

A Novel Tantallic Acid-Based Polymerizable Complex Route to LiTaO₃ Using Neither Alkoxides nor Chlorides of Tantalum

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Received March 17, 1999. Revised Manuscript Received August 3, 1999

A novel tantallic acid-based polymerizable complex (PC) route to LiTaO₃ was developed that uses neither alkoxides nor chlorides of Ta. Moisture-insensitive Ta₂O₅ was chosen as a starting source of Ta, and it was converted to a Ta-oxalate solution by means of the classic KHSO₄-oxalic acid method of Schoeller. Tantallic acid precipitated upon addition of ammonia solution to the Ta-oxalate solution. The freshly precipitated tantallic acid was soluble in a hot oxalic acid aqueous solution, and it was quite stable against hydrolysis. This water-resistant Ta precursor mixed with citric acid (CA), ethylene glycol (EG), and Li₂CO₃ was polymerized at 130 °C to produce a yellowish transparent polyester-type resin without undergoing precipitation, which after decomposition on heating at 350 °C was used as a powder precursor for LiTaO₃. Phase-pure LiTaO₃ in powder form was successfully synthesized at a reduced temperature (500 °C). The final LiTaO₃ powder calcined at 500–700 °C had a considerably large surface area in the range of 22–37 m²/g when compared with 1.4 m²/g for the conventional solid-state reaction powder of the same compound.

Introduction

Alkoxides of tantalum (Ta) are most frequently used as starting compounds in the sol-gel synthesis of Ta-based complex oxides. A major disadvantage of the alkoxide-based process is that Ta-alkoxide precursor solutions are extremely sensitive to moisture and have to be processed under a strictly dry atmosphere. Rapid hydrolysis of Ta-alkoxides may be circumvented by replacing a part of alkoxide ligands with other ligands such as acetic acid and acetylacetone, the technique of which has been successfully applied to the retardation of titanium and zirconium alkoxides.^{1–5} However, as long as expensive and highly moisture sensitive alkoxides are used as starting chemicals for producing such chemically modified Ta-alkoxide precursors, the commercial applicability of such systems is still greatly limited. Alternatively, tantalum pentachloride (TaCl₅) has been utilized as a tantalum precursor,⁶ since it is cheaper and less sensitive to moisture when compared with tantalum alkoxides. However, apart from possible degradation of optoelectronic properties of the final material due to a small concentration of residual chloride, unavoidable generation of corrosive HCl gas during processing is highly undesirable. We were there-

fore interested in exploring another precursor that enabled a less-corrosive processing with no need to work under inert atmosphere.

In this short paper, freshly precipitated tantallic acids (Ta₂O₅·*n*H₂O), which are readily prepared starting either from Ta₂O₅ or from metallic Ta by the KHSO₄-oxalic acid method of Schoeller^{7–9} familiar to analytical chemists, are used in combination with oxalic acid to circumvent the problem mentioned above. The precursor thus obtained can be best described as an aqueous solution of Ta-oxalate, which is then transferred as a starting source of Ta to the Pechini-type polymerizable complex (PC) processing based upon polyesterification between citric acid (CA) and ethylene glycol (EG).^{10–13} The feasibility of the present route is demonstrated in the powder synthesis of LiTaO₃ at 500 °C.

Experimental Section

a. Dissolution of Ta₂O₅ by the KHSO₄-Oxalic Acid Method of Schoeller and Preparation of Freshly Precipitated Tantallic Acid. The procedure for the dissolution of Ta₂O₅ and the subsequent preparation of tantallic acid is shown in Figure 1. A powdered mixture of 1.55 g of Ta₂O₅ and 55 g of potassium hydrogen sulfate (KHSO₄) was fused at 600 °C in a quartz beaker for 2 h. After cooling to room temperature, oxalic acid as a hot 10 wt % aqueous solution (500 mL) was used to dissolve the hydrogen sulfate melt. A clear transparent solution was then mixed with 150 mL of 28 wt %

