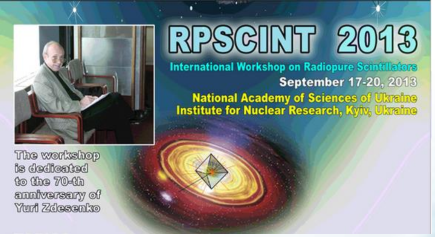

Influence of traps on the luminescent and scintillation properties of molybdates

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Outline

- **Self-trapping of charge carriers in inorganic solids and its influence on energy transfer processes.**
- **Self-trapped electrons and holes in molybdates. Manifestation in TSL curves and TSL spectra.**
- **Unusually high trapping efficiency in $ZnMoO_4$, co-existence of self-trapped electrons and holes.**
- **Influence of self-trapping on the luminescent and scintillation properties of the molybdates.**

Self-trapping of charge carriers

- **Trapping of electrons and holes is possible even in the ideal crystals without any impurity (self-trapping).**
- **Self-trapping of electrons and holes is possible due to their interaction with the crystals lattice. In some cases it results in the polarization of the local region of the crystal lattice, which immobilize the charge carrier.**
- **The well-known example of the self-trapped charge carrier is V_k center.**
- **Self-trapped electrons (STEL) and holes (STH) are stable at low temperatures and should influence the energy transfer processes in the cryogenic scintillating bolometers.**

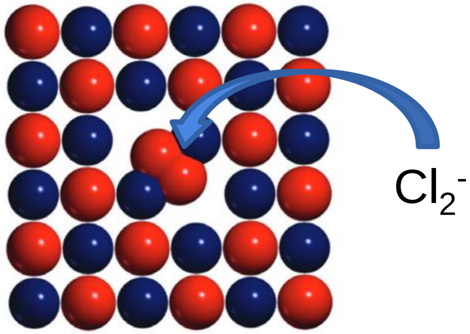
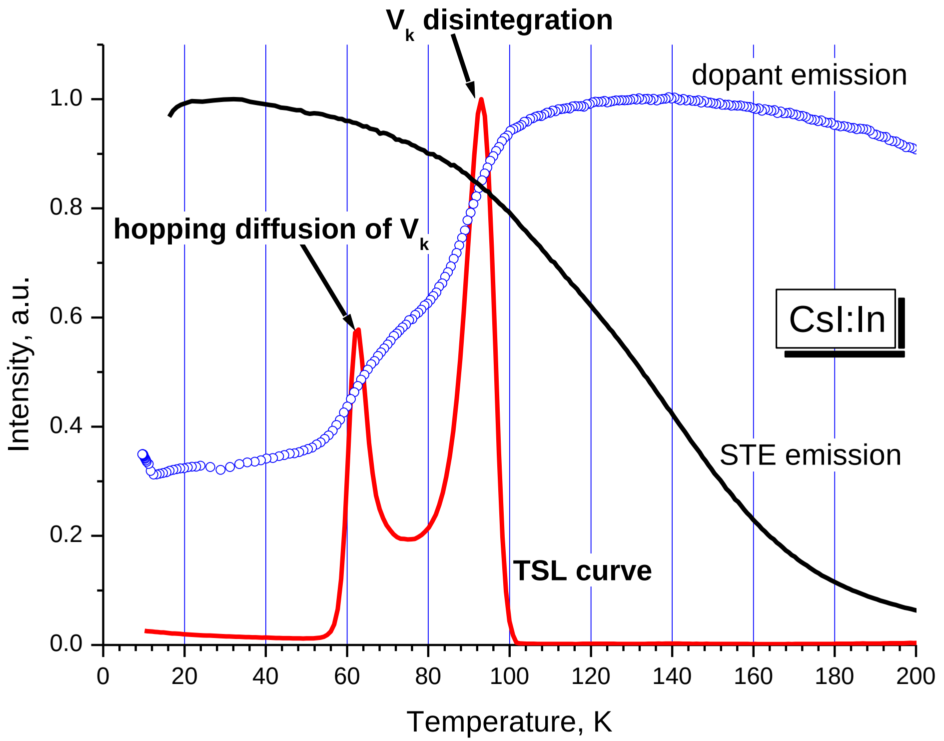


Fig. 13.12 A schematic of a V_K center in KCl.

Self-trapping of charge carriers

- **Influence of STH on the energy transfer processes. STH creation prevent the energy transfer to In impurity at low temperatures in CsI:In.**



Gridin et al, Channels of Energy Losses and Relaxation in CsI:M Scintillators (M=Tl, In), IEEE TNS, accepted for publication

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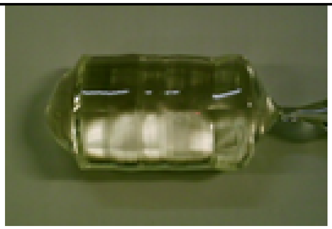
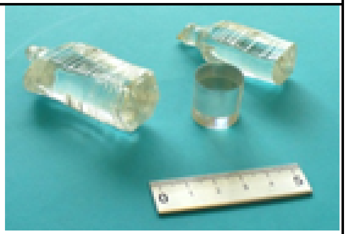
Self-trapping of charge carriers

Compound	Type of self-trapped carrier	Type of center	Disintegration temperature, K
CsCl	STH	Cl_2^- (V_k)	195
BaF_2	STH	F_2^- (V_k)	115
$PbWO_4$	STEL	$(WO_4)^{3-}$	40
$CaWO_4$	STH	O^-	150
Y_2SiO_5	STH	O^-	180
$PbCl_2$	STEL STH	Pb_2^{3+} Cl_2^-	125 51
SiO_2	No self-trapping		
$CaMoO_4$	**STH**	**O^-**	**150**
$SrMoO_4$	**STH**	**O^-**	**200**
$CdMoO_4$	**STH**	**O^-**	**69**
$PbMoO_4$	**STEL**	**$(MoO_4)^{3-}$**	**140 (?) 40 (?)**
$ZnMoO_4$	**?**	**?**	**?**

