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Hydrothermal synthesis of a Novel Transition Metal Oxyfluoride compound containing 2-Methylimidazole: Crystal Structure, and Characterization

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Abstract

Novel Molybdenum oxyfluoride compound $[Zn(C_4H_6N_2)_4][MoO_2F_4]$ consisting of tetrahedral $[Zn(C_4H_6N_2)_4]^{2+}$ cation, and octahedral $[MoO_2F_4]^{2-}$ anion have been successfully synthesized by a hydrothermal method in acidic conditions. Single crystal X-ray diffraction analysis confirms that the synthesized compound crystallized in the monoclinic space group, *P*2/*c*, and reveals a pseudo-one-dimensional structure through the strong inter-ionic hydrogen bonding interactions. The oxide and fluoride atoms form the inter-ionic hydrogen bonding network with the neighboring nitrogen or carbon atoms of the 2-methylimidazole ligand. The hydrogen bond network is attributable to the reduced BVS values of fluorides. The compound shows the qualitative IR vibrations for Mo-F and Mo-O bonds in the IR spectrum. The observed band gap ca. 3.18 eV is obtained from the octahedral distortion of Mo^{6+} cation in $[MoO_2F_4]^{2-}$ anions. The coordination bonding of fluorine and 2-methylimidazole ligands to Mo^{6+} and Zn^{2+} cations maintains the framework backbone of the title compound.

Keywords: Hydrothermal Reaction; Crystal Structure; Optical Band Gap; Hydrogen Bonding Network.

1. Introduction

Design and synthesis of novel metal oxyfluoride compounds composed of asymmetric moieties of transition metal cations and heterocyclic ligands are very important in crystal engineering due to their interesting properties [1-8]. Transition metal oxyfluoride compounds were used in different applied fields, such as gas storage, nonlinear optics, catalysis, luminescence, chemical separations, and sensing [9-12]. In particular, multidimensional frameworks of these compounds comprising highly polarizable d^0 and d^{10} transition metal ions, and organic electron donor ligands, connected via coordination bonds were reported earlier [13-15]. Based on the employed asymmetric moieties of metal oxyfluoride and organic linker, a variety of these materials exhibiting several geometries were explored [15-21]. Disordered structures for these compounds were observed because of the similar electronegativity and ionic size of fluorine and oxygen atoms. The polarizability matching and usage of multiple cations and organic linkers are required to generate the anisotropic geometries in the structures, which could influence the synthesis of crystallographically ordered transition metal oxyfluorides [22-26]. The organic linkers consisting of donor atoms, e.g.; nitrogen, oxygen, and phosphorous were broadly exploited to design these compounds, because of their higher hyperpolarizability, structural flexibility, and intermolecular interactions ability with metal centers [27, 28]. Especially, pyrazole, pyridine, and pyrazine derivatives were extensively used to synthesize of these materials due to their multiple modes of interaction and strong bonding affinity to different metal centers with additional properties [29-33]. Hydrogen bonds between the anionic metal polyhedra and the neighboring N-H bonds in the heterocyclic ligand derivatives could enhance the stability of structures [34-36]. Since the flexible nature of hydrogen bonds play a vital role in the designing of crystal structures as molecular building blocks [37, 38]. With the above ideas in mind, the current research attempts were focused on the synthesis of new transition metal oxyfluoride compounds by introducing the 2-methylimidazole ligand. In this work, compound $[Zn(C_4H_6N_2)_4][MoO_2F_4]$ consisting of d^0 transition metal $[MoO_2F_4]^{2-}$ anion and d^{10} transition metal $[Zn(C_4H_6N_2)_4]^{2+}$ cation were synthesized through a hydrothermal reaction. The metal-ligand bonding contributions and the hydrogen-bonding interactions of cationic and anionic polyhedra for the title compound are discussed based on the crystal structure, spectroscopic, and thermal measurements, as well as