Combined EPR and TSL study of charge trapping processes and energy transfer studied in lead molybdate

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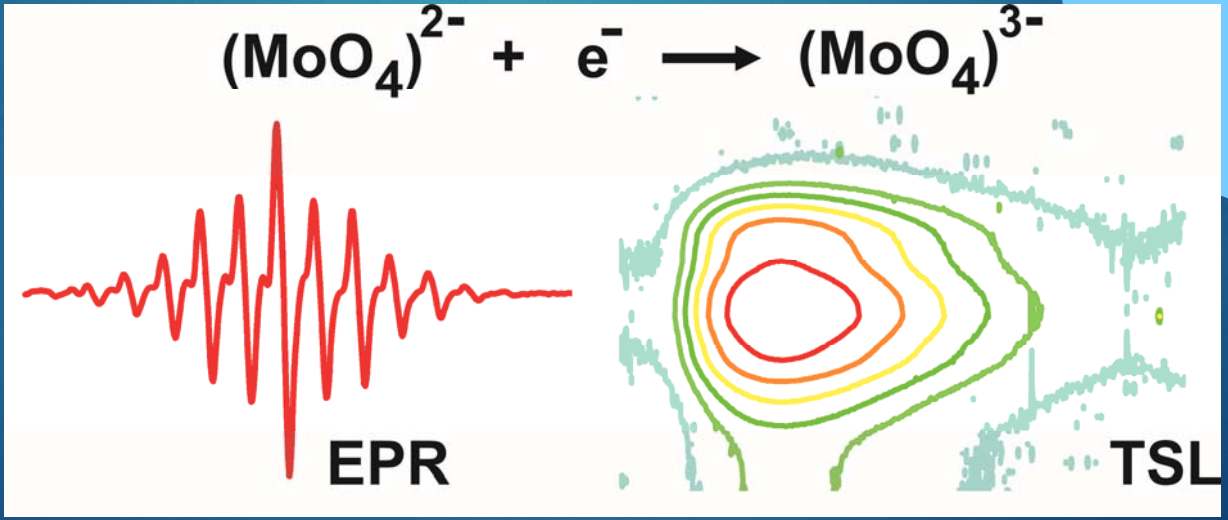
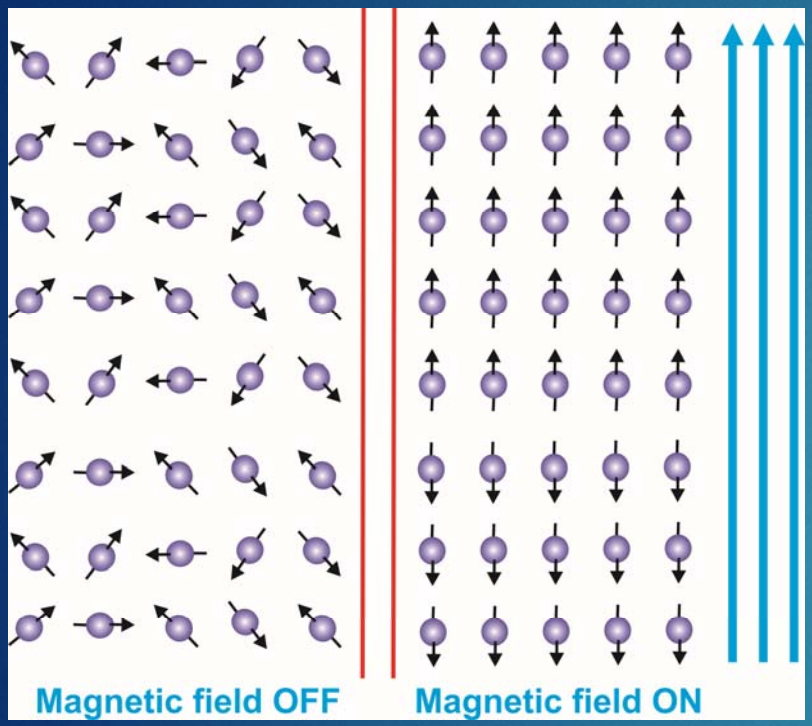
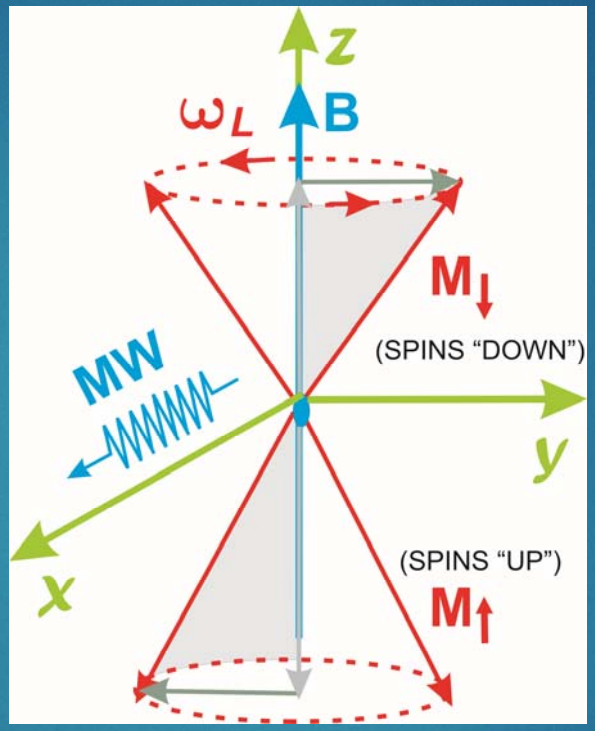


