. 1: $T = 444$ K with cadmium filter. 2: $T = 444$ K without cadmium filter. 3: $T = 300$ K with cadmium filter. 4: $T = 300$ K without cadmium filter.

crystals irradiated in an electrical field (Fig. 4). Pits, bubbles and dendrites appear on the surface and near the surface. The dark regions in Figs. 3 and 4 show the damages in crystals. The different degrees of opaque indicate that the depth of damage on the surface and near-surface layer is different (Fig. 4).

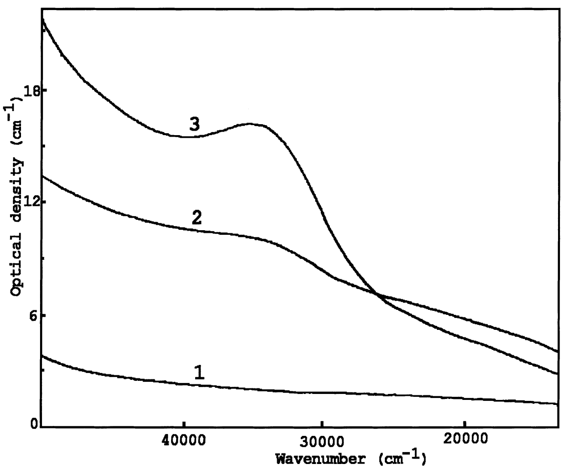

Fig. 2. The optical absorption spectra of lithium tetraborate. 1: before irradiation, 2: after irradiation of thermal neutron fluence 10^{16} cm^{-2} in electric field, and 3: after irradiation of thermal neutron fluence 10^{16} cm^{-2} without electric field.

4. Discussion

Fast and thermal neutron irradiation causes a great number of simple and complex radiation defects of lithium tetraborate. Due to large thermal neutron capture cross-section of lithium and boron the main part of radiation defects is directly connected to products of nuclear reaction. The lithium contains 7.42% of the isotope ^{6}Li with 950 barn capture cross-section for slow neutrons. The recoil atoms of tritium and helium with kinetic energy of 2.7 and 2.1 MeV and the Li^+-vacancies are created during the reaction:

$$^{6}\mathrm{Li} + \mathrm{n} \rightarrow {}^{3}\mathrm{H}\ (2.7\ \mathrm{MeV}) + {}^{4}\mathrm{He}\ (2.1\ \mathrm{MeV}).$$

Similarly, for the ^{10}B isotope (the capture cross-section is 3990 barn) the following reaction takes place:

$$^{10}\mathrm{B} + \mathrm{n} \rightarrow {}^{7}\mathrm{Li}\ (0.97\ \mathrm{MeV}) + {}^{4}\mathrm{He}\ (1.69\ \mathrm{MeV}).$$

Thus, the thermal neutrons produce energetic atoms of lithium, tritium, helium and lithium and boron vacancies in lithium tetraborate. The fast neutrons produce energetic atoms of oxygen, boron and lithium and its vacancies. The concentration of the radiation displacement defects can only be estimated approximately because there are no

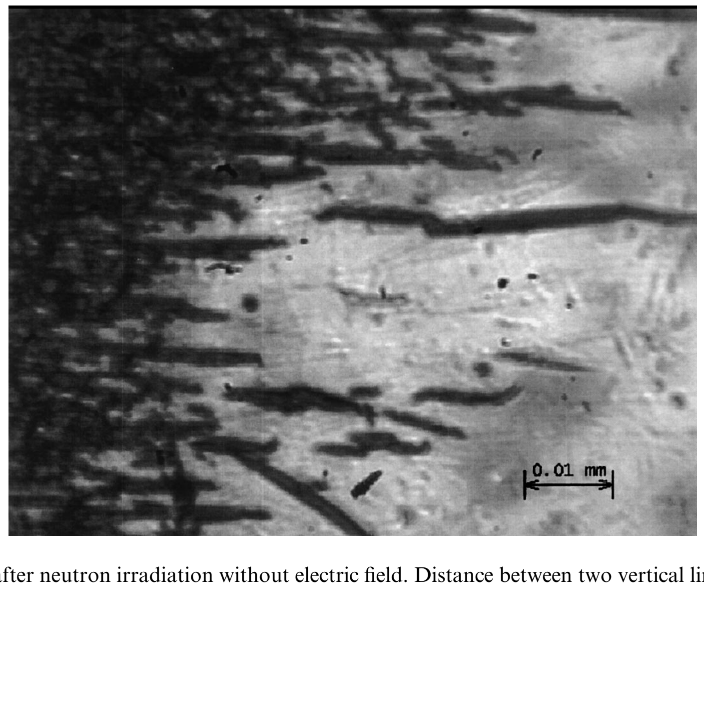

Fig. 3. The crystal surface after neutron irradiation without electric field. Distance between two vertical lines is equivalent to 0.01 mm.