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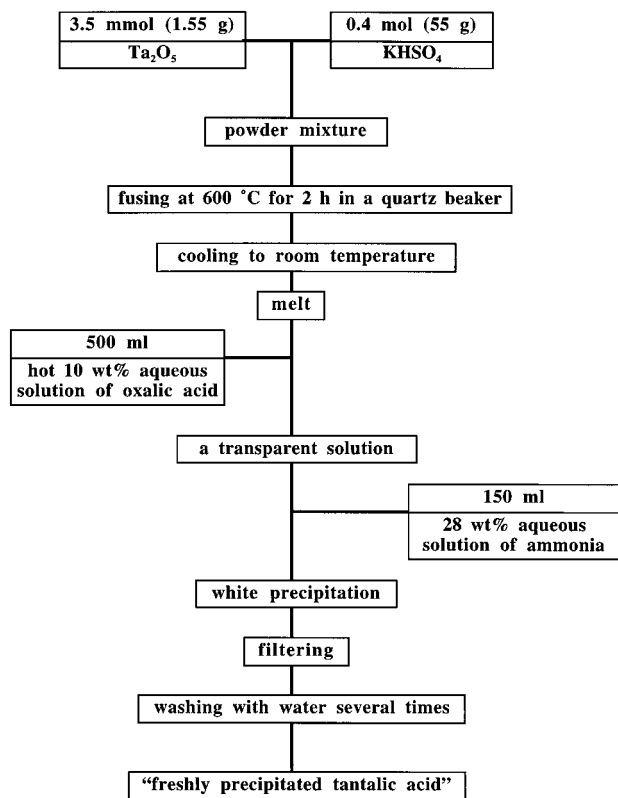


Figure 1. Flowchart for the dissolution of Ta_2O_5 and the subsequent preparation of tantalum acid.

ammonium solution to form a precipitation of tantalum acid. The precipitate was filtered and washed with distilled water several times. This washed precipitate is referred to as "freshly precipitated tantalum acid" hereinafter.

b. Preparation of LiTaO_3 by a Pechini-type PC Method Starting from Tantalum Acid. Figure 2 is a flowchart outlining the procedure followed to prepare LiTaO_3 by a Pechini-type PC method.^{10–13} A freshly precipitated tantalum acid (with ~ 10 mmol of Ta) was treated with oxalic acid as a hot 10 wt % aqueous solution (500 mL) to form a water soluble Ta-oxalate complex. The Ta concentration in this solution was determined by a standard gravimetric method. An excess of CA (35 mmol) relative to Ta (7 mmol) was added with continuous stirring to a measured volume of the original Ta-oxalate solution, followed by the addition of Li_2CO_3 (3.5 mmol) and EG (140 mmol). The clear transparent solution thus prepared, while stirred with a magnetic stirrer, was heated at ~ 130 °C to remove most of water and subsequently to accelerate polyesterification reactions between CA and EG. The prolonged heating at ~ 130 °C produced a viscous, bubbly mass that formed a dark-yellow transparent glassy resin upon cooling. No visible formation of precipitation or turbidity has been observed during the polymerization. Charring the resin at 350 °C for 2 h in a mantle heater resulted in a black X-ray amorphous solid mass, which is referred to as the "powder precursor" hereinafter. To minimize possible evaporation of lithium components during calcination at high temperatures,¹⁴ the powder precursor for LiTaO_3 was heat treated in static air for 2 h at relatively low temperatures between 400 and 700 °C.

For the purpose of comparison, LiTaO_3 was also prepared by the conventional solid-state reaction at 1050 °C in static air for 2 h using an intimate mixture of Li_2CO_3 and Ta_2O_5 achieved by mechanical grinding for 30 min.

c. Characterization of LiTaO_3 Powders. The powders produced after the heat treatments at temperatures between

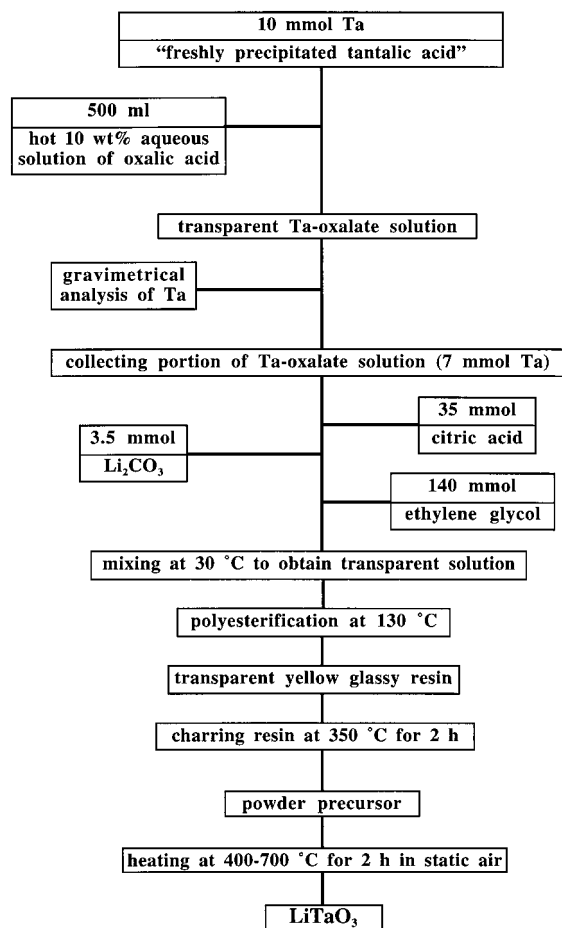


Figure 2. Flowchart for preparing LiTaO_3 by a Pechini-type polymerizable complex method.