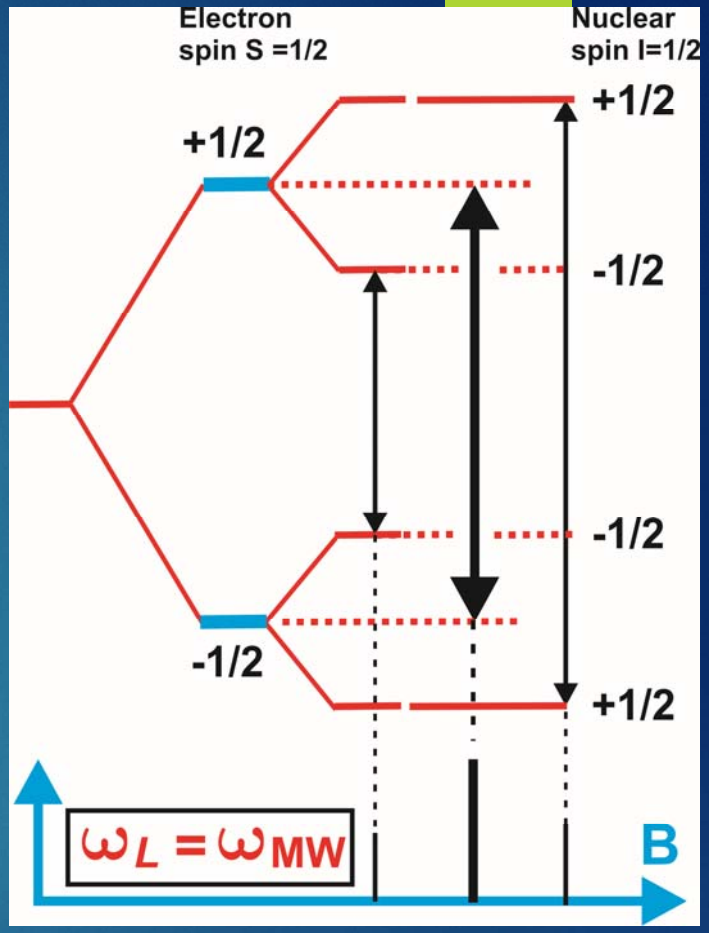
Speaker: Maksym Buryi, Ph.D.

Basic principles of EPR

Electron/nuclear spin system.





