LUMINESCENCE STUDY OF MOLYBDATES WITH CATIONS OF Li, Zn AND Mg

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MOTIVATION, OBJECTIVES AND EXPERIMENTAL DETAILS

- Potential application - cryogenic scintillating bolometry for the neutrinoless double beta decay detection and for the dark matter searching.
- Advantage of the molybdates with light cations is the absence of the long-lived isotopes of cations and relatively low density of the scintillating crystal.
- Study of the luminescent properties of **Li_2MoO_4, $MgMoO_4$, $ZnMoO_4$** and **$Li_2Zn_2(MoO_4)_3$** single crystals grown by Czochralski method was performed.
- Measurements were carried out at the Superlumi station, Hamburg (reflectivity, excitation, luminescence), laboratory set-up in Moscow State University (transmission, excitation, luminescence at RT) and in Claude Bernard University (TSL, phosphorescence), Lyon.

CHARACTERIZATION OF THE INVESTIGATED SAMPLES

	Li_2MoO_4	$Li_2Zn_2(MoO_4)_3$	$ZnMoO_4$	$MgMoO_4$
Photo of the boules				
Crystal size	Up to ∅25x100 mm		Up to ∅10x40 mm	Up to ∅15x40 mm

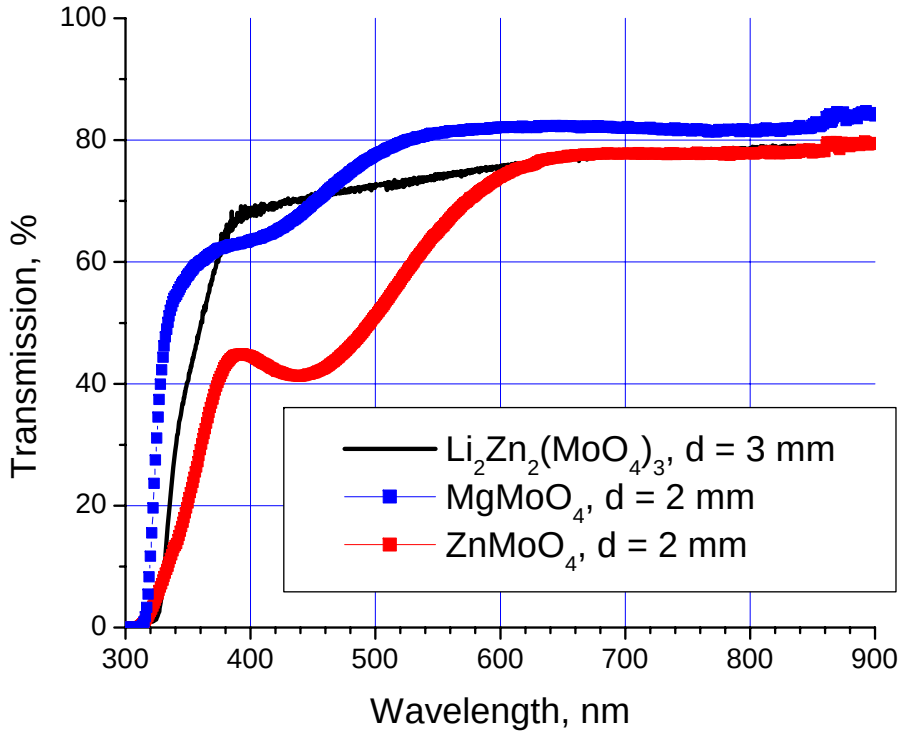
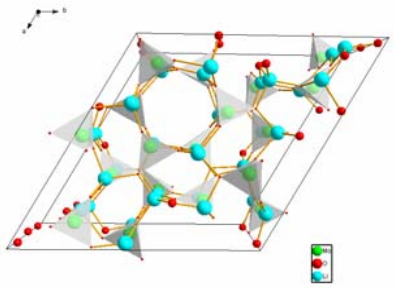
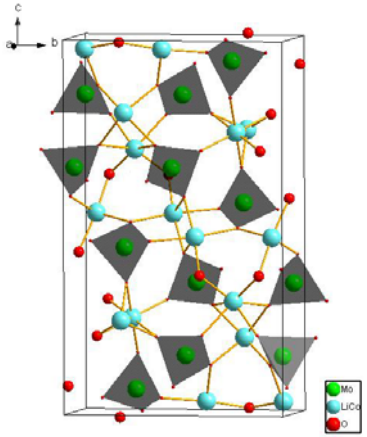
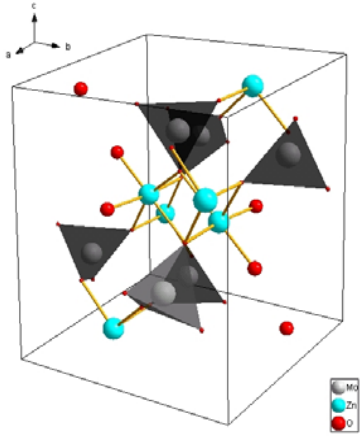
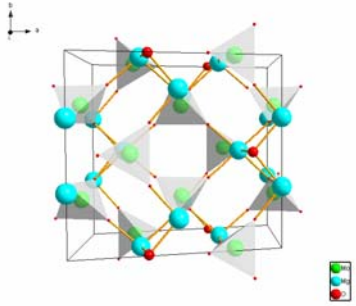