400 and 700 °C were characterized by X-ray powder diffraction (XRD) and Raman scattering techniques to identify various possible phases formed. A standard X-ray powder diffractometer (Model MXP^{3VA}, MAC Science Co., Ltd. Tokyo, Japan) was used with $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA. The Raman spectra were excited with the 363-nm line of an Ar laser and were measured at room temperature in a backscattering geometry. The scattered light was analyzed with a Jobin Yvon/Atago Bussan T64000 triple spectrometer with the first two stages connected in a subtractive dispersion, and collected with a liquid nitrogen cooled CCD (charge coupled device) detector. The specific surface area of the samples was measured by the conventional three-points BET method using a mixed gas of N_2/He (= 30.7/69.3) as absorbent (Model SA9601, Horiba Japan).

Results and Discussion

a. Underlying Chemistry in the Tantalum Acid-Based PC Method. The PC method is a kind of solution technology, which is based on polymerization between CA and EG to form a polyester-type resin inside which metal species should remain soluble to sustain the scale of their molecularly homogeneous mixing. Since the PC method involves a continuous step of polyesterification with dehydration, the starting solution system should be stable enough against the water that is intrinsically generated during the whole PC processing. In the PC synthesis of LiTaO_3 , a key to success is the choice of Ta materials. The candidate Ta material should satisfy the following prerequisites: (1) It should be soluble in a mixed solvent of EG and H_2O .

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(2) It should be stable enough to avoid hydrolysis. (3) Preferably, it should be inexpensive.

Undoubtedly, either Ta₂O₅ or metallic Ta is the cheapest raw material as a source of tantalum. However, neither of them can be used as a starting chemical for the PC synthesis of LiTaO₃, as they are not soluble in both EG and H₂O. Alkoxides of tantalum, previously used in the sol-gel synthesis of LiTaO₃,¹⁵⁻¹⁷ do not fulfill the three conditions mentioned above at all. Halides of tantalum such as TaCl₅ are soluble in EG and are lower in cost than Ta-alkoxides, but they are also unstable in the presence of water or humid air.

We thus decided to exploit the so-called "tantalic acid", often erroneously described as Ta(OH)₅ or HTaO₃, as a starting source of tantalum in the PC synthesis of LiTaO₃. The classic KHSO₄-oxalic acid method of Schoeller⁷⁻⁹ is applied to dissolution of tantalum pentoxide (Ta₂O₅), the technique being quite common for inorganic or analytical chemistry. When Ta₂O₅ is treated with potassium hydrogen sulfate (KHSO₄) at ~600 °C, high-temperature and high-concentration SO₃ produced via eq 1 reacts vigorously with Ta₂O₅ to form (K,Ta) binary sulfate.



A fusion cake including the binary sulfate is readily dissolved in a hot oxalic acid aqueous solution to form a Ta-oxalate solution. Tantalic acid now precipitates upon addition of ammonia solution to the Ta-oxalate solution. The entity of "tantalic acid" is not described as a single compound with a fixed composition, but it would be best described as a gelatinous precipitate Ta₂O₅·*n*H₂O rather than Ta(OH)₅ or HTaO₃. The freshly precipitated tantalic acid is soluble in a hot oxalic acid aqueous solution, the resulting solution of tantalum being quite stable against hydrolysis for a long period of time. Both tartaric acid and citric acid solutions serve equally well in preparing a stable solution of tantalum. Because of their inertness in the presence of water, these solutions can be used as convenient sources of Ta in the PC synthesis of LiTaO₃ or other Ta-containing complex oxides.

From a practical point of view, any precipitation must be avoided during the whole PC processing as it destroys the homogeneity maintained in the initial solution. It has been found in the present work that the temperature window at which neither phase separation nor formation of insoluble precipitates occurs throughout the resin formation is rather wide (between 80 and 160 °C), in contrast to the case of LaMnO₃ wherein formation of a transparent resin could be ascertained only in a narrow temperature region (90 ± 5 °C).¹⁸ Our belief is that Ta ions complexed with oxalic acid are each individually separated into a polyester network before unwanted hydrolysis and subsequent formation of precipitation occur.