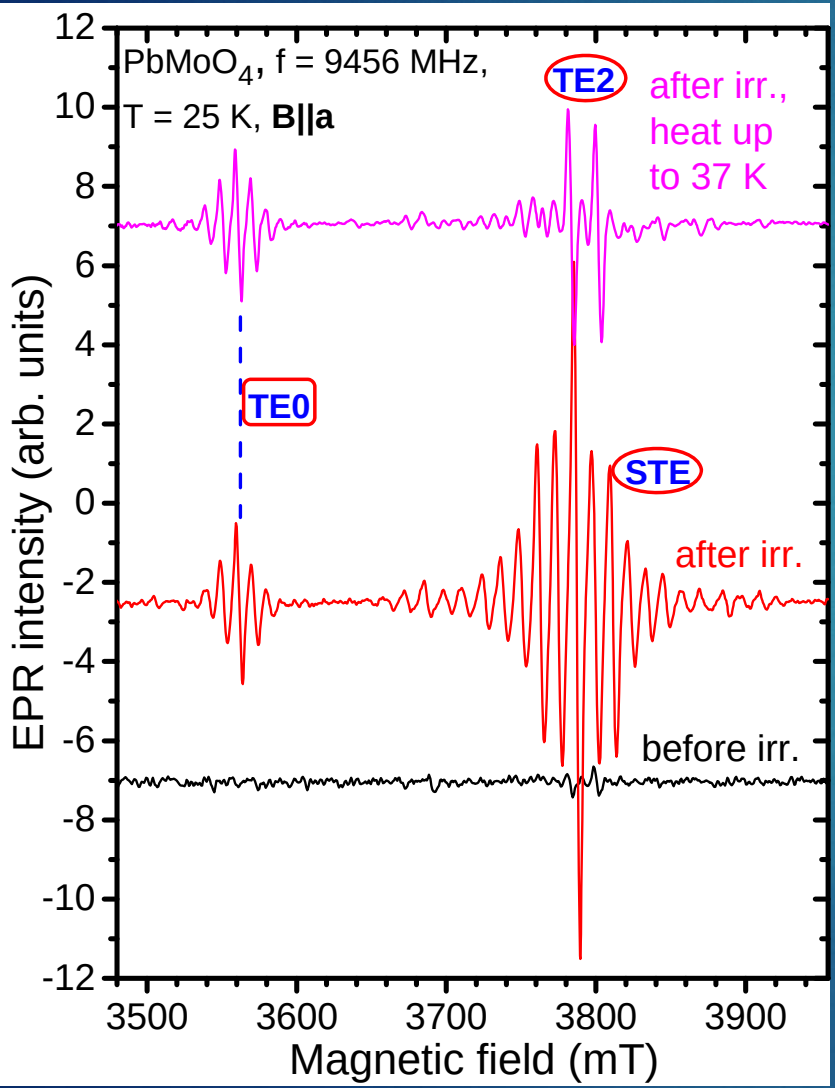


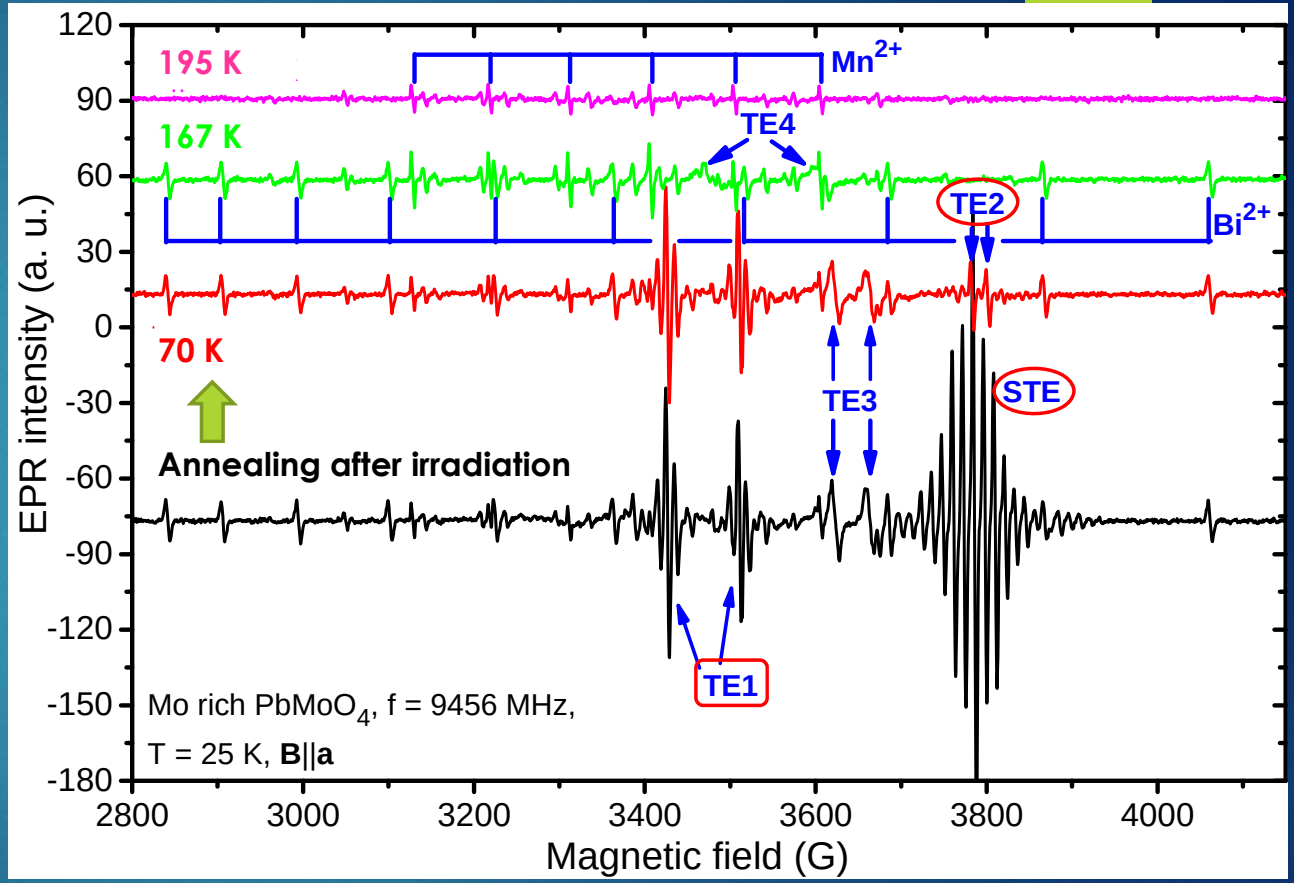
Spins ("up" and "down") produce magnetic moments. Magnetization (**M**) is the sum of the magnetic moments in a volume unit. The magnetization tumbles about the magnetic field (**B**) direction with the Larmor frequency ($\omega_L \sim |\mathbf{B}|$).

Absorption of microwaves (MW) occurs by reaching the $\omega_L = \omega_{MW}$ resonance condition. EPR signal is proportional to the $|\Delta\mathbf{M}| = |\mathbf{M}_\uparrow - \mathbf{M}_\downarrow|$ difference. Electron-nuclear interaction is also possible. It is called hyperfine (HF) when the nucleus and electron belong to the same ion and super hyperfine (SHF) in all other cases.

Schematic view of the energy levels in the spin system. Bold bar demonstrates EPR signal due to the +1/2↔-1/2 electron spin transition. Thin bars exhibit two transitions instead of one due to the splitting of the electron spin levels caused by the HF interaction. Since the $\omega_L \sim |\mathbf{B}|$ the $\omega_L = \omega_{MW}$ can be fulfilled by sweeping the magnetic field while the ω_{MW} = const.

Light irradiation induced defects in $PbMoO_4$



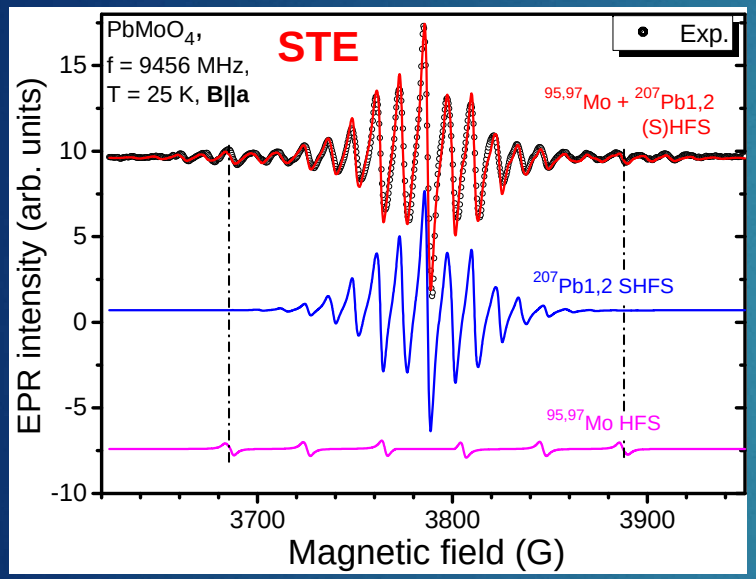


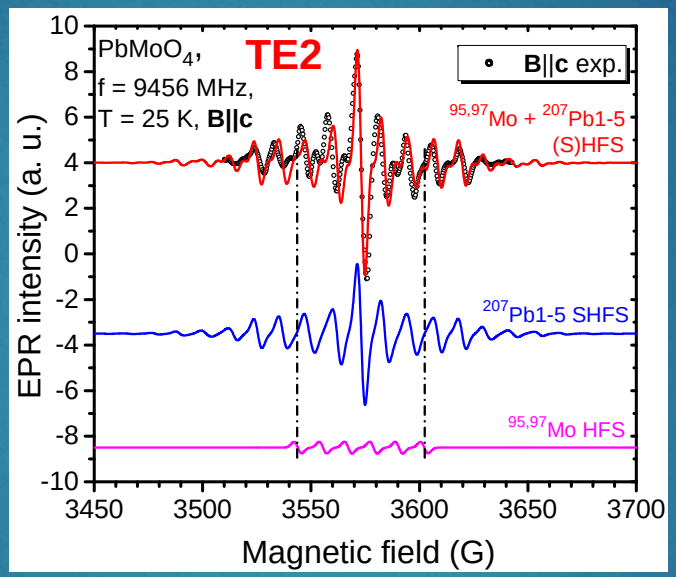
EPR spectra measured in undoped $PbMoO_4$ before and immediately after the 420 nm laser light irradiation.