Figure 1. Transmission spectra of molybdates at 300 K, d = 2 mm.

- Absorption band at 450 nm for $ZnMoO_4$ and 410 nm for $MgMoO_4$ resulted in the coloration of the investigated samples.

CRYSTAL STRUCTURE OF THE MOLYBDATE SINGLE CRYSTALS

	Li_2MoO_4	$Li_2Zn_2(MoO_4)_3$	$ZnMoO_4$	$MgMoO_4$
Space group	$R\bar{3}$ (C_{3i}^{2}) trigonal	Pnma orthorhombic	P-1 triclinic	C2/m monoclinic
Crystal structure				
Isolated MoO_4 complex?	Yes (6)	Yes (2)	Yes (3)	Yes (2)

SOME PHYSICAL AND CHEMICAL PROPERTIES

	Li_2MoO_4	$Li_2Zn_2(MoO_4)_3$	$ZnMoO_4$	$MgMoO_4$
ρ, g/см^3	3,08	4.38	4.37	3.82
Refraction index	1,722	1.97	1.98	1.82
Melting temperature, °C	700	890	986	1320

REFLECTIVITY

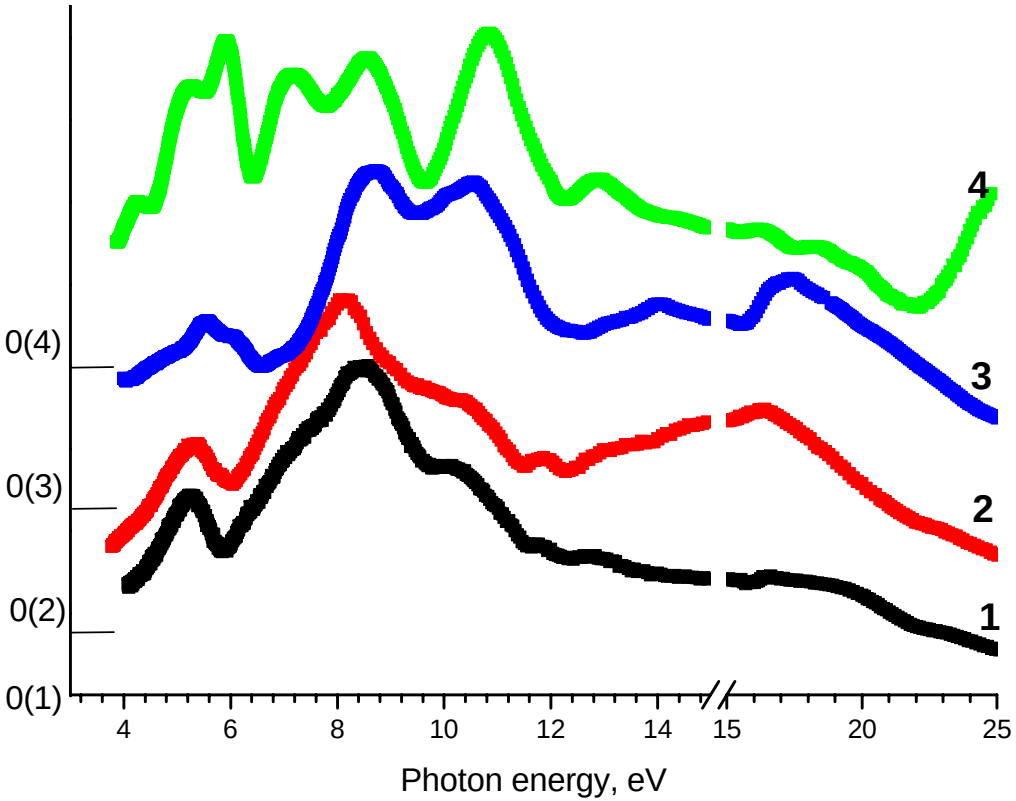


Figure 2. Reflectivity spectra at 10 K for

- $ZnMoO_4$ (curve 1),
- $Li_2Zn_2(MoO_4)_3$ (curve 2),
- $MgMoO_4$ (curve 3),
- Li_2MoO_4 (curve 4).

- Measurements were carried out on the freshly cleaved plane ($MgMoO_4$, $ZnMoO_4$) and vitreous ($Li_2Zn_2(MoO_4)_3$, Li_2MoO_4) surfaces of the samples.
- Reflectivity spectra for $Li_2Zn_2(MoO_4)_3$ and $ZnMoO_4$ are almost coincide, i.e. contribution of lithium electronic states in the bands formation is not significant.
- Reflectivity spectrum of Li_2MoO_4 demonstrates "pure" transitions in MoO_4 complex without contribution from the cation electronic states?

- **NOTE!** Anisotropy of the crystal structure should effect on the reflectivity spectra profile. E.g. it was observed for $MgMoO_4$.

LUMINESCENCE

Crystal	T, K	E_{max}, intrinsic band, eV	FWHM, eV	E_{max}, defect-related band, eV	FWHM, eV
$MgMoO_4$	10	2.3	0.64	1.9	0.43
$ZnMoO_4$	300	2.1	0.75		
$Li_2Zn_2(MoO_4)_2$	300	2.0	0.8		
Li_2MoO_4	10	2.1	0.67		

General properties of the intrinsic luminescence band of the molybdates

1. Broad elementary luminescence band in the visible spectral region;
2. Decay time exceeds 10^{-6} s (T = 10 K);
3. Luminescence is excited only in the fundamental absorption region of the crystal;
4. Similarity of the luminescence properties to other molybdates with isolated MoO_4 complex (i.e. scheelites);

Conclusion:

The intrinsic luminescence of the investigated molybdates can be attributed to the self-trapped exciton (STE) at isolated MoO_4 complex.

