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Chemical preparation of spherical lithium tantalate powder

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Spherical, micron size lithium tantalate powder was prepared by spray drying a lithium tantalate precursor using a mini spray dryer. Three chemical routes were used to prepare the lithium tantalate precursors, using lithium acetate and tantalum ethoxide as starting materials. The affects of processing parameters, such as solvent, drying temperature, and water, on the properties of the resulting powders were investigated. The as-dried powders were amorphous and became crystalline at a temperature as low as 450° C.

1. Introduction

The nature and quality of ceramic powders used in fabricating a final ceramic piece or device are the key to the overall process which determines the quality, yield, and performance of that final product. This is especially true for the powders used in the electronic ceramics. Important issues [1] related to ceramic powders including purity, particle size, size distribution, and the degree of agglomeration should be carefully controlled during powder production and later processing.

The synthesis of ceramic powders through chemical routes, such as precipitation from solution, or sol–gel processes, have recently received considerable attention [2–6]. It is mainly because these chemical routes can offer many advantages over conventional processes, such as high purity, and molecular homogeneity. The chemical routes have been used to prepare powders for electronic ceramics applications, such as $BaTiO_3$ [7, 8], $LiNbO_3$ [9], PLZT [10], and ZnO [11]. These results show that the powders exhibit high reactivity, and high purity, and can be densified at reduced temperatures.

The work reported here includes three chemical routes used to prepare lithium tantalate precursors, and preparation of powders by spray drying the precursors using a Buchi mini spray dryer. The effects of solvent, drying temperature, drying rate, and water on the physical properties of powder are investigated.

2. Experimental procedure

Spherical $LiTaO_3$ powders were prepared by spray drying lithium tantalate precursors using a Buchi mini spray dryer. The precursors were prepared using lithium acetate (Alpha Products, MA) and tantalum ethoxide (Alpha Products, MA) as starting materials. Fig. 1 shows two procedures used to prepare lithium tantalate precursor solutions. In the first method (Route 1), hydrous lithium acetate was first dissolved into methoxyethanol, and the dehydration was carried out at 125° C for 30 min. After the dehydration was complete, anhydrous lithium acetate was precipitated. The solution was cooled down to 70° C, and then an acetate precipitate was redissolved as soon as the temperature of the resulting solution was increased to 125° C. The refluxing process was continued for 2 h to complete the chemical reaction between lithium acetate and tantalum ethoxide. The resulting solution

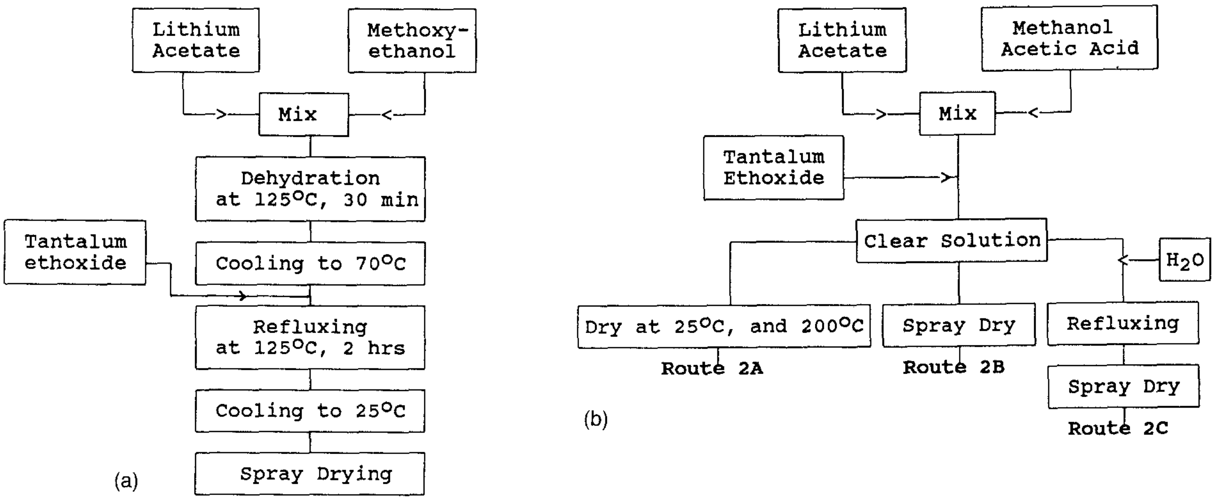

Figure 1 Two procedures used to prepare lithium tantalate precursors. (a) Route 1, (b) Route 2.

