HP/HT synthesis and in situ investigation of K doped Pb_2FeMoO_6 perovskite: tuning properties via A-site substitution

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The coexistence of magnetism and ferroelectricity requires very strict and specific symmetry conditions, which can be achieved in Pb-based double perovskites ($Pb_2BB'O_6$) due to the great tolerance of these systems to cationic substitutions and structural distortions. This study starts from the $Pb_2Fe^{3+}Mo^{5+}O_6$ (PFMO) system, a material that shows a semi-metallic to half-metallic transition at the FiM state (270 K) and an asymmetric magneto-resistivity below T_N. [1-2] In order to decrease the conductive character of the material, a strategy was devised to lower the electric charge on the A site and reduce the number of free electrons (by enhancing the Mo oxidation state) through the partial substitution of the Pb^{2+} ion with the alkali ion K^+.

The synthesis of $KPbFeMoO_6$ compounds was carried out using High Pressure/High Temperature (HP/HT) techniques with a multianvil press, which allows solid-state reactions in extreme regimes (up to 22 GPa and 2200°C). To find the best pressure-temperature stability conditions, the structural reactions were monitored in-situ in real-time via Energy-dispersive X-ray diffraction at the P61B Large-Volume press beamline at DESY.

The analysis of compounds ($K_xPb_{2-x}FeMoO_6$ with x=0.35-0.4) demonstrated the achievement of a phase isostructural to PFMO, with a perovskite purity of more than 92% considering some impurities and surface degradation products. Physical results reveal that the introduction of K^+ significantly modifies the material's behavior: the resistivity increases compared to PFMO, good dielectric constant values are recorded, and the magnetism shifts to a broad antiferromagnetic (AFM) transition with a T_N of ~50 K.

In conclusion, the combination of HP/HT synthesis and synchrotron investigations proves to be an indispensable approach to metastabilize unusual oxidation states, discover critical structural transformations that are completely inaccessible via standard ex-situ analysis, and fine-tune the properties of multifunctional materials. Further investigations, specifically at ESRF on ID14, will allow us to investigate iron and its surroundings.

1. C. Coppi et al., J. Crys. Growth, 632, 2024, 127629
2. F. Mezzadri et al., J. Mater. Chem. C, 2016,4, 1533-1542