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Preparation of $LiTaO_3$ powders at reduced temperatures by a polymerized complex method

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Abstract

A polymerized complex technique was utilized to prepare $LiTaO_3$ at reduced temperatures, viz. 500–600°C. A methanol–citric acid (CA) solution of $TaCl_5$ was found to be highly resistant to ambient moisture in air. Heating of a mixed-solution of methanol, CA, ethylene glycol (EG), Li and Ta ions with a molar ratio of [Methanol]:[CA]:[EG]:[Li]:[Ta]=1:0.1:0.4:0.01:0.01 at 130°C produced a yellow transparent polymeric gel without any precipitation, which after pyrolysis at 300°C was converted to a powder precursor for $LiTaO_3$. The formation of pure $LiTaO_3$ occurred during the heat treatment of the powder precursor at temperatures higher than 500°C in static air, which was confirmed by a combined analysis using XRD and Raman scattering techniques. No X-ray diffraction and Raman spectroscopic evidence for phase separation of crystalline Li_2CO_3 and Ta_2O_5 as distinct intermediates has been obtained during the thermal decomposition of the powder precursor.

Keywords: Tantalum precursor; Polymerized complex method; $LiTaO_3$

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1. Introduction

$LiTaO_3$ is currently one of the most widely used electrooptic materials because of its characteristic ferroelectric, piezoelectric and pyroelectric properties [1]. The traditional way of preparing $LiTaO_3$ powders is based on the solid-state reaction between fine particles of Li_2CO_3 and Ta_2O_5, which requires heat treatment at relatively high temperature (>1000°C) [2]. One of serious problems in processing $LiTaO_3$ by the traditional solid-state reaction route is the severe loss of lithium components due to its significant vapor pressure at the processing conditions, which makes difficult to control the stoichiometry [3]. Therefore, there is a strong need for methods that can control the stoichiometry and provide low temperature processing of lithium tantalate. Sol–gel processes based upon hydrolysis–condensation of alkoxides have been successfully applied to the low temperature (500–600°C) powder synthesis of $LiTaO_3$ [4–6]. In particular, utilization of a double metal ethoxide with a chemical formula $LiTa(OC_2H_5)_6$ has received considerable attention [5,6], since hydrolysis and condensation of such a double metal alkoxide with a controlled amount of water would result in the formation of a multicomponent gel with atomically mixed metal oxygen bonds of –Li–O–Ta–. A major disadvantage of the alkoxide-based process, however, is that the alkoxide precursor solution is extremely sensitive to moisture and has to be processed under a strictly dry atmosphere. We were therefore interested in exploring an alternative, that enabled the low-temperature (500–600°C) processing of $LiTaO_3$ under moisture non-free ambient circumstances. In this work, we present a modified Pechini-type polymerized complex (PC) route [7–11], based on polyesterification between citric acid (CA) and ethylene glycol (EG) that has been successfully used to synthesize $LiTaO_3$ at 500–600°C without any special care about moisture in air. A key to success in our PC route was to construct a suitable tantalum solution precursor enough stable against water. We demonstrate that a methanol–CA solution of $TaCl_5$ can be utilized as a stable Ta precursor, which retard any precipitation during the polymerization.

2. Experimental

2.1. Preparation of $LiTaO_3$ powders by PC method

The overall procedure for the synthesis of $LiTaO_3$ by the PC method is indicated in Fig. 1. $TaCl_5$ was chosen as a source of tantalum which is cheaper and much more

