Chemical Design of Highly Water-Soluble Ti, Nb and Ta Precursors for Multi-Component Oxides[†]

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Novel citric acid based Ti, Nb and Ta precursors that are highly stable in the presence of water were developed. No alkoxides of Ti, Nb and Ta were utilized in the preparation, instead much less moisture-sensitive metallic Ti, NbCl$_5$ and TaCl$_5$ were chosen as starting chemicals for Ti, Nb and Ta, respectively. The feasibility of these chemicals as precursors is demonstrated in the powder synthesis of BaTi$_4$O$_9$, Y$_3$NbO- and LiTaO$_3$. The water-resistant Ti precursor was employed as a new source of water-soluble Ti in the amorphous citrate method, and phase pure BaTi$_4$O$_9$ in powdered form was successfully synthesized at 800 °C. The Pechini-type polymerizable complex method using the water-resistant Nb and Ta precursors was applied to the synthesis of Y$_3$NbO- and LiTaO$_3$, and both the powder materials in their pure form were successfully synthesized at reduced temperatures, viz. 500-700 °C. The remarkable retardation of hydrolysis of these water-resistant precursors is explained in terms of the partial charge model theory.

Introduction

Numerous solution techniques have been developed to synthesize complex oxides with improved physical and chemical characteristics. Potentially, these methods can provide low temperature processing of oxides and the advantage of strict control over the stoichiometry of the constituents' elements. One such method for the low temperature synthesis of complex oxides is the so-called sol-gel technique that is based upon reactions of hydrolysis-condensation of metal alkoxides. One can find a prototypic example in the sol-gel synthesis of optoelectronic materials such as titanates, niobates and tantalates, in which pure and homogeneous products of tailored performance have been obtained in both powdered and film forms.[1,2]

In sol-gel based solution techniques for the synthesis of titanates, niobates and tantalates, water-free alcohol solutions of Ti-, Nb- or Ta-alkoxides are the most frequently utilized as titanium, niobium or tantalum precursors. A major disadvantage of the alkoxide-based process is that the alkoxide precursor solution, extremely sensitive to moisture, has to be processed under a strictly dry atmosphere. To prevent rapid hydrolysis of these alkoxides, a part of the alkoxide ligands was replaced by other ligands such as acetic acid and acetylacetone.[3-7] Nevertheless, as long as expensive and highly moisture sensitive alkoxides are used as starting chemicals to produce such chemically modified Ti-, Nb- or Ta-alkoxide precursors, one has to recognize that commercial applicability of such systems is still greatly limited.

To circumvent this problem, a process was developed to solubilize metallic Ti with hydrogen peroxide in the presence of citric acid to form a highly water-resistant peroxo-citrato-titanium complex. Similarly, novel water-resistant precursors of niobium and tantalum were prepared by dissolving NbCl$_5$ or TaCl$_5$ into methanol followed by the addition of citric acid to form a niobium or tantalum-citrato complex. Of particular importance is that no alkoxides of titanium, niobium and tantalum are required in the preparation of any of these precursors. These citric acid based precursors are highly stable against hydrolysis and, therefore, have potential applications for inexpensive and convenient aqueous synthesis of a variety of titanate, niobate and tantalate materials for ceramic and catalytic applications. The efficacy of the new aqueous titanium, niobium and tantalum precursors is demonstrated in the powder synthesis of BaTi$_4$O$_9$, Y$_3$NbO$_7$, and LiTaO$_3$.

