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Synthesis and spectroscopy of tetraborate glasses doped with copper

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ABSTRACT

Lithium and potassium–lithium tetraborate glasses doped with Cu ($Li_2B_4O_7$:Cu and $KLiB_4O_7$:Cu) of high optical quality were obtained from polycrystalline compounds by fast cooling of the corresponding melt. Cu impurity was added to the $Li_2B_4O_7$ and $KLiB_4O_7$ compounds in the form of a CuO oxide in the amounts of 0.4 and 1.6 mol.%. On the basis of EPR and optical spectroscopy (absorption, emission and luminescence excitation and kinetics) data analysis it was shown that the Cu impurity was incorporated into the tetraborate glass network as Cu^{2+} ($3d^9$) and Cu^{+} ($3d^{10}$) ions. The EPR spectra of Cu^{2+} centers were almost identical in glasses with the $Li_2B_4O_7$:Cu and $KLiB_4O_7$:Cu compositions and were characteristic for glassy compounds. The Cu^{2+} EPR spectra parameters (g-values, hyperfine constants and peak-to-peak linewidths) in the $Li_2B_4O_7$:Cu and $KLiB_4O_7$:Cu glasses were obtained at $T = 300$ K. The characteristic broad absorption band peaked near 750 nm was assigned to the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition of the Cu^{2+} centers. An intense absorption in the UV region ($\lambda < 350$ nm) was related to the $Cu^{2+} \rightarrow O^{2-}$ charge-transfer band. Broad emission bands with the maxima near 420 and 465 nm were observed in the luminescence spectra of the $Li_2B_4O_7$:Cu and $KLiB_4O_7$:Cu glasses. The emission bands, peaked near 420 and 465 nm, were characterized by single exponential decay with lifetimes $\tau = 23$ and 27 μs, respectively for the $Li_2B_4O_7$:Cu and $KLiB_4O_7$:Cu glasses (Cu content—1.6 mol.%) at $T = 300$ K. Both emission bands belonged to the Cu^{+} centers with different local environments or their distortion. A possible local structure for two types of Cu^{+} centers in a tetraborate glass network is discussed.

1. Introduction

Borate compounds (crystals and glasses), un-doped and doped with transition and rare-earth elements are very promising for quantum electronics and non-linear optics [1,2] scintillators and tissue-equivalent materials for thermoluminescent (TL) dosimetry [3–5], as well as γ and neutron detectors [6–8]. This also concerns lithium tetraborate crystals which are characterized by extremely high radiation stability [9,10], high transparency in a wide spectral range from VUV to far IR [11] and good TL properties [4–8].

It is technologically difficult, takes a long-time, and as consequence, it is very expensive to obtain tetraborate single crystals with different compositions by the Czochralski method. In addition to that, a very low velocity of the crystals growth and high viscosity of the melt lead to problems with the doping of tetraborate crystals. Thus, from the technological point of view the glassy (or vitreous) borate compounds are most prospective in comparison with the corresponding single crystals. On the other hand, the study of the electron and local structure of impurity and other point defects in complex oxide glasses, particularly in glasses with $Li_2B_4O_7$ (LTB) and $KLiB_4O_7$ (KLTB) basic compositions, poses an interesting scientific problem.

The electron paramagnetic resonance (EPR) and optical spectroscopy allow investigating the electron and local structure of point defects in crystals and corresponding glasses. Structural and corresponding spectroscopic data for crystalline analogies are needed for an interpretation of the EPR and optical spectra in complex oxide glasses [12,13].

Tetraborate compounds are good candidates to study the nature of point defects as boron-containing compounds, including tetraborates, can be obtained in both crystalline and glassy states.

