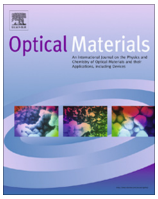
Optical Materials 36 (2014) 1754–1759

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



Luminescence spectroscopy and electronic structure of the $PbMoO_4$ and Pb_2MoO_5 single crystals

S. Nedilko [a], V. Chornii [a], Yu. Hizhnyi [a,*], M. Trubitsyn [b], I. Volnyanskaya [c]

[a] Taras Shevchenko National University of Kyiv, Volodymyrska St. 64, 01601 Kyiv, Ukraine
[b] Oles Honchar Dnipropetrovsk National University, Gagarina Ave. 72, 49010 Dnipropetrovsk, Ukraine
[c] Prydniprovs'ka State Academy of Civil Engineering, Chernyshevs'kogo St. 24a, 49600 Dnipropetrovsk, Ukraine

ARTICLE INFO

Article history:
Available online 1 April 2014

Keywords:
Luminescence
Electronic structure
Lead molybdate
Reflectivity

ABSTRACT

Intrinsic photoluminescence (PL) and electronic structure of Pb_2MoO_5 single crystal are first described and compared with corresponding properties of $PbMoO_4$ crystal. The PL properties of $PbMoO_4$ and Pb_2MoO_5 crystals grown by Czochralski method are studied under the VUV synchrotron radiation excitations (3.7–14 eV region of excitation photon energies) at $T = 8$ K. The electronic band structures of perfect $PbMoO_4$ and Pb_2MoO_5 are calculated by the Full-Potential Linear Augmented Plane Wave method. The Pb_2MoO_5 crystals reveal intensive PL band in the yellow–red spectral region peaking at ~600 nm. All studied $PbMoO_4$ samples reveal intensive PL band in the green spectral region and this band is accompanied by additional fast-decaying ($\tau \approx 3.5$ ns) component in the violet when the samples are grown with 30° orientation of seed with respect to the c axis. The excitation spectra of the violet component of $PbMoO_4$ reveal complex excitation band with main peak at 6.2 eV. It is assumed that the violet PL component of $PbMoO_4$ is generated by intra-center excitations from the ground to singlet excited states $^1A_1$–$^1T_{1,2}$ of the MoO_4^{2-} molybdate groups located near point defects in subsurface layer of the crystal. Strong anisotropy of reflectivity spectra of $PbMoO_4$ below 6 eV is a consequence of peculiarities of the electronic structure of the crystal and reflectivity bands at ~3.6 and ~4.3 eV are formed by band-to-band electronic transitions.

1. Introduction

The lead molybdate crystals $PbMoO_4$ are widely used at present as scintillation [1,2] and acousto-optic materials [3] and are also intensively studied as hosts for luminescent RE ions [4]. The photoluminescence (PL) properties of $PbMoO_4$ were investigated under various types of photoexcitations [5–11] and in particular, under excitation with synchrotron radiation in the VUV region of excitation photon energies [12]. The optical properties of Pb_2MoO_5 crystals were studied mainly from viewpoint of acousto-optic applications [13–16]. Intrinsic luminescence of Pb_2MoO_5 was studied so far only under Xe-lamp excitation [17].

As it was found recently, under excitation in the UV region, some Czochralski-grown samples of $PbMoO_4$ reveal an additional high-energy PL emission band near 400 nm with fast (nanosecond) decay [7,11]. In our studies of the set of $PbMoO_4$ crystals grown by Czochralski technique, we found that some $PbMoO_4$ samples when being grown at certain growing conditions (orientation of seed with respect to the crystalline axes) reveal such additional band. In the present paper, we report the excitation spectrum of this band for the first time. We also analyze the origin of $PbMoO_4$ luminescence taking into account results of the electronic band-structure calculations.

To our knowledge, intrinsic luminescence of Pb_2MoO_5 under the VUV synchrotron excitation has been never reported in literature. Existing assumptions on the origin of this luminescence were made on the ground of experimental data obtained only for polycrystalline powder samples Pb_2MoO_5 grown by a solid state reaction method [17]. In the present paper, we analyze the origin of intrinsic luminescence in Pb_2MoO_5 comparing the PL properties of Pb_2MoO_5 and $PbMoO_4$ and taking into account the results of the electronic structure calculations.