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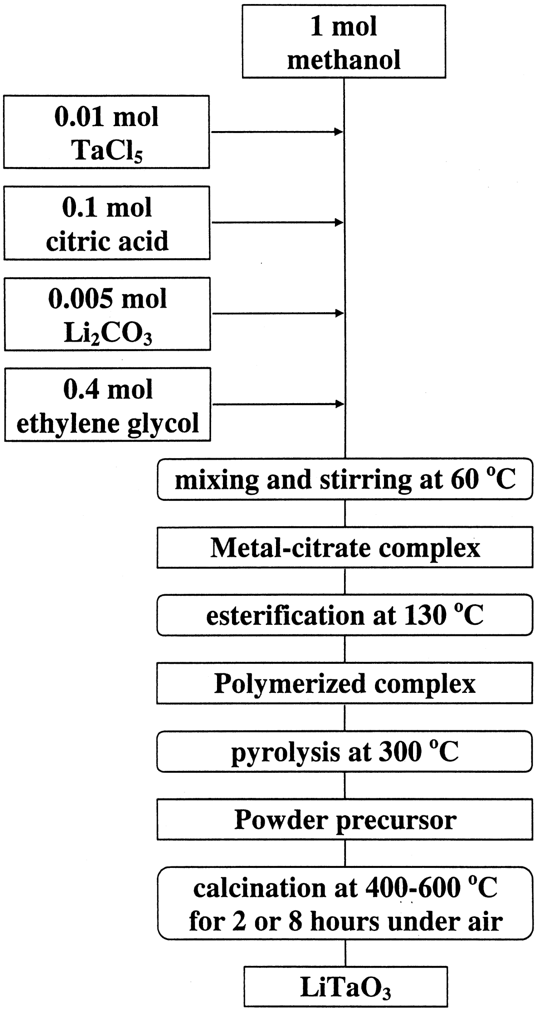

Fig. 1. Flow chart for the preparation of $LiTaO_3$ by polymerized complex method.

stable than Ta-alkoxides. 0.01 mol of $TaCl_5$ (3.58 g) was first dissolved into 1 mol of methanol (32 g=25 ml), followed by addition of CA (0.1 mol=19.2 g) with continuous stirring to produce moisture insensitive tantalum–CA complexes. After achieving complete dissolution of CA, 0.005 mol of Li_2CO_3 (5.37 g) was added and the mixture was magnetically stirred for 1 h to drive off carbon dioxides evolved in the decomposition reaction of lithium carbonate to produce a transparent solution. Subsequently 0.4 mol of EG (24.8 g=23 ml) was added to this solution. All the procedures described above were carried out at room temperature. The clear solution thus prepared, while stirred with a magnetic stirrer, was heated at ~60°C for 1 h to remove most of methanol. The solution was then heated up to ~130°C in order to accelerate esterification reactions between CA and EG. The prolonged heating at ~130°C produced viscous, bubbly mass that formed a 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 3 h in a box furnace resulted in a black solid mass, which was lightly ground into a powder with a Teflon rod. The powder thus obtained is called 'powder precursor' hereinafter. The powder precursor was heat-treated in a furnace at temperatures between 400 and 600°C for 2–8 h in static air, followed by natural furnace cooling to room temperature.

2.2. Characterization of powders

Thermogravimetry–differential thermal analysis (TG-DTA; Type-2020, MAC Science Company, Japan) was carried out to follow the decomposition and crystallization of precursors with a heating rate of 2°C/min in static air. The products after heat-treatments between 400 and 600°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., Tokyo, Japan) was used with Cu $K\alpha$ radiation at 40 kV and 40 mA at a scan rate of 4° (2θ) per min. 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.

3. Results and discussion

Fig. 2 illustrates the TG and DTA curves of the powder precursor for $LiTaO_3$ fired in static air using a heating rate of 2°C/min in the temperature range of 25–900°C. The TG curve indicates a small weight loss of ~2% up to ~100°C, a large steady weight loss of ~50% extending up to ~440°C, an abrupt weight drop of ~30% between 440 and 450°C, a very small weight loss of ~0.3% around 500°C and no further weight loss up to 900°C. The first TG weight loss is mostly due to dehydration. The last very small weight loss is probably attributed to the elimination of a trace of isolated carbon, which was confirmed by Raman spectroscopic data (shown later in Fig. 4). Exothermic DTA peaks are associated with the TG weight losses, and are indicative of organic combustion steps. The broad exothermic at ~330°C is attributed to decomposition of organic matter from the powder precursor. The large exothermic at ~440°C possibly represents the burn out of residual organic components. The small exothermic peak with an onset temperature at ~520°C is probably either due to burn out of the residual carbon or due to direct crystallization of $LiTaO_3$ from an amorphous component.