RELATIVE INTENSITY OF THE LUMINESCENCE COMPARED TO $CdWO_4$

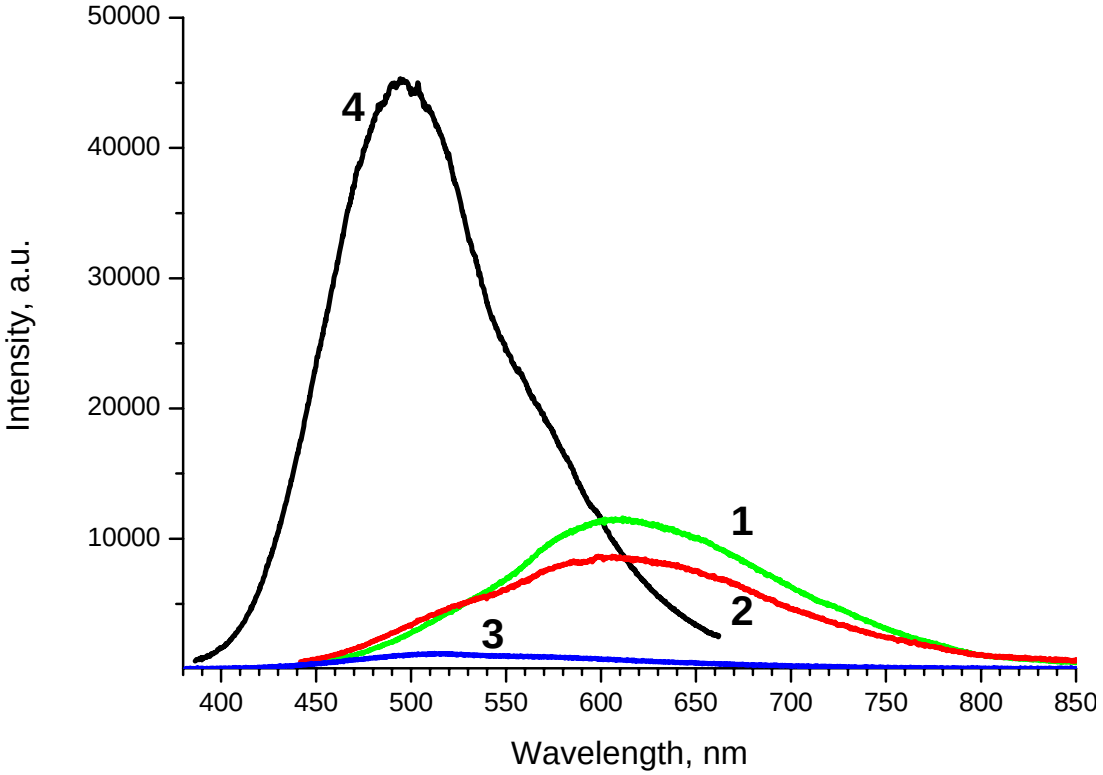


Figure 3. Relative intensity of the luminescence of

$ZnMoO_4$ (curve 1, E_{ex} = 4.3 eV),

$Li_2Zn_2(MoO_4)_3$ (curve 2, E_{ex} = 4.3 eV),

$MgMoO_4$ (curve 3, E_{ex} = 4.4 eV) and

$CdWO_4$ (curve 4, E_{ex} = 4.1 eV), T = 10 K.

- Luminescence spectra were measured in the same experimental conditions except for the excitation energy.
- Excitation energy corresponds to the first excitation peak at the edge of the fundamental absorption in order to exclude energy losses on the stage of charge carriers thermalization.
- Sample of $CdWO_4$ was cut from 1 cm^3 cube with light yield of 20000 ph/MeV at 300 K.
- The result is rather encouraging for $Li_2Zn_2(MoO_4)_3$ and $ZnMoO_4$.
- Luminescence intensity for Li_2MoO_4 and $MgMoO_4$ is of the same order of magnitude.
- Bend at 540 nm is connected with incorrect spectral sensitivity function of the set-up.