The electronic band structure of Pb_2MoO_5 is calculated here for the first time, whereas the electronic structure of $PbMoO_4$ was calculated and analyzed earlier [18–20]. For this reason, the present study does not focus on a detailed analysis of the electronic structure of $PbMoO_4$. Corresponding results of calculations are utilized here mainly for comparison with Pb_2MoO_5 case and for analysis of experimental reflectance spectra of lead molybdate.

---

[*] Corresponding author. Tel.: +380 675008524.
E-mail address: hizhnyi@univ.kiev.ua (Yu. Hizhnyi).

http://dx.doi.org/10.1016/j.optmat.2014.03.019
0925-3467/© 2014 Elsevier B.V. All rights reserved.

2. Experimental and calculation details

Single crystals of $PbMoO_4$ and Pb_2MoO_5 were grown from melts in a Pt crucible with a resistance heater 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 for each compound. Crystal seeds of various orientations were cut from oriented boule. Typical growth conditions are the following: 50 rpm rotation rate, 3 mm/h pulling rate, 30 °C/h cooling rate. The samples were grown at ambient air atmosphere with temperature fluctuation during crystal growing within ±0.2 °C.

Experiments with VUV radiation excitation were carried out on SUPERLUMI station at HASYLAB (DESY), Hamburg, Germany [21,22]. The photoluminescence (PL) spectra were obtained in 3.7–14 eV region of excitation energies at $T = 8$ K. Both the PL emission and excitation spectra were measured in time-integral regime in the limits of synchrotron radiation pulse with repetition time of 200 ns and duration of 0.128 ns. Photoluminescence and PL excitation spectra in the UV region of excitations were measured using powerful xenon lamp DKRSh-1500, primary monochromator DMR-4 and secondary double monochromator DFS-12. In both synchrotron and Xe-lamp experiments, the samples were put into helium-flow cryostat equipped with temperature stabilizing system. All measured PL emission and excitation spectra were corrected on system response.

Perfect $PbMoO_4$ crystal possess the scheelite-type lattice with space group $I\ 4_1/a$ and lattice constants: $\mathbf{a} = \mathbf{b} = 5.4312$ Å, $\mathbf{c} = 12.1065$ Å, $\boldsymbol{\alpha} = \boldsymbol{\beta} = \boldsymbol{\gamma} = 90°$ [23]. The unit cell of this material has four formula units of $PbMoO_4$. Pb_2MoO_5 crystal possess the lanarkite-type lattice with space group $C\ 2/m$ and lattice constants: $\mathbf{a} = 14.2058$ Å, $\mathbf{b} = 5.7592$ Å, $\mathbf{c} = 7.2844$ Å, $\boldsymbol{\alpha} = \boldsymbol{\gamma} = 90°$, $\boldsymbol{\beta} = 114.29°$ [24].

The $PbMoO_4$ crystal comprise molecular anionic groups MoO_4^{2-} which exist in form of distorted tetrahedra with S_4 point symmetry group (all Mo–O distances are equal to 1.774 Å). The Pb_2MoO_5 crystal also possess isolated MoO_4^{2-} irregular-tetrahedral groups (average Mo–O distance is 1.777 Å). Another peculiarity of Pb_2MoO_5 structure is existence of infinite Pb–O zigzag-like chains along the z crystallographic direction (closest Pb–O distances in the chains are 2.298 Å). Every fifth oxygen atom in Pb_2MoO_5 lattice belongs to Pb–O chains (such atoms are denoted here as O^{ch}), whereas all other oxygen atoms belong to MoO_4^{2-} groups.

The electronic structures of perfect $PbMoO_4$ and Pb_2MoO_5 crystals were calculated by Full-Potential Linear Augmented Plane Wave (FP-LAPW) method within the framework of density-functional theory (DFT) using the WIEN2k program code [25]. Calculations were performed using Perdew and Wang generalized gradient approximation for the exchange-correlation potential [26]. The relativistic effects were treated in the scalar relativistic approximation. The energy of separation between core and valence states was chosen as −10.0 Ry. The muffin-tin (MT) radii R_{MT} were chosen from the condition of "almost touching" MT spheres. The potential and charge density in the MT-spheres were expanded in spherical harmonics with $l_{max} = 10$. The plane wave cutoff parameter $R_{MT}K_{max}$ was equal to 7.0. The magnitude of the largest vector G_{max} in charge density Fourier expansion was 12.0. The convergence criterion was chosen as the 0.0001 Ry convergence of total energy. The modified tetrahedron method was used for the Brillouin zone (BZ) integration [27].

