Investigation of Molybdate Single Crystals with Light Cations

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Molybdates are found to be perspective candidates for using as scintillators for neutrinoless double beta decay process registration. Main attention is focused on the crystals with the scheelite type structure. As it was shown for the series of scheelite type molybdates, luminescence intensity and decay depend on the cation's ionic radius and its electron structure [1]. Thus the cation's electron states in the conduction and valence bands modify luminescence properties of the molybdates. In the present work Li_2MoO_4 and $MgMoO_4$ single crystals were studied. Presence of the isolated tetrahedrons of MoO_4^{2-} and extremely light weight of the cation allows to emphasize the role of the MoO_4^{2-} group in the luminescence process and in the process of energy bands building.

Reflectivity, luminescence emission and excitation spectra were studied at the SUPERLUMI station settled in the synchrotron radiation channel I of DORIS III storage ring [2]. Reflectivity and luminescence excitation spectra were measured in the energy range of 3.5 - 25 eV at the temperatures 10 and 300 K. Luminescence spectra were measured using ARC SpectraPro SP-308 monochromator working in spectrograph mode and were normalized on the function of the registration route spectral sensitivity.

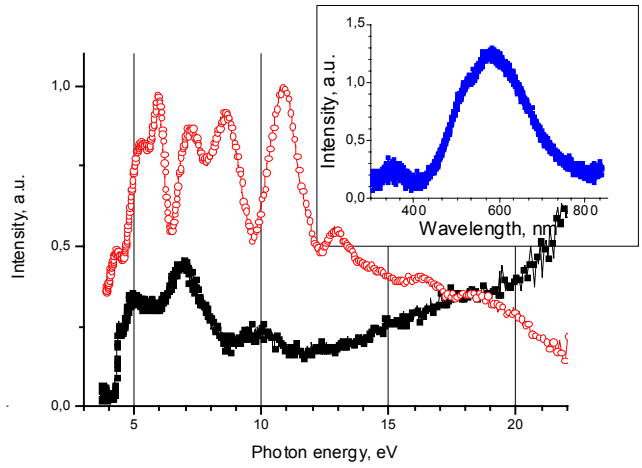

Figure 1. Reflectivity (squares) and luminescence excitation (red open circles), λ_{lum} = 580 nm for Li_2MoO_4, 10K. In the inset – emission at E_{ex} = 15.5 eV.

At RT luminescence of Li_2MoO_4 and $MgMoO_4$ signal crystals was not observed. However at 10K luminescence was found for both investigated crystals (fig. 1,2). Both molybdates show non-elementary emission band with several components. Complex structure of the luminescence band may be due to the presence of two overlapped luminescence bands. Decay time of the luminescence exceeds 10^{-6} s. Presence of the MoO_4^{2-} isolated tetrahedrons in Li_2MoO_4 allows to suggest that the shortwave band (shoulder at 515 nm) that caused by electron transition in isolated MoO_4^{2-} complex and longwave (peak at 580 nm) caused by defects in the crystal (oxygen vacancy in MoO_4 complex) similarly to the scheelite type molybdates. Luminescence of $MgMoO_4$ has maximum at 510 nm and shoulder in the region of 550 – 560 nm. We ascribe the shortwave luminescence to the distorted MoO_4 complex because in $MgMoO_4$ crystal only distorted MoO_4 tetrahedrons exist.

Reflectivity of the lithium molybdate is presented in fig. 1. The first peak at 4.15 eV is obviously caused by the reflection from the back side of the crystal. It is known that the transmission edge of this crystal is 4.2 eV at RT [3] and it shifts to the high energy region when the temperature decreases. To our knowledge there are no calculations of the energy bands structure for lithium molybdate. However we suggest that the contribution of the electron states of the lightest lithium cation in the valence and conduction bands building

is negligibly small. Thus reflectivity spectrum in the fundamental absorption region is determined by electron transactions on the MoO_4^{2-} complex.