In molybdates:

- **charge carriers are self-trapped at the MoO_4 complex, which is the emission center.**
- **Pb 6s states prevents self-trapping of the holes in $PbMoO_4$.**

Objects of the study

	$CaMoO_4$	$SrMoO_4$	$PbMoO_4$	$ZnMoO_4$
Space group	C_{4h}^6(I4$_1$/a), tetragonal			P-1, triclinic
Photo of the bulk crystal			No photo	
Contaminating impurities	Ba (100 ppm), Sr (60 ppm), Na (30 ppm), Ag (10 ppm), W (10 ppm)	Si (70 ppm), Ca (20 ppm), Cl (15 ppm), W (10 ppm), Ba (10 ppm)	W (300 ppm), Ca (40 ppm), S (10 ppm), Bi (4 ppm), K (4 ppm)	W (200 ppm), Si (40 ppm), Cd (4 ppm)
Intrinsic trap centers	Hole center O^-	Hole center O^-	Electron center MoO_4^{3-}	?
Release temperature, K	150 [Z.Physik(B) 35 (1979) 1]	200 [J.Lumin. 22 (1981) 419]	140 [PSS b 89 (1978) 375] 40 [J.Lumin. 33(1985) 315]	?

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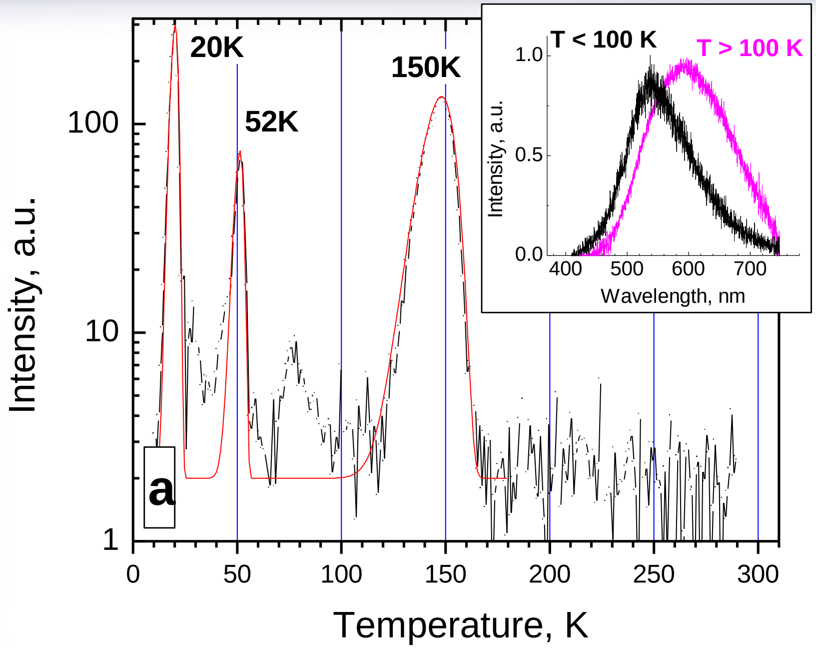
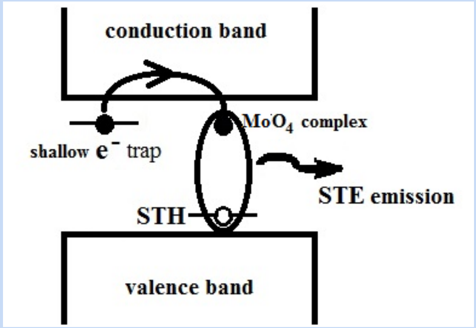
STH in $CaMoO_4$

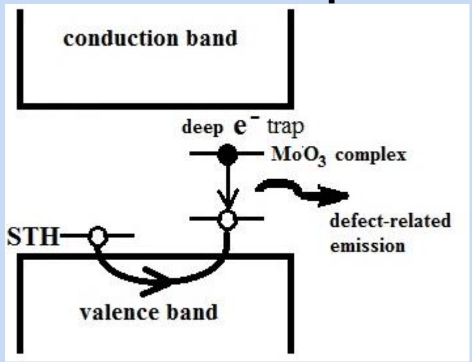


Compound	Type of self-trapped carrier	Type of center	Disintegration temperature, K
$CaMoO_4$	STH	O^-	150
$SrMoO_4$	STH	O^-	200
$PbMoO_4$	STEL	$(MoO_4)_3^-$	140 40
$ZnMoO_4$	?	?	?

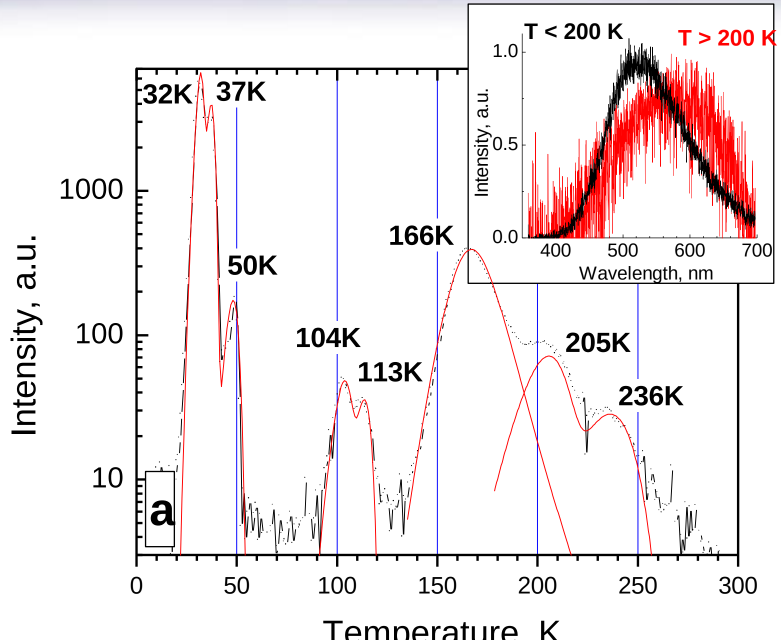
Scheme of the processes, which are responsible for the TSL peaks at 20 and 52 K:



Scheme of the processes, which are responsible for the TSL peak at 150 K:

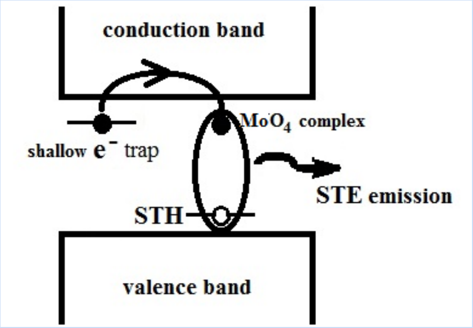


STH in $SrMoO_4$

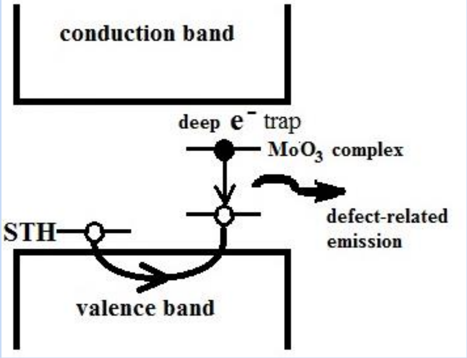


Compound	Type of self-trapped carrier	Type of center	Disintegration temperature, K
$CaMoO_4$	STH	O^-	150
$SrMoO_4$	STH	O^-	200
$PbMoO_4$	STEL	$(MoO_4)_3^-$	140 40
$ZnMoO_4$	?	?	?

Scheme of the processes, which are responsible for the TSL peaks below 200 K:



Scheme of the processes, which are responsible for the TSL peaks above 200 K:



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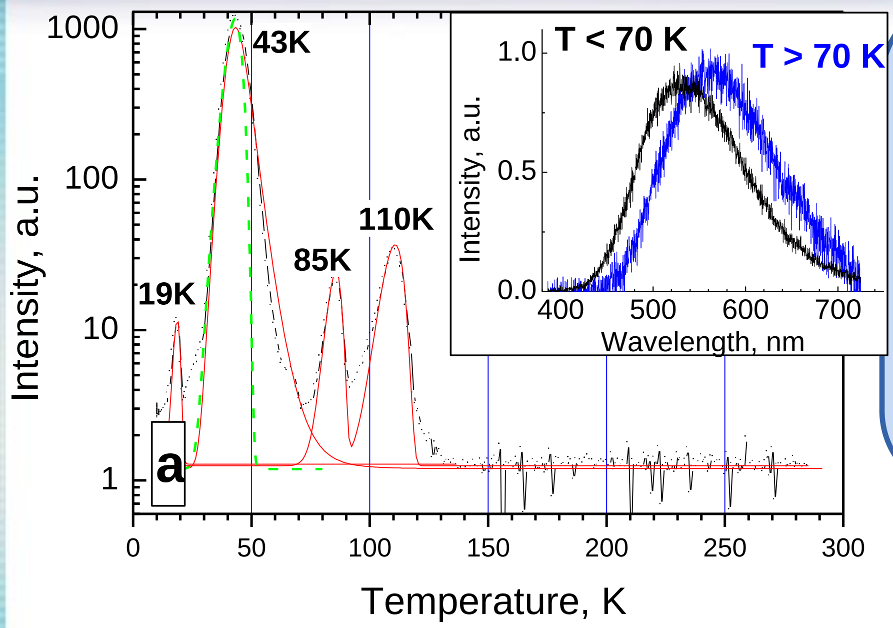
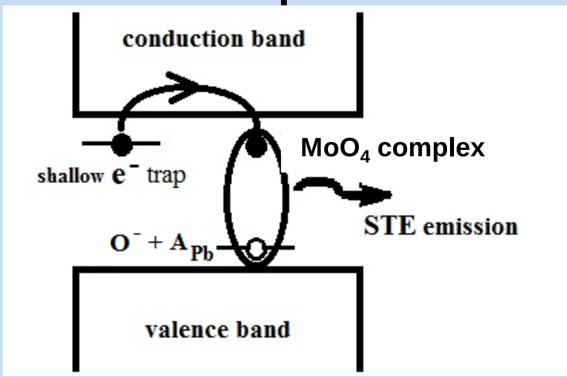
STEL in $PbMoO_4$

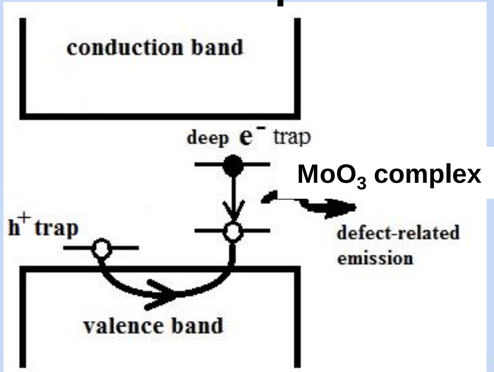


Compound	Type of self-trapped carrier	Type of center	Disintegration temperature, K
$CaMoO_4$	STH	O^-	150
$SrMoO_4$	STH	O^-	200
$PbMoO_4$	STEL	$(MoO_4)_3^-$	140 40
$ZnMoO_4$	?	?	?

