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Efficient Synthesis of Stoichiometric Lithium Tantalate Powder by a Solid-State Combustion Route

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Stoichiometric lithium tantalate (SLT) powder was prepared by a solid-state combustion method from the raw powder of Li_2CO_3 , Ta_2O_5 , and urea, which is characterized by a short reaction time and relatively low temperatures. The urea, added into the mixture (Li_2CO_3 and Ta_2O_5), serves as a fuel and an inducer to produce intermediate compounds and cause a solid-state combustion reaction as well. Various temperatures and urea contents were employed to optimize the synthesis of SLT. The chemical process and the quality of LiTaO_3 powder were investigated by X-ray diffraction, electron microscope, thermogravimetry, and Raman spectroscopy. The optimized synthesis shows great capability to reduce the volatilization of lithium-ion and presents an efficient way to manufacture high-quality SLT.

Keywords LiTaO_3 ; Solid-state combustion; Synthesis; Urea.

INTRODUCTION

Multifunctional materials lithium tantalate (LiTaO_3 , LT) and lithium niobate (LiNbO_3 , LN) have a lot in common including their structures, physical properties, and the applications. Both LT and LN are the most excellent and widely used materials in the applications of piezoelectric, ferroelectric, surface acoustic wave (SAW), electro-optic, and nonlinear optics [1–5]. LiNbO_3 and LiTaO_3 are stoichiometric oxides, and metal ratios Li/Ta and Li/Nb close to 1 result in greatly improved performance in the applications. Compared with LiNbO_3 , LiTaO_3 possesses higher value of light damage and lower coercive electric field, which makes it more suitable for quasi-phase-matched devices. In addition, mirror polished LiTaO_3 wafers are extensively used in the manufacture of high-frequency SAW devices which play an important role in advanced communication field. However, for the growth of LiTaO_3 and LiNbO_3 crystal and the polycrystalline device, the preparation of high-quality stoichiometric powder is always a key challenge.

A variety of synthetic methods have been reported to prepare LiNbO_3 powder with different properties in various application areas, such as solid-state synthesis, sol-gel process, complex formation reaction, spray

drying synthesis, and hydrothermal synthesis [6–12]. Similar to the methods of LiNbO_3 preparation, the synthesis methods of LiTaO_3 can also affect the composition, density, and even the growth direction. And these physical traits may consequently vary the properties and the quality of LiTaO_3 powder. The solid-state synthesis, which is the most widely used method to produce LiTaO_3 powder for single crystal growth, requires a high temperature (1250°C) and a long heat treatment time (48 h). Furthermore, on account of the serious volatilization of Li_2O at high temperature, it is hard to harvest the pure single-phase stoichiometric LiTaO_3 from solid-state synthesis. Tantalum alkoxides are also frequently used in sol-gel synthesis of Ta-based complex oxide [13]. The main drawback of alkoxide-based synthesis is that the precursor solution (Ta-alkoxide) is easy to hydrolyze and has to be processed in a bone-dry atmosphere. The use of tantalum pentachloride (TaCl_5) has been reported as a starting source which is cheaper and insensitive to moisture [14]. However, besides the small bit of residual chloride in final samples, unavoidable generation of HCl gas is also undesired. Furthermore, in the hydrothermal synthesis of lithium tantalate, the output is quite low. In general, the above methods cannot meet the requirement of industrial production for high-cost and complex process. An efficient and economical method to synthesize stoichiometric lithium tantalate (SLT) is urgently needed.

It is known to all that the conventional solution combustion route becomes an optimal technique to synthesize high-quality multicomponent oxides from soluble nitrates. The molecular-scale reactions via the solution combustion require shorter diffusion length

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than the grain-to-grain reactions in solid state [15]. These reaction conditions are useful to synthesize the material whose performance is very sensitive to slight composition change. For example, the volatilization of Li_2O in high temperature is a top concern for the synthesis of stoichiometric LiTaO_3 [15]. On the other hand, the solid-state calcination synthesis also represents an attractive method to produce different oxides for its simplified reaction process [16–21], but its high temperature and heterogeneous process cannot keep the exact proportion of initial components. To solve these problems, urea is hereby added in raw powders to improve the thermal and chemical reaction efficiencies [18, 19]. During the whole reaction process, the melted urea (fluid state) which releases a large amount of heat during decomposition is helpful for the component reaction and diffusion. This method induces a self-sustained reaction, which turns the raw mixture into desired well-crystalline compositions. What needs to be mentioned is that, unlike the solution combustion route, carbonate (Li_2CO_3) and oxide (Ta_2O_5) are not soluble in molten urea and the liquid phase disappears before the desired phase (LiTaO_3) is formed. This implies that our method is a standard solid-state reaction. Urea is not a solvent but a fuel and an inducer to reduce reaction temperature. As a result, the integration of the conventional endothermic solid-state reaction and the combustion reaction is obviously impressive. The reaction temperature can be lowered and reaction time shortened.