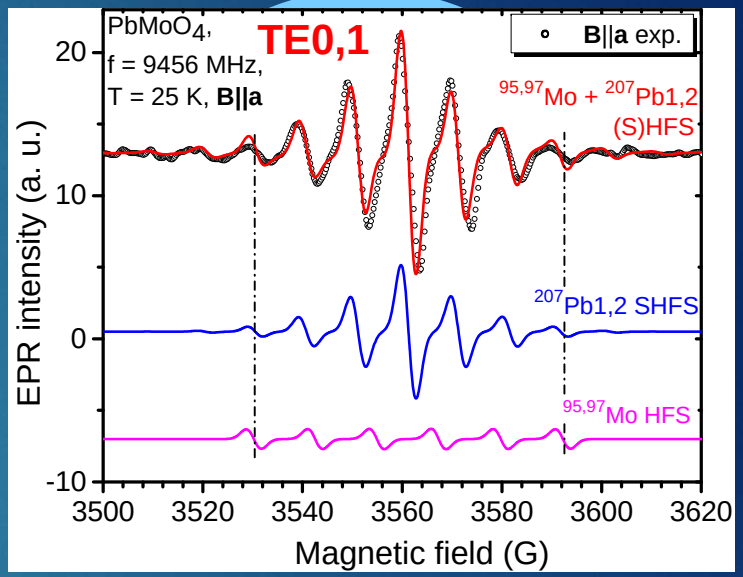
EPR spectra measured in Mo rich $PbMoO_4$ after the 420 nm laser light irradiation. **Three more new centers were created compare to the undoped lead molybdate.**

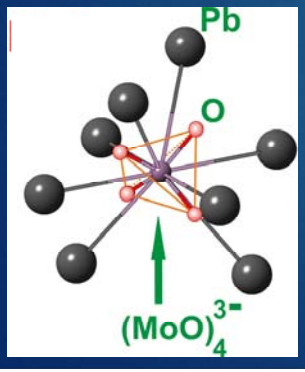
Light irradiation induced defects in $PbMoO_4$

M. Buryi, V. Laguta, M. Fasoli, F. Moretti, M. Trubitsyn, M. Volnianskii, A. Vedda, M. Nikl, **Electron self-trapped at molybdenum complex in lead molybdate: an EPR and TSL comparative study, J. Lumin. (2017). In press. DOI: https://doi.org/10.1016/j.jlumin.2017.07.066**



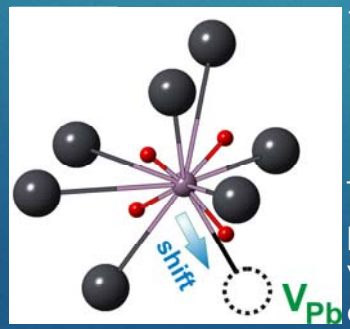






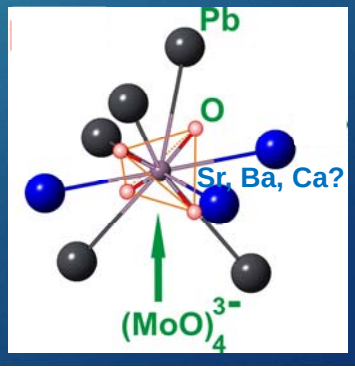
Contributions from the intrinsic $^{95,97}Mo$ and 8 ^{207}Pb nuclei. **Axial spectrum.**

Regular molybdenum site. **$(MoO_4)^{2-} + e^- \rightarrow (MoO_4)^{3-}$. The center does not survive above 40 K.**



The intrinsic $^{95,97}Mo$ and 7 ^{207}Pb nuclei. **Non-axial spectrum.**

The Mo regular site perturbed by a lead vacancy. The center exists up to 85 K.

