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Spectroscopy of Cu- and Ag-doped single crystal and glassy lithium tetraborate: luminescence, optical absorption and ESR study

M.Ignatovych, V.Holovey[*], *T.Vidoczy*[**], *P.Baranyai*[**], *A.Kelemen*[***], *V.Laguta*[****], *O.Chuiko*[****]

Institute of Surface Chemistry, National Academy of Sciences of Ukraine, 17 Gen. Naumov St., 03164 Kyiv, Ukraine
[*]Institute of Electron Physics, National Academy of Sciences of Ukraine, 21 Universitetska St., 88000 Uzhgorod, Ukraine
[**]Photoscience Laboratory, BUTE and CRC, HAS, P.O.Box 17, Budapest 1525, Hungary
[***]Institute of Isotopes, CRC, HAS, P.O.Box 77, Budapest 1525, Hungary
[****]Institute for Problems of Material Science, National Academy of Sciences of Ukraine, 3 Krzyzhanovsky St., 03142 Kyiv, Ukraine

Photoluminescence (PL), optical absorption (OA) and ESR spectra have been studied to characterize Cu- and Ag-doped single crystal and glassy $Li_2B_4O_7$ (LTB). The attribution of LTB:Cu glass PL as one arising from the sets of Cu^+ ions with slightly different local environments is proposed. The OA spectra of Cu-doped single crystal and glass are different in the UV and VIS ranges. The OA and PL features of LTB:Ag single crystal and glassy are different from each other.

Исследованы спектры фотолюминесценции (ФЛ), оптического поглощения (ОП) и ЭПР для характеристики монокристаллов и стекла тетрабората лития (ТБЛ), легированных Cu и Ag. Предложена интерпретация ФЛ стекла ТБЛ:Cu, как обусловленной набором Cu^+ ионов в несколько отличных локальных окружениях. Спектры ОП монокристаллов и стекла отличаются как в УФ, так и в видимой части спектра. Показано, что спектры ОП и ФЛ монокристаллов и стекла ТБЛ:Ag также различны.

Doped lithium tetraborates (LTB) are well-known dosimetric materials; their chemical and isotopic compositions provide separate detection of neutron and gamma doses. Doped LTB crystals possess an unique feature of tissue equivalency, therefore, those are applied widely as the thermoluminescent (TL) detectors for personal and clinical dosimetry [1–3]. Despite the commercial production of some doped LTB and their very successful applications, the basic physical characteristics, such as the nature of emitting centers responsible for luminescence and TL mechanism, are still ambiguous. It is not clear, even for the most comprehensively studied Cu-doped LTB, the role of dopant and host lattices as well as the Cu valence state are still unclear. Nor known is, whether favorable or detrimental are the single crystal or glass modification for its good TL properties.

Recently, we have reported for the first time the results of time-resolved photoluminescence (PL) and radioluminescence (RL) study of Cu- and Eu-doped lithium tetraborate (LTB) depending on the dopant content and host modification [4, 5]. This work is a continuation of the above approach. The

spectral investigation under steady state excitation and emission photoluminescence (PL), time-resolved PL, optical absorption (OA) and ESP techniques for characterization of Cu- and Ag-doped lithium tetraborate (LTB) are here reported in more detail.

There are several reasons to study LTB:Ag. It has been reported [1, 3] that in the development of highly sensitive TL detectors, Ag was used as a co-dopant to basic Cu-activated LTB. Besides, it has been shown that the dopants in LTB:Cu as well as in LTB:Ag are directly involved in formation of new effective TL-centers [6]. At the same time, the photoluminescence studies of LTB:Ag are very restricted. To our best knowledge, there is only one quite recent publication where optical transmittance and excitation-emission experimental spectra of LTB:Ag single crystal are displayed, but without any further discussion [7].

Single crystals of LTB:Cu and LTB:Ag were grown by Czochralski technique from high purity (at least 99.99 %) precursor compounds. Glassy samples were prepared by melting doped single crystals to ensure the same stoichiometry and dopant content. The dopant contents in the samples estimated by atomic absorption spectroscopy have been found to be of 0.0007–0.05 mass.% Cu and of 0.002–0.004 mass.% Ag. The PL spectra were recorded using a Perkin-Elmer LS50B luminescence spectrometer equipped with a pulsed xenon lamp. That instrument makes it possible to measure phosphorescence using selectable time delays between excitation and detection.