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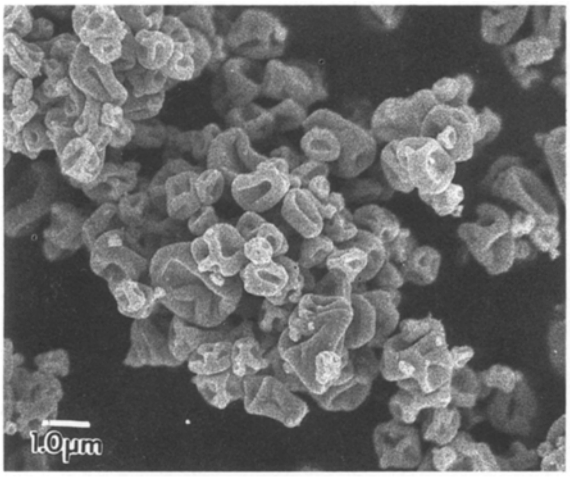

Figure 2 SEM micrograph of the powder prepared by Route 1.

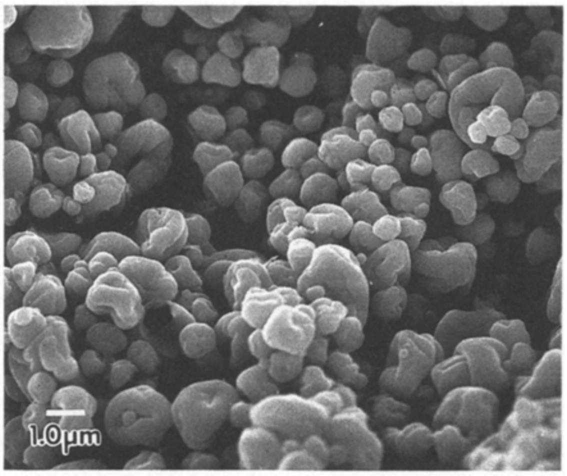

Figure 4 SEM micrograph of the powder prepared by Route 2B at 200° C.

was cooled down to room temperature, and then spray dried using a mini spray dryer. In Route 2, the lithium tantalate precursor solution was prepared by dissolving hydrous lithium acetate in methanol containing glacial acetic acid (30 : 1 by weight). After the solution became clear, an equal molar quantity of tantalum ethoxide was added to give a 1 : 1 molar ratio of Li and Ta. The resulting solution was clear, and was equally divided into three parts. The first part was dried at room temperature for 4 weeks, then at 200° C for 24 h, and the second part was immediately spray dried. To the third part (one litre solution) 0.3 mol H_2O was added, and then the resulting cloudy solution was refluxed at 80° C in air for 16 h. After the refluxing was complete, the cloudy solution was spray dried.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to measure the weight loss and energy of transition of powders as a function of temperature at a heating rate of $10° C min^{-1}$ in air. The crystallization behaviour of as-dried powders fired in air at various temperatures was studied by X-ray diffraction analysis. Particle size and particle morphology were examined using a scanning electron microscope (SEM). Particle size distributions were determined using an image analyser, and 200 to 300 particles were sampled. Specific surface areas and pore size distributions of the powders calcined at various temperatures in air for two hours were determined by multipoint nitrogen BET measurement. The equivalent spherical diameters of the particles were calculated based upon the BET results.

3. Results and discussion

Fig. 2 shows a typical SEM micrograph of the powder prepared by Route 1 and spray dried at an inlet temperature of 200° C. The powder is irregular and contains a lot of large dimples on the particle surface. The particle size, determined from SEM micrograph, is in the range of 0.5 to 4 μm. The same result is found for the powder spray dried at 160° C. XRD analysis of the powders calcined at 450° C for 2 h shows that pure crystalline lithium tantalate, without lithium oxide or tantalum oxide present, is obtained. Route 1 powder is not spherical and not suitable for use in the electronic ceramics, thus no further discussion is to be presented.