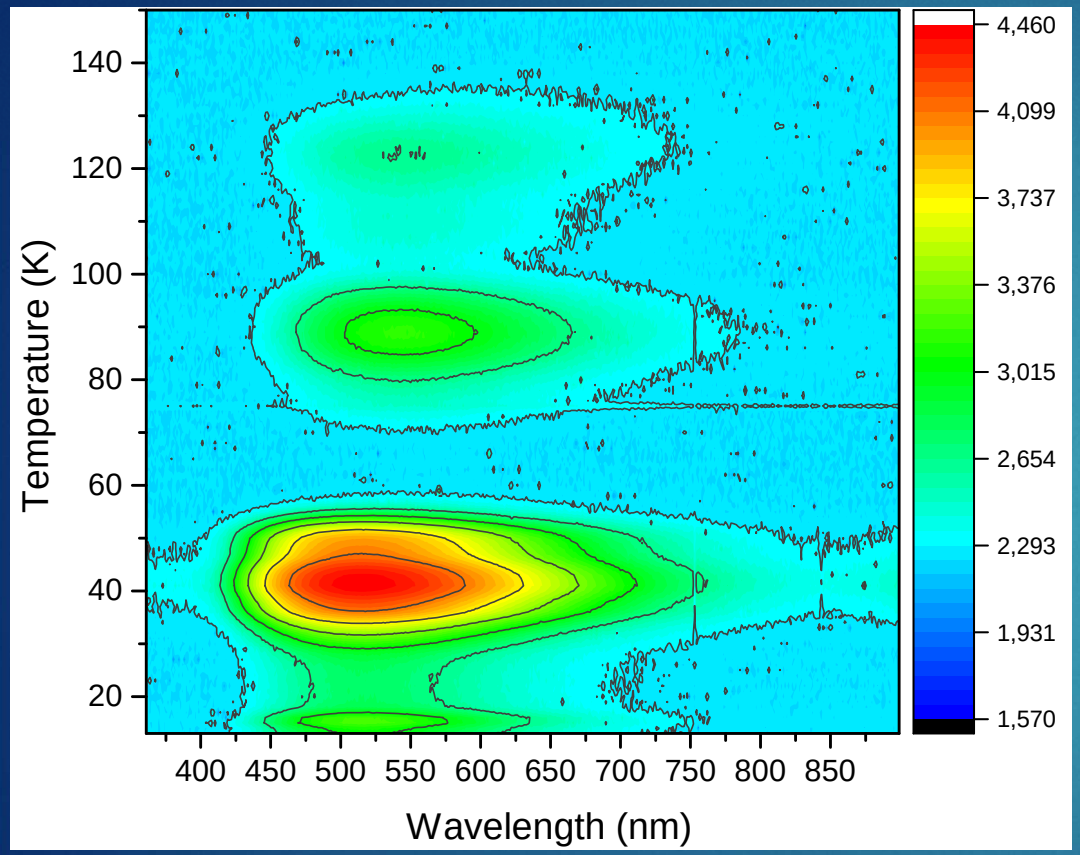


The intrinsic $^{95,97}Mo$ and 4-5 ^{207}Pb nuclei. **Axial spectrum.**

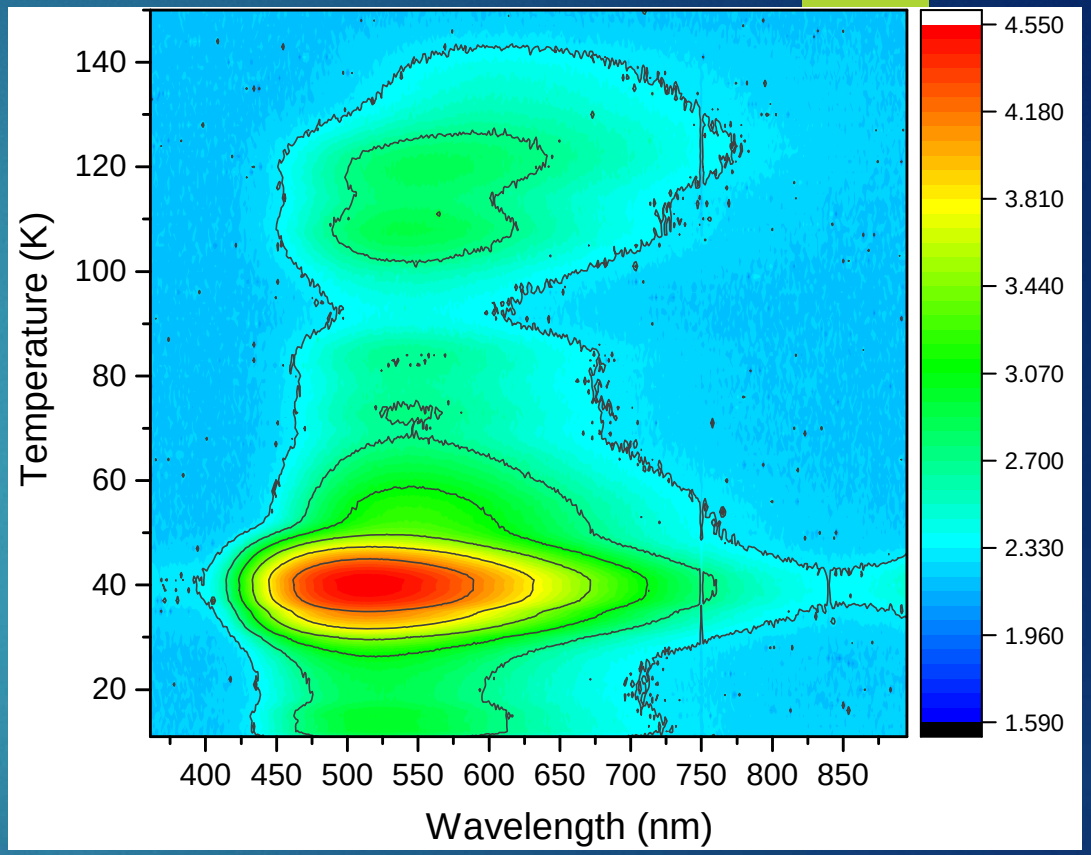
The Mo regular site with 3-4 lead ions replaced by other ions of similar ionic radii. The center exists up to 65, 165 K.

TSL and thermal stability study

In collaboration with the Department of Materials Science, University of Milano-Bicocca



Contour plot obtained from spectrally resolved TSL measurements in undoped $PbMoO_4$. The 90 K, 550 nm group of peaks is stronger than the 125 K, 570 nm one.



Contour plot obtained from spectrally resolved TSL measurements in the Mo rich $PbMoO_4$. Main group of peaks at around 40 K and 525 nm is almost unchanged, however it overlaps with the new peaks absent in the undoped lead molybdate sample. Significant changes occurred to the 90 K, 550 nm and 125 K, 570 nm groups.

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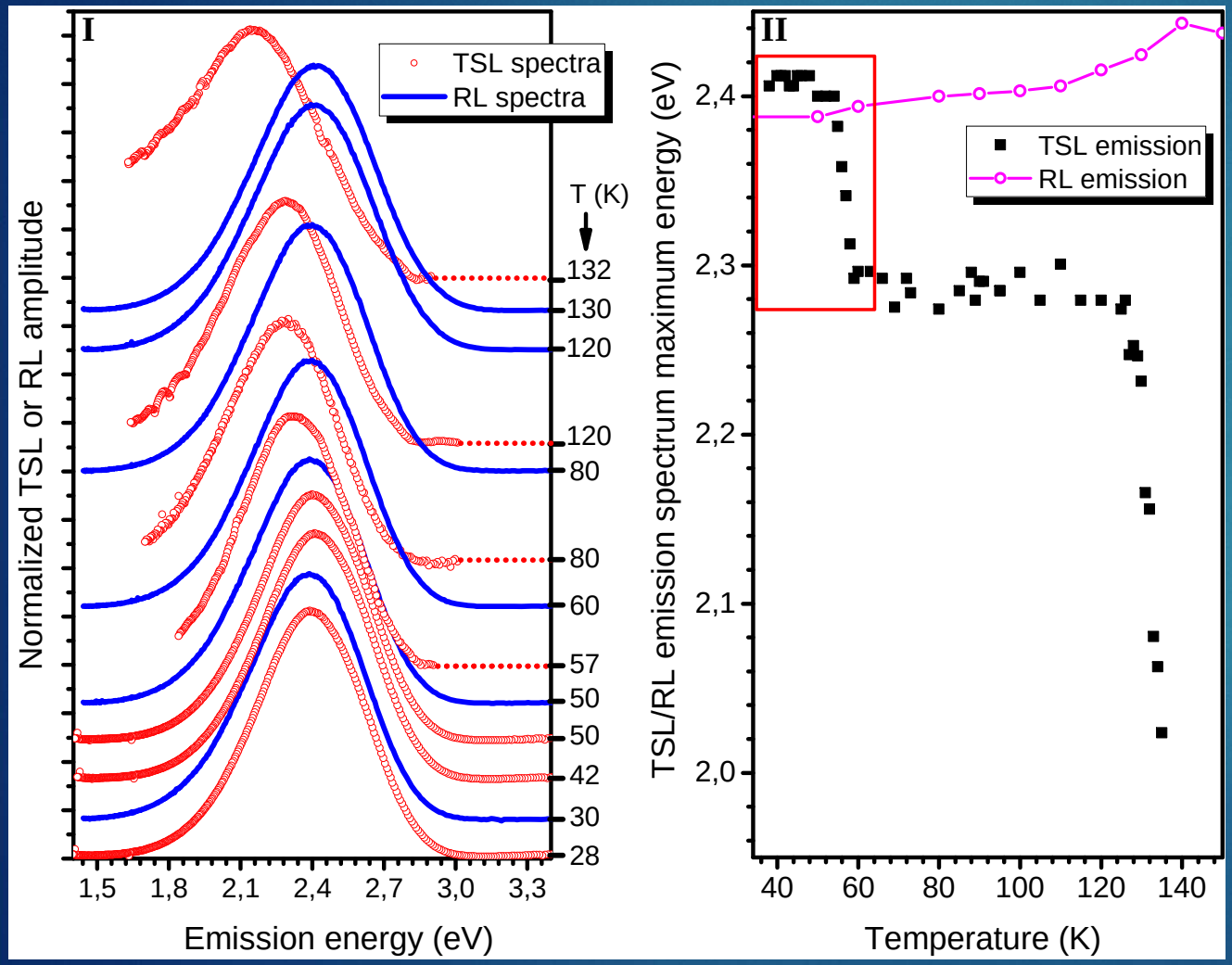