The time-resolved PL was excited by the fourth harmonic (266 nm) of a Nd–YAG laser (60 mJ/pulse), and the emission was monitored through a $f/4.0$ monochromator with an EMI 9783R photomultiplier. The signal was stored in a digital oscilloscope (Tektronix TDS 210), the average of 64 measurements has been evaluated with standard spreadsheet program. The optical absorption spectra of Cu- and Ag-doped LTB referenced to undoped samples were measured using a JASCO V-550 UV-VIS spectrophotometer. All optical spectra were taken at room temperature. ESR spectra were registered using an Oxford cryostat in the temperature range 25–300 K by a home-made high sensitivity spectrometer.

LTB:Cu samples. LTB:Cu single crystals with various copper content exhibit two UV bands at 240 and 260 nm in the excitation spectrum and a single emission band at

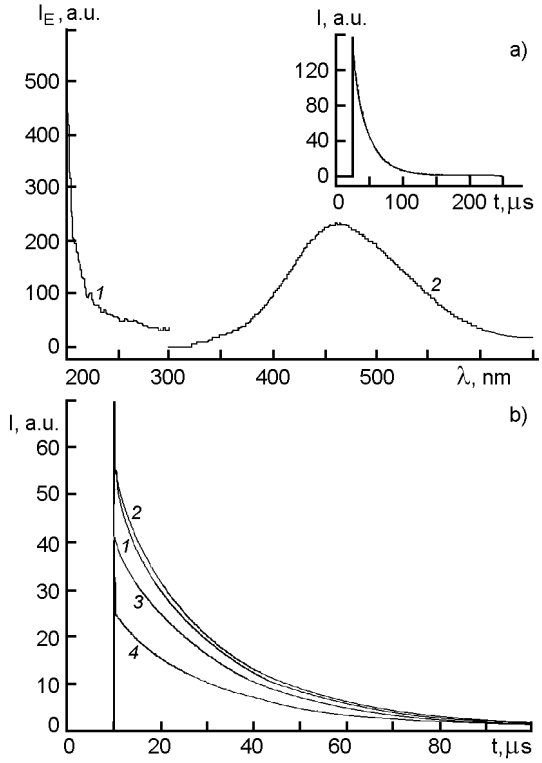

Fig. 1a. Photoluminescence (PL) of Cu-doped lithium tetraborate glass sample. *1* — excitation, *2* — emission, in the inset: decay curve at 490 nm, τ = 22.532 μs.

Fig. 1b. Photoluminescence decay curves of Cu-doped lithium tetraborate glass sample at various wavelength emissions: (*1*) 430 nm (τ = 21.296 μs), (*2*) 460 nm (τ = 21.422 μs), (*3*) 490 nm (τ = 22.532 μs), (*4*) 520 nm (t = 23.052 μs).

about 370 nm. The emission intensity increases with increasing Cu content in the sample without any change in the spectral shape. Besides, it has been found that the emission spectra shapes are independent of the excitation wavelength (in the range of 200–300 nm) as well as the excitation spectra remain the same upon monitoring different emission wavelengths. Such PL features together with the single-exponential emission decay suggest strongly the only type of emitting centers in LTB:Cu single crystals. The observed PL pattern and a long lifetime (τ = 23.753 μs) evidence that the emission of LTB:Cu is caused by $3d^9 4s \rightarrow 3d^{10}$ triplet transition in Cu^+ ions [8, 9].

The PL of LTB:Cu glass samples shows a remarkable difference in the excitation and emission spectral patterns and their intensities as well. Fig. 1a represents typical PL

spectra with the decay curve for Cu-doped glassy sample. A considerable broadening, red shift, and the intensity decrease is observed in the emission of glassy LTB:Cu while the excitation is substantially blue-shifted as compared to the observed for the relevant (with the same copper content) single crystal.

