

Optical and luminescent properties of a series of molybdate single crystals of scheelite crystal structure

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The luminescent and reflectivity spectra of a series of the molybdates with the scheelite crystal structure were investigated using synchrotron radiation. The main features in reflectivity spectra in the energy range of 3.2–40 eV were analyzed. The luminescence spectra were measured under X-ray excitation and their relative intensities were explained in the frames of the configuration curves model.

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1 Introduction Molybdate single crystals with scheelite crystal structure are extensively used in acousto-optical devices (CaMoO_4 and PbMoO_4) and appeared to be perspective candidates for usage as laser crystals (SrMoO_4). Moreover molybdate crystals could be used as scintillators for the neutrinoless double β decay experiment [1]. ^{100}Mo isotope (natural abundance is 9.6 %) is a double β decay nuclide, so the development of a scintillator containing Mo in itself is a problem of great interest. Here we present the results of our investigation of a series of the molybdates: CaMoO_4 , SrMoO_4 , BaMoO_4 and PbMoO_4 (results on the latter two crystals were also presented in [2]). The investigations of luminescent and optical properties of a series of isostructural crystals are of a particular interest because they allow to work out generic trends in the properties of a family of crystals as well as to define specific features of particular crystals.

2 Experimental Luminescence emission, kinetics and excitation spectra as well as reflectivity of the molybdates were measured at the SUPERLUMI station (HASYLAB, Hamburg, Germany) [3]. Measurements were carried out in the energy range of 3.7–40 eV at temperatures from 10 to 300 K. Reflectivity in the energy range of 3.5–25 eV was also measured at the VUV station of the SIBERIA-1 storage ring. Reflectivity of PbMoO_4 in the energy region of 3.2–4.5 eV was measured in the laboratory. Luminescence spectra under X-ray excitation were measured at the experimental station on beamline 5.6 of the storage ring SIBERIA-2 (electron energy of 2.5 GeV) at the Kurchatov Center of Synchrotron Radiation (Moscow, Russia). In these experiments luminescence was excited by a white beam of SR which passed through Be-foil. Luminescence spectra measured under X-ray excitation were not corrected for the spectral response of the detection system.

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The barium molybdate single crystal was grown from the solution in the melt and other molybdates were grown using Czochralski method. Calcium and strontium molybdates were grown in the Laser Materials and Technology Research Center of GPI (Moscow) and lead and barium molybdates were grown in VNIISIMS (Vladimir region). The relative orientation of crystallographic axes of the samples to the \mathbf{E} vector of the incident SR was taken into account during the reflectivity measurements for anisotropic PbMoO_4 and BaMoO_4 . Orientational effects were not studied for CaMoO_4 and SrMoO_4 samples, moreover, X-ray structure analysis revealed twinning for CaMoO_4 . Spectra were measured from freshly cleaved surface except barium molybdate for which natural surface was used for the measurements.

3 Results and discussion

3.1 Reflectivity spectra Reflectivity in the energy region from 3.7 to 15 eV for a set of the scheelite type molybdates are presented in Fig. 1A. We already analyzed reflectivity of PbMoO_4 and BaMoO_4 [2]. For the lead molybdate it was shown that an additional peak with the maximum at 3.6 eV (at RT) is due to the transitions $6s^2 \rightarrow 6s6p$ in Pb^{2+} ion with possible exciton creation. For the lead molybdate the main features were assigned to the electronic transitions within the MoO_4^{2-} complex. In spite of vague orientation of the calcium and strontium molybdates in this energy region their reflectivity structure is analogous to that of barium tungstate. We suppose that reflectivity peaks of CaMoO_4 , SrMoO_4 in this region are also 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 [4]. The maximum and half-width of the first reflectivity peak in CaMoO_4 and SrMoO_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 and 5.3 eV for SrMoO_4) gives us an estimate of the bandgap in these compounds. More accurate estimation of the bandgap can be done from the absorption spectra, which are calculated from the reflectivity using Kramers-Kronig relations. These calculations will be made soon.

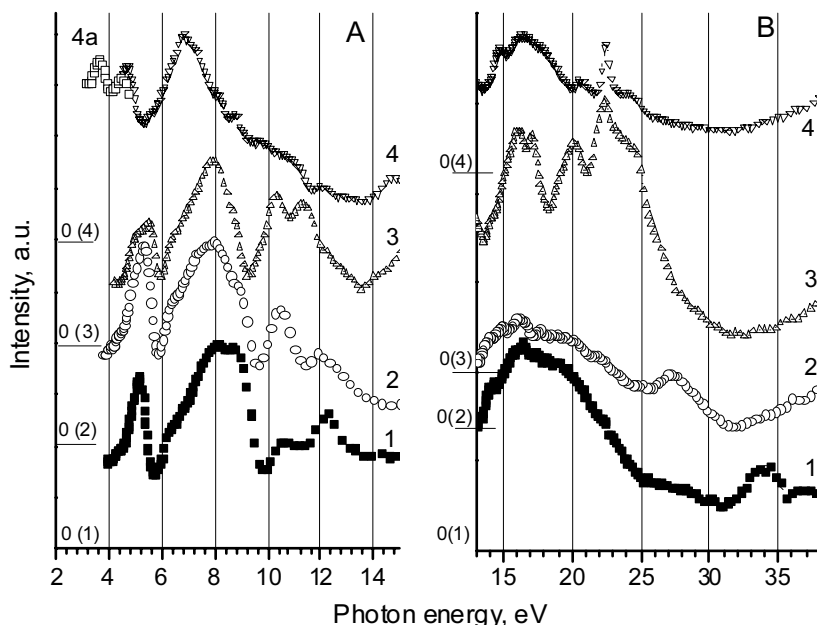


Fig. 1 Reflectivity of CaMoO_4 (1), SrMoO_4 (2), BaMoO_4 (3) and PbMoO_4 (4) at 10 K. 4a - Reflectivity of PbMoO_4 , measured on the laboratory equipment at RT. For BaMoO_4 and PbMoO_4 reflectivity presented for the “parallel” orientation of \mathbf{c} and \mathbf{E} .