LUMINESCENCE EXCITATION SPECTRA OF $Li_2Zn_2(MoO_4)_3$ AND $ZnMoO_4$

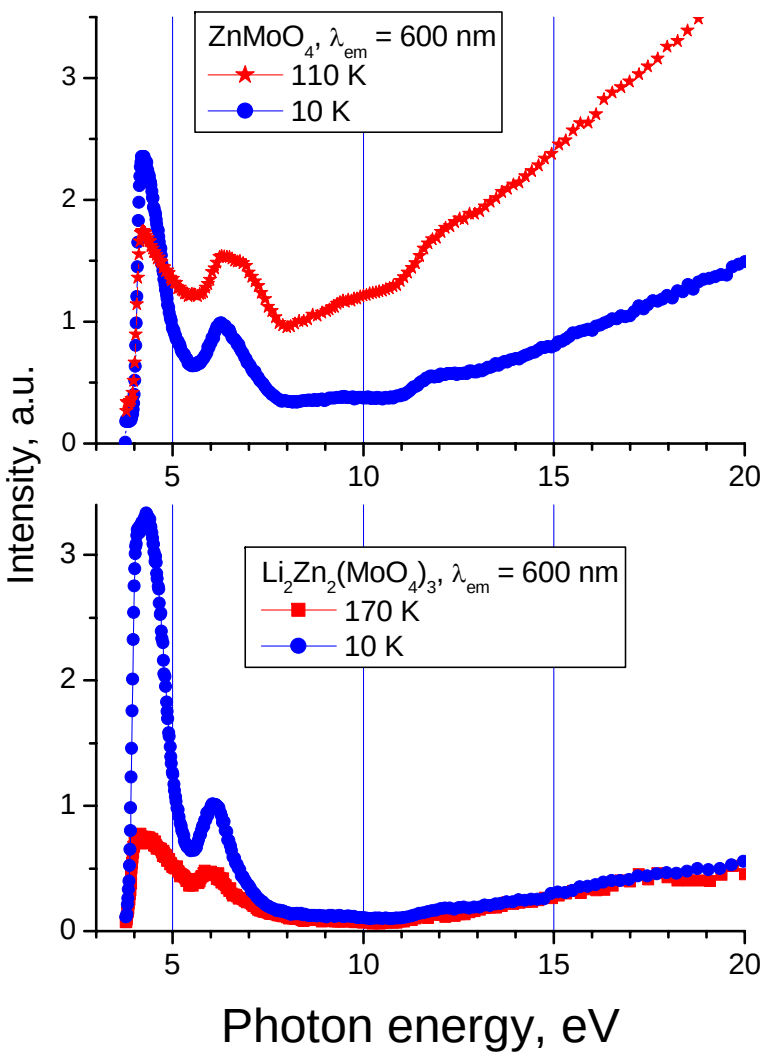


Figure 4. Luminescence excitation spectra of $ZnMoO_4$ and $Li_2Zn_2(MoO_4)_3$ at different temperatures, λ_{em} = 600 nm.

- Excitation spectra contain information about the light yield of the scintillator.
- At the low temperature (10 K) significant decrease of the intensity with the increase of excitation energy is connected with the presence of the effective competitive relaxation channel of electron excitations.
- As the temperature increases the probability for the separated electron and hole to be bound into the exciton increases for $ZnMoO_4$ whereas for $Li_2Zn_2(MoO_4)_3$ no increase was observed.
- As the concentration of the defects in $Li_2Zn_2(MoO_4)_3$ is much less than in $ZnMoO_4$ the peculiarities of the energy bands structure may be the reason.

