Design of molecular species for synthesis of advanced ceramic materials†

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In view of their solubility in organic solvents, ease of purification due to their volatility and facile hydrolysability, alkoxides of metals have been gaining increasing importance as precursors for the preparation of oxide ceramic materials by the sol-gel process. Synthesis and characterization of a number of soluble, volatile bi- and poly-metallic alkoxides in the author’s laboratories have added a new facet to the chemistry of metal alkoxides as these provide unique examples of coordination species stabilised by bridging alkoxy bonds between different metals. Molecular design of extraordinary homogeneous advanced ceramics has become a distinct possibility by employing a prefabricated volatile heterometal alkoxide, with a composition suited to that of the targeted material as a precursor in the sol-gel process. Care is required in some cases to introduce less hydrolysable auxiliary ligands like β-diketones at the metal centres at which hydrolysis rates tend to be faster. The high over-all purity, with sometimes desired limits of impurities, is a dominant factor in attaining the predicted functionality of a product and it is possible to control this factor using the metal alkoxide route.

During the last decade or so, ceramics and glasses have transformed gradually from ‘stone age’ to ‘space age’ materials. The unexpected discovery of super-conducting properties of some oxide ceramic has ushered an unprecedented interest in the field of ceramics as a whole with special emphasis on oxide ceramics for which novel methods of synthesis are being currently devised.

Conventional routes for the synthesis of ceramics both on laboratory and industrial scale consist of fusion, powder mixing and precipitation from solution. A procedure of powder compaction followed by firing at high temperatures has been generally employed for production of solid ceramic bodies with microstructures suitable for the desired application(s). Generally, a fine-grained distribution leads to enhanced strength for engineering ceramics and control of grain size is more essential for opto-ceramics. However, even a slight non-homogeneity or undesirable chemical impurities can have serious deleterious effects on high temperature mechanical behaviour of engineering ceramics and electrical properties of electroceramics. These conventional routes are also not generally suitable for producing desired forms, such as fibrous materials and coatings.

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Alternative procedures are, therefore, being suggested to obviate the above difficulties. The conventional methods, in general, depend on the disintegration of larger masses into microstructural phases that have suitable applications. Such microstructures can also be built by the condensation of simpler species (or precursors) at the molecular level. This has been achieved in some cases by the CVD (chemical vapour deposition) or the SSG (solution-sol-gel) processes. The steps in the SSG (or SG) process can be represented by Fig. 1.

In the place of metal salts like nitrates or acetates, which were previously used, metal alkoxides are now strongly preferred as precursors in the MOCVD and SSG processes, as these are volatile and soluble in organic solvents, making their purification rather easy. By modifying the initial concentration of solutions, mode of hydrolysis and gelation rate, etc., the final ceramic can be obtained in the desired forms or shapes as thin films or fibre.

In addition to the ease of purification and the possibilities of obtaining the final ceramic product in the desired shape/form at much lower sintering temperatures than those required in the conventional process, a striking homogeneity has been generally noticed in the sol-gel process which employs a mixture of numerous metal alkoxides in the original solution. Dislich had conjectured as early as 1971 that in addition to the gain of 10⁴-10⁵ in the intimacy (over the usual particle size in the conventional process) of physical mixing of the alkoxide precursors, the extraordinary homogeneity of the product indicated the formation of new chemical bonds amongst alkoxides of different metals in the starting precursor solution.

The lack of communication between chemists and ceramicists was evident by the reaction of audience when the author presented at Kyoto in 1987, the extensive work on metal alkoxides emanating from his research group since the late 60's and which had been presented in the form of invited lectures at several international conferences on coordination chemistry. Surprised by the extensive work already available on actual isolation and characterization of a series of bimetallic alkoxides, Dislich mentioned about his conjecture (1971) on the possibility of new chemical bond formations amongst 7-8 metal alkoxides used by him in the precursor solution. Following the remarks of Dislich, the author has been led to synthesize a number of novel heterometal alkoxides, which have an extraordinarily high thermal stability, as depicted by the fact that many of these can be distilled unchanged under reduced pressure.

M is a bivalent metal like Be, Mg, Zn, Cd, Fe(II), Co(II), Ni(II), Cu(II); M is a trivalent metal like Y, Ln, Fe(III), etc. and L, L' and L'' are ligands like \([\text{Al(OPr')₄}]^⁻; \text{[Zr₂(OPr')₆]}^⁻; \text{[Nb(OPr')₄]}^⁻; \text{[Ta(OPr')₆]}^⁻\).

The formation of these heterometal alkoxides can be easily understood on the basis of a simple coordination model involving alkoxy bridges between different metal atoms, similar to the oligomerization of simple metal alkoxides, arising from bridges between the same metal atoms (see structures I, II and III).

The higher stability of such a methoxy bridge between dissimilar metals was demonstrated as early as 1975 by the formation of a bimetallic species, \((\text{MeO})₄\text{Nb(μ-OMe)}₂\text{Ta(OMe)}₄\) in an equimolar solution of the two constituent dimeric methoxides. It has been confirmed by the actual crystal structure determination in a few cases. Besides their use as precursors for heterometal oxide ceramics, the significance of such stable polymetal systems prepared by the author's group has been recognized as compounds containing 2, 3 or 4 metals in a cluster molecule.
In addition to heterometal alkoxides, the alkoxide chemistry of metals like yttrium, bismuth, and bivalent metals like copper and alkaline earths has received unprecedented attention in view of their potential applicability in preparation of superconducting materials and insolubility and non-volatility of the alkoxides of bivalent metals with simple alcohols.

Obviously, the far-reaching potential of such heterometal alkoxide systems has opened up new dimensions of the sol-gel process as illustrated by the following few examples:

(i) Preparation of lithium niobate/tantalate fibres from Li[Nb/Ta(OR)₃]: in this paper, Mackenzie et al. have shown that a greater homogeneity in the final ceramic material is obtained when the preformed bimetallic ethoxide is used in place of a mixture of constituent ethoxides.

(ii) Preparation of potassium niobate from K[Nb(OR)₃]: in this paper, Mackenzie et al. have shown that a greater homogeneity in the final ceramic material is obtained when the preformed bimetallic ethoxide is used in place of a mixture of constituent ethoxides.

(iii) Preparation of potassium niobate from K[Nb(OR)₃]: in this paper, Mackenzie et al. have shown that a greater homogeneity in the final ceramic material is obtained when the preformed bimetallic ethoxide is used in place of a mixture of constituent ethoxides.

(iv) Synthesis of superconductor YBa₂Cu₃O₇₋ₓ from soluble alkoxide Y-Ba-Cu precursors.

As mentioned earlier also, the difference in geometries of (MeO)Al[μ-OOMe]₃Ni[μ-OOMe]Al(OOMe) and (PrO)₃Al[μ-OPr]₃Ni[μ-OPr]₃Al(OPr)₃ opens up the possibility of synthesizing two types of ceramic materials with the same overall composition, e.g., NiAlO₃.

The synthesis of heterometal alkoxides and their use as precursors in the sol-gel process have thus, in addition to some other possibilities, opened a new route for the 'Molecular Design of Materials'. Even for the preparation of semi-conductors by MOCVD techniques, the use of a 'single-source' precursor (in which different elements are incorporated in the desired ratio) has been found to improve the quality of the final material remarkably.

References