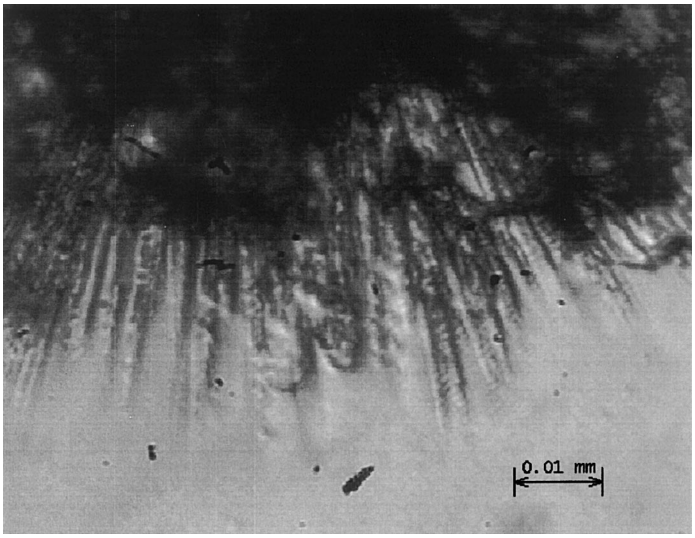

Fig. 4. The crystal surface after neutron irradiation with electric field. Distance between two vertical lines is equivalent to 0.01 mm.

precise data of threshold energy. At a fluence of about 10^{17} cm^{-2} the defect concentration is 0.2×10^{19} cm^{-3}. Therefore, it can be expected that the changes of the optical absorption of lithium tetraborate under irradiation with fast neutrons are connected with the formation of oxygen, lithium and boron recoil atoms and the corresponding vacancies, interstitials atom and more complex defects. The irradiation with mixed neutron flux (thermal, resonance and fast neutron) creates additional nuclear reaction products – helium, tritium and lithium atoms and increases the concentration of lithium and boron vacancies. We neglect the accompanied γ-irradiation that practically does not change the concentration of the recoil atoms.

The additional absorption in the region of 43 500–33 300 cm^{-1} (230–300 nm) produced by electrons of an energy of 4.7 MeV is caused by oxygen vacancies with localized electrons [12]. The electron irradiation does not lead to the change of the 20 000 cm^{-1} (500 nm) absorption band. But the annealing characteristics of this maximum are different. The more complete and exact results are given for lithium tetraborate annealed after fast neutron irradiation [15]. The color center connected with the band in 24 000–18 200 cm^{-1} (415–550 nm) is less thermally stable. We do not observe this band under fast and thermal neutron irradiation at high temperature. The influences of fast and thermal neutrons are revealed as increase of the absorption in the whole spectral interval. It is likely that both anion and cation vacancies take part in the formation of the absorption spectra. To our opinion the great difference in additional absorption of lithium tetraborate irradiated with and without Cd-filter is connected with elastic scattering of the recoil atoms ^{3}H, ^{4}He and ^{7}Li. Primary absorption of thermal neutrons and energy emission in the surface layer possibly can be the reason for the creation of complex defects. An applied electric field creates the displacement of charged particles, that leads to the appearance of the micrononhomogeneous region in the crystal and thus the decrease of the intensity of absorption bands. The irradiation damages not only the surface of the crystal but also the deeper layers.

5. Conclusion

The results obtained in this study are summarized as follows:

1. The changes of the absorption spectra are connected with defects created by elastic scattering of fast neutrons and by capture reaction of thermal neutrons.

2. Primary absorption of thermal neutrons possibly can cause the complex defects and the formation of disordered fields on the surface and near-surface layers of the single crystals of lithium tetraborate.
3. An applied electric field induces the displacement of charged particles, creating the micro-nonhomogeneous regions in the crystal leading to a decrease of the intensities of the absorption bands.

Acknowledgements

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