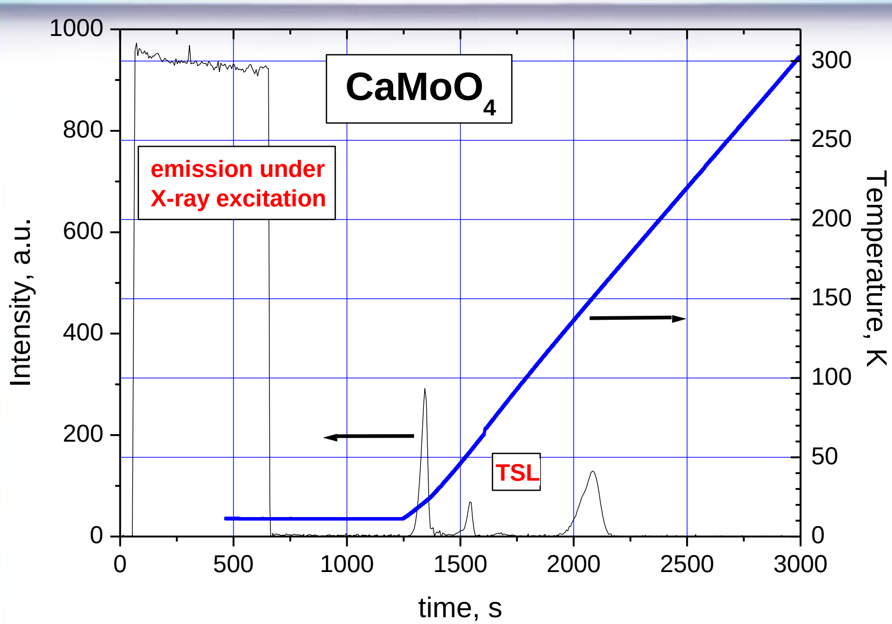
Scheme of the processes, which are responsible for the TSL peaks below 70 K:



Scheme of the processes, which are responsible for the TSL peaks above 70 K:



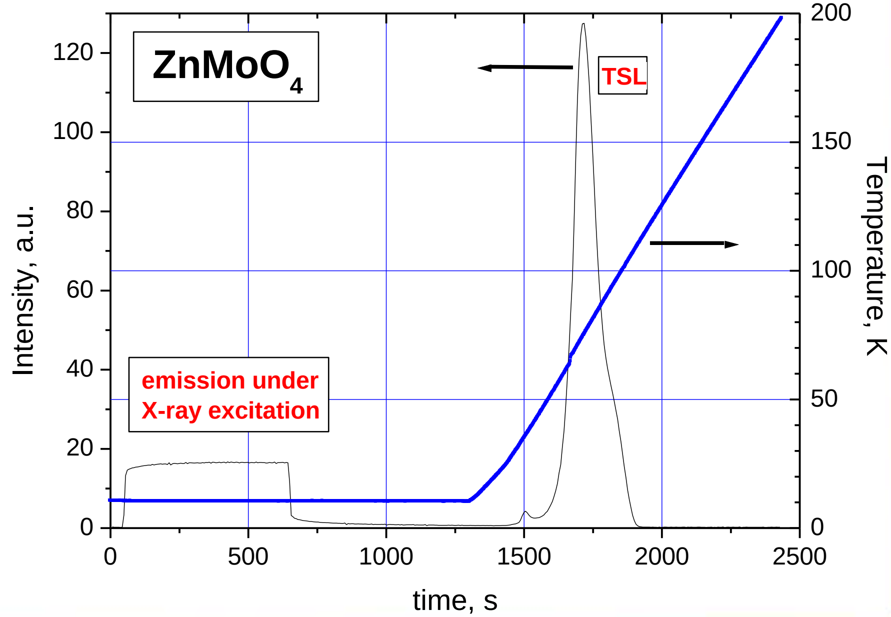
Efficiency of trap centers



Integrated intensity of TSL relatively to the integrated intensity of emission under X-ray excitation:

$CaMoO_4$ – 5% **$SrMoO_4$** – 3%

$PbMoO_4$ – 20% **$ZnMoO_4$** – 150%



Traps prevents energy transfer to the emission centers in **$ZnMoO_4$**. Can we avoid the negative influence from the traps?

