Szczecin, 6.09.2021

mgr inż. Marta Karolewicz

Supervisor: dr hab. inż. Elżbieta Tomaszewicz, prof. ZUT

Abstract of PhD thesis:

New materials based on doped calcium molybdate – their synthesis, characterization and application possibilities

Divalent and trivalent metal tungstates and molybdates constitute a large and important group of materials. They exhibit many different types of crystal structures, and show also excellent chemical resistance as well as high thermal durability. For these reasons, molybdates and tungstates are very good hosts for *d*- and *f*- electron metal ions.

This PhD thesis concerns studies of materials that have not been described in the literature so far, and obtained with using calcium molybdate doped with manganese ions (Mn^{2+}) as well as co-doped with rare earth ions (RE^{3+} = Pr^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+} or Yb^{3+}). New materials are substitutional and vacancied solid solutions described by the following formulas: $Ca_{1-x}Mn_xMoO_4$ ($0 < x \leq$ max. 0,15), $Ca_{1-x}Mn_x(MoO_4)_{0,50}(WO_4)_{0,50}$ ($0 < x \leq$ max. 0,15) and $Ca_{1-3x-y}Mn_y\square_xRE_{2x}(MoO_4)_{1-3x}(WO_4)_{3x}$ ($0 < x \leq$ max. 0,25, $0 < y \leq$ max. 0,0667, and $\square$ denotes as vacancies in the crystal lattice of a solution). For the synthesis of new solutions, a high-temperature solid-state reaction method, a combustion reaction as well as a co-precipitation method were used. In cooperation with the Institute of Physics PAS in Warsaw, undoped calcium molybdate as well as Mn^{2+}-doped and Nd^{3+}-co-doped $CaMoO_4$ single crystals were grown by the Czochralski method.

New materials were analysed using the following research techniques: X-ray powder diffraction (XRD), UV-vis spectroscopy, infrared spectroscopy (IR), scanning electron microscopy connected with X-ray analysis (SEM/EDX), high-resolution transmission electron microscopy (HRTEM). Moreover, the density of new doped materials was determined using a pycnometric method. The melting point of some doped samples was estimated using a pyrometric method. In cooperation with other research groups in Poland, magnetic and electrical properties of new materials were examined.

The XRD results revealed the formation of tetragonal, scheelite-type materials belonging to $I4_1/a$ symmetry. The unit cell constants increased or decreased, in most cases non-linearly, with increasing Mn^{2+} and RE^{3+} contents in samples under study. The doped materials obtained by high-temperature sintering contained irregular grains and their average size was ~20 μm. Some part of microcrystals were connected together to form larger agglomerates with the size of ~50 μm. Nanocrystalline materials contained homogeneous and oval grains with

their average size ranging from 20 to 50 nm were obtained by combustion and co-precipitation methods.

New materials melt and their melting point changes significantly with increasing concentration of both dopants. Melting point doped samples was lower than the melting point of pure matrix (1753 K).

The values of direct optical band gap (E_g) as well as Urbach energy (E_U) of Mn^{2+}-doped and RE^{3+}-co-doped calcium molybdato-tungstates were determined using UV-vis spectroscopy. It was found that all materials are insulators and their E_g values are higher than 3,50 eV. Furthermore, both optical band gap and Urbach energy change non-linearly with increasing concentration of Mn^{2+} and RE^{3+} ions in samples under study.

The dielectric results revealed that new doped materials show low energy losses and dielectric permittivity within the temperature range of 76-300 K. These values do not depend on temperature, frequency of external electric field as well as Mn^{2+} and RE^{3+} ions contents. These results show that new solid solutions are promising materials for application in lossless capacitors. The doped molybdato-tungstates are also potential phosphor and scintillation materials.

Marta Kaniewiaz
6.09.2021