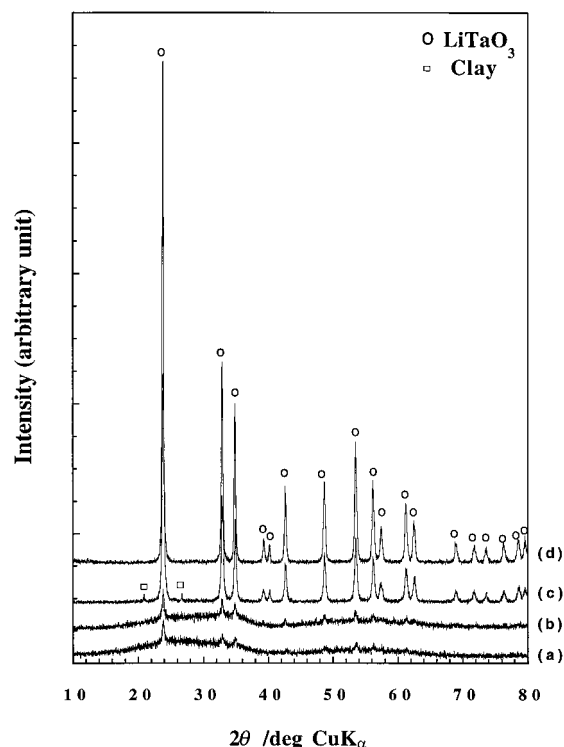


Figure 3. XRD patterns of the products obtained after calcining the powder precursor for LiTaO₃ in air for 2 h at (a) 400, (b) 450, (c) 500, and (d) 700 °C. Peaks marked with squares (□) are attributed to reflections of a clay on a sapphire holder used for the XRD measurement.

b. Structural Evolution of LiTaO₃ and Purity.

XRD patterns of the products obtained after calcining the powder precursor for LiTaO₃ in air at four different temperatures are shown in Figure 3. The starting precursor (not shown here) was primarily amorphous in structure, characterized by a broad continuum in XRD pattern. Partial crystallization has occurred during the heat treatment at 400 °C (Figure 3a), but the broad continuum characteristic of the amorphous component persists in the powder calcined at 450 °C (Figure 3b). Complete crystallization then occurred when the powder precursor was heat treated at 500 °C (Figure 3c). The width of the principal lines somewhat sharpens when the calcination temperature is increased up to 700 °C (Figure 3d), but the overall shape of the pattern remains almost unchanged. No foreign crystalline phases such as Li₂CO₃ were detected by XRD.

The purity of the LiTaO₃ samples was further checked by Raman spectroscopy, a technique which is capable of detecting impurities consisting of very small crystallites that are not easily identified with the XRD technique because of their diffuse reflections. In particular, Raman spectroscopy is quite suitable for detection of residual amorphous carbons, which give rise to a characteristic broad band around 1600 cm⁻¹. Figure 4 shows the corresponding Raman spectra of the same samples used for the XRD analysis. All the Raman spectra exhibit no significant scattering between 1300 and 1700 cm⁻¹, thus proving our specimen is virtually free of carbons. The Raman spectra also show no evidence for the presence of Li₂CO₃ because of the complete absence of the strongest Raman peak at ~1080 cm⁻¹ characteristic of Li₂CO₃.

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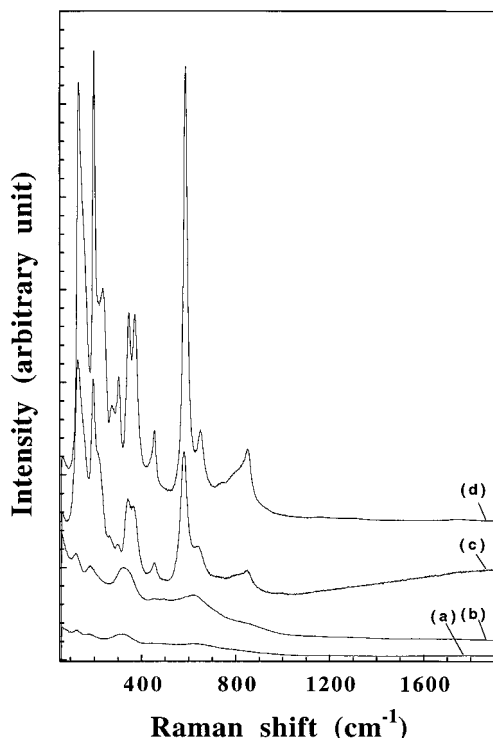


Figure 4. Raman spectra of the products obtained after calcining the powder precursor for LiTaO₃ in air for 2 h at (a) 400, (b) 450, (c) 500, and (d) 700 °C.

c. Merits of the PC Method for LiTaO₃ Synthesis.