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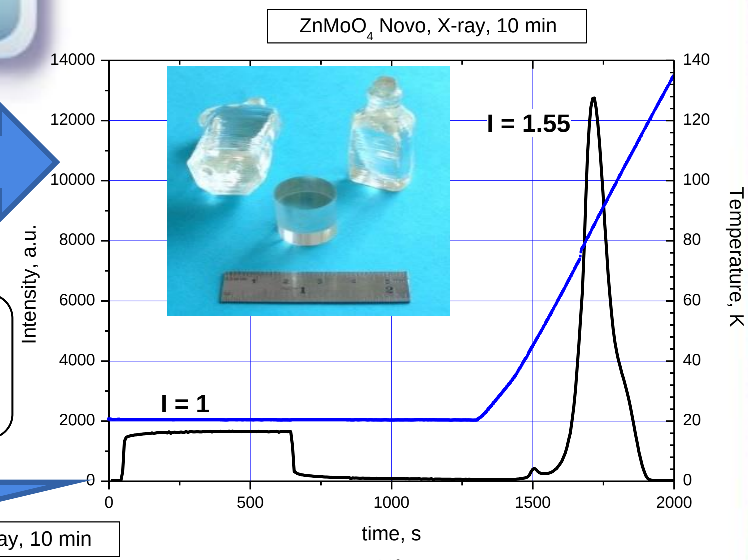
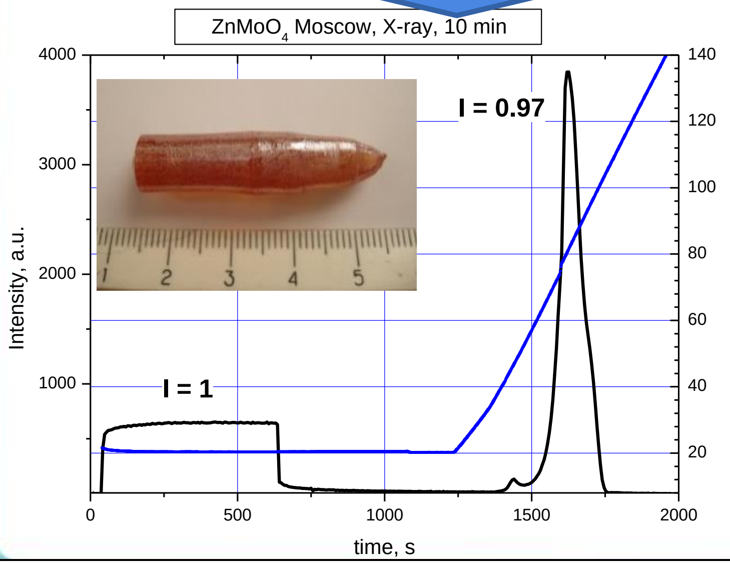
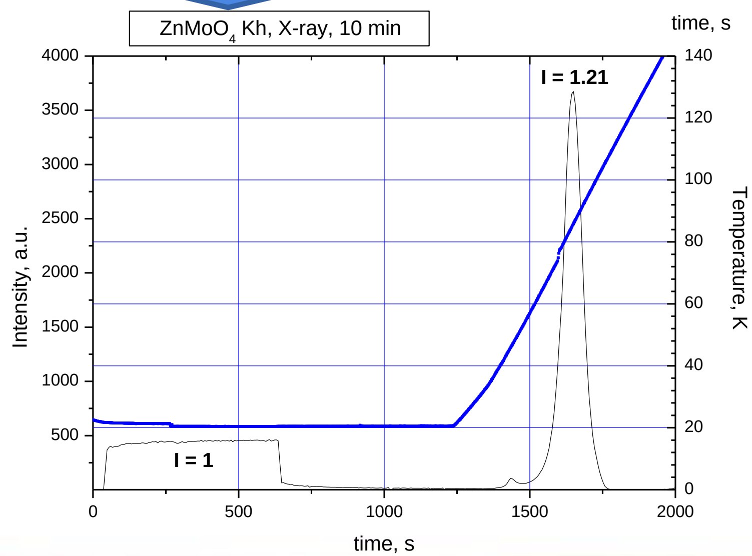
Efficiency of trap centers in $ZnMoO_4$

Low gradient Czochralski method
NIIC SRAS (Novosibirsk) 2011



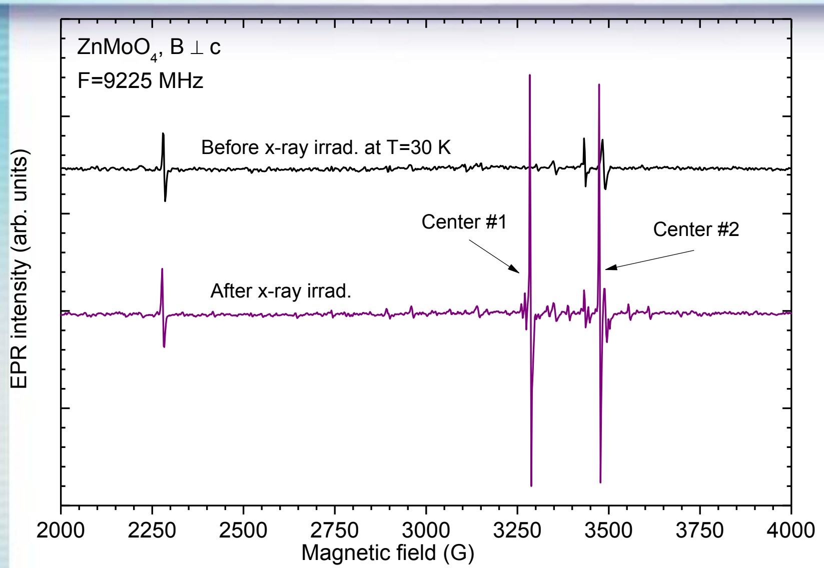
Conventional Czochralski method
GPI RAS (Moscow) ISMA (Kharkov)



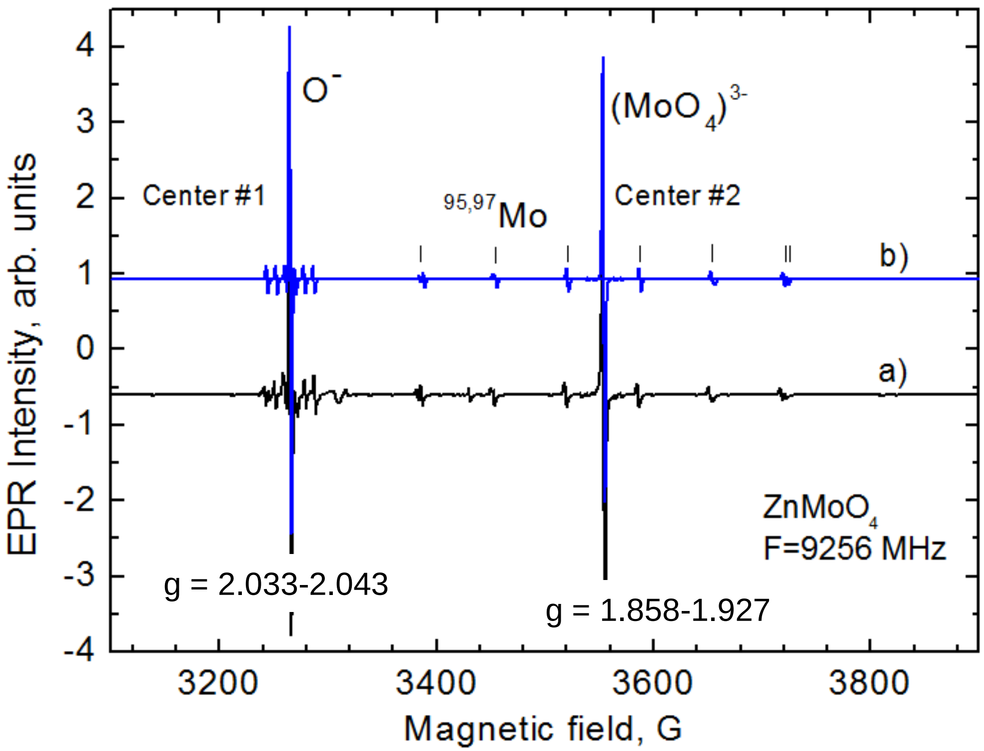


Improvement of optical quality of $ZnMoO_4$ crystal increases concentration of traps?

