Reflectivity and luminescence of $SrWO_4$, $SrMoO_4$ and $CaMoO_4$

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Here we present the results of our investigation of the calcium and strontium molybdate and strontium tungstate single crystals with the scheelite crystal structure. $CaMoO_4$ is known to be used in acousto-optical devices and $SrMoO_4$ and $SrWO_4$ are appeared to be perspective candidates for usage as laser crystals [1].

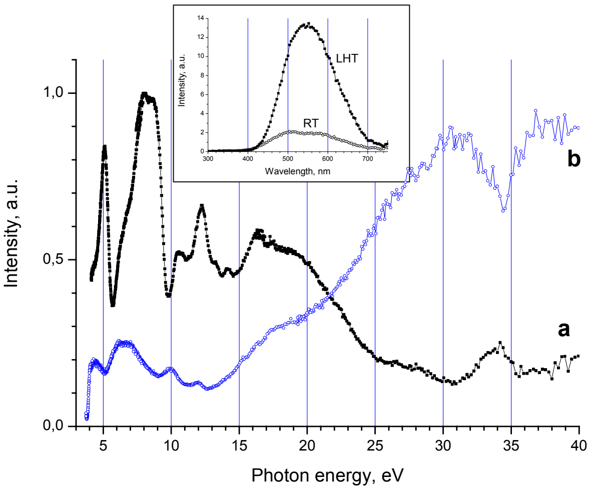

Figure 1. Reflectivity (a) and luminescence excitation (b), λ_{em} = 520 nm spectra of $CaMoO_4$ at LHT. In the inset – luminescence of $CaMoO_4$ at λ_{ex} = 110 nm.

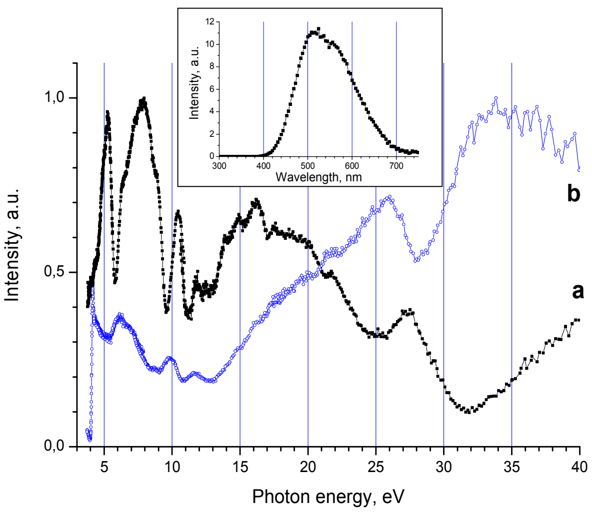

Figure 2. Reflectivity (a) and luminescence excitation (b), λ_{em} = 510 nm spectra of $SrMoO_4$ at LHT. In the inset – luminescence of $SrMoO_4$ at λ_{ex} = 110 nm.

Luminescence emission and excitation spectra as well as reflectivity of the investigated crystals were measured at the SUPERLUMI station (HASYLAB, Hamburg, Germany). Measurements were carried out in the energy range of 3.7-40 eV at temperatures from 10 to 300 K. The luminescence spectra were corrected on the photomultiplier tube sensitivity. Crystals were grown in the Laser Materials and Technology Research Center of GPI (Moscow). The relative orientation of crystallographic axes of the samples to the **E** vector of the incident SR was taken into account during the reflectivity measurements for anisotropic $SrWO_4$.. Spectra were measured from freshly cleaved surface.

Reflectivity in the energy region from 3.7 to 30 eV for a set of the scheelite type crystals are presented in fig.1-3. In spite of vague orientation of the calcium and strontium molybdates in the energy region of 3.7-15 eV their reflectivity structure is analogues to that of barium molybdate. Analogously to the reflectivity of $PbMoO_4$ and $BaMoO_4$ analysed in [2] we suppose that the reflectivity peaks of $CaMoO_4$, $SrMoO_4$ in this region are also mainly due to the electronic transitions within MoO_4^{2-} complex. This suggestion is confirmed by the calculations of electronic structure of the valence and conduction bands of $CaMoO_4$ [3]. The maximum and half-width of the first reflectivity peak in $CaMoO_4$, $SrMoO_4$ and $SrWO_4$ remain constant at RT and LHeT. Since it is not of the excitonic origin, the position of its maximum (5.1 eV for $CaMoO_4$, 5.3 eV for $SrMoO_4$ and 6.1 eV for $SrWO_4$) gives us an estimate of the bandgap in these compounds. More accurate estimation of the bangap can be done from the absorption spectra, which are calculated from the reflectivity using Kramers-Kronig relations.

