

Luminescent Properties of MgWO_4 Crystals

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Abstract. Luminescent properties of magnesium tungstate were investigated. Two samples of MgWO_4 single crystals grown by different methods were studied. Only intrinsic luminescence attributed to exciton emission was detected for the both samples and. It was shown that the temperature dependence of the low-energy edge in the excitation spectra obeys Urbach rule. Steepness coefficient that was deduced from this dependence indicates self-trapping of excitons in MgWO_4 . The absence of cation d states in the valence band is a distinctive feature of MgWO_4 that is shown to be manifested in the luminescence excitation spectra.

Key words: MgWO_4 , luminescence, excitation spectra, reflectivity, Urbach rule.

I. INTRODUCTION

Luminescent properties of MgWO_4 are known from 1940, when it was used as a phosphor for fluorescent lamps [1]. It demonstrates a broad intensive luminescence band in the blue spectral region (470 nm) that is not quenched up to the room temperatures [2]. Recently this material also attracted attention of researchers due to prospects of application as a scintillator in rare event search [3, 4]. Magnesium tungstate is of particular interest for such application due to the advantageous combination of heavy and light elements in its composition [3]. However phase transition below melting point in MgWO_4 is a serious obstacle for growth of the bulk single crystals that are required for the detectors. Only recently magnesium tungstate crystals of $\sim 1 \text{ cm}^3$ volume were obtained for the first time by the flux growth method [5]. The performance of MgWO_4 as a scintillator has been demonstrated in [3], however the photoelectron output from MgWO_4 was found to be only about 35% that of CdWO_4 . Relatively low output may not be due to the potential worse quality of the crystal but have physical background. Magnesium tungstate has at least one feature, which distinguish it from other representatives of wolframite group (CdWO_4 and ZnWO_4). Absence of d states of Mg (that are initially vacant) in the lower part of the valence band may lead to the changes in the energy conversion to luminescence quanta in MgWO_4 . So, the aim of this work is to study the luminescent properties of MgWO_4 and energy transfer mechanisms to the emission centers taking into account this feature of the band structure of MgWO_4 crystals.

II. EXPERIMENTAL

Investigated MgWO_4 single crystals (MgWO_4 (Kh) sample) were grown by flux method in the Institute for

Scintillation Materials (Kharkiv, Ukraine). Also measurements were carried out on the sample of MgWO_4 (V) grown from the melt in VNIISIMS (Alexandrov, Russia).

The luminescence excitation and emission spectra as well as the reflection spectra were measured at the Superlumi station (DESY, Germany) at the synchrotron radiation line I of the DORIS III storage ring in the temperature range 10–300 K. Some luminescence and excitation spectra under UV excitation at room temperature were obtained at the laboratory set-up.

III. RESULTS AND DISCUSSION

Luminescence spectra and luminescence excitation spectra of the investigated samples at the room temperature are presented in Fig. 1. The luminescence of MgWO_4 , excited in the region of direct exciton creation (4.1 eV), is characterized by the single intense wide-band emission peaking at 2.45 eV and with full width of half maximum 0.7 eV. The luminescence is of intrinsic origin and is usually ascribed to the radiative annihilation of excitons [6]. No luminescence signal was detected at the excitation energies below 3.8 eV, that indicates the absence of luminescence associated with the crystal structure defects or the inadvertent impurities.

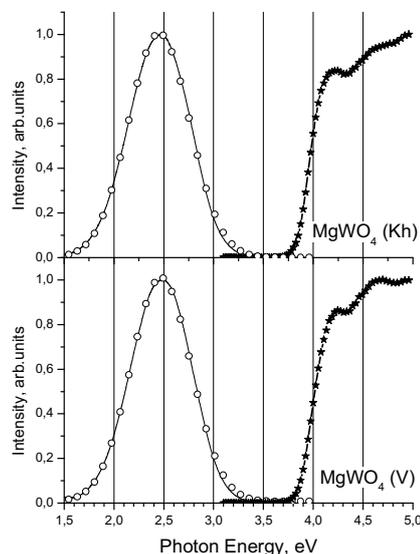


Fig. 1. Emission spectra of MgWO_4 (Kh) and (V) samples at $E_{\text{ex}} = 4.1 \text{ eV}$ and luminescence excitation spectra at $E_{\text{em}} = 2.5 \text{ eV}$, $T = 300 \text{ K}$.

In Fig. 2 the temperature dependence of the edge of the luminescence excitation spectra is presented. Edge shifts to the low energy region with the temperature increase from 10 to 290 K. A similar temperature-dependent shift is characteristic for the Urbach tail of the fundamental absorption edge. The excitation spectra generally coincide with the absorption spectra at the relatively low values of the

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absorption coefficient. Therefore the excitation spectra at the edge of the fundamental absorption region can also be simulated with the well-known Urbach formula [7]:

$$\alpha(E) = \alpha_0 \exp\left(-\sigma \frac{E_0 - E}{kT}\right), \quad (1)$$

where k – is the Boltzmann constant, E_0 and α_0 – coordinates of intersection point of Urbach curves prolonged in area of large values of absorption coefficient, σ is the empirical slope coefficient.