EPR data on $ZnMoO_4$



- Two paramagnetic centers are created under X-ray irradiation at T = 30 K.



- The center #1 is of hole-type, created as a result of a hole trapping at lattice oxygen ion.
- The center #2 is of electron – type, and is created by trapping of an electron by $(MoO_4)^{2-}$ complex.

Thermal stability of paramagnetic centers in $ZnMoO_4$

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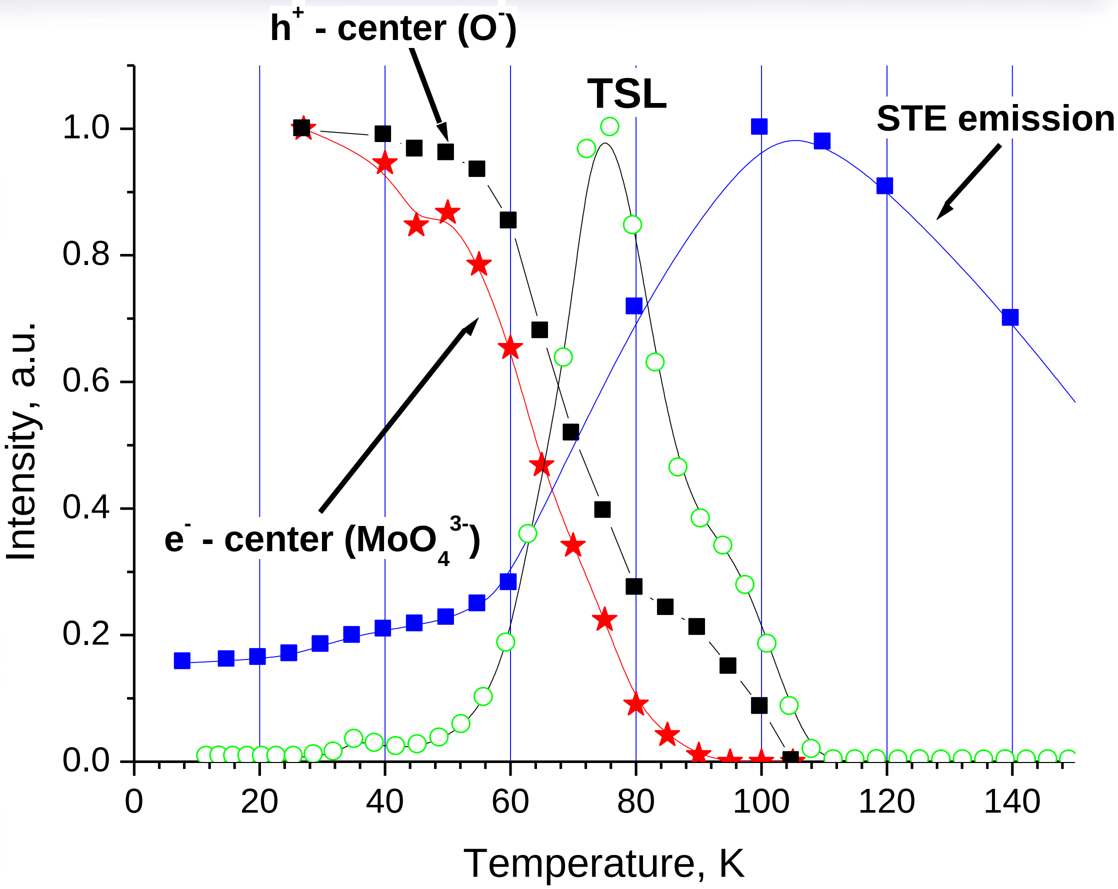
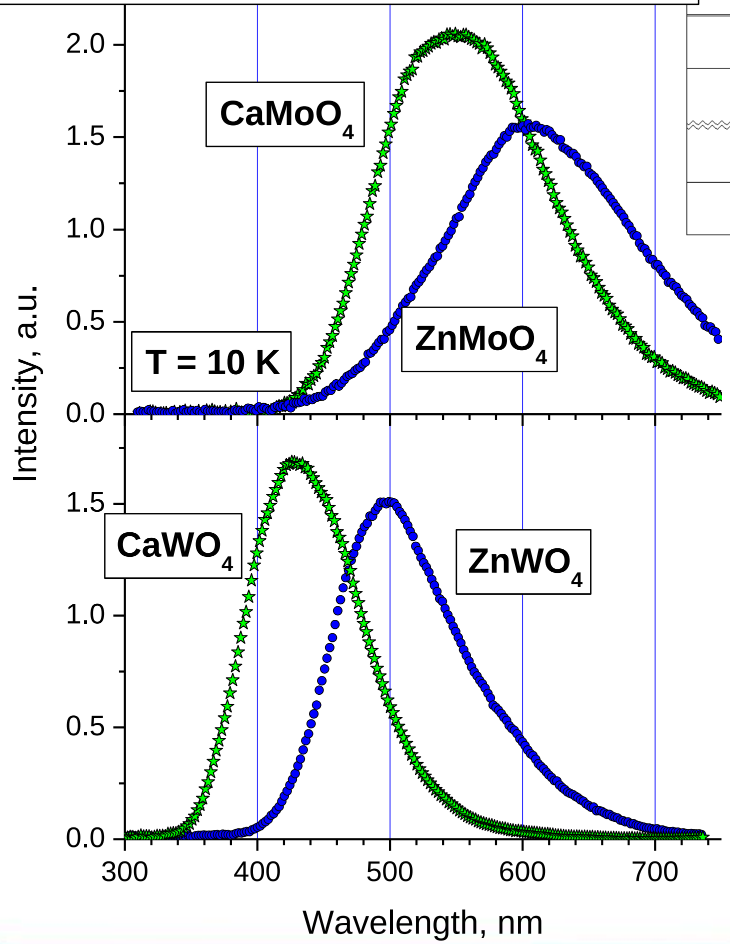


- Both types of charge carriers are immobile at the low temperatures.
- It may be the main reason for low scintillation yield of $ZnMoO_4$ at low temperatures.

