Luminescence in Gadolinium Molybdate Single Crystals under VUV and XUV Excitations

I.A. Gofman, V.A. Pustovarov and S.O. Cholakh

Ural Federal University, 620002, Mira str. 21, Yekaterinburg, Russia

Luminescent properties of molybdates have recently been a subject of intensive research using synchrotron radiation. By now, crystals with scheelite structure were studied [1], also specific investigations were held on molybdate crystals with light cations [2], magnesium [3] and zinc molybdates [4]. Some of the materials were shown to be prospective for use as cryogenic scintillating bolometers in the search of neutrinoless double beta decay [5]. Molybdates also attract researchers’ attention because the nature of the luminescent centers is still not clear to the end.

The object of the present study was a rare-earth molybdate $\beta$-Gd$_2$(MoO$_4$)$_3$ (GMO) with tetragonal structure (Pba$_2$ space group). We studied two groups of crystals – nominally pure single crystals cut perpendicular to c-axis, and single crystals with radiation induced defects (irradiated under fast electrons, E=10 MeV, fluence F=2·10$^{16}$ electrons/cm$^2$).

PL spectra in the energy range 1.3 - 6.2 eV, PL excitation spectra and reflection spectra (17°) in the energy range 3.7 - 21 eV were measured at T=7.5 K at the SUPERLUMI station (Beam-line I). The 0.3 m ARC SpectraPro-308i monochromator equipped either with the R6358P (Hamamatsu) photomultiplier or cooled CCD camera was used to analyse luminescence. The PL excitation spectra were corrected for the equal number of the exciting photons using sodium salicylate, whereas the PL spectra are presented without any corrections. In the XUV region PL spectra (2.5 - 7.0 eV), PL excitation spectra (60 - 450 eV) as well as PL decay kinetics were measured at T=8.5K using SR from the BW3 beam-line. Undulator radiation was further monochromatized by a Zeiss SX700 monochromator. The PL spectra were measured by an 0.4 m vacuum monochromator (Seya-Namioka scheme) equipped with an microchannel plate-photomultiplier (MCP 1645, Hamamatsu). The PL excitation spectra were corrected for incident flux using photodiode AVUX-100.

PL spectra of both crystals are shown in the Figure 1. PL spectrum of the pure GMO crystal is a broad band in the green region, typical with molybdates. It consists of two explicit subbands $E_{em}=2.21$ eV and $E_{em}=2.45$ eV with relative intensity dependent on the excitation energy. This type of behaviour was not observed for any of other molybdates, pointing to the responsibility of crystallographic peculiarities for this phenomenon. In particular, GMO structure shows several non equivalent crystallographic positions for MoO$_4^{2-}$ tetrahedra. PL spectrum of defective crystal is shifted to the red side ($E_{em}=1.92$ eV), together with its excitation peak at $E_{exc}=3.92$ eV. These parameters are characteristic of the molybdate additional emission peak previously observed in scheelite compounds [6]. This is an important result because we thus show that this type of defects can be obtained both by synthesis and radiation modification. The nature of the defect center is still under discussion.

The reflection spectra and PL excitation spectra of the pure and defective crystals are shown in the Figures 2 and 3, respectively. The absorption edge tails in both cases lie lower than 4.0 eV and therefore are inaccessible for available equipment. From laboratory measurements we know that radiation induced slight yellow coloration of the crystals and shifted the absorption edge to lower energy. PL excitation spectra of the pure crystal show two peaks which can be attributed to the allowed transitions in the MoO$_4^{2-}$ tetrahedra. Relative intensity of the higher energy peak is also dependent on the emission wavelength monitored. Sharp lines of Gd$^{3+}$ absorption are well resolved at the PL excitation spectra. This result indicates that energy transfer exists from cationic to anionic sublattice.

Luminescence excitation spectra in the XUV region showed sharp structures in the region of the core levels of the atoms present in the crystal, e.g. near 1s(O) level (peak at 542 eV) and 4d$_{5/2}$(Gd) level (see Figure 4). Presence of the minima in the spectra point to the high mobility of the electronic excitations created by XUV photons. The main peculiarity of the luminescence spectra under XUV-excitation was that Gd$^{3+}$ $^6P_3\rightarrow^8S_{7/2}$ lines appeared (see Figure 3, inset). Together with
the presence of gadolinium lines in the excitation spectra this means that 4f levels of Gd$^{3+}$ mix significantly with 2p orbitals of O$^{2-}$ contributing to the top of the valence band in GMO.

Figure 1: The PL spectra of pure GMO crystals, $E_{\text{exc}}=6.2$ eV (1), $E_{\text{exc}}=4.4$ eV (2) and defective GMO samples, $E_{\text{exc}}=3.9$ eV. $T=7.5$ K, detector - CCD-camera.

Figure 2: The reflection spectrum (1) and PL excitation spectra $E_{\text{em}}=2.58$ eV (2) and 2.02 eV (3) of the pure GMO crystal. Inset: fragment of the PL excitation spectrum near Gd$^{3+}$ excitation lines, $T=7.5$ K.

Figure 3: The PL excitation spectrum $E_{\text{em}}=1.9$ eV of the defective crystal. Inset: PL spectrum of the pure crystal, $E_{\text{exc}}=142$ eV, $T=8.5$K.

Figure 4: Luminescence excitation spectrum of pure GMO sample in the region of 4d(Gd) edge at $T=8.5$ K.

Acknowledgements: The authors are grateful to Prof. V.Ya. Shur for granting the crystals, Dr. V.Yu. Ivanov and S.I. Omelkov for help in measurements on BW3 channel, F.G. Neshov and F.M. Klinov for managing electron irradiation of GMO crystals.

References