In Route 2A, the size of the as-dried powder was reduced using pestle and mortar, and a typical micrograph is illustrated in Fig. 3. Powder is chunk-like and has a large particle size, 2 to 200 μm. This type of powder is not suitable for later powder processing. The powder prepared in Route 2B with an inlet

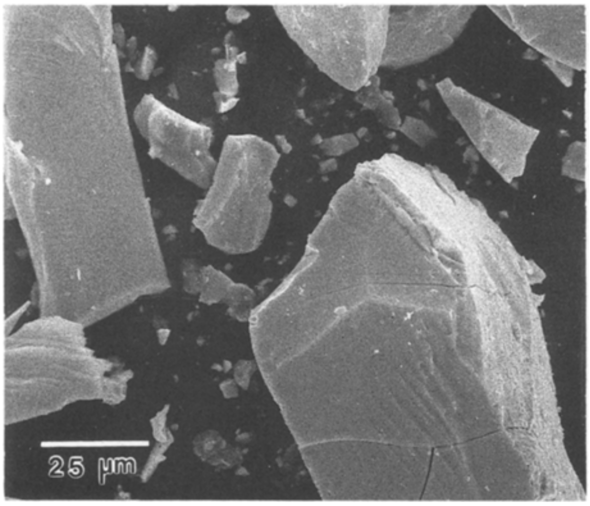

Figure 3 SEM micrograph of the powder prepared by Route 2A.

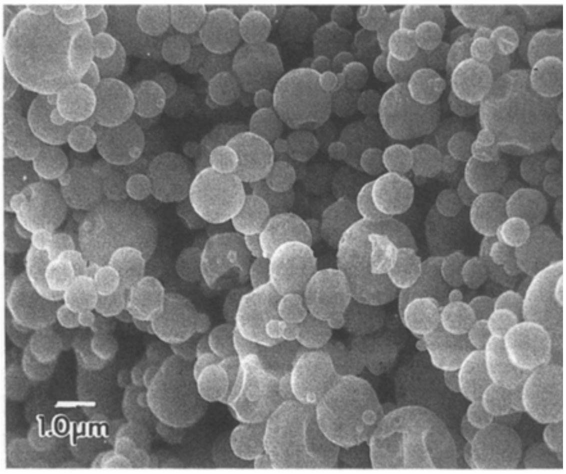

Figure 5 SEM micrograph of the powder prepared by Route 2B at 160° C.

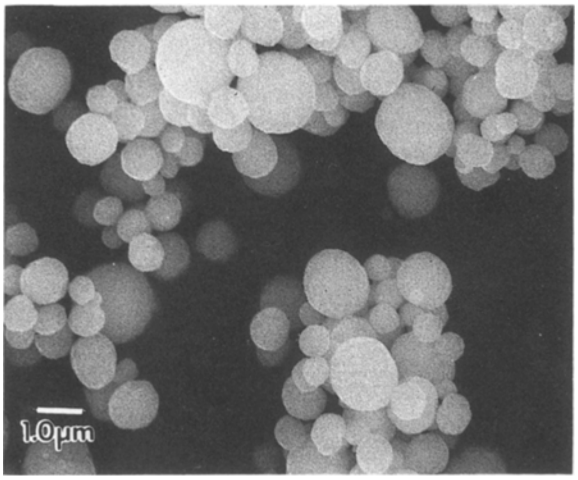

Figure 6 SEM micrograph of the powder prepared by Route 2C at 160° C.

temperature of 200° C is given in Fig. 4. The powder is granular-like, and contains a lot of dimples on the surface. The dimple size is also a function of spray drying temperature; the smaller dimple is obtained for the powder prepared at lower spray drying temperatures. For example, Fig. 5 gives powder prepared at an inlet temperature of 160° C, showing that the powder contains less and smaller dimples than that prepared at 200° C. This can be caused by the difference in volume shrinkage and the shrinkage rate of particles during spray drying. The as-dried powder is a mixture of lithium acetate and tantalum ethoxide, thus a large volume change and a high shrinkage rate can be expected during spray drying. In addition, the volume shrinkage and the shrinkage rate increase with increasing spray drying temperature. The larger volume change and shrinkage rate, however, could create a non-uniform shrinkage in particle, and thus forming larger dimples on the particle surface.

The powder prepared by Route 2C at an inlet temperature of 160° C is illustrated in Fig. 6, indicating that a smooth, and spherical powder is produced. The same result is observed for the powder spray dried at 200° C. This can be due to the fact that the as-dried powder is a mixture of hydroxides, which have a small and uniform volume change in particle during spray drying. Thus, spherical particles can be prepared, even at a high spray drying temperature of 200° C. Fig. 7 shows a typical cumulative size distribution, determined from SEM micrograph using an image analyser. The particle size is in the range of 0.3 to 3.4 μm, and has a mean size of 1.2 μm and a geometric standard deviation of 1.41. The particle morphology and particle size distribution remain unchanged after the powders are calcined at 500 or 800° C in air for 2 h, and an SEM micrograph is shown in Fig. 8.

