Luminescence and electronic excitations in KBe$_2$BO$_3$F$_2$ crystals

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The report presents the results of a study of the dynamics of electronic excitations in modern non-linear optical crystals of KBe$_2$BO$_3$F$_2$ (KBBF) [1] obtained by the means of the low-temperature luminescence vacuum ultraviolet spectroscopy with nanosecond time resolution. The experimental data were obtained on the decay kinetics of photoluminescence (PL), the PL emission spectra in the energy range from 3.7 eV to 21 eV (0.32 nm resolution) were measured for these crystals at the SUPERLUMI experimental station of HASYLAB under selective photoexcitation with synchrotron radiation (SR). Time-resolved spectra were recorded in two independent time windows (TWs) set for detection of luminescence signal within 0.5–2.3 ns (TW1) and 14–58 ns (TW2) relative to the beginning of the SR pulse. Time-integrated (TI) spectra were recorded within the full time range available between two sequential excitation pulses, viz. 192 ns. The measurements were performed in the ultra-high-vacuum chamber (up to $10^{-9}$ mbar) at 7 K. Simultaneously with the excitation, the reflection spectra were recorded at an angle of incidence 17.5$^\circ$. All the examined crystals were grown at the Institute of Geology and Mineralogy SB RAS (Novosibirsk, Russia) by spontaneous crystallization method (see more details in Ref. [2]). Photoexcitation of KBBF at photon energies $E_{ex} = 3.7–21$ eV at $T = 7$ K produces broad-band PL emission with a maximum at 3.6–4.2 eV, Fig. 1. The observed PL band comprises three Gaussians at 3.03, 3.88 and 4.30 eV. The 3.03 emission band can be excited only at the crystal transparency band. Two other PL bands at 3.88 and 4.30 eV are efficiently excited in the host absorption band of KBBF. In addition, two low intensive bands at 2.2 eV (FWHM=0.2 eV) and 4.5 eV (FWHM=0.8 eV) can be excited only at 6.5 and 8.7 eV.

Figure 1: Left panel – The PL emission spectra (TI) recorded upon excitation at 6.3 – (1), 8.7 – (2) and 11.1 eV – (3) for KBBF crystal at 7 K. Right panel – The PL emission spectrum recorded in the 2.5–6.2 energy range by the means of CCD-camera for KBBF crystal upon excitation at 11.1 eV at 7 K.

Figure 2 presents the time-resolved PLE spectra recorded monitoring emission at 4.1 eV the reflection spectrum for KBBF crystal at 7 K. In the low energy region 5.0–8.0 eV the PLE intensity is fairly low. At 8.0–10.0 eV PLE intensity increases by the factor 20 peaking at 8.7 and 10.6 eV. The
low temperature reflection spectrum shows peak at 9.7 eV. On the basis of these spectra our estimation of $E_g = 10.6–11.0$ eV. The PL decay kinetics curves were recorded monitoring emission at various energies over the energy range 2.9–4.4 eV for KBBF crystal $T = 7$ K upon excitation at either 8.7 or 11.1 eV. All the PL time responses were the same in profile. The PL decay kinetics is monoexponential in shape. The measured lifetime of the PL decay kinetics was always equal to $\tau = 2$ ns. The longer decay components of the micro- and millisecond time range are presented in our measurements as a pedestal. The amplitudes ratio for the exponent to pedestal is about 0.96, Fig. 2. The obtained experimental data pointed out a dominated excitonic pathway of excitation of the 3.88 eV PL emission band. In fact, the theoretical calculations of the KBBF electronic structure [3] predicted that the lowest energy excitations are due to electron transitions from 2p oxygen levels, forming the valence band top, onto the hybridized boron-oxygen orbitals, forming the conduction band bottom. In the other words, we are dealing with electronic transitions inside the boron-oxygen anionic group. This picture is very typical for other borate crystals studied by us previously (see for example [4]). At the same time, several PL emission bands in the visible and ultraviolet spectral region at 3.03 and 4.30 eV should be assigned to luminescence of the lattice defects. At energies above $E_g$ the shape of the PLE spectra points out the possible participation of recombination processes in the PL excitation. However, further detailed studies of the lattice defects are necessary to better understand the channels of creation and decay of electronic excitations in KBe$_2$BO$_3$F$_2$ crystals.

References