The optical spectra of lithium tetraborate crystals and glasses doped with Cu (LTB:Cu) have been investigated by different authors [6–8,14,15]. Particularly in [14] it has been shown by optical spectroscopy that the multivalent states of impurity transition ions for non-irradiated LTB:Cu crystals and glasses, “as-grown” in the air, obtained from melted crystals are characteristic and the copper impurity is revealed as Cu^{+} and Cu^{2+} ions. At the present time, the emission spectra and luminescence kinetics of Cu^{+} centers have been investigated in LTB:Cu single crystals [6,7] and glasses [8,14–17],

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however, the peculiarities of the Cu^{+} luminescence properties of LTB:Cu glasses have not been clearly explained to this day. The EPR spectra of the Cu^{2+} paramagnetic ions in the LTB:Cu crystal and glass at different temperatures, typical for crystalline and glassy compounds, have been presented in [16], however, their spin Hamiltonian parameters have not been determined. In [18] we have reported for the first time the parameters of the Cu^{2+} EPR spectra in $Li_2B_4O_7$:Cu and $KLiB_4O_7$:Cu glasses.

On the basis of the referenced data analysis it can be concluded that at the present time the EPR and optical spectra of LTB:Cu glasses doped with Cu have been studied insufficiently. The results of optical and EPR spectroscopy for new crystal and glass with $KLiB_4O_7$:Cu compositions have not been published up to now. The presented work is devoted to detailed EPR and optical investigations of the LTB:Cu and KLTB:Cu glasses and to determining the electron and local structure for paramagnetic and luminescence copper centers in their network on the basis of the obtained and referenced spectroscopic and structural data.

2. Glass synthesis, experimental equipment and characterization of samples

LTB:Cu and KLTB:Cu glasses were obtained in the air from corresponding polycrystalline compounds according to a standard glass synthesis using the technological conditions developed by the authors. Carbonates (Li_2CO_3 and K_2CO_3) and boric acid (H_3BO_3) of high chemical purity (99.999%) in the corresponding proportion were used for a solid state synthesis of the $Li_2B_4O_7$ and $KLiB_4O_7$ polycrystalline compounds. Cu impurity was added to the $Li_2B_4O_7$ and $KLiB_4O_7$ compounds in the form of a CuO oxide of the chemical purity in the amounts of 0.4 and 1.6 mol.%. The LTB:Cu and KLTB:Cu glasses were obtained by fast cooling of the corresponding melts which were heated about 100 K higher than their melting temperature ($T_{melt}=1190$ and 1080 K, respectively) to exceed the glass transition points.

The non-controlled and copper paramagnetic impurities in the obtained glasses were registered by the EPR technique using modernized commercial X-band spectrometers of the SE/X-2013 and SE/X-2544 types ("RADIOPAN", Poznań, Poland), operating in the magnetic field high-frequency (100 kHz) modulation mode at room temperature. The microwave frequency was measured using a 5350 B Hewlett Packard microwave frequency counter and a DPPH g-marker ($g=2.0036\pm0.0001$). The parameters of the registered EPR spectra were obtained by a computer analysis of the experimental data.

The optical absorption, luminescence excitation and emission spectra as well as luminescence kinetics were registered in the UV–VIS spectral range at room temperature. The optical absorption spectra were recorded with a Varian Model 5E UV–VIS–NIR spectrophotometer. The emission and luminescence excitation spectra were acquired with a Dongwoo (model DM711) scanning system consisting of an excitation monochromator with the 150 mm focal length and an emission monochromator with the focal length of 750 mm equipped with a photomultiplier and an InGaAs detector. The spectral response of the whole emission system was calibrated in the $400\div800$ nm spectral region against the reference source. The resulting signal was analyzed by a Stanford (model SRS 250) boxcar integrator and was stored in a personal computer.

The luminescence decay curves were recorded with a Tektronix (model TDS 3052) digital oscilloscope at $T=300$ K. Excitation was provided by a Continuum Surelite I Optical Parametric Oscillator (OPO) pumped by a third harmonic of an Nd:YAG laser ($\lambda=355$ nm) and the emitted light was filtered using a grating monochromator GDM with 1000 mm focal length.