I. TSL (red circles) and RL (blue solid lines) emission spectra (with assymetric band) measured at different temperatures. The shift of the maximum towards lower energies is clearly visible for the TSL spectrum.

II. Temperature dependence of the TSL spectra maximum energy. On the contrary the RL spectra have very weak tendency to the higher energies at higher temperatures till 140 K reaching a plateau.

Both undoped and Mo rich $PbMoO_4$ demonstrated this phenomenon.

It was also observed in the extra pure arch$PbMoO_4$ within the 10-60 K range (red oblong in Fig. II).

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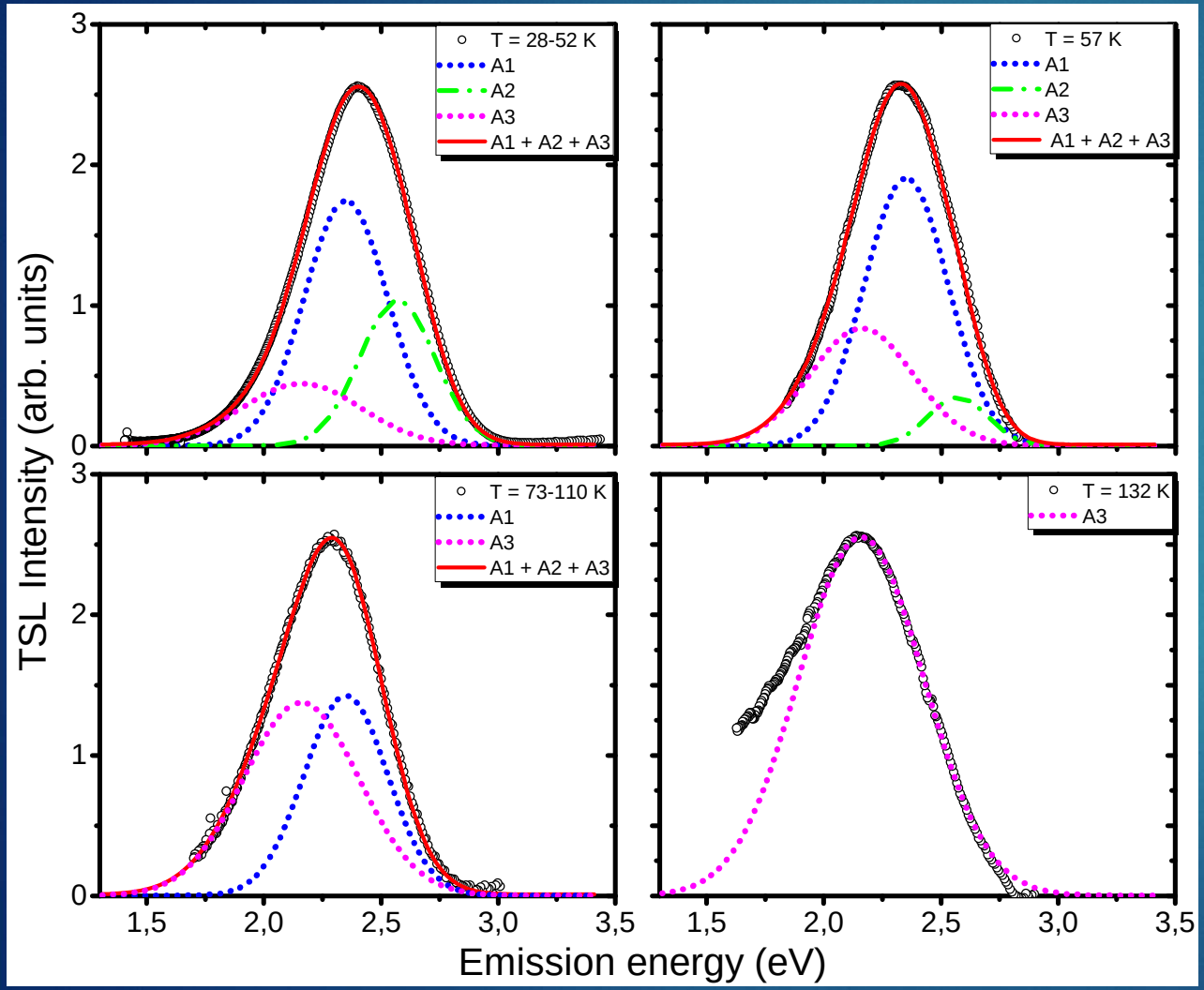

On example of the undeoped $PbMoO_4$ the chosen TSL emission spectra (measured at certain temperatures mentioned in figures) have been approximated by the calculated ones **supposing** them to be composed of three different A1-A3 Gaussian components with the following features:

A1 – maximum at 2.35 eV, FWHM = 0.42 eV;

A2 – maximum at 2.57 eV, FWHM = 0.30 eV;

A3 – maximum at 2.16 eV, FWHM = 0.63 eV.

Spectral shift is due to different fading rate of a single component with increasing temperature.