Such features are observed in the steady-state PL spectra of Cu-doped glassy samples within the whole investigated copper content range. For samples with low copper concentration, the intensity decrease is so dramatic that their emission spectra are comparable with that of non-doped samples in the range of 350–450 nm. For these cases, the time-resolved PL was applied and it was revealed that while the lifetime of weak emission for LTB:Cu is in the microsecond range, the emission of the non-doped samples was quenched after 250 ns [5].

Our measurements of OA revealed two weak UV bands at 240 and 260 nm in the spectrum of the single crystal. In OA spectrum of glassy sample (with the same total Cu content), a high intensity band at about 250 nm dominates that is well-known as the charge-transfer (CT) band of $O^{2-} \rightarrow Cu^{2+}$. The presence of Cu^{2+} ions in the glassy samples luminescence-silent in the UV range can explain the observed decrease in the emission intensity, while the reabsorption caused by intensive CT band positioned at 250 nm can account for the blue-shifted "tail-like" excitation spectrum.

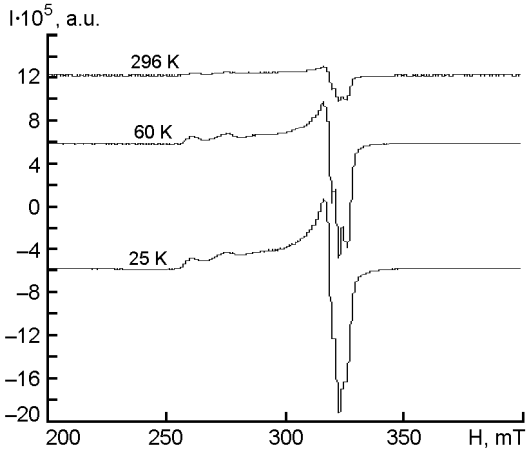

Fig. 2. ESR spectra of Cu-doped lithium tetraborate glass sample: temperature dependence.

In kinetic study (Fig. 1b), the decay curves measured for different emission wavelengths (within broad limits in the range of 430 to 520 nm) and evaluated lifetimes found to be in the range of τ = 21.296 to 23.052 μs appear to be quite similar and also close to that obtained for LTB:Cu single crystal (τ = 23.753 μs). It is important to note that such kinetic data were confirmed within the whole examined Cu content range. It is also worthwhile that in the microsecond domain, undoped samples (neither single crystal, nor glassy one) did not show any detectable luminescence in the range of Cu-doped samples emission. That is