Experimetal Section

Preparation of BaTi$_4$O$_9$. BaTi$_4$O$_9$ was prepared using a new water-resistant titanium precursor by the so-called amorphous citrate method.[8] Powders of metallic Ti and barium carbonate were used as starting sources of Ti and Ba, respectively. A precisely weighed metallic Ti powder was dissolved in an aqueous alkaline solution containing hydrogen peroxide, forming a yellow transparent Ti solution. An excess of citric acid with CA/Ti=10/1 was dissolved in this Ti-solution with continuous stirring to produce water-resistant titanium precursor, followed by the addition of barium carbonate with Ba/Ti = 1/4. After complete dissolution of BaCO$_3$, the mixture was heat-treated on a hot plate set at 300 °C to remove excess solvent and other volatile components. The prolonged heat-treatment produced a puff-like solid mass that was heat-treated in a mantle heater set at 450 °C to eliminate most carbons. The resulting white powder was referred to as "powder precursor" for BaTi$_4$O$_9$. The powder precursor was heat-treated in a furnace at 700 °C and 800 °C for 2 h in static air.
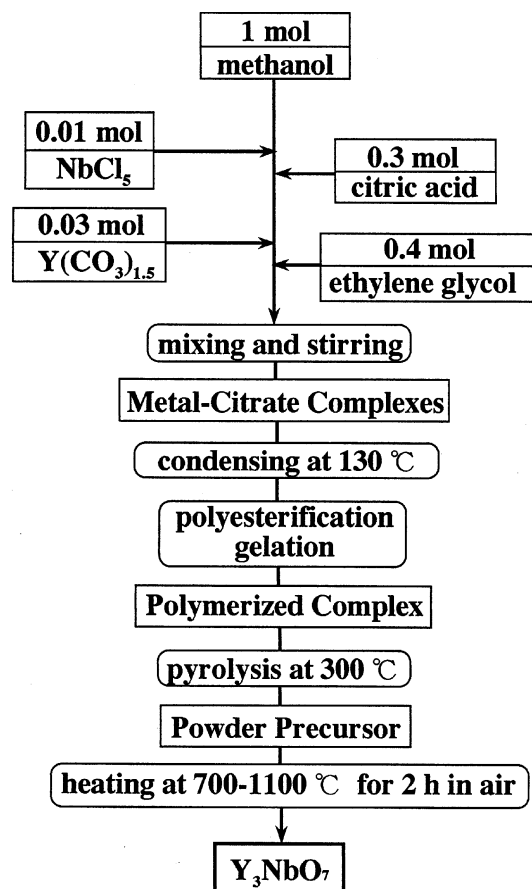
Figure 1. Flow chart for preparing Y₃NbO₇ by a modified Pechini-type polymerizable complex method.

Preparation of Y₃NbO₇ and LiTaO₃.   Figure 1 is a flow chart outlining the procedures followed to prepare Y_3NbO_7 by a modified Pechini-type polymerizable complex (PC) method.[9-12] Below we describe the process for preparing ~10 g of Y_3NbO_7. $NbCl_5$ was chosen as a source of niobium, which is much less expensive and more stable than Nb-alkoxides. One mol of methanol (64 g-50 mL) was used as a solvent to dissolve 0.02 mol of $NbCl_5$ (5.4 g). A large excess of CA (0.6 mol – 115.2 g) relative to niobium (0.02 mol) was added with continuous stirring to the $NbCl_5$/methanol solution to produce a solution of niobium-CA complexes, which can be expected to remain stable with respect to hydrolysis for several months. After achieving complete dissolution of CA, 0.06 mol of $Y(CO_3)_{1.5}$ (10.74 g) was added and the mixture was magnetically stirred for 1 h, producing a transparent solution of Y- and Nb-CA complexes. Subsequently, 0.8 mol of EG (49.6 g-46 mL) was added to this solution. The clear solution thus prepared was stirred with a magnetic stirrer while being heated at ~130 °C to remove most of the methanol and to accelerate polyesterification reactions between CA and EG. The prolonged heating at ~130 °C produced a viscous, bubbly mass that formed a brown transparent glassy resin upon cooling. No visible formation of precipitation or turbidity was observed during the polymerization. Charring the resin at 300 °C for 2 h in a box furnace resulted in a black solid mass, which is referred to as

the "powder precursor" for Y_3NbO_7. The powder precursor was heat-treated in a furnace at temperatures between 700 °C and 1100 °C.

LiTaO₃ was prepared by a modified Pechini-type PC method in a way similar to that described above for Y_3NbO_7 except that $TaCl_5$ and $Li_2(CO_3)$ were used as starting sources of Ta and Li, respectively.[13] In order to minimize possible evaporation of lithium components during calcination at high temperatures, the powder precursor for LiTaO₃ was heat-treated at relatively low temperatures viz. between 400 °C and 600 °C.

Results and Discussion

Structural evolution of BaTi₄O₉, Y₃NbO₇ and LiTaO₃.   The XRD patterns of powders obtained after calcining the powder precursor for $BaTi_4O_9$ in air at 700 °C and 800 °C for 2 h are shown in Figure 2. The powder precursor fired at 700 °C was primarily amorphous in structure, as shown by a broad continuum in the XRD pattern in Figure 2(a). Drastic crystallization occurred during the heat treatment of the powder precursor in air at 800 °C for 2 h (Figure 2(b)). All the well-defined peaks in the XRD pattern of Figure 2(b) exhibited a pure orthorhombic phase of $BaTi_4O_9$ in good agreement with the diffraction pattern observed for this compound by Phule *et al..*[14] It is known that $BaTi_4O_9$ is very difficult to synthesize in its pure form at temperatures below 1000 °C. For instance, $BaTi_4O_9$ has been synthesized by the conventional solid-state reaction route, which involves mixing $BaCO_3$ and TiO_2, followed by repeated cycles of grinding and firing at high temperatures (1000-1300 °C).[15-18] Attempts to synthesize $BaTi_4O_9$ at lower temperatures have been carried out by sol-gel techniques using metal-alkoxides, but, unexpectedly, firing gels at 1100 °C[14] or 1300 °C[19] was required to obtain phase pure $BaTi_4O_9$. Therefore, should be stressed that probably for the first time $BaTi_4O_9$ has been synthesized in this work at temperatures as low as 800 °C using a new water-soluble titanium precursor by the amorphous citrate method. $BaTi_4O_9$ also has been successfully prepared by the Pechini-type PC technique at an even
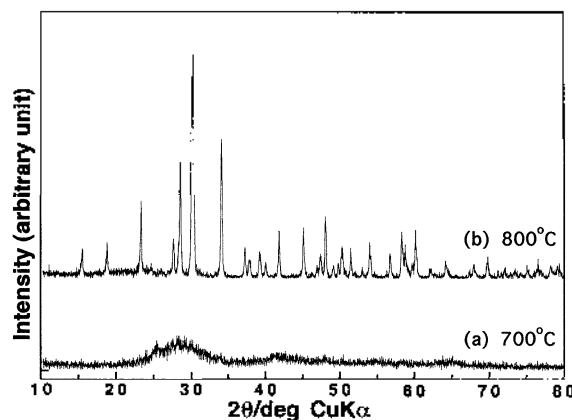

