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Physicochemical properties of $ZnCr_2Se_4$ spinel doped with selected d- and f-electron elements (summary)

As part of this work, the synthesis of doped poly- and monocrystalline compounds based on $ZnCr_2Se_4$ was planned and carried out, and then their physicochemical characteristic was determined. The inspiration for the research consisted in its unusual physicochemical properties.

This compound has a spinel structure and is a p-type semiconductor with a spiral magnetic structure. The d- and f-electron elements manganese, holmium and neodymium were chosen as admixtures, guided by different values of effective magnetic moment compared to chromium ions on III oxidation state. The synthesis of poly- and monocrystalline compounds was based on solid phase reactions (ceramic method for polycrystalline compounds and chemical vapour transport for growth of single crystals). X-ray methods (diffraction, SEM, XPS), magnetic measurements (SQUID, strong fields), electric measurements (four-point method), and thermal analysis (DSC/TG) were used to develop the characteristics of the compounds obtained.

In the $Zn_{1-x}Mn_xCr_2Se_4$ polycrystalline system, single-phase compounds in the x = 0.1÷0.5 range were obtained, which was confirmed by an X-ray study. The lattice and anion parameters increase linearly with an increase in the Mn^{2+} amount, which is consistent with the difference in the radii values between Zn^{2+} and Mn^{2+} ions. Magnetic measurements showed an antiferromagnetic ordering in the obtained compounds as well as a superexchange interaction between chromium and manganese ions. XPS studies confirmed the presence of manganese ions on the II oxidation state and chromium ions on the III oxidation state. Thermal analysis showed that the increase in the amount of Mn^{2+} ions affects the stability and resistance of doped compounds compared to pure $ZnCr_2Se_4$.

In the $ZnCr_2Se_4$:Ho system, single crystals with well-formed walls and edges were obtained. The chemical composition of the obtained single crystals and their structural parameters were determined using an X-ray study. Based on these studies, it was found that holmium ions occupy octahedral positions, together with chromium ions, and the general formula for single crystals can be written as $Zn[Cr_{2-x}Ho_x]Se_4$. The network parameters increase linearly with the increase in the holmium amount, which is consistent with the difference in the radii values between Cr^{3+} and Ho^{3+} ions. Magnetic measurements have shown that the obtained single crystals exhibit an antiferromagnetic order and a metamagnetic transition. A significant influence of holmium ions on short-range ferromagnetic interactions, effective magnetic moments, and exchange integrals for the first and second coordination zones was observed. Thermal analysis confirmed the thermal stability of the obtained single crystals to about 800°C.

In the $ZnCr_2Se_4$:Nd system, good quality single crystals were obtained, which were examined using X-ray in order to determine their structure and chemical composition. Based on these studies, it was found that neodymium ions occupy tetrahedral positions, together with zinc ions, and the general formula for single crystals can be written as $(Zn_{1-x}Nd_x)Cr_2Se_4$.

The lattice parameters increase linearly with the increasing amount of neodymium, which is consistent with the difference in cation radii of Zn^{2+} and Ho^{3+} ions. Based on magnetic measurements, it was found that the obtained single crystals are antiferromagnetics and exhibit short-range ferromagnetic interactions. Measurements of electrical conductivity showed semiconductor properties and a metal-insulator transition for single crystals with a lower amount of Nd^{3+} ions, at T_{MI} = 330 K for x = 0.08 and 360 K for x = 0.05. Thermal measurements confirmed the thermal stability of single crystals $(Zn_{1-x}Nd_x)Cr_2Se_4$ to a temperature of about 700°C.