TEMPERATURE DEPENDENCE OF LUMINESCENCE INTENSITY OF $ZnMoO_4$

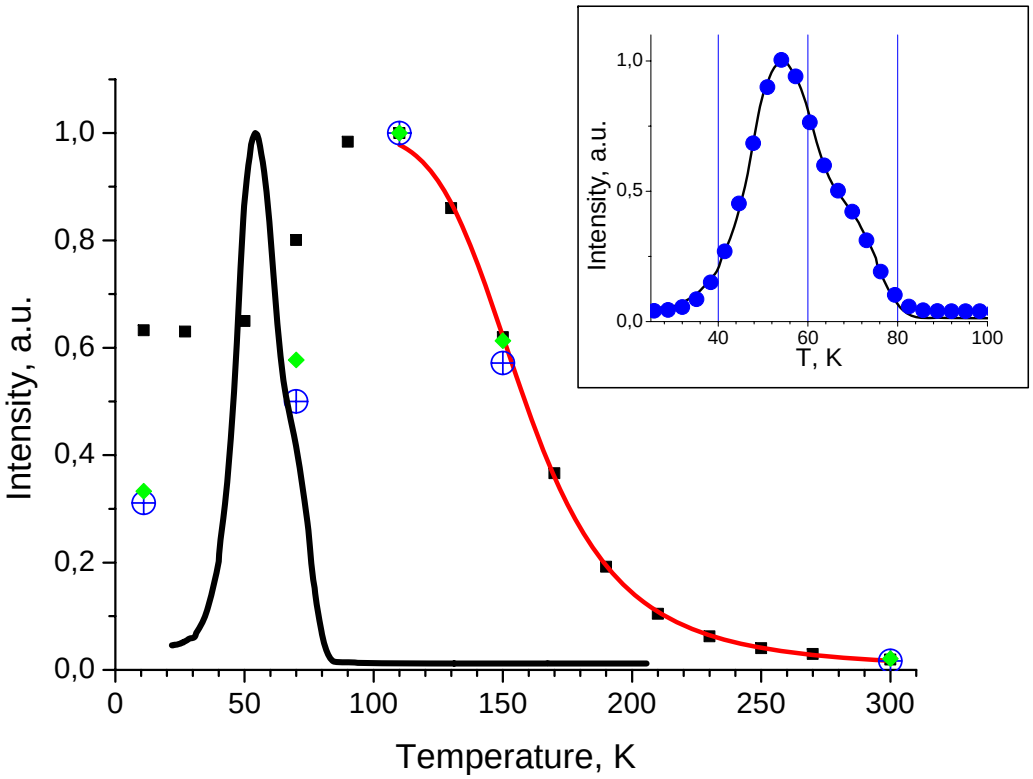


Figure 5. Temperature dependence of the luminescence integrated intensity of $ZnMoO_4$ at the excitation energy that:

slightly exceeds E_g - 6.5 eV (black squares)

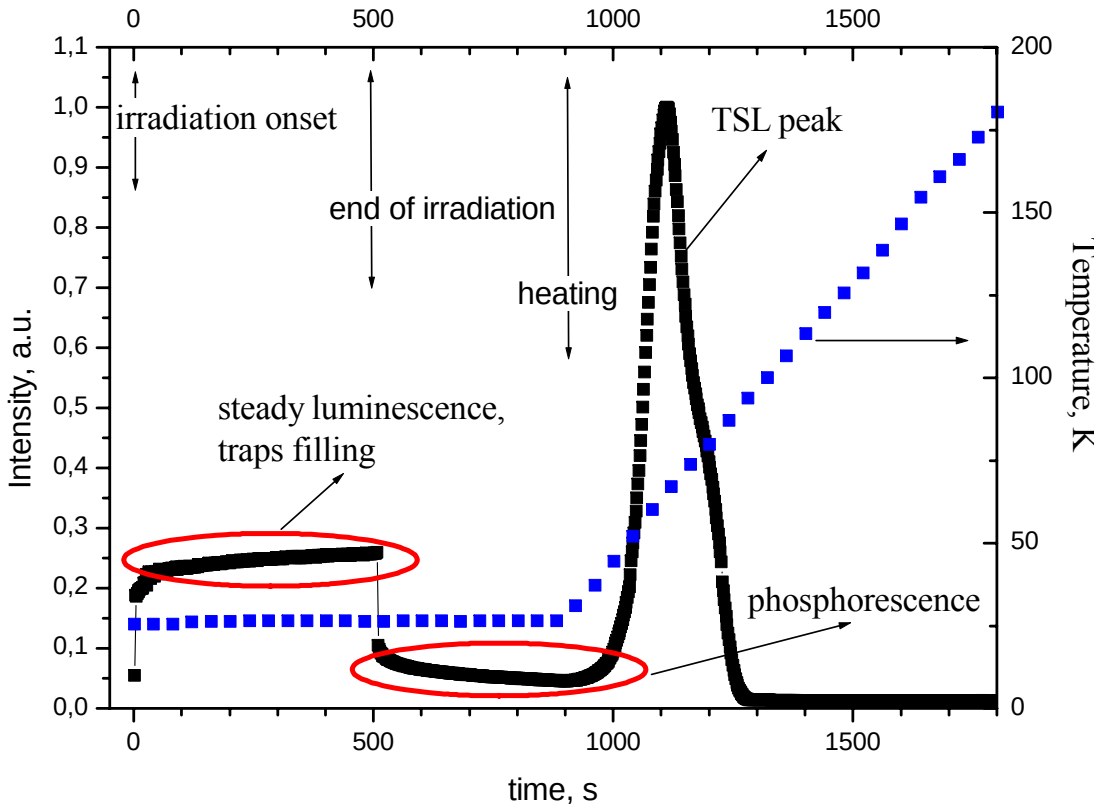
slightly less than $2E_g$ - 10 eV (blue circles)

exceeds $2E_g$, - 15 eV (green lozenges).

