Luminescence properties of the Pb$_2$MoO$_5$ single crystals doped with Cu ions

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Abstract. Photoluminescence (PL) emission and PL excitation spectra of the undoped and Cu-doped Pb$_2$MoO$_5$ grown by Czochralski technique are obtained and analyzed. The complex wide PL emission band in 450-750 nm spectral range was observed for both pure and Cu-containing crystals under photoexcitation with ultraviolet light. The short-wavelength component of the PL has been associated with luminescence centers related to MoO$_4^{2-}$ anionic groups. Long-wavelength the PL component with maxima near 600 nm was observed for both pure and Cu-doped crystals and it is described to manifestation of the crystal defects.

1. Introduction

Optical properties of the double lead molybdate Pb$_2$MoO$_5$, single crystals have been studied due to the perspectives of this material application in the acousto-optic devices [1, 2]. In the same time due to the photochromic effect, peculiar to the lead molybdate family, their application is still limited [3]. As it follows from the literature both Mo [4] and Pb deficiency [5] can lead to a photochromic effect in PbMoO$_4$, for example. Obviously, that non-stoichiometric composition of the crystals promotes the creation of the various types of defects in the crystals structure. The situation can be partially managed by the specific doping of the crystals with impurity ions. The dopants will affect the quantity of the defects and influence their role. As was reported, the PbMoO$_4$ doping with Bi$^{3+}$ and Ba$^{2+}$ ions leads to lowering of the photo-induced coloring of the compound [3]. So, it is possible that isovalent to Pb$^{2+}$ ion doping can change an optical quality of the Pb$_2$MoO$_5$ crystals. Therefore the role of the defects in the optical properties determination is an important issue for developing of high quality optical materials based on the Pb$_2$MoO$_5$ crystals.

Optical methods, in particular luminescence spectroscopy, can be efficiently used to analyze the role of defects on the physical processes in oxide crystals. Luminescence properties of the undoped and impurity-containing molybdates are interesting in itself for elaboration of the scintillation and luminescent materials. To our knowledge, there are only two papers on luminescence properties of the nominally un-doped Pb$_2$MoO$_5$ crystals [6, 7], while no paper deals with luminescence of the impurity-containing double lead molybdate.

In the present paper we studied the luminescence properties of both pure and Cu-doped Pb$_2$MoO$_5$ crystals and have tried to find an influence caused by Cu ions. The possible origin of the investigated crystals luminescence is also discussed.
2. Sample preparation and experimental set-up
The Pb$_2$MoO$_5$ single crystals were grown from melts in a Pt crucible by the conventional Czochralski technique. The melts were prepared by heating of PbO and MoO$_3$ oxides (purity rating 99.99%) taken in stoichiometric ratio. Typical growth conditions are the following: 50 rpm rotation rate, 3 mm/h pulling rate, 30°C/h cooling rate. The samples were grown in ambient air atmosphere with temperature fluctuation during crystal growing within ±0.2°C. The Pb$_2$MoO$_5$:Cu crystals were synthesized in the same way from a melt that contains 0.03 wt. % of the CuO.

The PL emission and PL excitation spectra in the ultraviolet (UV) region of excitations were measured using a Xenon lamp DKsSh-150, primary monochromator MDR-12 and secondary monochromator MDR-23. The samples were put into a helium-flow cryostat for the luminescence study. The PL emission and excitation spectra were corrected on system response.

3. Results and discussion
The PL emission spectra of Pb$_2$MoO$_5$ and Pb$_2$MoO$_5$:Cu crystals at liquid helium temperature (4.2 K) are presented on the Figure 1. It is clearly seen from the figure that both pure and Cu-doped crystals reveal a wide complex PL band in the 450 - 750 spectral region. At least, two components can be distinguished in the PL spectra of the un-doped Pb$_2$MoO$_5$ crystals under long-wave ultra-violet (UV) excitation at $\lambda_{ex} = 350$ nm.

The short-wavelength (“green”) PL component has a maximum at 520 nm and was observed earlier [6]. This green PL is mainly excited in the narrow excitation band with maxima near 350 nm (3.54 eV) in excitation spectra. This asymmetric PL excitation band is accompanied with a shoulder in the range 275 - 340 nm and low intensity excitation band which is manifested as the wing located in the range 250 - 275 nm (Figure 2, top).

Figure 1 shows also the long-wavelength (“orange”) component of the un-doped Pb$_2$MoO$_5$ photoluminescence with maximum near 590 nm. This PL clearly observed under excitation at shorter wavelengths, $\lambda_{ex} = 330$ and 300 nm, and the low intensity “red” component of the PL can be also distinguished in the range 625 - 750 nm. The mentioned orange and red components are mainly excited in the shorter UV wavelength range in comparison with the PL excitation of the green.
luminescence, 250 – 340 nm, but at the same time we have to note the excitation at the longer wavelengths range: 360 – 380 nm (see the curves on the Figure 2, top). We should note that only orange photoluminescence of the un-doped PbMoO₅ crystal was earlier observed for excitation with synchrotron radiation in vacuum ultraviolet (VUV) spectral region (λ < 200 nm) [7].

