Spin-orbit coupling in $Ca_{1-x}Mn_x(MoO_4)_{0.50}(WO_4)_{0.50}$ solid solution (where $0 < x \leq 0.15$)

T. Groń[1], M. Piątkowska[2], E. Tomaszewicz[2], M. Oboz[1], H. Duda[1]

[1]*University of Silesia, Institute of Physics, ul. Uniwersytecka 4, 40-007 Katowice, Poland*
[2]*West Pomeranian University of Technology, Szczecin, Faculty of Chemical Technology and Engineering, Department of Inorganic and Analytical Chemistry, Al. Piastów 42, 71-065 Szczecin, Poland*

Molybdates and tungstates of calcium are characterized by high thermal stability and chemical resistance. These compounds are used in electronics and optoelectronics as matrix laser crystal and scintillation materials. $Ca_{1-x}Mn_x(MoO_4)_{0.50}(WO_4)_{0.50}$ (where $0 < x \leq 0.15$) was prepared by solid phase reaction to give a new substitutional solid solution. Mixtures containing $CaWO_4$, $CaMoO_4$ and $MnMoO_4$ were heated in air and in the 12-hour steps in temperatures of the range 900-1150°C. X-ray diffraction measurements at room temperature showed that the solid solution under study crystallized in tetragonal scheelite type structure with the space group of $I4_1/a$. The calculated lattice parameters (a and c) of the tetragonal unit cell decreased with increasing content of Mn^{2+} ions in the structure solution of $Ca(MoO_4)_{0.5}(WO_4)_{0.5}$. The Ultraviolet–visible and near-infrared measurements showed that all phases of $Ca_{1-x}Mn_x(MoO_4)_{0.50}(WO_4)_{0.50}$ are insulators with the energy gap above 3.5 eV.

The electrical conductivity $\sigma(T)$ and the *I-V* characteristics have been measured with the aid of the DC method in the temperature range 77 – 400 K using a KEITHLEY 6517B Electrometer/High Resistance Meter. The thermoelectric power *S(T)* was measured in the temperature range 300 – 600 K with the aid of a Seebeck Effect Measurement System (MMR Technologies, Inc., USA). The magnetic properties were measured in the zero-field cooled (ZFC) and field cooled (FC) mode using a Quantum Design Physical Properties Measurement System.

The results of the electrical and magnetic measurements showed insulating behaviour with small values of the *p*-type electrical conductivity of $\sigma \sim 10^{-10}$ S/m independent of the manganese content, ferrimagnetic long-range interactions for x=0.01 and 0.03 as well as paramagnetic behaviour for x=0.125 and 0.15. The ferromagnetic short-range interactions in the content range $0.01 \leq x \leq 0.10$ and antiferromagnetic ones above x=0.10 were observed. There was no splitting between the ZFC and FC magnetic susceptibilities for any phase, which means no spin frustration. The most interesting observation is the spin–orbit coupling driven from the Brillouin fit at 2 K of the magnetization versus H/T. With the increase of manganese content the Landé factor decreases from g=1.75 for x=0.01 to g=0.66 for x=0.15. That is, the contribution of the orbital magnetic moment strongly increases with increasing content of manganese ions. The strong spin-orbit coupling was observed for the $ZnRE_4W_3O_{16}$ (RE=Nd, Gd, Dy, Ho) [1] and $Co_2Sm_2W_3O_{14}$ tungstates [2]. However, for the $AgY_{1-x}Gd_x(WO_4)_2$ solid solution the spin-orbit coupling was not observed [3].

[1] P. Urbanowicz, E. Tomaszewicz, T. Groń, H. Duda, A.W. Pacyna, T. Mydlarz, H. Fuks, S.M. Kaczmarek, J. Krok-Kowalski, J. Phys. Chem. Sol. 72 (2011) 891–898.
[2] P. Urbanowicz, E. Tomaszewicz, T. Groń, H. Duda, A.W. Pacyna, T. Mydlarz, H. Fuks, S.M. Kaczmarek, Solid State Phenom. 170 (2011) 1–4.
[3] E. Tomaszewicz, H. Fuks, J. Typek, B. Sawicki, M. Oboz, T. Groń, T. Mydlarz, Ceram. Int. 41 (2015) 5734–5748.