Fig. 9 shows the TGA result of the powder prepared by Route 2B. It shows that the weight loss mainly occurs at two temperature regions, 50 to 300° C and 500 to 575° C, and has a total weight loss of 30 wt %. The total weight loss is consistent with the spray dried powder containing a mixture of lithium acetate and tantalum ethoxide. The weight loss, 28 wt %, in the first temperature region is due to the evaporation of residual solvent, the combustion of organic species, or the decomposition of the starting materials. In the second region 2 wt % loss resulted from the crystallization of lithium tantalate powder is found. No weight loss takes place at temperature above 600° C. The DTA data for the powder prepared by Route 2B is also given in Fig. 9. Two exothermic peaks and one endothermic peak associated with the two weight loss regions in the TGA curve are observed.

Three distinct weight loss regions and a total weight loss of 14 wt % are found in the TGA data, as shown in Fig. 10, for the powder prepared by Route 2C. The total weight loss is much less than that found for the powder prepared by Route 2B, suggesting that the as-dried powder consists of a mixture of hydroxides, or a precursor of lithium tantalate compound. Most of the weight losses take place in the first two regions, between 50 and 650° C, and are believed to be due to the removal of associated solvent, or the decomposition of hydroxides. Crystallization of lithium tantalate powder happens at 700° C, which results in a small weight loss. The DTA curve shown in Fig. 10 gives four exothermic and one endothermic peaks which are related to the weight losses in the TGA curve. The crystallization temperature of the Route 2C powder, 700° C, is higher than that prepared by Route 2B, 575° C, based upon the TGA–DTA results.

XRD analysis of the powder prepared by Route 2B and calcined at various temperature in air for 2 h shows that the as-dried powder is amorphous up to 450° C where strong $LiTaO_3$ peaks, without Li_2O or Ta_2O_5 peaks present, are found (see Fig. 11). This suggests that lithium acetate and tantalum ethoxide

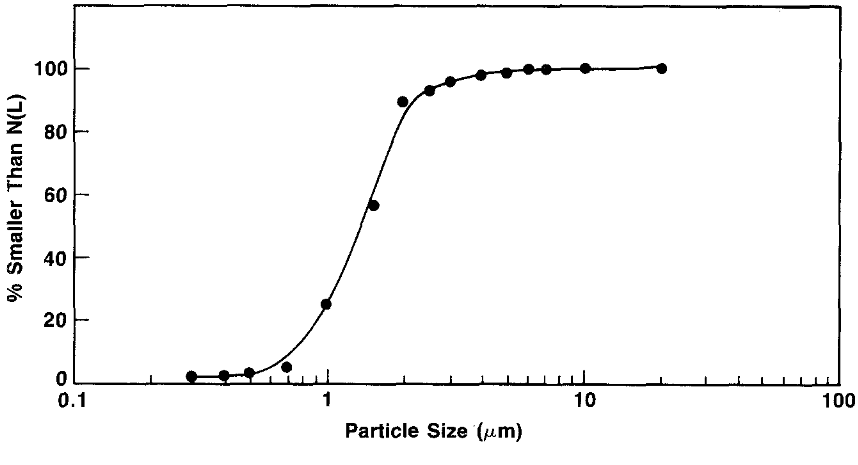

Figure 7 Cumulative particle size of the Route 2C powder prepared at 160° C.

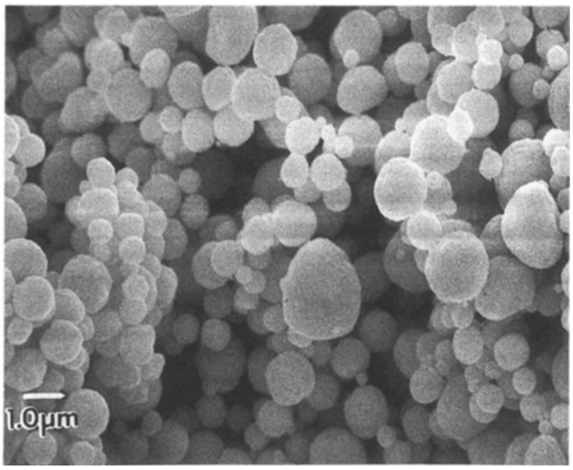

Figure 8 SEM micrograph of the Route 2C powder calcined at 800° C in air for 2 h.