Black line – TSL spectrum after X-ray irradiation.

- Thermal quenching of the luminescence is observed at T > 110 K. Red dot line demonstrates the thermal quenching approximation with Mott formula, $E_{activation}$ = 117 meV.
- Luminescence intensity also decreases in the low-temperature region. Intensity depends on the mean distance between the separated electron and hole.
- Existence of a thermal barrier to the STE creation is proposed to explain the observed dependence.
- TSL peak position (55 K) coincides with the luminescence intensity rise. TSL peak was decomposed into two elementary peaks in the first order kinetics approximation (see the inset). Trap's ionization energies were calculated as 32 and 54 meV.

LUMINESCENCE, PHOSPHORESCENCE AND TSL SPECTRA OF $ZnMoO_4$



- Sample was irradiated with X-rays for 500 s at T = 20 K. Luminescence intensity slightly increased during the irradiation that is evidence of the taps filling.
- After the end of X-ray irradiation the phosphorescence has been observed.
- At t = 900 s from the beginning of the irradiation the sample was heated with the heating rate of 10 K/min. Non - elementary TSL peak appears with the maximum at 55 K.
- Luminescence spectrum measured in the TSL peak coincides with the steady luminescence.

Figure 6. Luminescence at the continuous X-ray excitation, phosphorescence and thermo stimulated luminescence of $ZnMoO_4$ under X-ray excitation.

KINETIC MODEL FOR THE ENERGY RELAXATION IN ZINC MOLYBDATE

$$\frac{\partial n_{ex}}{\partial t} = -\frac{n_{ex}(t)}{\tau_{rad}} - \omega_q e^{-\frac{E_q}{kT(t)}} n_{ex}(t) + \varepsilon n_e(t) n_h(t) + I(t) r_{ex}$$

$$I(t) = \begin{cases} I_0, & t < t_0 \\ 0, & t \geq t_0 \end{cases}$$

$$\frac{\partial n_t}{\partial t} = -\omega_t e^{-\frac{E_t}{kT(t)}} n_t(t) + k n_h(t)(n_{t0} - n_t(t))$$

$$\frac{\partial n_h}{\partial t} = \omega_t e^{-\frac{E_t}{kT(t)}} n_t(t) - k n_h(t)(n_{t0} - n_t(t)) - \varepsilon n_e(t) n_h(t) + I(t)(1 - r_{ex})$$

$$kT(t) = \begin{cases} kT_0, & t < t_{T0} \\ kT_0 + \beta(t - t_{T0}), & t \geq t_0 \end{cases}$$

$$\frac{\partial n_e}{\partial t} = -\varepsilon n_e(t) n_h(t) + I(t)(1 - r_{ex})$$

