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From Oxalate-based Heterometallic Compounds to nanocrystalline Ca-Cr Oxides

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Metal-organic coordination systems may exert a variety of specific properties including porosity, conductivity, or luminescence and have potential applications in various fields, from heterogeneous catalysis to supramolecular magnetism. Recently, these systems are exploited as molecular precursors by thermal decomposition for the preparation of mixed-metal oxide [1-3]. Since this synthetic route is relatively new and unexplored, there are few reported examples of nanomaterials obtained in this way. The heterobimetallic polymeric compounds [CaCr2(bpy)2(C2O4)4]•0.83H2O}n (1) and {[CaCr2(phen)2(C2O4)4]•0.33H2O}n (2) (bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline) were synthesized and characterized. The crystal structure of 2 is reported: the [Cr(phen)(C2O4)2]− unit, through the two oxalate groups, acts as a chelating ligand towards Ca cations, resulting in one-dimensional (1D) double zigzag chains, formed of diamond-shaped units. The ability of compounds 1 and 2 to act as the single-source precursors for the formation of the CaII–CrIII oxides was explored by thermal analysis (TGA and DTA) in the stream of the synthethic air or nitrogen, powder X-ray diffraction and IR spectroscopy. The heat treatment of 1 and 2 resulted in the formation of mixed-metal oxide phases, CaCrO4, α-CaCr2O4 and β-CaCr2O4. Thermal processing of compounds at 1100 °C in the stream of air, led to the appearance of the orthorhombic β-CaCr2O4 phase as the major crystalline oxide, together with CaCrO4. By heating the samples up to 1100 °C in nitrogen flow, only β-CaCr2O4 phase was formed, whereas the heating at 1400 °C caused the crystallization of two polymorphs, α-CaCr2O4 and β-CaCr2O4. J.P. acknowledge financial help from the Croatian Academy of Sciences and Arts. This work has been supported by HAZU grant “XBroad – program za brzo i točno određivanje mikrostrukturnih parametara iz proširenja difrakcijskih linija polikristalnih uzoraka” and "Nanokristalni oksidi prijelaznih metala: Mikrovalna sinteza i strukturna svojstva"

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