In the energy region above 15 eV spectral features were observed, which were individual for each investigated molybdate attributed to the excitation of the highest-lying core levels of the cations (Fig. 1B). A pronounced doublet at 20.74 and 22.46 eV and some of low-intensity reflectivity peaks in the

energy region of 19–25 eV in PbMoO_4 were assigned to the cationic core excitons with the hole component on the Pb^{2+} 5d levels [5]. The group of the reflectivity peaks in the energy range from 17 to 30 eV in BaMoO_4 can be assigned to the creation of cation core excitons on Ba^{2+} ion and to the electronic transitions from 5p level of Ba^{2+} to the conduction band as it was observed in BaWO_4 [6] or in BaF_2 [7].

On the other hand no 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 [7]. According to [4] calcium levels were positioned in the upper part of the conduction band. Interaction of these transitions with the continuum of the transitions from the valence band to the upper part of the conduction band can result in the decay of core exciton. A similar situation is observed for SrMoO_4 – there are no pronounced features in 22–24 eV energy region but a broad maximum is observed at 27 eV. 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.

Thus the structure of the upper core cation excitons is more pronounced for molybdates with heavier cations (Ba, Pb). We suppose that in the discussed series of the molybdate single crystals 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. As a result core cation exciton peaks in the reflectivity spectra disappear in molybdates with relatively light cations (Ca, Sr). However there is no such dependence e.g. for the fluorides [7] or oxides [11] of these metals were the above mentioned core cation excitons have a pronounced structure in the reflectivity spectra.

3.2 Luminescence spectra The luminescence spectra of a series of molybdates measured under X-ray excitation are presented in fig.2. Commonly, the luminescence of the molybdates excited with photons with energies exceeding the bandgap value consists of a single "green" luminescence band with the maximum at 490–550 nm [8] and it is attributed to the radiative transitions within MoO_4^{2-} -complex. The possible exception is the luminescence of the lead molybdate. In our previous paper we suggested the participation of the lead electronic states in forming of the emission center or in the energy transfer to the center. The measurements were carried out under the same conditions therefore we can get the information about the relative intensities of the luminescence bands in these molybdates. Spectra are plotted on logarithmic scale for clearness, as the relative intensity of luminescence changes by hundred times from the brightest (calcium molybdate) to the weakest one (barium molybdate). The values of the relative

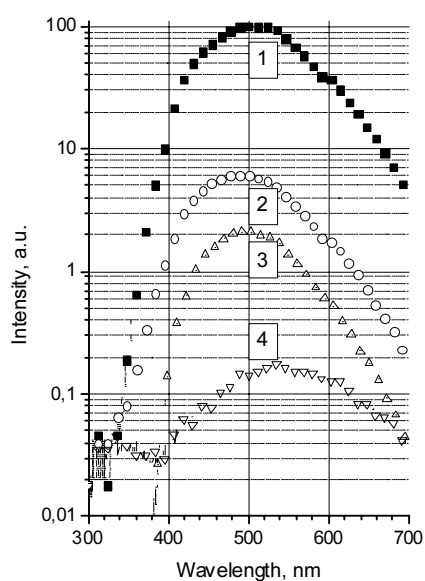


Fig. 2 Luminescence spectra of CaMoO_4 (1), SrMoO_4 (2), PbMoO_4 (3) and BaMoO_4 (4) under X-ray excitation, RT.

Table 1 Relative intensity of luminescence in molybdates.

Crystal	Luminescence maximum (nm)	Relative intensity of the luminescence	Cation ionic radius (angstroms) [10]
CaMoO ₄	500	100	0,99
SrMoO ₄	484	6.15	1,12
PbMoO ₄	492	2.08	1,20
BaMoO ₄	522	0.18	1,34

intensities of the samples luminescence are presented in the table (the luminescence intensity of calcium molybdate was taken as 100%). Decrease of the luminescence intensity in the row CaMoO₄ - SrMoO₄ - PbMoO₄ - BaMoO₄ correlates with the increase of ionic radius of the given cations (see Table 1). According to [9] this phenomenon can be explained in the frames of the configuration curves model because the shift of the excited state parabola (parabola offset) depends on the cation ionic radius. The larger is the cation ionic radius, the greater is the parabola offset value, and, accordingly, the greater is the probability of nonradiative electron relaxation from the excited state.

It should be noticed that the measurements were carried out on the samples grown using two different methods. Relative intensity and spectral structure of the luminescence may depend on the growth technique so the relative intensity values of the luminescence are not absolutely correct.

4 Conclusion The main features in reflectivity spectra in the energy range of 3.2–40 eV were explained for series of the molybdates with scheelite crystal structure. The bandgap values were estimated for CaMoO₄ and SrMoO₄. It was supposed that in the discussed molybdates 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. The relative intensities of the measured luminescence bands were explained in the frames of the configuration curves model.

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