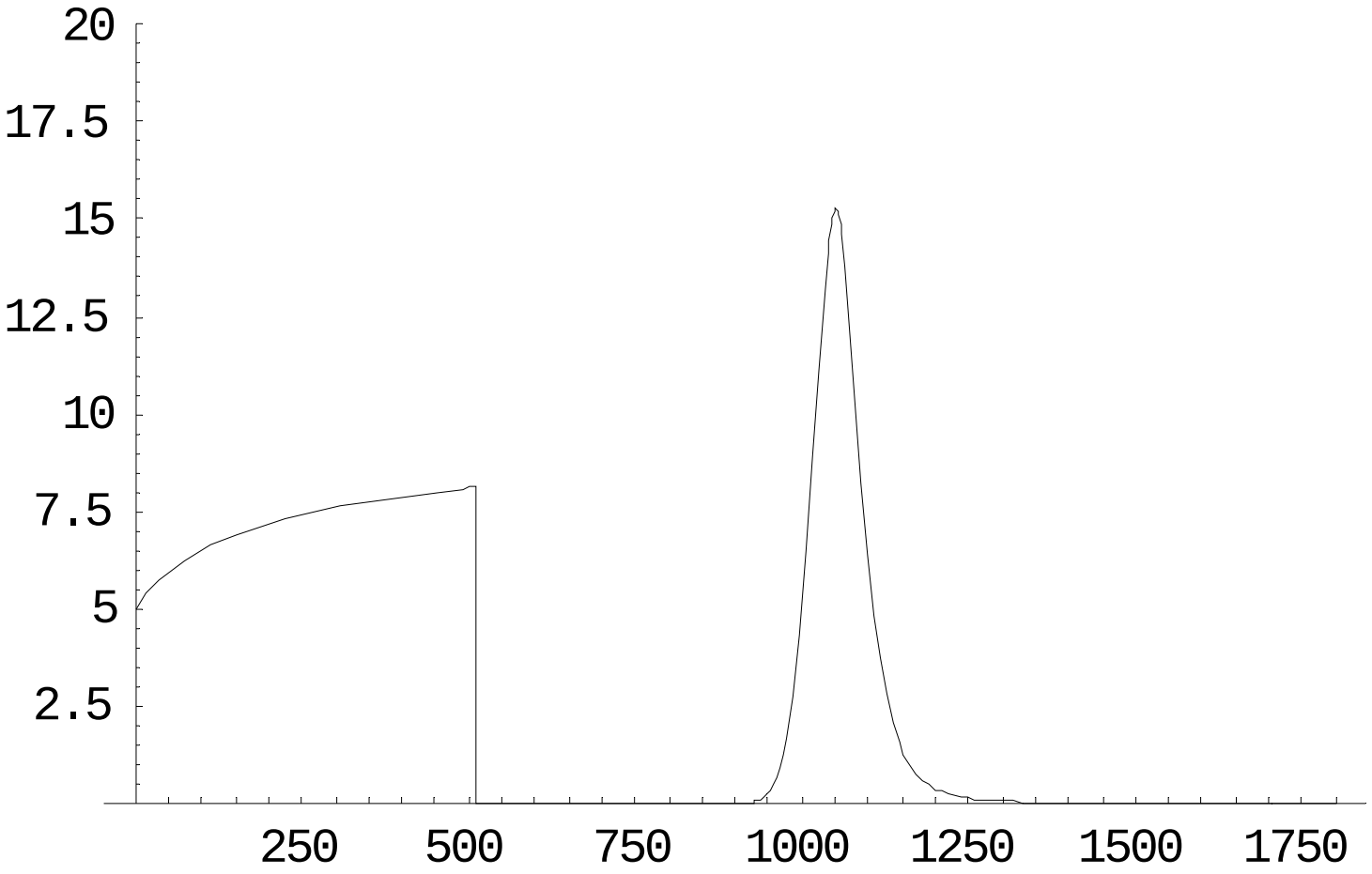
The model accounts for

1. direct exciton creation under the incident radiation
2. bound of the free electrons and holes into the exciton
3. electron capture at the trap (trap parameters were obtained from TSL)
4. thermal quenching of the luminescence (parameters were obtained using approximation with Mott formula)

Variable parameters:

- probability of for free electron and hole to be bound into the exciton — ε = variable
- probability for the electron to be captured by the trap — k = variable
- part of excitons directly created under X-ray radiation — r_{ex} = variable

SOME RESULTS OF THE MODELLING



$r_{ex} = 0.5$; $\varepsilon = 0.1$; $k = 0.01$

The model can't describe:

1. Phosphorescence
2. Simultaneously - relative intensity of the steady luminescence and TSL peak and time dependence of steady luminescence intensity

New parameters should be added!! I.E. existence of the thermal barrier for free electrons and holes to be bound into the exciton.

Benefits and disadvantages of the zinc molybdate as a scintillator

+ Absence of the long-lived isotopes of cations and relatively low density of the crystal
+ Rather high (up to 25 %) luminescence intensity as compared to cadmium tungstate
+ Possibility of effective energy transfer to the luminescence centers at the high-energy excitation
+ Peculiarities of the energy band structure because of the 3d states of zinc?

- Complexity in growing of the crystal
- Poor optical quality of the investigated sample
- Presence of the thermal barrier to the STE creation at low temperatures
- Phosphorescence

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