are intimately mixed in the as-dried powder, and react quickly to form lithium tantalate powder. Lithium oxide or tantalum oxide could form when the as-dried powder was calcined at temperatures below 450° C, however, no conclusive evidence was found. This could be due to the fact that the oxide powders are too small to be detected by XRD before they form lithium tantalate powder. Calcination at temperatures above 450° C causes a rapid chemical reaction between lithium oxide and tantalum oxide to form lithium tantalate, and a significant growth in crystallite size, thus yielding very strong XRD peaks.

Fig. 12 shows XRD results for the powder produced by Route 2C and calcined at various temperatures in air for 2 h. No significant diffraction peaks are observed at a temperature up to 450° C where very small lithium tantalate peaks, compared with the XRD results shown in Fig. 11, are found. The

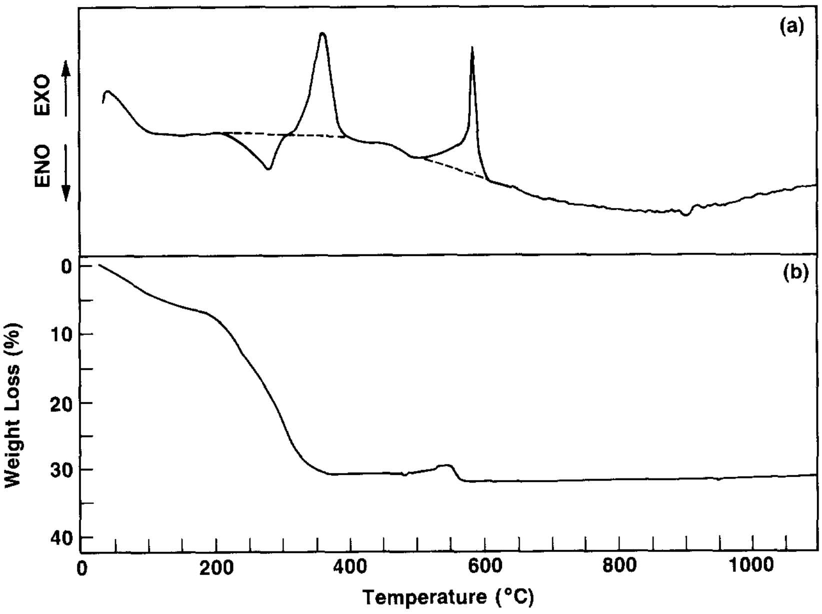

Figure 9 (a) DTA and (b) TGA results of the Route 2B powder at a heating rate of 10° C/min in air.

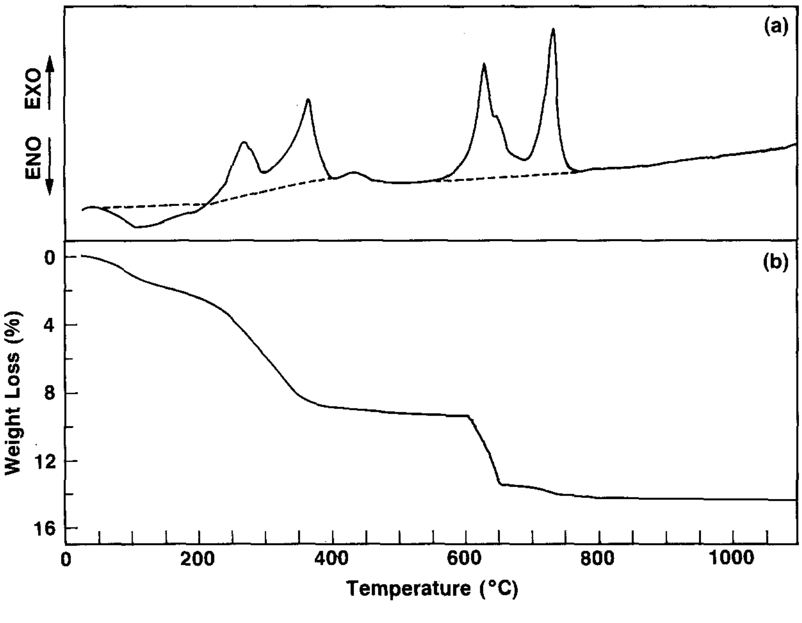

Figure 10 (a) DTA and (b) TGA results of the Route 2C powder at a heating rate of 10° C/min in air.