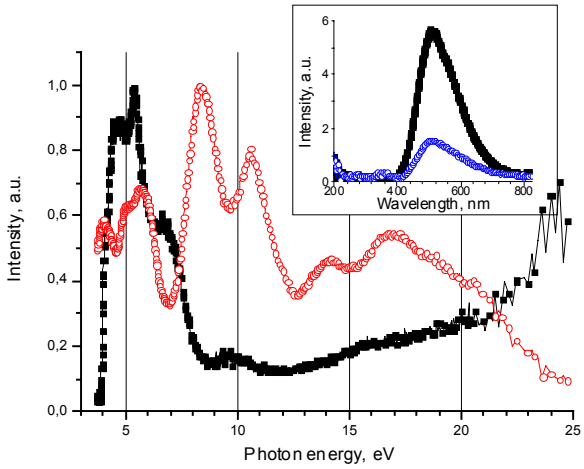

Figure 2. Reflectivity (squares) and luminescence excitation (red open circles), λ_{lum} = 500 nm for $MgMoO_4$, 10K. In the inset – emission at E_{ex} = 15.5 eV (blue circles) and 5.4 eV (black squares).

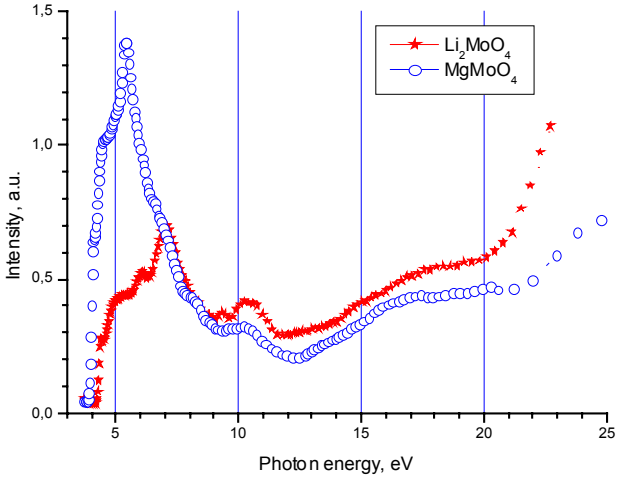

Figure 3. Volume quantum yield for the diffusion length of the electronic excitations L = 5 nm for Li_2MoO_4 and $MgMoO_4$.

Calculation of the density of states using first principle of density functional theory DFT was performed for β-$MgMoO_4$ [4]. Valence band structure of β-$MgMoO_4$ is determined by orbital O 2*p* and Mo 4*d* hybridization. Moreover as a result of DFT calculations for the series of $MeMoO_4$, (Me = Mg, Fe, Co, Ni, Cu, Zn) it was found that the density of states of the cation is neglectible comparing with density of molybdenum d states in the bottom of conduction band. Thus $MgMoO_4$ reflectivity structure is due to the transitions in MoO_4 group. Difference in the reflectivity spectra of Li_2MoO_4 and $MgMoO_4$ may be caused by the MoO_4 group distortion in the latter crystal and also by the unknown orientation of the crystallographic axis of the samples.

Calculation of the volume quantum yield was carried out from the luminescence excitation spectra using the diffusion model of the near surface losses [5]. Such calculations allow to take into account the influence of the portion of the radiation absorbed by the crystal and the factor of the near surface losses on the quantum yield. In energy region from 5.5 to 8.5 eV the volume quantum yield value of $MgMoO_4$ decreases that is typical for the excitonic type of luminescence [5]. As for Li_2MoO_4 the there is no pronounced decrease thus the recombination type of the luminescence is proposed for this compound. However in the latter crystal the excitation was measured at the maximum of the low energy band that is due to the defects and the volume yield in this case gives information about the type of the low energy luminescence band. In the photon energy range above 12.6 eV for $MgMoO_4$ and 11.8 eV for Li_2MoO_4 the increase of $\eta_{vol}(h\nu)$ is observed that is due to the electronic excitation multiplication (EEM) phenomenon. In the energy region where EEM process starts only located near the top of valence band electrons could take part in this process. With the further increasing of the excitation energy electrons from the depth of the valence band could also take part in this process that leads to the further increase of $\eta_{vol}(h\nu)$.

The support of grants DFG 436 RUS 113/437, RFBR 03-02-17346, NSh 1771.2003.2 is gratefully acknowledged.

References

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