The XRD patterns of powders obtained after calcining the powder precursor in static air at different temperatures are shown in Fig. 3 in a 2Θ range of 10–80°. The starting precursor (not shown here) and the powder calcinated at

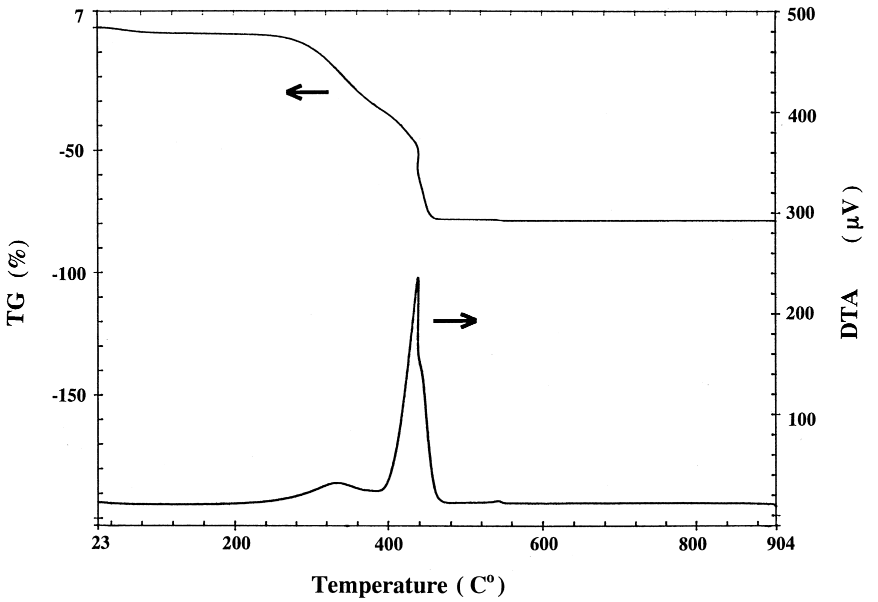

Fig. 2. TG and DTA curves of powder precursor in static air with a heating rate of 2°C/min.

400°C were primarily amorphous in structure, as shown by a broad continuum in XRD pattern in Fig. 3a. Time-dependent crystallization has occurred during the heat treatment at 450°C (Fig. 3b,c), but the XRD data indicate imperfect transformation from an amorphous component to crystalline $LiTaO_3$ even after the prolonged heat treatment up to 8 h (Fig. 3c). The amorphous component persists in the powder calcinated at 475°C for 2 h (Fig. 3d). Complete crystallization has then occurred when the powder precursor was heat-treated at 500°C for 2 h (Fig. 3e). While the powder calcinated below 500°C was slightly gray, the powder calcinated above 500°C was white, which is usually indicative of complete burnout of the residual carbon consistent with both TG analysis (Fig. 2) and Raman spectroscopic data (Fig. 4). Of particular importance is that except for the amorphous component no reflections from foreign crystalline phases such as Li_2CO_3 were observed in XRD during the whole series of heat-treatments (Fig. 3a–f). However, it should be noticed that crystallites of dimensions less than about 100 nm give rise