The obtained un-doped LTB and KLTB glasses are uncolored and characterized by a high transparency in the $330\div2500$ nm spectral range. According to [8] un-doped LTB glasses are transparent in the $281\div2760$ nm region, whereas nominally-pure LTB single crystals reveal high transparency in a very wide ($167\div3200$ nm) spectral range [11]. The obtained LTB:Cu and KLTB:Cu glasses are lightly blue (CuO—0.4 mol.%) and aquamarine (CuO—1.6 mol.%) in color and they are characterized by high optical quality. EPR and optical spectra characteristic for glassy (or vitreous) compounds were observed in all the LTB:Cu and KLTB:Cu samples. The spectra are presented in Figs. 1–4 and discussed in Section 3.

3. Results and discussion

3.1. EPR spectroscopy of tetraborate glasses doped with Cu

It should be noted that a characteristic EPR signal with $g_{eff}=4.29\pm0.01$ was observed in all the LTB:Cu and KLTB:Cu glasses (Fig. 1, a). The same signal with less intensity was also observed in the un-doped and rare-earth doped LTB and KLTB glasses. In the investigated samples the integral intensity of the EPR signal with $g\cong4.29$ is comparable with the Cu^{2+} signal intensity (Fig. 1, a). The first explanation of the signal at $g_{eff}\cong4.29$ in the glass network was proposed by Castner et al. [19] on the basis of a spin Hamiltonian in the form given by Bleaney and Stevens [20]:

$$\hat{H} = \beta\cdot\left(B\cdot g\cdot\hat{S}\right) + D\left[S_z^2-1/3S(S+1)\right] + E\left(S_x^2-S_y^2\right) \quad (1)$$

where D and E are the axial and orthorhombic crystal field terms, respectively. At the present time it is generally acknowledged [21] that the signal with $g_{eff}\cong4.29$ originates from isolated $3d^5$-ions (Fe^{3+} and Mn^{2+}) for a large second-order ligand field splitting in which the value of the $|E/D|$ ratio lies in the vicinity of its maximum value of 1/3 (for fully rhombic symmetry $|E/D|=1/3$). Several types of fully

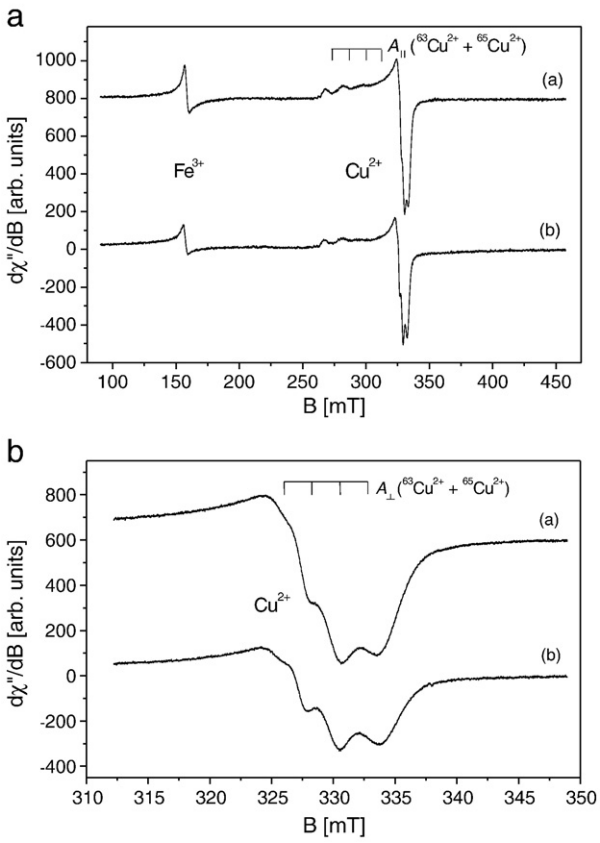

Fig. 1. Complete (a) and central part (b) of X-band EPR spectra of LTB:Cu (a) and KLTB:Cu (b) glasses, containing 0.4 mol.% of Cu, recorded at $T=300$ K.