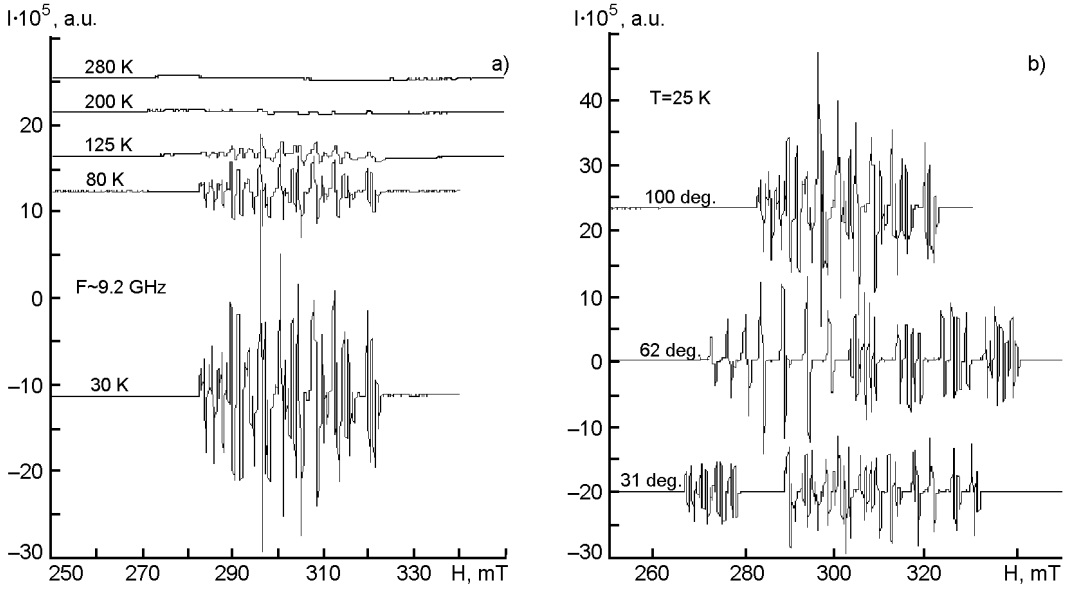

Fig. 3. ESR spectra of Cu-doped lithium tetraborate single crystal: (a) temperature dependence, (b) angular dependence.

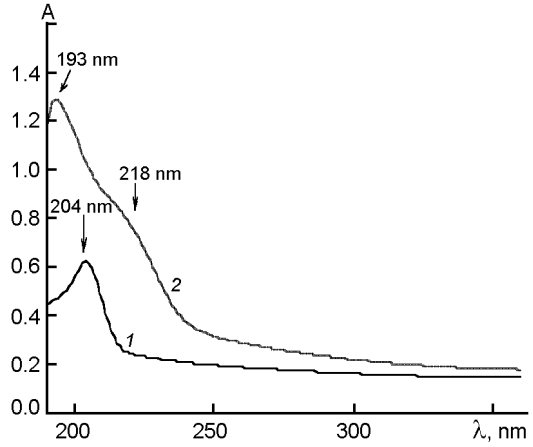

Fig. 4. Optical absorption of Ag-doped lithium tetraborate samples: (*1*) single crystal, (*2*) glass.

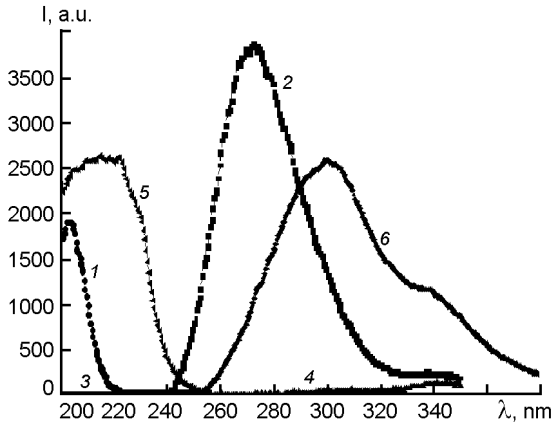

Fig. 5. Photoluminescence of Ag-doped samples. Comparison of single crystal and glassy samples: (*1*) and (*2*), excitation and emission spectra of the Ag-doped single crystal, (*3*) and (*4*), those of the non-doped single crystal, (*5*) and (*6*), those of the Ag-doped glassy sample.

why we also attribute (despite of exhibited difference in the PL features) the PL of LTB:Cu glass samples as that arising from metal-centered $3d^9 4s \rightarrow 3d^{10}$ triplet transition of numerous Cu^+ ions with slightly different local environments.

It was already mentioned that the OA spectrum clearly shows the presence of Cu^{2+} ions only in LTB:Cu glass samples, while no evidence thereof is observed in spectrum of LTB:Cu single crystals. At the same time, in several publications devoted to thermoluminescence of LTB:Cu single crystals, it is just Cu^{2+} ions, that are considered as TL centers [6], though not being confirmed experimentally. The ESR technique has been proved to be particularly sensitive to paramagnetic Cu^{2+} ions, therefore, it is used widely to detect those in various media [10]. But as far as we know, in the ESR study of LTB:Cu single crystals reported before, ESR signals of Cu^{2+} ions were not yet registered [6].