A2 origin: $\mathbf{(MoO_4)^{4-} + 2h^+ \leftrightarrow (MoO_4)^{2-}}$ **(unstable)**

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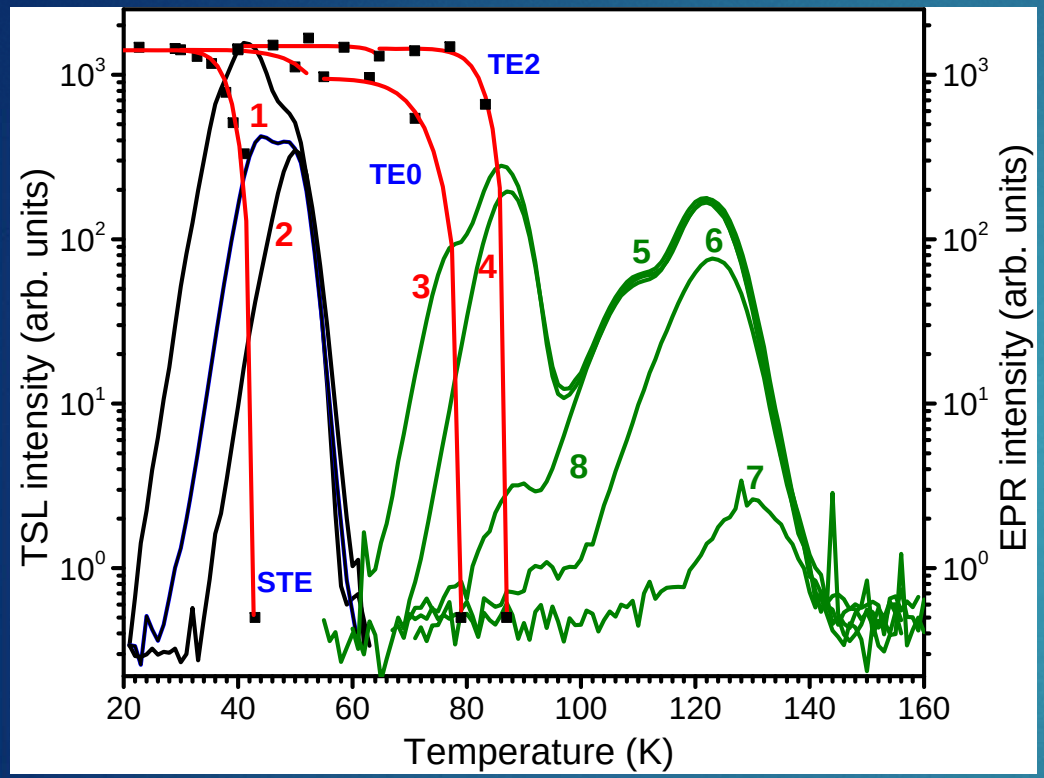
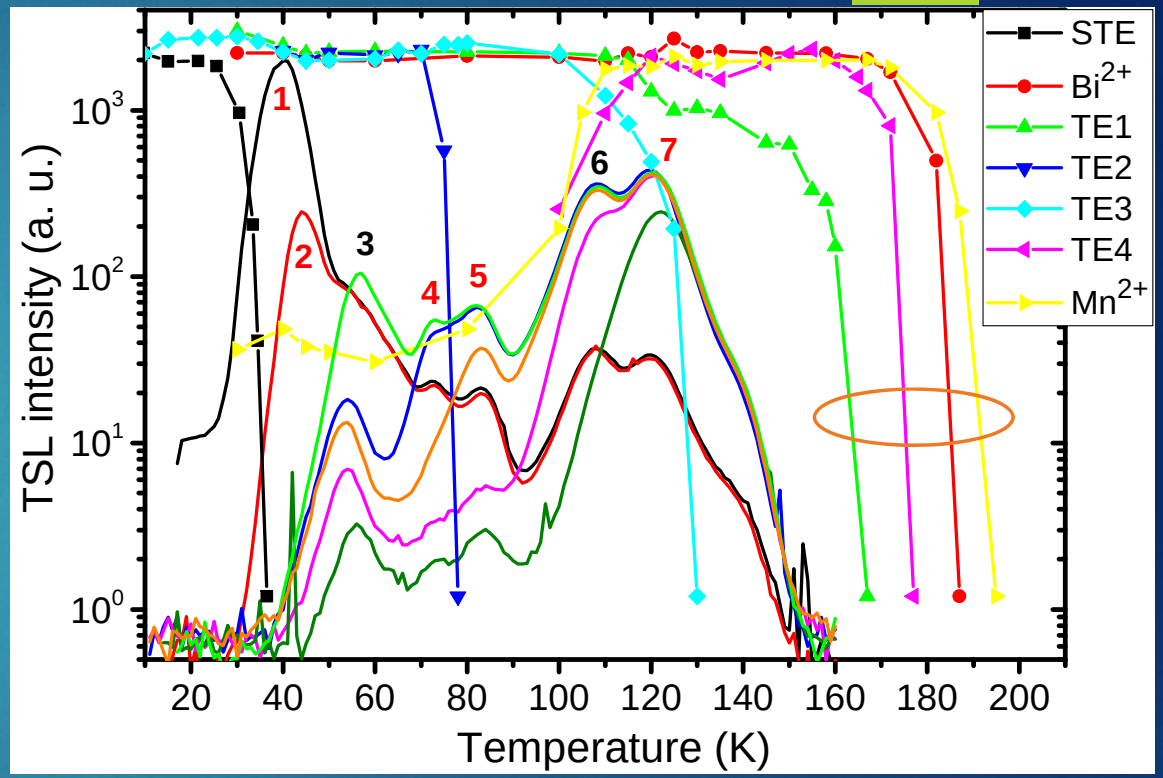


TSL glow curves measured after partial cleaning at different stop temperatures. The numbered peaks correspond to: 1 – 43 K, 2 – 47 K, 3 – 83 K, 4 – 87 K, 5,8 – 97 K, 6 – 120 K, 7 – 130 K. EPR intensity thermal decay curves (dots) approximated by the calculated curves (red) demonstrate correlation with some peaks.



TSL glow curves measured after partial cleaning at different stop temperatures. The numbered peaks correspond to: 1 – 40 K, 2 – 44 K, 3 – 57 K, 4 – 70 K, 5 – 83 K 6 – 110 K, 7 – 122 K. EPR intensity thermal decay curves (line + symbol) demonstrate correlation with some peaks. Decays of the TE1,4 and Mn^{2+} and Bi^{2+} EPR signals are connected somehow.