Figure 2. XRD patterns of the products obtained after calcining the powder precursor for $BaTi_4O_9$ in air for 2 h at (a) 700 and (b) 800 °C.

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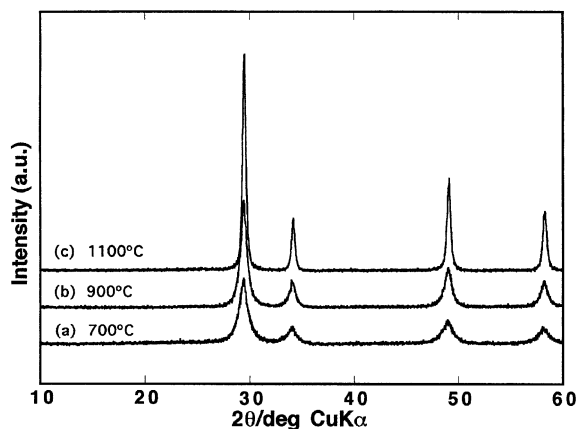
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Figure 3. XRD patterns of the products obtained after calcining the powder precursor for Y₃NbO₇ in air for 2 h at (a) 700, (b) 900 and (c) 1100 °C.

lower temperature of 700 °C.[20,21] Note that the amorphous citrate method differs from the Pechini-type PC method in that the latter process involves polyesterification between CA and EG, while the former process involves no polymerization,[10,12] and that the Pechini-type PC process generally suffers from its own unique problem, such as effective removal of carbon-containing organic polymers, despite the fact that the maximum chemical homogeneity can be achieved in the PC method.[10,12]

The XRD patterns of powders obtained after calcining precursors for Y₃NbO₇ and LiTaO₃ in air at various temperatures are shown in Figure 3 and 4 respectively. The Y₃NbO₇ crystallization had occurred already during the heat treatment of the powder precursor in air at 700 °C for 2 h (Figure 3(a)). The broadened XRD lines of the sample at 700 °C are due to the fact that it consists of ultrafine particles. All XRD patterns of the powders heat treated above 700 °C exhibited a pure cubic phase of Y₃NbO₇ with a fluorite structure.[22,23] Note that the present PC technique produces a phase pure Y₃NbO₇ at reduced temperatures, as opposed to the conventional solid-state reaction methods in which temperatures higher than 1400 °C are required for a nearly single-phase material.[22] Similarly, complete crystallization of LiTaO₃ occurred when its powder precursor was heat treated at 500 °C for 2 h (Figure 4(e)). Lowering the operational temperature is of particular importance in the synthesis of complex oxides with elements having a significant vapor pressure even at relatively low temperatures. The synthesis of LiTaO₃ is a case in point. In fact, the severe loss of lithium components due to its significant vapor pressure at temperatures higher than 600 °C[24] makes it difficult to control the stoichiometry of complex oxides having Li as a component. The operative temperature (500 °C) in the present PC synthesis of LiTaO₃ is low enough to avoid the volatilization of lithium componenty during calcination and high enough to fully crystallize LiTaO₃. It should be stressed that no reflections from foreign crystalline phases were observed in XRD pattern the present during the series of heat-treatments of the powder precursors for Y₃NbO₇ and LiTaO₃ (Figures 3 and
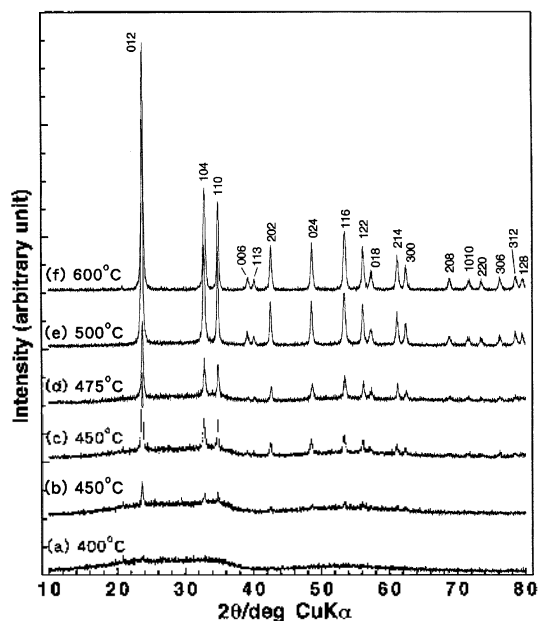