Now, our first results on comparative ESR study of single crystals and glassy LTB:Cu are presented. Fig. 2 shows representative ESR spectra of LTB:Cu glass sample; the spectra are rather similar to known of Cu^{2+} ions in the oxide amorphous media [10]. The spectra of Cu^{2+} ions are anisotropic with weak $g_{\|}$ components arising from 3/2 nuclear spin of Cu^{63} and Cu^{65} isotopes and display an apparent temperature dependence (Fig. 2). Figs. 3a and 3b represent ESR spectra of LTB:Cu single crystal. The low-temperature (125–25 K) spectra of LTB:Cu single crystal display a hyper-fine (HF) structure (with splitting from Cu^{63} and Cu^{65} isotopes (Fig. 3) and angular dependence (Fig. 4). As we see, the spectral patterns are essentially different as compared to that for the glassy sample. Thus, ESR spectra directly prove the presence of Cu^{2+} ions not only in glass sample, but also in the single crystal, though their spectral patterns are considerably different. The ESR study using oriented LTB:Cu single crystals is in progress, and we hope that a further fitting procedure will provide information concerning the site symmetry of Cu^{2+} ions and their location.

LTB:Ag samples. As mentioned above, the evidences of very promising TL properties of Ag-doped (or containing Ag as a co-dopant) LTB detectors appeared in the recent literature [1–3], however, their photoluminescence was investigated rather poorly.

Fig. 4 represents OA spectra of Ag-doped samples. As we see, the single-band absorption at 204 nm is observed for LTB:Ag single crystal while the absorption of glassy sample is broader and red-shifted as a whole and contains two bands with the maxima at 193 and 218 nm. In good correspondence with the OA data are the observed excitation spectra of Ag-doped samples presented in Fig. 5. It follows that for LTB:Ag single crystal, the excitation single band is located within 203–215 nm with maximum at 206 nm, while the excitation for glassy sample is clearly broader and red-shifted up to 240 nm. Both single crystal and glassy Ag-doped samples exhibit an intense luminescence in the near UV region. LTB:Ag sin-

gle crystal exhibits a single-band emission at about 272 nm; whereas emission of LTB:Ag glassy sample is broader, red-shifted and displays apparent two maxima at 300 and 340 nm.

Measurements of emission dependence on the excitation wavelength for LTB:Ag single crystal have also been performed. It has been shown that the PL emission band positioned at 272 nm has the highest intensity when excited by 210 nm and is shape-independent under excitation within 203–215 nm range. Also the excitation spectra remain unchanged under monitoring different emission wavelengths. Such PL features point that there is only one type of luminescent centers in LTB:Ag single crystal.

Monovalent silver and copper are d^{10} ions; but while the luminescence of Cu^+ in various media had been studied widely and fundamentally [8, 9], the situation is quite different with PL investigation of Ag^+ ion. G.Blasse in his monography states "about the Ag^+ ion less is known but what is known shows a similarity with Cu^+ data" [9]. Substantiating by this analogy, we propose an attribution of OA and PhL of LTB:Ag single crystal as metal centered $4d^95s \leftrightarrow 4d^{10}$ transitions in the same type of Ag^+ ions.

OA and PL spectral patterns of LTB:Ag glassy sample can preliminary be explained as those caused by the presence of at least two non-equivalent Ag^+ ion types. The observation of two apparent bands in OA and emission spectra of glassy LTB:Ag is in agreement with this assumption. The luminescence decay of these emission bands at 300 and 380 nm were measured and lifetimes were found to be equal to 13.026 μs and 21.968 μs, respectively.

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Спектроскопія легованого Cu та Ag монокристалічного та склоподібного тетраборату літію: дослідження люмінесценції, оптичного поглинання та ЕПР

М.Ігнатович, В.Головей, Т.Відоці, П.Бараньяї, А.Келемен, В.Лагута, О.Чуйко

Досліджено спектри фотолюмінесценції (ФЛ), оптичного поглинання (ОП) та ЕПР для характеристики монокристалічного та склоподібного тетраборату літію (ТБЛ), легованого Cu та Ag. Запропоновано інтерпретацію ФЛ скла ТБЛ:Cu як такої, що зумовлена набором Cu^+ іонів у дещо відмінних локальних оточеннях. Спектри ОП монокристалів та скла ТБЛ:Cu відрізняються один від одного як в УФ, так і у видимій ділянках спектра. Спектри ОП монокристалів та скла ТБЛ:Ag також відрізняються один від одного.