The energy dispersion curves $E(\mathbf{k})$, partial densities of electronic states (PDOS) and optical constants were calculated using well-known relations implemented in the WIEN2k program package [25]. The $E(\mathbf{k})$ curves were calculated along segments in the $\mathbf{k}$-space which connect certain special points of the Brillouin zones of tetragonal and monoclinic lattices [28] of $PbMoO_4$ and Pb_2MoO_5 crystals, respectively. Calculations of PDOS were carried out for 35 nonequivalent sampling $\mathbf{k}$-points in the irreducible parts of the Brillouin zones and it was assured that further increase of the number of $\mathbf{k}$-points does not lead to significant changes of calculated PDOS distributions for each considered crystal. The reflectivity spectra R_{ii} are calculated for three orthogonal polarizations of a light beam (i = x, y, z) in the case of normal incidence (corresponding relations can be found in our previous paper [29]).

3. Results and discussion

3.1. PL spectroscopy

Under the VUV synchrotron radiation with λ_{ex} in 90–330 nm range, the lead molybdate $PbMoO_4$ crystals reveal intensive PL emission band in the green–orange spectral region with peak position at ~530 nm (2.33 eV) (see Fig. 1a). The PL emission band with analogous peak position and half-width was observed earlier for other $PbMoO_4$ samples at low temperature under various photoexcitation wavelengths [7–9,12]. At $\lambda_{ex} = 200$ and 225 nm, the main emission band of $PbMoO_4$ is accompanied by a well-distinguished shoulder in the short-wavelength side (see corresponding curves in Fig. 1a). This shoulder evidently points to existence of additional PL component in the violet spectral region (350–450 nm). Such a component peaking near 420 nm is depicted in Fig. 1a by a dashed line. An additional band in the violet region (peaking near 400 nm)

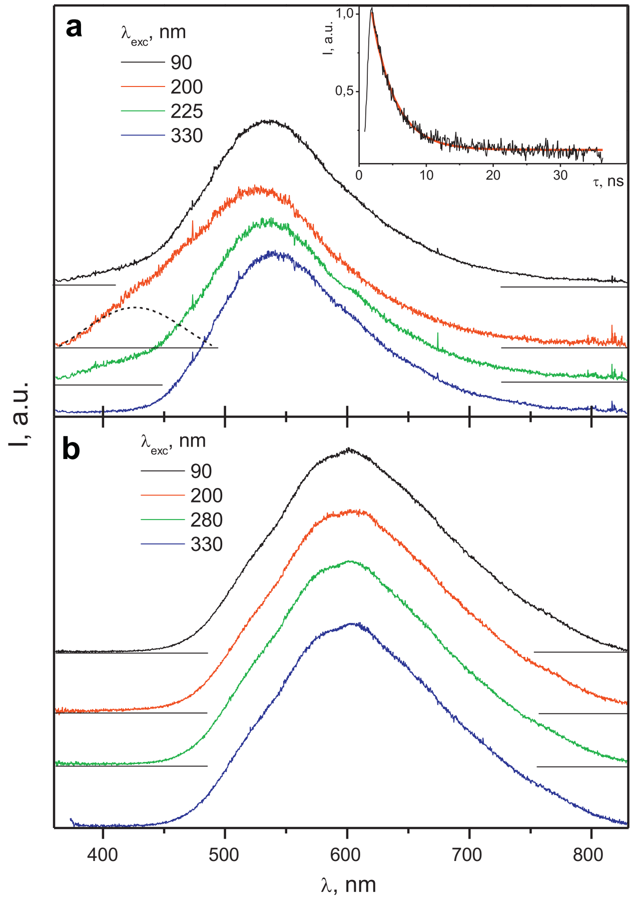


Fig. 1. PL emission spectra of $PbMoO_4$ (a) and Pb_2MoO_5 crystals (b), $T = 8$ K. Inset: decay kinetics of PL signal measured at $\lambda_{ex} = 200$ nm and $\lambda_{reg} = 400$ nm (black line) and its approximation with single exponential (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)