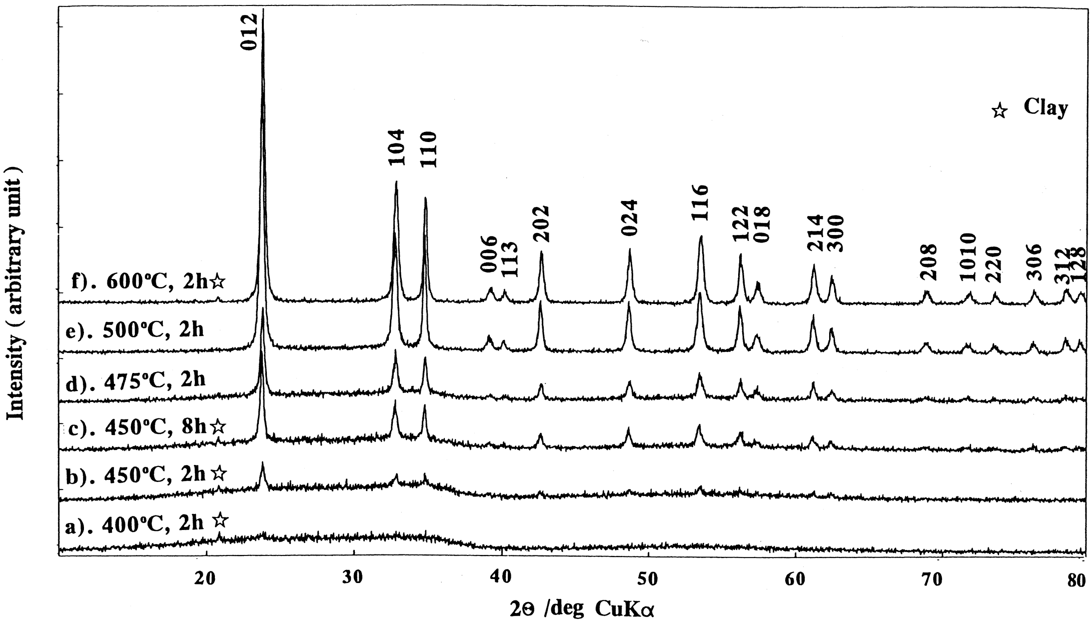

Fig. 3. XRD patterns of the calcined powders in air for 2 h at (a) 400, (b) 450, (d) 475, (e) 500 and (f) 600°C, and for 8 h at (c) 450°C. Peaks marked with ☆ are from reflections of a clay on a sapphire holder used for the XRD measurements.

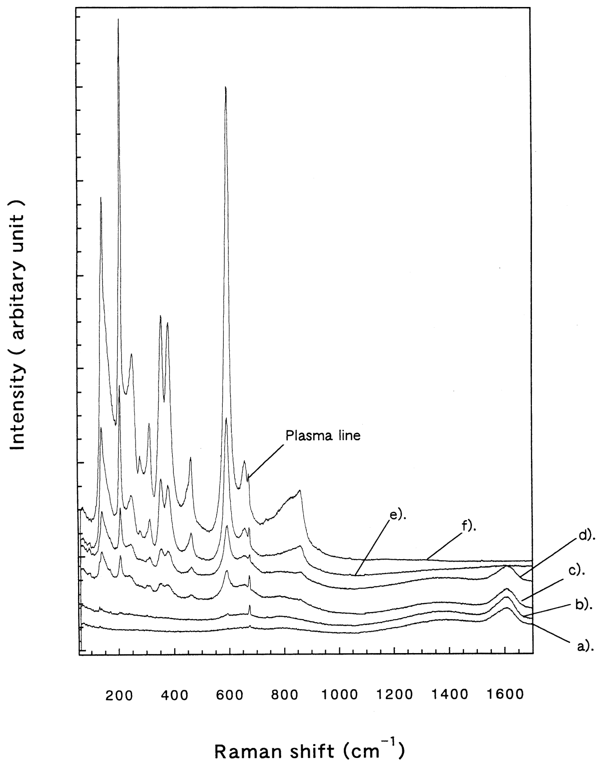

Fig. 4. Raman spectra of the calcined powder in air for 2 h at (a) 400, (b) 450, (d) 475, (e) 500 and (f) 600°C, and for 8 h at (c) 450°C.