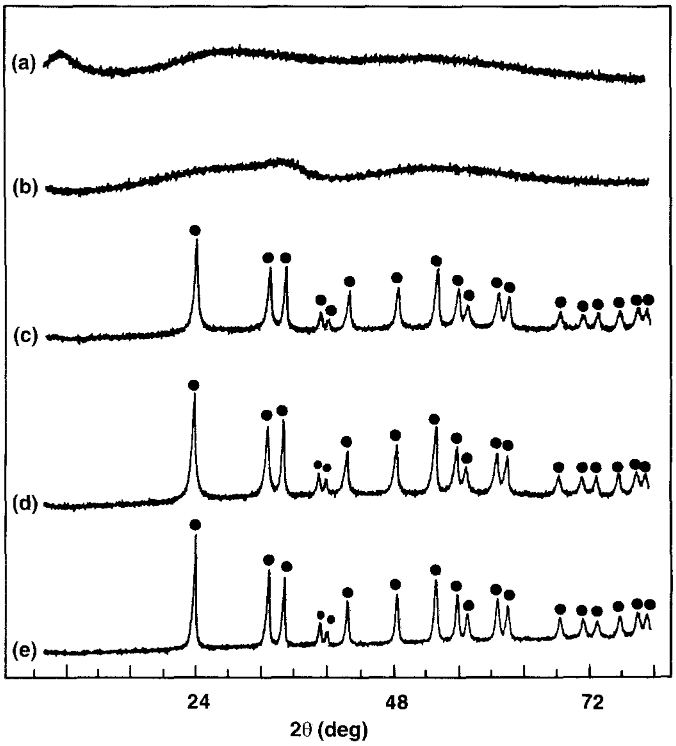

Figure 11 XRD results of the Route 2B powder calcined at various temperatures in air for 2 h. (a) as-dried, (b) 350° C, (c) 450° C, (d) 550° C, (e) 700° C. (● $LiTaO_3$).

XRD peaks remain at the same angles and become stronger with increasing calcination temperature. As noted in Figs 11 and 12, it can be found that powder prepared by Route 2C is more difficult to get crystalline lithium tantalate than that produced by Route 2B. This can be caused by the difference in tantalum oxide particle size. The larger tantalum oxide powder reacting with the same size of lithium oxide powder gives a slower crystallization rate of lithium tantalate. The size of the tantalum oxide powder prepared in Route 2C is controlled by the size of the tantalum hydroxide powder, precipitated by the hydrolysis of tantalum ethoxide during refluxing, which is much larger than that prepared by direct oxidation of tantalum ethoxide in Route 2B. The XRD results of Route 2C powder are similar to those observed in the sol–gel derived $LiTaO_3$ [12], where the hydrolysis of tantalum ethoxide or lithium tantalate precursor also proceeds before forming gels.

The BET surface area data of the powder calcined at various temperatures in air for 2 h is shown in Fig. 13. The as-dried powder prepared by Route 2B has a BET surface area of $3\,m^2\,g^{-1}$, corresponding to an equivalent spherical diameter of 1 to 2 μm which is close to SEM particle size. Calcination at 450° C causes an increase in surface area, up to $35\,m^2\,g^{-1}$, which is due to the decomposition of lithium acetate and tantalum ethoxide or the formation of small