TSL and thermal stability study

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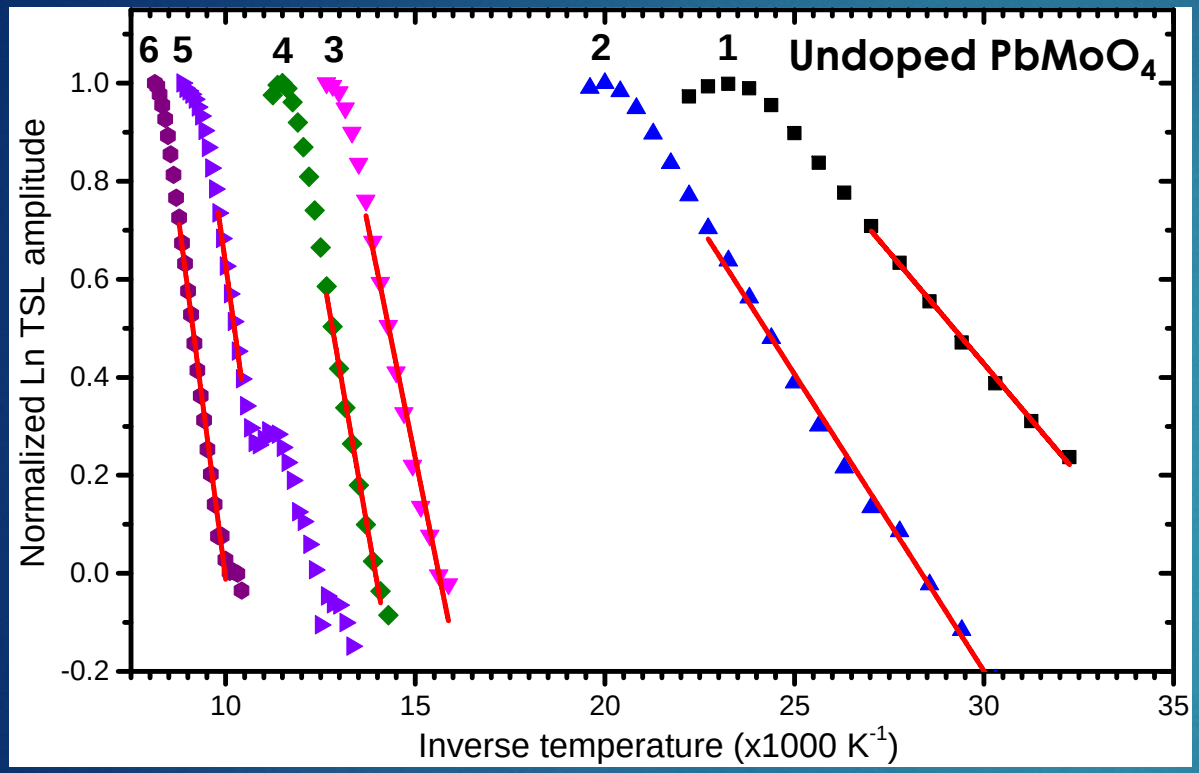

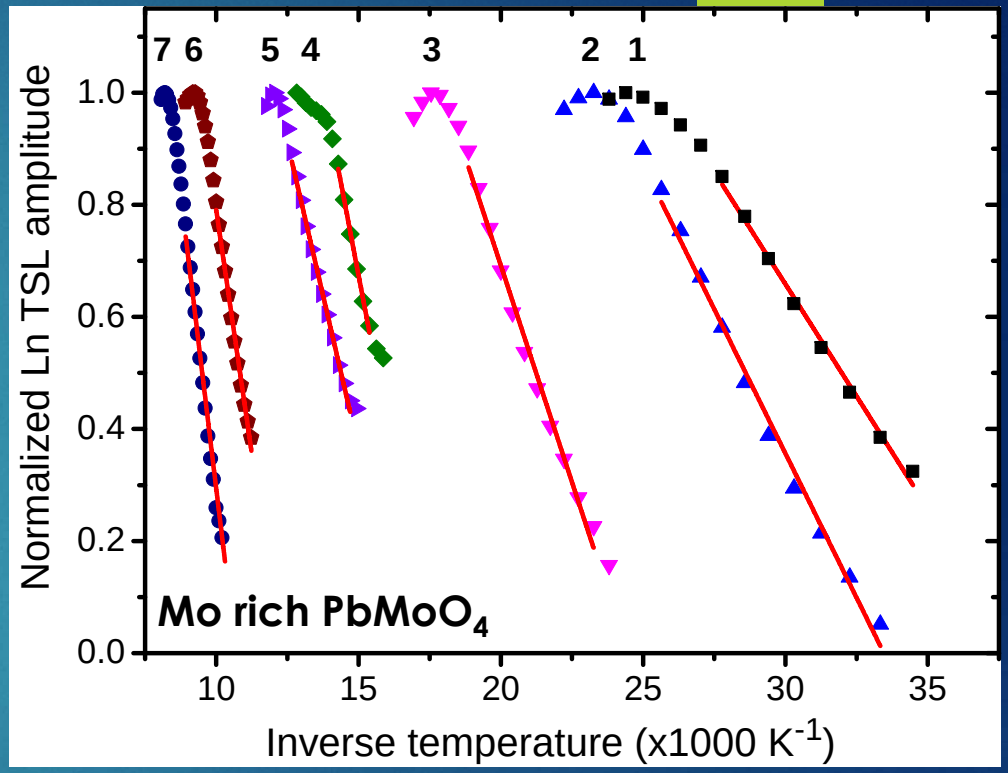

Initial rise technique applied to the chosen peaks (numbered) in both undoped and Mo rich $PbMoO_4$. Red solid lines are fitting curves. Comparing calculated trap depths (~0.05-0.2 eV) and frequency factors (~10^4-10^6 s^{-1}) with those determined from the fitting of EPR spectra intensity thermal decay curves, the "1-2", "3" and "4" have been referred to the STE, TE0, TE2 centers in the undoped $PbMoO_4$ and the "1-2", "4-5" and "7" to the STE, TE2, TE3 in the Mo rich $PbMoO_4$, respectively.

Conclusions

- Self-trapped electron has been discovered, as an intrinsic feature of a lead molybdate similarly to a lead tungstate.
- Other electron traps are connected with accidental impurities and non-regularity within the lattice.
- No paramagnetic hole traps like e.g. O^- defect were found.
- Emission spectrum is multicomponent. The shift with temperature towards lower energies, most likely, originates from different fading rate of each single component.
- Crystal growth from the Mo rich melt leads to larger amount of charge traps.

Thank you for your attention!