

SYNTHESIS AND MICROSTRUCTURAL PROPERTIES OF CUBIC CsMnMoO₃F₃ OXYFLUORIDE

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Oxyfluorides containing the six-coordinated species of the (MO₃F₃)³⁻ type in a crystal lattice keep rather often a cubic structure in spite of anion pseudo-octahedral local symmetry. These units are inherently strongly polar due to the displacement of a central atom towards oxygen atoms. There exist at least two reasons of cancelling the separate octahedron dipole moments associated with the F/O ligands disordering and/or with the relative orientations of neighboring octahedral units. Such a situation is realized, for instance, in two crystal families with the following general formulas A⁺₂(A⁺)MO₃F₃ and A⁺A²⁺MO₃F₃ (M = hexavalent transition metal). They are characterized by elpasolite-type crystal lattice (space group *Fm-3m*, *Z* = 4) and defect pyrochlore structure (space group *Fd-3m*, *Z* = 8) related to RbNiCrF₆, respectively. The present investigations are aimed at synthesizing CsMnMoO₃F₃ oxyfluoride and determination of the structural, thermal, magnetic and electronic parameters over a wide temperature range.

Polycrystalline CsMnMoO₃F₃ was synthesized in the form of yellow-orange colored powder. (NH₄)₃MoO₃F₃, Cs₂CO₃ (99.9%) and MnCO₃ (99.9%) were used as starting materials. Initially, the (NH₄)₃MoO₃F₃ single crystals were prepared by the method reported elsewhere. The MnCO₃ powder was prepared by the reaction between water solutions of MnCl₂ (99.9%) and NH₄HCO₃ (99.9%) just before synthesis of the complex. White-pink precipitate was filtered under vacuum and washed once with water and three times with acetone. Then the powder was air-dried under ambient conditions. The product contains 42.7 mass% of manganese that gives brutto-formula MnCO₃·0.7H₂O. To obtain CsMnMoO₃F₃, the initial components were mixed in a stoichiometric ratio governed by the reaction:



The interaction of reagents, even at room temperature, was supported by the smell of ammonia appeared on grinding the mixture. Solid state synthesis was produced with two stages. Initially, the powder mixture was heated in a platinum cup at *T* = 200-300°C with stirring up to complete ammonia evolution. Then the powder was calcined in closed platinum crucible at *T* = 500°C for 0.5 h. The fluorine content in final product was controlled by H₂SiF₆ distillation. The micromorphology of the final product was observed by scanning electron microscopy (SEM) with the help of LEO 1430 device. The powder diffraction data of CsMnMoO₃F₃ for Rietveld analysis were collected at room temperature with a Bruker D8-ADVANCE powder diffractometer (Cu-Kα radiation, θ-2θ geometry) and linear VANTEC detector. The elpasolite-related crystal structure of CsMnMoO₃F₃ has been refined by Rietveld method at *T* = 298 K (space group *Fm-3m*, *a* = 10.59141(4) Å, *V* = 1188.123(8) Å³; *R*_B = 3.44 %).

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