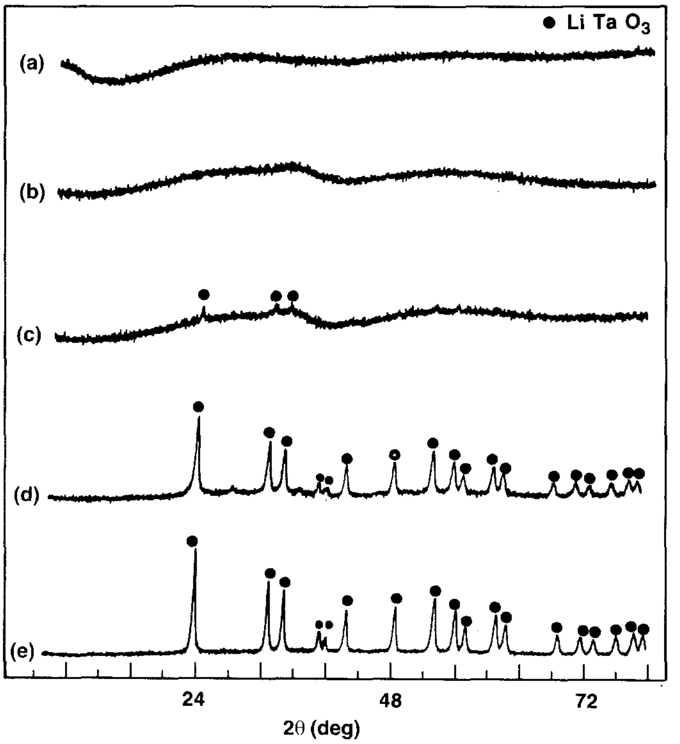

Figure 12 XRD results of the Route 2C powder calcined at various temperatures in air for 2 h. (a) as-dried, (b) 350° C, (c) 450° C, (d) 550° C, (e) 700° C. (● $LiTaO_3$).

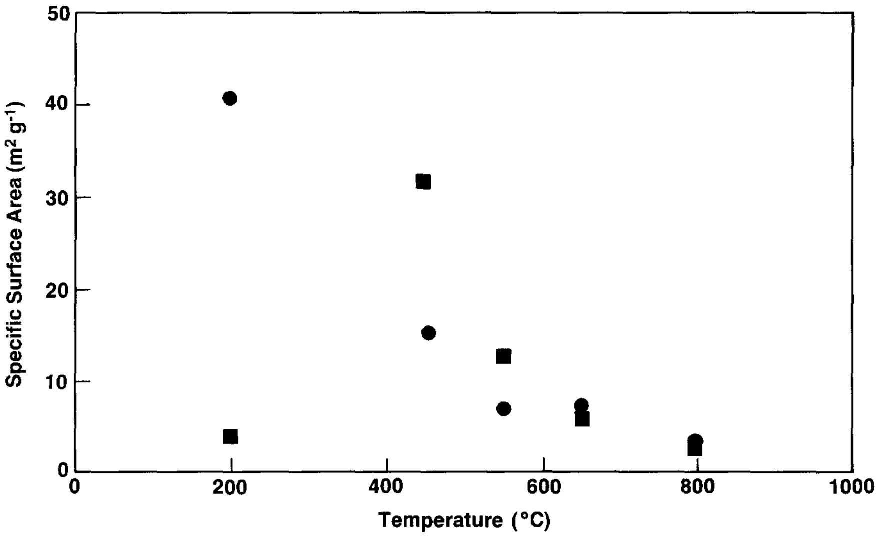

Figure 13 BET surface area results of the Route 2B (■) and Route 2C(●) powders calcined at various temperatures in air for 2 h.

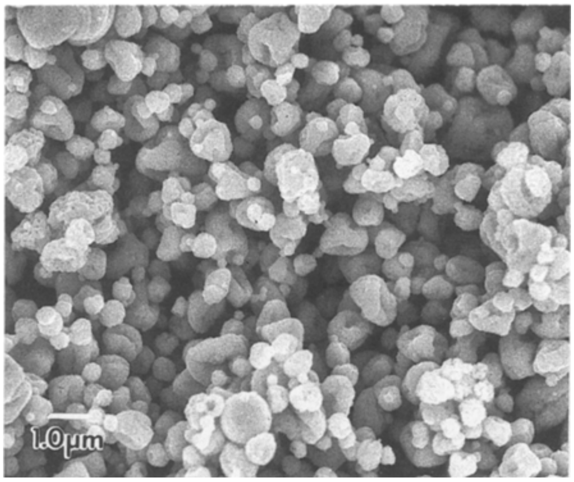

Figure 14 SEM micrograph of the Route 2B powder calcined at 800° C in air for 2 h.

lithium tantalate powder. The surface area decreases with increasing calcination temperature due to partial densification, from 35 $m^2 g^{-1}$ at 450° C to 3 $m^2 g^{-1}$ at 800° C. Fig. 14 shows a typical SEM micrograph of the Route 2B powder calcined at 800° C. It illustrates that the particle is partially densified to form porous agglomerates. The pore size distribution of the Route 2B powder calcined at 800° C for 2 h is given in Fig. 15. It shows that the pore sizes are in the range of 10 to 100 nm, and the mean size is 28 nm.