Scintillation properties and self-trapping

emission of STE under direct excitation



	E_g, eV	Emission peak, nm	Light yield, ph/MeV (T ~ 10 K)
$CaMoO_4$	4.4	540	**15000**
$ZnMoO_4$	4.3	595	**500**
$CaWO_4$	4.9	420	**16000**
$ZnWO_4$	4.6	490	**19000**

$$N_{ph} = \frac{E}{\beta E_g} S Q$$

Q ($CaMoO_4$) ~ Q($ZnMoO_4$)
E_g ($CaMoO_4$) ~ E_g ($ZnMoO_4$)

Energy losses occurs at the stage of migration of charge carriers to the emission centers.

S($CaMoO_4$) > S($ZnMoO_4$)

Self-trapping prevents migration of both – electrons and holes in $ZnMoO_4$.

Conclusion

Intrinsic trapping centers for electrons and holes co-exist in $ZnMoO_4$. The immobility of charge carriers at $T < 50$ K results in the substantial decrease of the probability of STE creation with consequent worsening of the luminescent properties at low temperatures and in the unusually low scintillation light yield of $ZnMoO_4$.

Acknowledgements

The financial support from 7th FP INCO.2010-6.1 grant agreement No 266531 (project SUCCESS), Mobilitas ESF program (grant MTT83), Estonian Research Council – Institutional Research Funding IUT02-26 and RFBR 11-02-01506-a grants is gratefully acknowledged.

Thank you for your attention!

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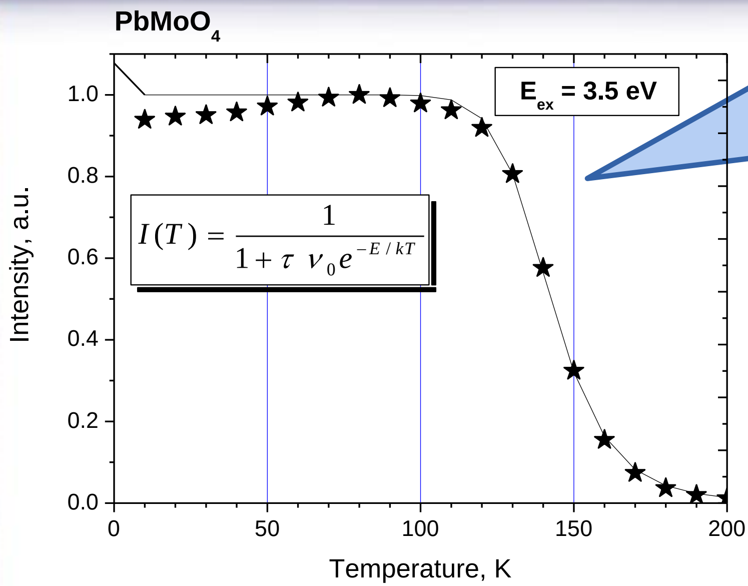
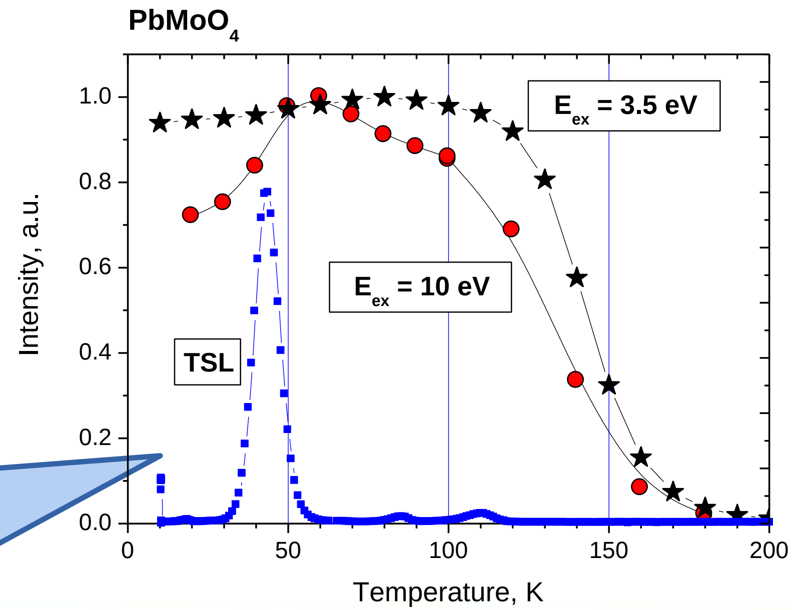
Scintillation properties and self-trapping. $PbMoO_4$