Figure 4. XRD patterns of the products obtained after calcining the powder precursor for LiTaO₃ in air for 2 h at (a) 400, (b) 450, (d) 475, (e) 500 and (f) 600 °C, and for 8 h at (c) 450 °C.

4). The success in lowering the crystallization temperature to 500-700 °C may indicate an improved level of mixing of cations in each powder precursor.

Chemical design of water-resistant Ti, Nb and Ta-precursors using the partial charge model. Alkoxides of Ti, Nb and Ta, most commonly used in the sol-gel solution technique, are highly reactive with water. The reaction between water and a metal alkoxide having the general formula $M(OR)_n$ is given by Eq. (1), where M is a metal ion and R is an alkyl group:

$$M(OR)_n + xH_2O \rightarrow M(OH)_x(OR)_{n-x} - xROH \qquad (1)$$

The relative reactivity of $M(OR)_n$ with water can be qualitatively understood by use of the so-called "Partial Charge Model (PCM)" theory developed by Livage et al..[4] The larger the negative partial charge of OR ($\delta(OR)$) in $M(OR)_n$ the higher the probability that the hydrolysis occurs because of increasing coulomb is interaction between OR in $M(OR)_n$ and the positive charge of H in H₂O. Replacement of OR in $M(OR)_n$ by X (Eq. (2)) leads to a new precursor whose chemical reactivity can be modified noticeably:

$$M(OR)_n - zX + zH^- \rightarrow M(X)_z(OR)_{n-z} + zROH \qquad (2)$$
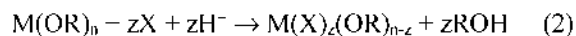
An example of the above can be seen in the hydrolysis of $Ta(OCH_3)_5$ and its modification by Cl⁻. We were aware that a methanol solution of $TaCl_5$ was less sensitive to ambient moistures in air, compared with the corresponding methanol solution of $Ta(OCH_3)_5$.[13] NMR spectroscopies reveal formation of a new chloro-methoxide with a composition close to $Ta(Cl)_2(OCH_3)_3$.[25] On proceeding from $Ta(OCH_3)_5$ to $Ta(Cl)_2(OCH_3)_3$, the partial charge on OCH₃ ($\delta(OCH_3)$), which can be deduced from the PCM theory, changes from -0.10 to -0.05. The smaller negative charge of $\delta(OCH_3)$ for

$Ta(Cl)_2(OCH_3)_3$ means that the protonation of the coordinated OCH_3 is less probable, and, therefore, can be used to explain why the hydrolysis is depressed by the introduction of Cl and not OCH_3. A more efficient way to retard the hydrolysis of alkoxides is to introduce organic complexants such as citric acid (CA) into the original precursor solution. Let us suppose that a part of methoxide in $Ta(OCH_3)_5$ is replaced by CA to form $[Ta(CA)(OCH_3)_3]$. The partial charge on OCH_3 for this new species was calculated to be $+0.35$, meaning that the protonation of OCH_3 is much less probable when compared with both $Ta(OCH_3)_5$ and $Ta(Cl)_2(OCH_3)_3$. Thus, it can be anticipated that the CA modified Ta precursor solution does not form hydroxide precipitates even in the presence of excess water, as has indeed been confirmed by experiment.[25] Similarly, formation of hydroxide precipitates of titanium or niobium has been avoided by using the CA modified Ti or Nb precursor solution, and the remarkable retardation of its hydrolysis is well explained by the PCM theory.

Conclusion

Citric acid based Ti, Nb and Ta solutions, prepared starting from non-alkokides such as metallic Ti, $NbCl_5$ and $TaCl_5$, are excellent precursors for water-based processing of complex oxides, including these metals. All of these precursors are readily prepared and are utilized for the synthesis of complex oxides at reduced temperatures, viz. 500-800 °C. The partial charge model qualitatively explains the hydrolysis behavior of metal alkoxides and their chemical modifications, and, therefore, plays a role in designing water-resistant compounds.

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