The present PC technique produces a phase-pure LiTaO₃ at reduced temperatures, as opposed to the conventional solid-state reaction method, in which a heat treatment of a mixture of Li₂CO₃ and Ta₂O₅ at a relatively high temperature (>1000 °C) is required for a single-phase material.¹⁹ The conventional solid-state reaction technique suffers from the problem related to the severe loss of lithium components due to its significant vapor pressure at the processing conditions, which makes difficult to control the stoichiometry.¹⁴ For this reason, many attempts were made to lower the synthetic temperature of LiTaO₃ by employing solution techniques. One such technique for the low-temperature synthesis of LiTaO₃ is the so-called sol-gel technique based upon hydrolysis-condensation of alkoxides,¹⁵⁻¹⁷ particularly the one using a double-metal ethoxide with a chemical formula LiTa(OC₂H₅)₆.^{16,17} Indeed, lowering the synthesis temperature of LiTaO₃ down to 500–600 °C has been reported in these sol-gel studies.¹⁵⁻¹⁷ However, the expense and extreme large sensitivity to moisture of Ta-alkoxides limit their practical applicability; the latter nature of Ta-alkoxides, reactivity toward water, requires not only the use of a glovebox for shutting out unnecessary moisture from outside sources but also rather elaborate experimental procedures, such as complete elimination of water from all starting chemicals, including the solvent. The main purpose of this paper was therefore to explore alternative, which enabled the low-temperature (500–600 °C) processing of LiTaO₃ without the need to work in a strictly moisture-free atmosphere. The XRD results shown in Figure 3 indicate that our PC technique, starting from tantallic acid, fulfills the low-temperature

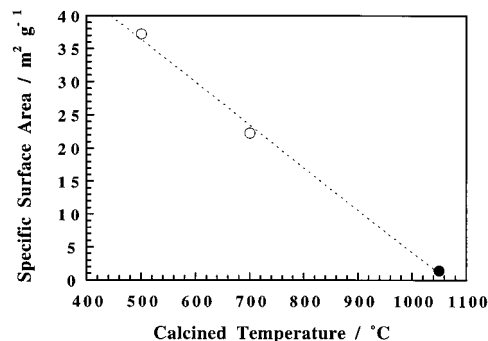


Figure 5. Specific surface areas of the PC-derived powders calcined at 500 and 700 °C (○) and of the powder prepared at 1050 °C by the conventional solid-state reaction method (●). A dotted straight line is guide for eye.

requirement. The operating temperature (500–700 °C) in our PC synthesis of LiTaO₃ is low enough to avoid the volatilization of lithium components during calcination and high enough to fully crystallize LiTaO₃.

For certain applications such as a catalytic application, the material needs to be prepared at temperatures as low as possible, since the lower synthesis temperature leads to a high-surface area material, i.e., a material with improved catalytic activity may be obtained. From this point of view, LiTaO₃ conventionally produced by the solid-state reaction technique is not suitable for use in catalysts, since the large grain growth owing to the high-temperature heat treatment lowers the surface area of the resultant material. Indeed, the specific surface area of such a powder prepared at 1050 °C by the conventional solid-state reaction method was quite low, typically less than 1.5 m²/g (Figure 5). Figure 5 also includes specific surface area data for the two samples prepared at 500 and 700 °C by the PC technique, demonstrating a large value of 37 and 22 m²/g, respectively.

Conclusion

A freshly precipitated tantallic acid, which is readily prepared by starting from inexpensive Ta₂O₅ and by using the KHSO₄-oxalic acid method of Schoeller, was an excellent starting source of Ta for the Pechini-type PC processing. Tantallic acid reacted readily with oxalic acid to afford a water-resistant precursor, which can best be described as an aqueous solution of Ta-oxalate. The Ta-oxalate solution was quite stable during a prolonged polymerization at 130 °C, and consequently Ta ions complexed with oxalic acid appeared to be individually separated into a polyester network before unwanted precipitates formed. The present PC method using tantallic acid is a convenient manner of synthesizing LiTaO₃ at reduced temperatures (500–700 °C) with a relatively large specific surface area in the range of 22–37 m²/g.

Acknowledgment. Financial support by “Research for the Future” Program no. JSPS-RFTF96R06901 from The Japan Society for the Promotion of Science is greatly acknowledged (Research Coordinator: Professor M. Yoshimura of Tokyo Institute of Technology (TIT)).

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