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Synthesis, structure and physicochemical properties of spinel compounds doped with selected elements: p-, d- and f- electronics

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Chromium spinels with general formula ACr_2X_4, (where *A* is a divalent cation: Cu, Cd, Hg, Mg, Fe or Zn, and *X* is a divalent anion: O, S, or Se, and Cr^{3+} ion is in the $3d^3$ configuration) belong to the group of compounds with many potential applications, especially for use in electronic and thermoelectric devices [1-3]. The compounds ACr_2Se_4 (A = Cd, Cu, Zn) belonging to the family of spinels, crystallize to a cubic structure (space group *Fd*-3*m*, No. 227). The value of lattice parameter is above 10 Å and the value of the fractional coordinate *u* is about 0.250 Å. Selected spinels ($CuCr_2Se_4$, $CdCr_2Se_4$, $ZnCr_2Se_4$) have different physical properties. The $CuCr_2Se_4$ compound is a ferromagnetic and has metallic conductivity (T_C = 460 K, Θ_{CW} = 465 K, C_M = 2.50 K/mol, μ_{sat} = 4.94 μ_B), $CdCr_2Se_4$ is a ferromagnetic and p-type semiconductor (T_C = 130 K, Θ_{CW} = 200 K, μ_{sat} = 5.30 μ_B, μ_{eff} = 5.49 μ_B), while the spinel $ZnCr_2Se_4$ is a p-type semiconductor with a spiral magnetic structure (T_N = 21 K, Θ_{CW} ~ 115 K, C_M = 3.54 K/mol, μ_{sat} = 6.1 μ_B, μ_{eff} = 5.90 μ_B). It is possible to improve the physicochemical properties of the ACr_2Se_4 compounds using of some dopants. This effect depends on many factors. The most important of them are the size of the ion radius, ion placement in the spinel structure (tetra- or octahedral position), coordination number (CN) and type of chemical bond. The question is, how the introduction of third cation to the crystal lattice of ACr_2Se_4, influences on the crystal structure and physicochemical properties of the parent compound.

In this lecture, the researches of physical and chemical properties of ACr_2Se_4 doped selected elements (Ni, Sn, Mn, Dy) will be presented. The seleno-spinels were synthesized by ceramic method (for polycrystalline samples) and by chemical vapour transport in order to obtain single crystals. The obtained samples were characterized using various method: X-Ray diffraction, SEM, SQUID, XPS, DSC/TG, XANES, NPD, Mössbauer spectroscopy. Depending on the substitution of one of the elements (magnetic or non-magnetic), a strong influence on the properties of the parent compound is observed, for example: **(1)** a spin-glass-like behavior in the $ZnCr_2Se_4$:Sn single crystals [4], **(2)** AFM order and the strong short-range FM interactions in the single crystals $ZnCr_2Se_4$:Dy was observed [5], **(3)** increase of FM interactions in the polycrystalline $ZnCr_2Se_4$:Mn [6], **(4)** weaker ferromagnetic interactions in the $CdCr_2Se_4$:Mn single crystals [7], **(5)** increase of AFM interactions in the $CuCr_2Se_4$:Ni single crystals [8].

References

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