Common features in the reflectivity of $CaMoO_4$ and $SrMoO_4$ are also observed in the energy region 13-25 eV that can be attributed to the transitions from the valence band to the upper states of the conduction band. In the energy region above 20 eV spectral features were observed, which were similar for the strontium molybdate and tungstate and different for the calcium molybdate. This features can be attributed to the excitation of the highest-lying core levels of the cations. It worth noting that there is no excitonic-type features related to the Ca 3p core level were found in the region 25 – 30 eV in $CaMoO_4$. This is not always the case for Ca compounds; a pronounced reflectivity peak at ≈28 eV is observed in $CaCO_3$, CaF_2 and $CaSO_4$ that is due to the creation of core exciton with hole component on 3p Ca^{2+}. Nevertheless in $CaMoO_4$ we observe a broad reflectivity peak with the maximum at 34 eV that is due to the electron transitions from 3p Ca^{2+} to the conduction band [4]. A similar situation is observed for $SrWO_4$ and $SrMoO_4$ – there are no pronounced features in 22-24 eV energy region but a broad maximum is observed at 27 eV.

It worth noting that the structure of the upper core cation excitons is more pronounced for molybdates and tungstates with heavier cations (Ba, Pb). We suppose that the contribution of the cation electronic levels to the bottom of the conduction band decreases with the decrease of the atomic number of the cation for the molybdates and tungstates. As a result core cation exciton peaks in the reflectivity spectra disappear in molybdates and tungstates with relatively light cations (Ca, Sr). Actually according to [3] calcium levels were positioned in the upper part of the conduction band. However there is no such dependence e.g. for the fluorides [4] or oxides [5] of these metals were the above mentioned core cation excitons have a pronounced structure in the reflectivity spectra.

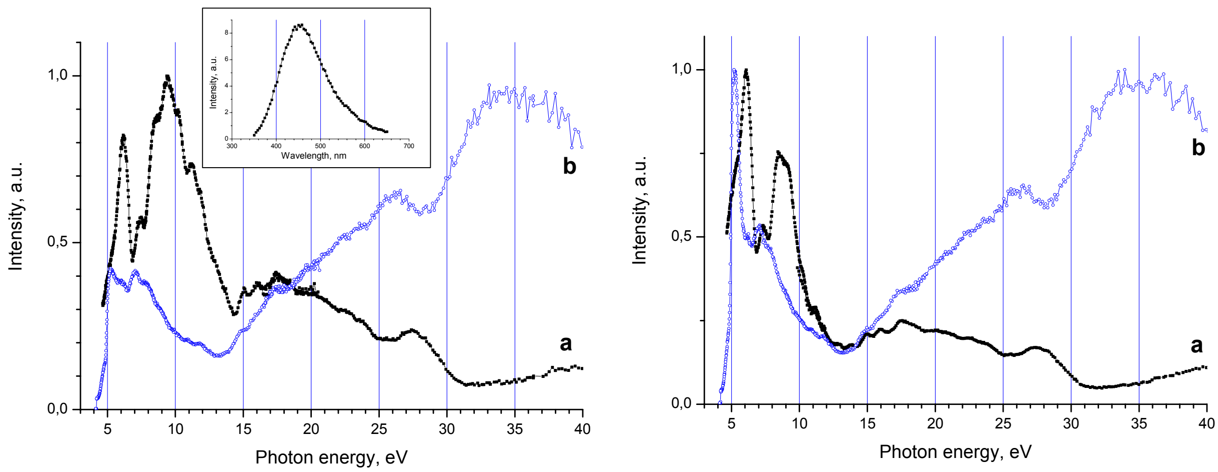

Figure 3. Reflectivity (a) and luminescence excitation (b), λ_{em} = 450 nm spectra of $SrWO_4$ for the perpendicular (rigth) and parrallel (left) orientation of the axis **c** of the crystal and electric vector **E** of the incident synchrotron radiation, LHT. In the inset – luminescence of $SrWO_4$ at λ_{ex} = 60 nm.

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