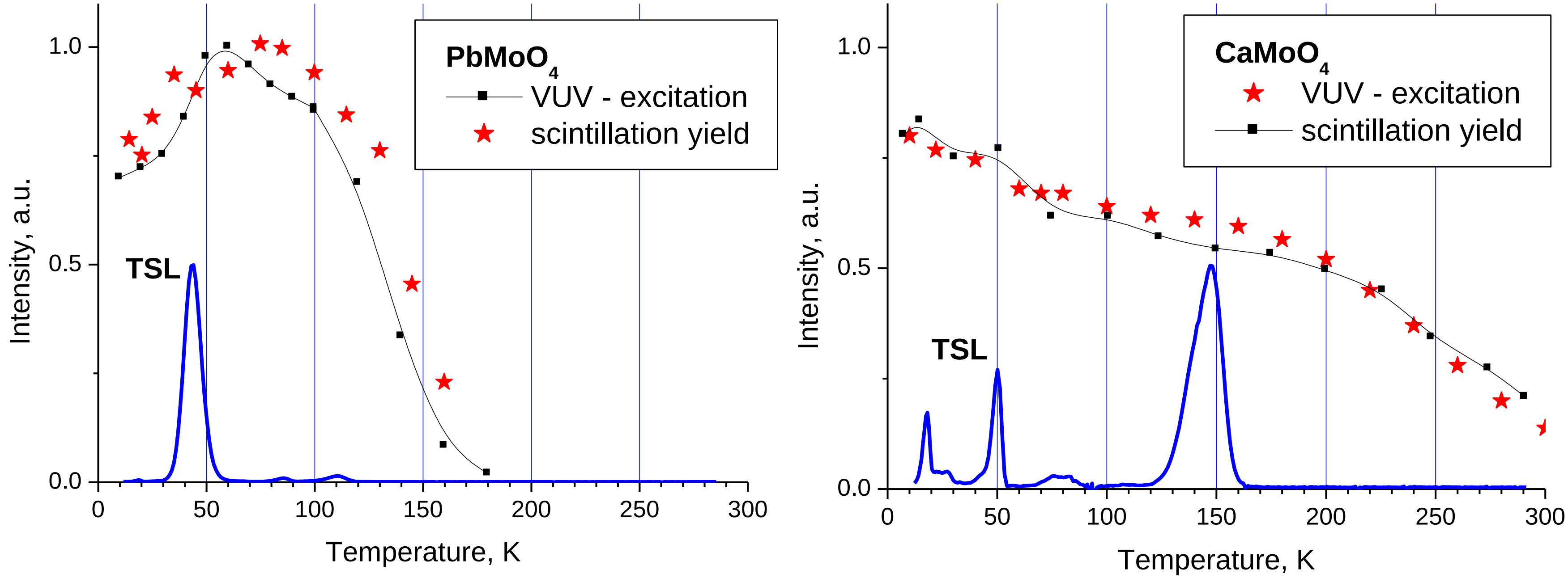


- When excitation energy corresponds to the direct creation of exciton, the temperature dependence of luminescence is determined by the intra-center quenching.



- When excitation energy exceeds the bandgap value separated charge carriers may be intercepted by another relaxation channels.

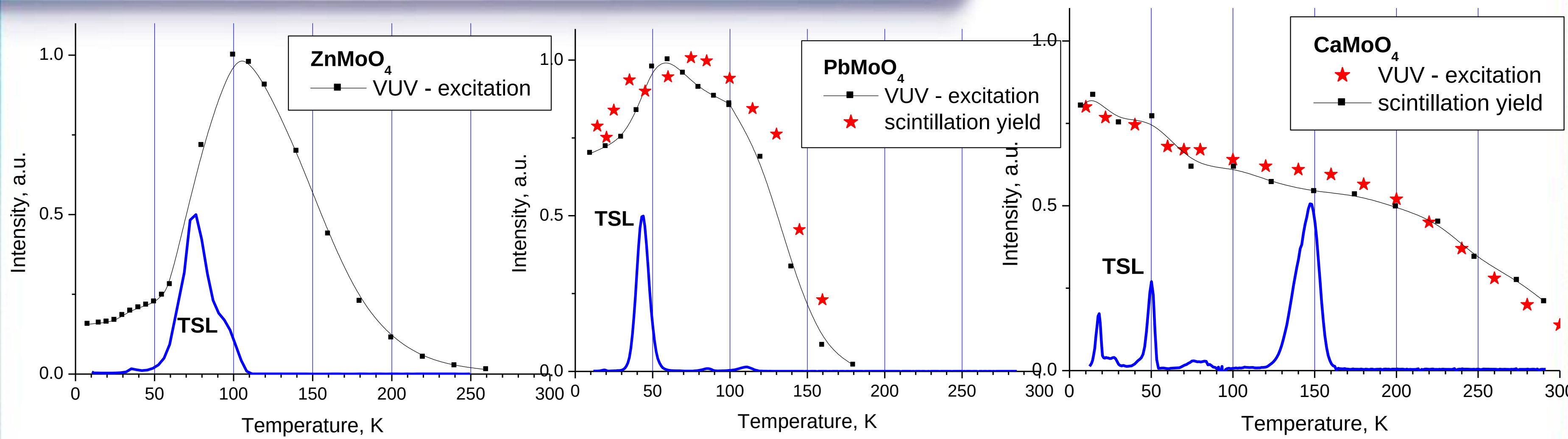
Luminescence properties and scintillation yield



- The suppression remains at the same level for excitation with alpha particles.
- VUV spectroscopy allows to make conclusions about the scintillation yield (in some cases).

data on scintillation light yield of $PbMoO_4$ were obtained in [Danevich et al NIM. A 622 (2010) 608]
data on scintillation light yield of $CaMoO_4$ were obtained in [Mikhailik et al PSS (b) 247 (2010) 1583]

Scintillation yield



data on scintillation light yield of $PbMoO_4$ were obtained in [Danevich et al NIM. A 622 (2010) 608]
data on scintillation light yield of $CaMoO_4$ were obtained in [Mikhailik et al PSS (b) 247 (2010) 1583]

	$CaMoO_4$	$SrMoO_4$	$PbMoO_4$	$ZnMoO_4$	
Space group	$C_{4h}^6(I4_1/a)$, tetragonal			P-1, triclinic	
Intrinsic trap centers	O^-	O^-	MoO_4^{3-}	MoO_4^{3-}	O^-
Release temperature, K	150	200	40	76	97