Magnetic and electric properties of Nd^{3+} and Mn^{2+}-co-doped calcium molybdato-tungstate single crystals

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Divalent metal molybdates and tungstates with tetragonal scheelite-type structure (space group $I4_1/a$, No. 88) both un-doped as well as activated with di- or/and trivalent ions are very interesting materials because of their excellent properties. Micro-/nanocrystalline as well as single crystals samples of these materials could be widely applied as efficient phosphors [1], solid state lasers [2], scintillators [3], and microwave dielectrics [4]. Calcium molybdate ($CaMoO_4$) and calcium tungstate ($CaWO_4$) as members of scheelite family are highly ionic compounds with a small contribution of a covalent bonding. Band gaps determined from the band dispersion calculations [5] indicated that both compounds are direct band gap insulators with the E_g values of: 3.41 eV for $CaMoO_4$, and 4.09 eV for $CaWO_4$. Our earlier magnetic and electric research of microcrystalline $Ca_{1-3x-y}Mn_y\square_xNd_{2x}(MoO_4)_{1-3x}(WO_4)_{3x}$ solid solution (when $0.0050 \leq x \leq 0.2000$ and $y = 0.0200$, where $\square$ denotes vacant sites) obtained by high-temperature annealing of ternary $MnMoO_4/Nd_2(WO_4)_3/CaMoO_4$ mixtures showed a paramagnetic behavior with long-range ferrimagnetic and short-range antiferromagnetic interactions in these materials as well as a weak *n*-type electrical conductivity with stronger activation of 1.0 eV above 300 K in the intrinsic region [6].

In this work, $Ca_{1-3x-y}Mn_y\square_xNd_{2x}(MoO_4)_{1-3x}(WO_4)_{3x}$ molybdato-tungstate single crystals ($x = 0.005$ or $x = 0.0099$ and with constant Mn^{2+} ions concentration, *i.e.* $y = 0.005$) have been grown by the Czochralski method in an inert atmosphere and subjected to structural, magnetic and electrical studies. The static magnetic susceptibility of as-grown single crystals was measured in the temperature range of 2–300 K and recorded both in zero-field-cooled and field-cooled mode using a Quantum Design SQUID magnetometer. Electrical conductivity $\sigma(T)$ of doped single crystals was measured by the dc method using a KEITHLEY 6517B Electrometer/High Resistance Meter. Thermoelectric power S(T) was measured within the temperature range of 77–400 K using a Seebeck Effect Measurement System (MMR Technologies). Our studies have shown that replacing diamagnetic Ca^{2+} ions with paramagnetic Nd^{3+} ones with the content not exceeding of 0.02 and having a screened 4*f*-shell revealed a significant effect of orbital diamagnetism and Van Vleck's paramagnetism, residual electrical conductivity without intrinsic region and a change of sign of the Seebeck coefficient at ~230 K as well as the Fermi energy (~0.04 eV) and the Fermi temperature (~500 K), determined from the diffusion component of thermopower suggesting the presence of shallow acceptor and donor levels.

[1] C.R. Ronda, T. Jüstel, and H. Nikol, *J. Alloy Compd.* **277**, 669 (1998).
[2] G. Boulon, *Opt. Mat.* **34**, 499 (2012.
[3] V.B. Mikhailik, S. Henry, H. Kraus, and I. Solskii, *Nucl Instrum Methods Phys. Res. A* **583**, 350 (2007).
[4] E.S. Kim, S.H. Kim, and I.B. Lee, *J. Eur. Ceram. Soc.* **26**, 2101 (2006).
[5] Y. Zhang, N.A.W. Holzwarth, and R.T. Williams, *Phys. Rev. B* **57**, 12738 (1998).
[6] B. Sawicki, E. Tomaszewicz, M. Guzik, T. Groń, M. Oboz, H. Duda, S. Pawlus, and P. Urbanowicz, *Ceram. Int.* **49**, 944 (2023).