CRYSTALLINE SALTS WITH PEACOCK–WEAKLEY TYPE HETEROPOLY ANION $Na_9[Ln(W_5O_{18})_2]\cdot nH_2O$ (Ln = LANTHANIDE): SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES

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New procedure for synthesis of isostructural sodium heteropoly decatungstolanthanidates(III) with Peacock–Weakley type anion $Na_9[Ln(W_5O_{18})_2]\cdot 35H_2O$ (Ln = La–Yb) in $Ln(NO_3)_3 – Na_2WO_4 – HNO_3 – H_2O$ solutions with a ratio $\nu(Ln) : \nu(W) = 1:10$, acidified up to $Z = \nu(HNO_3)/\nu(Na_2WO_4) = 0.80$, were elaborated (Mariichak O.Yu., *et al.* Patent of Ukraine No. 121322, 2017). The synthesized salts were characterized by Single Crystal X-ray analysis (Fig. 1), FT-IR and FT-Raman spectroscopy, and scanning electron microscopy.

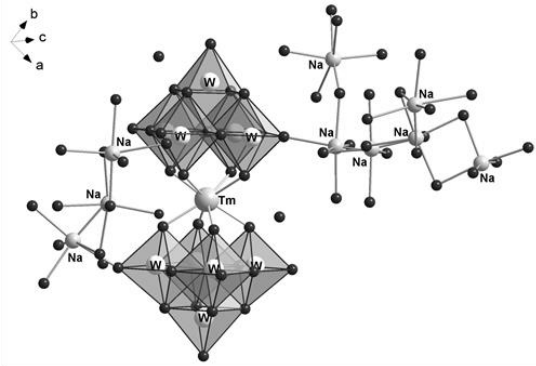

Fig. 1. Structure of the $Na_9[Tm(W_5O_{18})_2]\cdot 35H_2O$

Magnetic properties of $Na_9[Ln'(W_5O_{18})_2]\cdot 35H_2O$ (Ln' = Tm, Yb) were characterized. The Tm(III) derivative was found to exhibit slow relaxation of its magnetization with an energy barrier of 62 K. $Na_9[Tm(W_5O_{18})_2]\cdot 35H_2O$ is a rare example of Tm(III)-based SMM.

By comparing the interatomic distances and bond lengths for a series of normal ($Na_9[Ln(W_5O_{18})_2]\cdot nH_2O$) and acid salts ($K_3Na_4H_2[Ln(W_5O_{18})_2]\cdot nH_2O$, $Na_6H_3[Sm(W_5O_{18})_2]$x x28H_2O, $Na_8H[Gd(W_5O_{18})_2]\cdot 30H_2O$) the influence of the Ln-heteroatom on the structural parameters in Peacock–Weakley type heteropoly anion $[Ln(W_5O_{18})_2]^{9-}$ (Ln = La–Yb) was analyzed. The influence of the Ln-heteroatom on the structural parameters in the lanthanide-containing lacunary Keggin type heteropoly anion $[Ln(\alpha\text{-}PW_{11}O_{39})_2]^{11-}$ and metatungstate isopoly anion $[Ln_2(H_2O)_{10}W_{22}O_{71}(OH)_2]^{8-}$ was discussed.

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