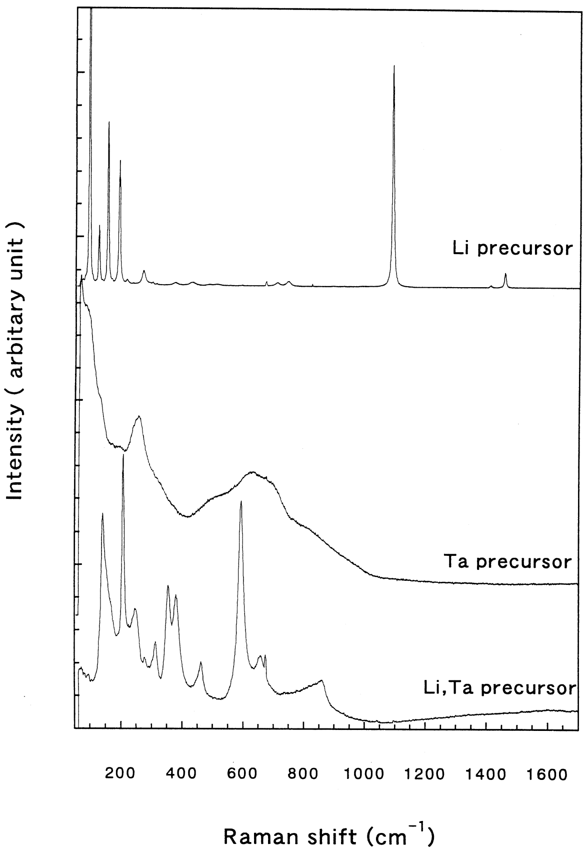

Fig. 5. Raman spectra of products obtained by calcining powder precursors in static air at 500°C for 2 h: precursors containing only Li (Upper), only Ta (Middle), and both Li and Ta (Bottom).

to line broadening of XRD, which deteriorates the ability of the XRD technique to detect such impurities.

The powders used for the XRD analysis were therefore further characterized using Raman spectroscopy, a technique which is capable of detecting impurities consisting of very small crystallites not easily identified with the XRD technique. Fig. 4 gives Raman spectra of decomposition products of the powder precursor at 400–600°C. The spectrum (Fig. 4a) of the powder calcinated at 400°C exhibits a characteristic broad band around 1600 cm^{-1}, which is probably attributed to the residual carbon [12,13]. The band at 1600 cm^{-1} remained up to 475°C (Fig. 4d), and it completely disappeared at temperatures higher than 500°C (Fig. 4e,f). Thus the small weight loss observed around 500°C in the TG curve (Fig. 2) can be reasonably connected with the disappearance of the 1600 cm^{-1} Raman band. Consistent with the XRD data (Fig. 3), Raman peaks characteristic of $LiTaO_3$ showed up already at 450°C (Fig. 4b), and they developed rapidly with increasing the heating temperature (Fig. 4c–f). A matter of very important concern is then to know whether Li_2CO_3 and Ta_2O_5 are distinct intermediate phases formed prior to the formation of $LiTaO_3$ during the thermal decomposition of the powder precursor. For this purpose, we have measured Raman spectra of decomposition products of similarly prepared powder precursors containing only Li or Ta, and they are compared with that of $LiTaO_3$ as shown in Fig. 5. The Raman spectra of the Li and Ta precursors calcinated at 500°C indicate the presence of Li_2CO_3 and Ta_2O_5, respectively. Some peaks, for instance a sharp peak at 1080 cm^{-1} characteristic of Li_2CO_3 (the upper spectrum of Fig. 5) and the strongest scattering around 100 cm^{-1} characteristic of Ta_2O_5 (the middle spectrum of Fig. 5), do not overlap with the Raman spectrum of $LiTaO_3$ (the bottom spectrum of Fig. 5), and therefore they can be used as sensitive probes for detecting them in a given sample. Turning back to the Raman spectra of our samples in Fig. 4, we can conclude that no phase separation of Li_2CO_3 and Ta_2O_5 has occurred during the thermal decomposition of the powder precursor because of the complete absence of their characteristic Raman peaks mentioned above (Fig. 5).

