Electronic and optical properties of NaTi$_2$(PO$_4$)$_3$ materials

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Double alkaline and other metal (aluminum, indium, titanium) phosphates like MAl(In)P$_2$O$_7$, MTiOP$_4$, MT$_2$(PO$_4$)$_3$, M$_3$Ti$_3$P$_5$O$_{20}$ (M = Na, K) are well known as multifunctional materials [1]. In this work we study the properties of NaTi$_2$(PO$_4$)$_3$ system in crystalline and amorphous form.

The investigated compounds were obtained by the “melting solution” method from the initial blend of Na$_2$O - M$^{III}$O$_3$ - P$_2$O$_5$ – TiO$_2$ common composition in 650 - 1050 C temperature region at ambient atmosphere conditions. Photoluminescence (PL) and PL excitation spectra of the samples were obtained in 4.2 - 300 K temperature region. Reflection, excitation and luminescence spectra were investigated using synchrotron radiation in the energy region 3.5 – 20 eV. Calculations of NaTi$_2$(PO$_4$)$_3$ crystal electronic structure were performed using the WIEN2k package [2]. Reflection spectra $R$ were calculated for the case of normal incidence with neglecting of the off-diagonal components of dielectric tensor.

Eight clearly distinguished bands are observed in the NaTi$_2$(PO$_4$)$_3$ reflection spectra in 3.5 – 20.0 eV region (Fig. 1). Bands with maxima positions at 5.05 and 11.97 eV are the most intensive in the spectrum (Fig. 1, curve 1). An intensive band in 1.75 – 3.25 eV (400 – 700 nm) region is observed in the luminescence spectra of NaTi$_2$(PO$_4$)$_3$ crystals under excitation by synchrotron radiation at 10 K (Fig. 2). Position of the band maximum ($E_{max} \approx 2.5$ eV ($\lambda_{max} \approx 500$ nm)) is practically independent on excitation energy in 3.7 - 7.5 eV region. The luminescence intensity of the amorphous form samples is less by an order than in the case of the crystal, and the emission spectra are more complex when obtained at the same temperature and excitation energies (Fig. 2, curve 2).

The luminescence band of the amorphous form is a superposition of two components. One of the components corresponds to the emission band of the crystal, while another one is shifted to long-wavelength side ($E_{max} = 2.1$ eV, $\lambda_{max} = 583$ nm).

The photoluminescence spectra are also complex. Indeed, the PL spectra obtained under excitation at $E_{ex} = 3.54$ eV ($\lambda_{ex} = 350$ nm) contain in 350 – 700 nm spectral region an intensive band with maximum at 2.28 eV (543 nm) and few weak bands on both sides of the main band in the 2.5 - 3 eV and 1.75 – 2.1 eV spectral regions (Fig. 2, curve 3). All mentioned above PL bands are observed in the same region where the luminescence under the high-energy excitation was observed. The peak position of the red emission band lies at 1.62 eV (765 nm) (Fig. 2).

Figure 1: Experimental reflection (1), excitation of luminescence (2, 3) and calculated reflection (4) spectra of NaTi$_2$(PO$_4$)$_3$ crystals (1, 2, 4) and amorphous form (3); T = 10 K (1-3); $\lambda_{reg} = 530$ nm (2, 3).
At monochromatic laser excitation ($\lambda_{ex} = 337.1$ nm) the weak PL bands disappear and only the band near 2.28 eV is observed in 3.5 – 1.5 eV region at 4.2 K (Fig. 2, curve 4). The fine structure appears on the high-energy edge of the red PL band with peak positions near 1.671, 1.661, and 1.651 eV (~742, 746, and 751 nm) (Fig. 2, insert).

We have to mention that experimental data on reflection and excitation of luminescence in general agree with results of the calculations. There is also agreement in many details. Unfortunately, the orientation of the crystal axes of the sample in experiment was not known, therefore we use for analysis the averaged spectra calculated for the $x$- and $z$-polarizations of the incident $E$ vector ($R_x+R_z$)/2 (Fig. 1, curve 4). The bands in experimental reflection at 3.8, 5.05, and 6.64 eV, the minima at 7.5 and 13.5 eV are well reproduced in the calculated curve. Some discrepancies between the calculation and experimental results are evident in the region between 7.5 and 13.5 eV. The presented above general agreement allowed us to use the results of the calculations for interpretation of experimental data as on reflection as well as on the luminescence of the investigated materials [3].

We can make some preliminary assumptions concerning the mechanisms of emission. The obtained data evidences that it is a superposition of self emission and emission caused by defects. We ascribe the emission in 1.75 – 3.25 eV (400 – 700 nm) region to self emission of the host materials. The self emission can apparently have two origins: a) Emission of first origin is caused be the electronic transitions with charge transfer from titanium to oxygen (Ti $d$ - O $p$). This emission dominates in luminescence of the amorphous form and appears as a low-energy shoulder of the PL band of the crystals (Fig. 2, curves 1, 2); b) Annihilation of the localized excitons created after excitation with energy 4.03 eV is the second origin of the self emission. This emission peaks at $E_{max}$ = 2.5 eV ($\lambda_{max}$ = 500 nm) and dominates in luminescence of the crystal.

The amorphous form is characterized by unfavorable conditions for creation of excitons, as the long range ordering is absent in it. Moreover, the amorphous form is characterized with significant amount of lattice defects that leads to energy losses before localizing that is why the excitonic luminescence of the amorphous form is quenched. The first type of the self emission can be observed at these conditions.

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References