The knowledge of the band gap value, E_g, could simplify the analysis of the PL excitation spectra and the PL origin. Unfortunately no papers which deal with E_g of the PbMoO₅ compound are available at present. However, we know that thin samples of the un-doped double lead molybdate crystals are transparent for spectral region λ > 336 nm and the region of the high absorption starts at 230 nm [8]. Taking into account the high absorption of most oxide materials in the region of the band-to-band transitions we have full reason to assume that the band gap of PbMoO₅ is not lower that 3.7 eV (this value correspond to wavelength 336 nm). Because the maximum of the green PL excitation band (3.54 eV) is close to the above mentioned value, it probably indicates the “excitonic” origin of the green luminescence. It should be noted the green luminescence band position as well as it’s excitation spectrum is similar to the case of the PbMoO₅ luminescence and it is generally accepted that luminescence of the PbMoO₅ is related to radiative decay of excitons which localized at molybdate groups of the crystal. So, it is likely that green component of the PbMoO₅ PL has the same origin. This is a radiative decay of excitons which are localized at the MoO₃²⁻ molybdate groups.

As for the orange and red the PL components it is not so easy to speak about their origin. In fact, the VUV and UV excitations, obviously, correspond to band-to-band transition in PbMoO₅ crystal and it would be useful to engage available data on the electronic band structure calculations. It has been found earlier, the distribution of the partial density of states of the PbMoO₅ indicates that Pb-O chains contribute to the band-to-band absorption edge [7]. Therefore, mentioned chains or rather Pb²⁺ ions bounded with oxygen in its surrounding may play an important role in luminescence excitation. At the same time, the orange and red PL bands were observed for a number of molybdate and analogues tungstate compounds under excitation not only in VUV and UV regions, but in the region of crystals transparency and that is characteristics detail – in the spectral range located near excitonic excitation band at longer wavelengths [9-14]. That is why, those types of the PL are assigned to the various complex luminescence centers which can include two charged matrix cation (or its vacancy), molecular group (molybdate or tungstate), oxygen vacancy (or F, F⁺, F⁵⁺, etc. – center formed on the site of the oxygen vacancy) [see e.g. 15]. Our measured excitation spectra (Figure 2, top) show the similar characteristic details, so we can assume that the orange and red components of the PbMoO₅ PL can be assigned to the similar luminescence centers, but no more reliable conclusions about the origin of the orange and red luminescence of un-doped PbMoO₅ crystals can be done on the basis of the data available at present.

Doping of the PbMoO₅ crystal with Cu leads to the disappearance of the green photoluminescence band (Figure 1, b) and corresponding to it a band in the PL excitation spectra (Figure 2, b). The orange PL bands are still observed but have somewhat lower intensity if compared to the un-doped samples. As for the red PL, its contribution to the spectra can be distinguished clearly.

There are at least two possible ways of the Cu ions location in the PbMoO₅ crystal matrix can lead to vanishing the green component of the PL by copper impurity. We have to regard two charge variant of the Cu substitution for the Pb²⁺ in crystal lattice. First of them is Cu²⁺ substitution for the Pb²⁺. If the Cu²⁺ substitutes for the Pb²⁺ in crystal lattice the changes in nearest oxygen surrounding seem to be indispensable (the ionic radii of the Pb²⁺ and Cu²⁺ are strongly different: 1.26 and 0.80 Å respectively).

The other way is more complicated. This is related to other charge state of copper ion – Cu⁺. It was reported for similar PbWO₄ compound that impurities of copper are mainly in the Cu⁺ state, but not in the Cu²⁺ state [16]. We can expect a similar situation for the PbMoO₅:Cu case. An incorporation of the Cu⁺ ion on the Pb²⁺ site requires charge compensation, so, the additive oxygen vacancies have to be formed in the PbMoO₅:Cu⁺ crystals. Note, that ionic radii of the Pb²⁺ and Cu⁺ are also different: 1.26 and 0.98 Å respectively. Possibility of the Cu⁺ ions substitution for Pb²⁺ is in accordance with the results of the PbMoO₅:Cu crystal electronic band structure calculations, which were performed by us recently with Wien2k package [17]. Of course, some doubts arise due to approximate character of
calculation based on the density functional theory quantitative analysis of the state occupations. Nevertheless it is likely that in the Pb$_2$MoO$_5$ crystal the Cu$^{+}$ ions on Pb$^{2+}$ positions can exist.

In both cases, some of the MoO$_4^{2-}$ anionic groups in Pb$_2$MoO$_5$:Cu crystals are more distorted than in un-doped Pb$_2$MoO$_5$ that results in their losing the capability to localize excitation energy and future emit the “green” light as result of the excitons decay.

Orange and red components of the Pb$_2$MoO$_5$:Cu crystal luminescence are of the same origin as ones for the un-doped Pb$_2$MoO$_5$. Some changes in the shapes of the emission and excitation spectra of the orange and red luminescence can be related with changes of the various types of defects content and related with them centers of mentioned luminescence. This issue, charge state of the Cu ions as well as nature of the orange and red photoluminescence requires further research, in particular by time resolved spectroscopy, of both un-doped and doped with different content of the Cu ions Pb$_2$MoO$_5$ crystals.

4. Conclusions

Studied samples of the un-doped Pb$_2$MoO$_5$ crystals grown by Czochralski technique reveal complex photoluminescence bands with two main components maxima at 520 and 590 nm respectively. The PL excitation spectra of short-wavelength, “green”, component reveal narrow band at 350 nm accompanied with a shoulder on the side of the lower wavelengths. Doping of the Pb$_2$MoO$_5$ crystal with a low amount of Cu leads to vanishing of green photoluminescence as well as to disappearance of the band with maxima at 350 nm in the PL excitation spectra. This green luminescence was attributed to radiative decay of localized excitons.

The changes in luminescence properties of Cu-doped samples in comparison with pure crystals are ascribed to the increasing of the defects concentration (i.e. oxygen vacancies) in crystal lattice.

The origin of the orange and red long-wavelength luminescence of the Pb$_2$MoO$_5$ crystals requires further research.

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