HETEROMETAL ALKOXIDES AS PRECURSORS IN THE SOL–GEL PROCESS

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ABSTRACT

The preparation of a series of bimetallic alkoxides during the last three decades has been followed by a successful synthesis of intriguingly stable heterometal alkoxides containing three or four different metal atoms in the same molecular species during the past five years.

The increasing importance of the use of mixtures of a number of metal alkoxides as precursors for the preparation of a wide variety of novel ceramics by the SOLUTION–SOL–GEL (S–S–G) process has led to the possibility of molecularly designing a single source precursor suited to the composition of the targeted final ceramic. This has been made feasible by the extraordinary stability of the framework of heterometal alkoxides, which appears to remain intact during the initial hydrolysis reactions in the S–S–G process.

The characterization (by sophisticated physicochemical techniques including X-Ray crystal structure determination in some cases) of these heterometal alkoxides has added a new class of heterometal coordination systems which are found to be uniquely stable without the presence of metal-metal bonds or auxiliary ligands like CO, etc., generally required for stabilizing polymetallic systems known so far. A clearer understanding of their structural features is providing not only a valuable insight into the mechanism of their reactivity in the S–G process, but is resulting in refinements which enhance the
capabilities of the procedures for the synthesis of more and more novel materials.

1. INTRODUCTION

The term 'Heterometal Alkoxides' has itself a historical perspective reflecting the development of their chemistry also. Beginning with the evidence for formation of the 'alkoxo salts', e.g., [NaAl(OR)₄] in the titration of basic alkali alkoxides with less electropositive metal alkoxides in nitrobenzene by Meerwein, et al.⁴, a large number of so called 'double alkoxides' of various elements were synthesized² in the laboratories of Rajasthan University, including the characterization of a few very interesting (from the point of view of volatility and solubility in organic solvents) examples, e.g., [NaZr₂(OR)₉], which had been described earlier by Bartley and Wardlaw³. The first review entitled 'Chemistry of double alkoxides of various elements' appeared² in 1971, followed by a general survey⁴ of double alkoxides and another review⁵ dealing with the chemistry of transition metal alkoxides.

The first tri-metallic alkoxides:

[(PrO₂)₂Be(μ-OPr)₂Be(μ-OPr)₂Zr(μ-OPr)₃] and
[(PrO₂)₂Be(μ-OPr)₂Be(μ-OPr)₂Nb(μ-OPr)₄] were synthesized in 1985 by Mehrotra and Agrawal⁶ followed by the work on tri- and tetra-metallic alkoxides of copper⁷ and other 3d transition metals⁸.

An interaction⁹ at the 4th International Workshop on 'Glasses and Glass-Ceramics from Gels' (Kyoto, July 1987) with Dislich¹⁰, who as early as 1971 had conjectured about the formation of such polymetallic complexes in the precursor solution of a mixture of many metal alkoxides, led to the first publication¹¹ entitled 'Polymetallic Alkoxides - Precursors for Ceramics' in which a variety of possible applications of such systems as precursors in the Sol-Gel Process was envisaged by Mehrotra¹². Realizing that the term 'Polymetal Alkoxides' could be confused with the associated