A large BET surface area, 42 $m^2 g^{-1}$, is obtained for the as-dried powder prepared by Route 2C. This large surface area corresponds to an equivalent spherical diameter of 50 to 100 nm which is much smaller than that of SEM size shown in Fig. 6. It indicates that each individual powder is very porous, and consists of a lot of tiny particles, such as tantalum hydroxide formed by the hydrolysis of tantalum ethoxide. The surface area decreases with increasing calcination temperature, down to 3 $m^2 g^{-1}$ at 800° C which is the same as that of Route 2B powder. The pore size distribution of the Route 2C powder calcined at 800° C is also depicted in Fig. 15. It shows that most of the pore sizes are in the range of 7 to 30 nm, and the mean size is 14.5 nm which is much smaller than that of Route 2B powder, 28 nm. A typical SEM micrograph for the Route 2C powder calcined at 800° C for 2 h is shown in Fig. 16, indicating that the powder is very porous and the pore size is close to BET pore size.

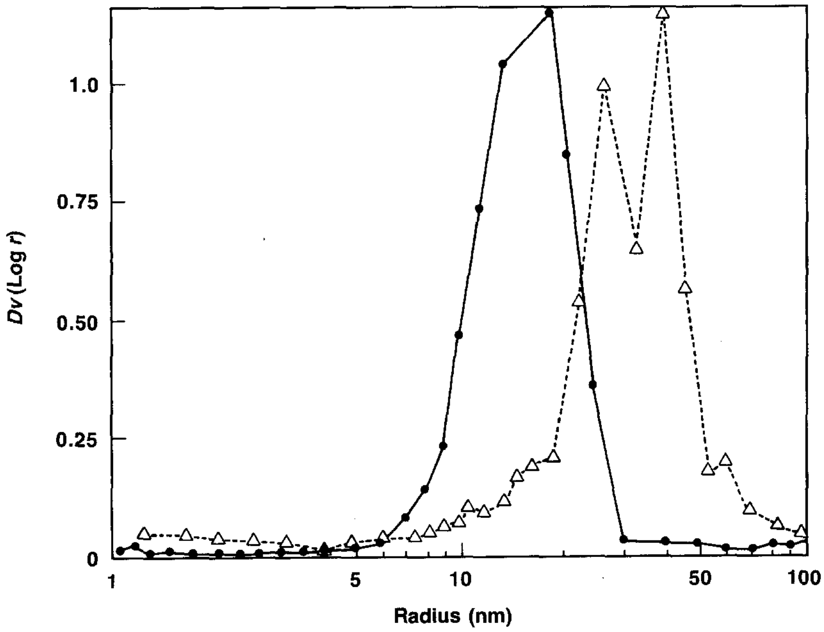

Figure 15 Pore size distributions of the Route 2B (△) and Route 2C (●) powders calcined at 800° C in air for 2 h.

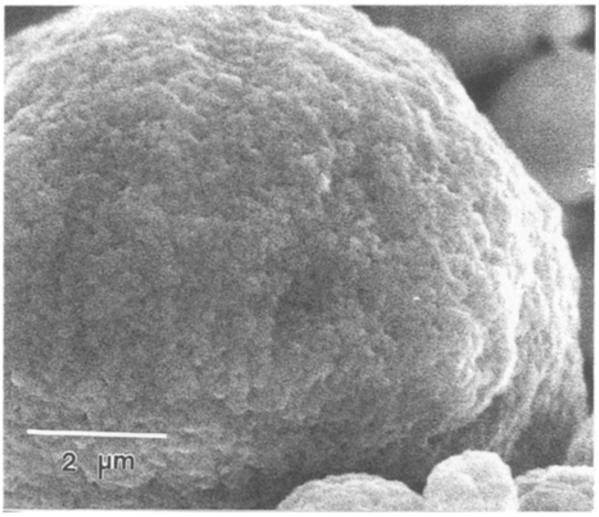

Figure 16 SEM micrograph of the Route 2C powder calcined at 800° C in air for 2 h.

4. Conclusions

Spherical, micrometre size $LiTaO_3$ powders are synthesized by spray drying lithium tantalate precursors, which are prepared using lithium acetate and tantalum ethoxide as starting materials. The as-dried powders are amorphous and crystallized directly to $LiTaO_3$, without the presence of Li_2O or Ta_2O_5, at a temperature as low as 450° C which is 350° C lower than that observed in the case of mixed oxides [12].

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