No phase separation of Li_2CO_3 and Ta_2O_5 in significant amounts may evidence our Li–Ta powder precursor prepared by the PC technique to be compositionally homogeneous. The contiguous ions of Li and Ta in the pyrolyzed product can therefore react with each other with a minimum of diffusion at relatively low temperatures (500°C) to form homogeneous and stoichiometric $LiTaO_3$. The PC technique forms a striking contrast to the conventional solid-state reaction technique as has been demonstrated in Fig. 6: i.e. while $LiTaO_3$ formed at 500°C as a single phase by the PC technique (the upper pattern of Fig. 6), formation of $LiTaO_3$ through the solid-state reaction

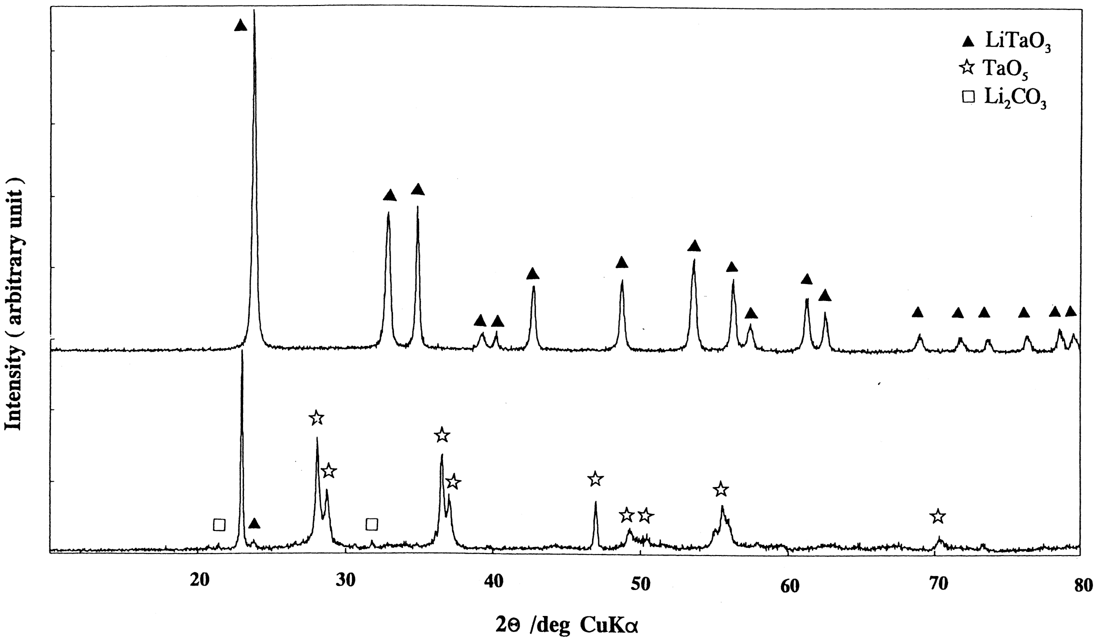

Fig. 6. XRD patterns of products obtained by calcining the PC powder precursor (Upper) or by solid-state reactions between Li_2CO_3 and Ta_2O_5 (Lower) at 500°C for 2 h.

between Li_2CO_3 and Ta_2O_5 was greatly restricted at the same temperature (the lower pattern of Fig. 6). The temperature (i.e. 500°C) at which $LiTaO_3$ forms by the PC technique is low enough to avoid the volatilization of lithium components during calcination and high enough to fully crystallize $LiTaO_3$.

4. Conclusion

A pure $LiTaO_3$ has been successfully synthesized by heat-treating the PC powder precursor in air at 500°C for 2 h. The success in lowering the processing temperature for $LiTaO_3$ down to 500°C may indicate an improved level of mixing of Li and Ta cations in the PC precursor.

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