

**MOLECULAR PRECURSORS BASED ON HETEROMETALLIC
BISMUTH(III)-VO(II) OR -Cu(II) COORDINATION COMPOUNDS**

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With respect to physical properties that are important for the advanced technology, a major challenge has become multimetallic bismuth(III) oxides due to their broad spectrum of potential applications. Among heterometallic Bi(III) oxide materials, Bi₄V₂O₁₁ has been extensively studied for its fascinating ionic conducting behavior, while Bi₂CuO₄ is the basic compound for producing high-temperature Bi-Cu-M-(M')-O superconductors.

A convenient synthetic strategy used to control the stoichiometry and microstructure of the oxide materials is the single-source molecular precursor (SSMP) method. We have, therefore, examined the ability of polyaminopolycarboxylate (PAPC) ligands to connect two different metal centres of a desired ratio in coordination compounds which could serve as SSMP for heterometallic oxides. In this line, we started a systematic investigation of the influence of PAPC ligands from the heterometallic precursors on thermal degradation process, on composition and morphology of the final residue. The major objective was to elucidate the factors that would lead to the desired pure mixed-oxides of uniform grain size and morphology.

Considering this, we synthesized five coordination compounds of general formula M(X)_y{Bi(PAPC)}₂·nH₂O (M = VO²⁺, Cu²⁺; PAPC = edta⁴⁻, cdta⁴⁻, X = blank or 2,2'-bipyridyl; y = 1 or 2; n = 5-14) as single-source molecular precursors for Bi₄V₂O₁₁ and Bi₂CuO₄ heterometallic oxides.

Beside single crystal X-ray structure determination, the decomposition behaviour of the precursors has been studied by temperature controlled X-ray powder diffraction (TCXRD), performed under static or flowing air at different heating rates. Scanning electron microscopic (SEM) observations were carried out to correlate the precursor's composition and grain microstructure (size and morphology) of the residues at the final stage of the thermal treatment.

In view of preparing single phases, it comes out that the degradation process under static air at 10 °C·min⁻¹ heating rate provides an optimal reaction only in case of precursors VO[Bi(edta)]₂·10H₂O (**1**), [VO(bpy)][Bi(edta)]₂·14H₂O (**2**) and Cu[Bi(cdta)]₂·5H₂O (**5**), since the final residues, after cooling to room temperature, were the expected pure Bi₄V₂O₁₁ and Bi₂CuO₄, respectively. Considering similar crystal structures of **1** and **2**, it appears that the presence of ancillary *bpy* ligand is the main reason for the different order of intermediates appearance throughout thermo-degradation pathway. As a result, this is the only case when pure γ-Bi₄V₂O₁₁ is formed as the only crystalline material before the sample is cooled to room temperature.

The SEM images of the powders, resulted after heating the precursors to 600°C, confirmed the presence of porous agglomerates with sizes in the 1-70 μm range, depending on the starting compound. The agglomerates were formed of strongly interpenetrated spherical or ellipsoidal grains (0.3-3 μm), the smallest grains being present in the residues produced by *cdta*-based precursors.

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