The results of the simulation for the temperatures of 10, 100, 150, 200, 250 and 290 K are presented as the straight lines in the Fig. 2. The deviation of the experimental curves from the simulated ones in the high-energy region is due to the saturation of the radiative transitions when the incident radiation is completely absorbed in the crystal. The steepness parameter σ as well as the parameter E_0 was deduced from the simulation. The latter was obtained as 4.65 - 4.75 eV for the different temperatures. It is known that the E_0 parameter corresponds to the position of the excitonic peak. Pronounced sharp peak was observed in the reflectivity spectra just around 4.7 eV (Fig. 2, inset (b)). The peak profile is temperature dependent and characteristic for the excitonic peaks.

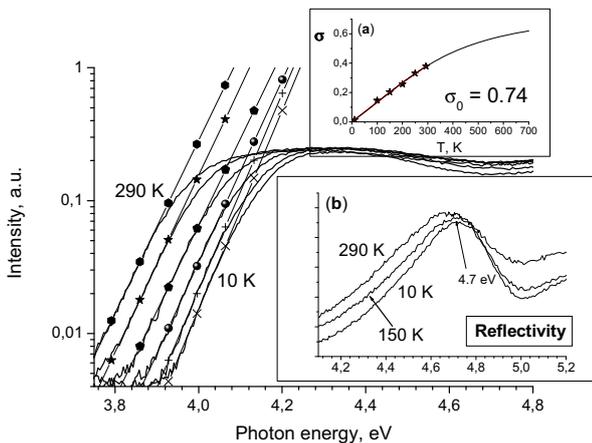


Fig. 2. Low-energy edge of the excitation spectra at $T = 10, 100, 150, 200, 250, 290$ K (line) and its fitting to the Urbach rule (dots+line) for MgWO_4 (V). In the inset (a): temperature dependence of the empirical slope coefficient σ and its fitting to the formula (2). In the inset (b): temperature dependence of the exciton peak in reflectivity.

The obtained values of σ coefficient were used to determine the slope coefficient which governs the propensity for self-trapping. Actually σ is temperature dependent, according to

$$\sigma = \sigma_0 \frac{2kT}{\hbar\omega_p} \tanh\left(\frac{\hbar\omega_p}{2kT}\right), \quad (2)$$

where $\hbar\omega_p$ is the energy of the principal interacting phonon mode and σ_0 is the limit of σ at high temperature. This temperature dependence of σ comes from the fact that the average vibrational amplitude of an ensemble of quantum mechanical oscillators is not linear in T at low temperature, but tends to the zero-point amplitude [7]. The value of $\sigma_0 = 0.74$ was obtained from the fitting that is presented in Fig. 2, inset (a). It implies self-trapping of the excitons in MgWO_4 since the values below unity are inherent for the self-trapping.

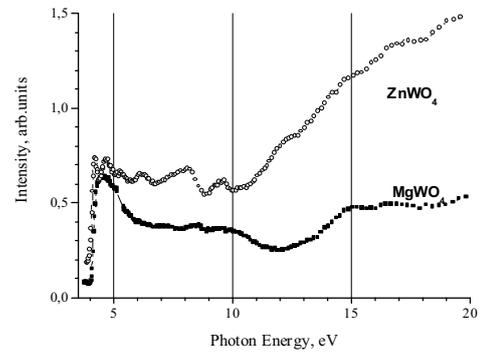


Fig. 3. Excitation spectra of the intrinsic emission ($E_{em} = 2.5$ eV) of zinc and magnesium tungstates at $T = 10$ K.

Luminescence excitation spectrum of MgWO_4 (Kh) in the fundamental absorption region is presented in Fig. 3 together with the spectrum of ZnWO_4 . The latter was grown by Czochralski technique in the Institute for Scintillation Materials (Kharkiv). In the region of the low-energy onset, where the direct creation of excitations occurs, the intensity of excitation spectra differs only slightly due to the comparable efficiency of energy conversion into luminescence quanta in these tungstates. However at higher energies the excitation spectrum of MgWO_4 demonstrates considerable decrease of intensity. The most remarkable discrepancy in the spectra of MgWO_4 and ZnWO_4 is observed at $E_{ex} > 10$ eV. In this energy region the electronic transitions from the lower part of the valence band to the conduction band occurs. Absence of the d states of Mg in the lower part of the valence band is supposed to be responsible for the observed difference.

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