In the present work, an efficient technique of one-step preparation of stoichiometric LiTaO_3 powder was demonstrated by employing the solid-state combustion method. Different calcination temperatures and various amounts of urea were investigated. The possible mechanism and the optimized chemical process were proposed. Our results indicate that this technique can be applied in mass production of stoichiometric LiTaO_3 powder.

MATERIALS AND METHODS

High-purity starting materials of Li_2CO_3 (4N purity) and Ta_2O_5 (4N purity) powders were mixed with a molar ratio of $\text{Li}/\text{Ta}=1:1$ for all the samples. Various urea (5N purity) contents were added into the mixture. Particularly, the mass ratio of urea to ($\text{Li}_2\text{CO}_3 + \text{Ta}_2\text{O}_5$), R , was 0.5:1, 1:1, 2:1, 3:1, and 4:1, respectively. The mixtures were finely grounded and then calcined in a muffle furnace at 500°C, 600°C, 650°C, 700°C, and 800°C for 6 h, respectively. The obtained LiTaO_3 products were investigated by powder X-ray diffraction (XRD, D-MAX 2200 VPC, RIGAKU). The role of the urea was investigated by thermogravimetry-Fourier transform infrared spectrometry (STA-IR, STA449F3/Nicolet 6700, NETZSCH/ThermoFisher Scientific, USA). Field emission scanning electron microscope (SEM, JSM-6330F) was used to analyze the morphology of LiTaO_3 powder. Raman spectrum was carried out in a Renishaw inVia Laser Micro-Raman Spectrometer using 633 nm laser. To measure Li/Ta composition, a SLT sample (800°C) with the mass ratio of 1:3 was chosen.

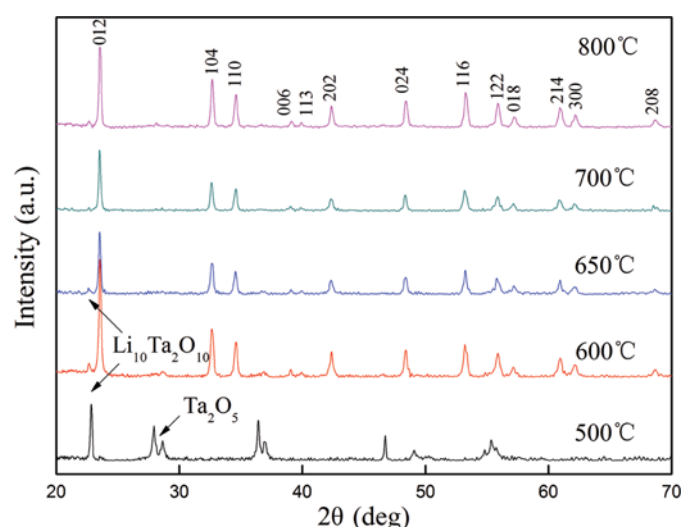


FIGURE 1.—The XRD patterns of the powder with the urea/ $(\text{Li}_2\text{CO}_3 + \text{Ta}_2\text{O}_5)$ mass ratio of 4:1 sintered at 500°C, 600°C, 650°C, 700°C, and 800°C, respectively.

RESULTS AND DISCUSSION

The XRD patterns of powders produced at different temperatures and mass ratios are given in Figs. 1 and 2, respectively. The LiTaO_3 structure can be assigned from the sharp reflections. Using d -spacing value, we assigned each peak as its corresponding crystallographic plane.

Figure 1 shows the XRD pattern of the LiTaO_3 powders sintered at temperatures ranging from 500°C to 800°C for 6 h with the mass ratio of 4:1. When the calcination temperature is lower than 650°C, besides the LiTaO_3 main phase, the diffraction peaks of Li-rich phase ($\text{Li}_{10}\text{Ta}_2\text{O}_{10}$) and Ta_2O_5 are also detected. When the temperature increases, $\text{Li}_{10}\text{Ta}_2\text{O}_{10}$ phase gradually

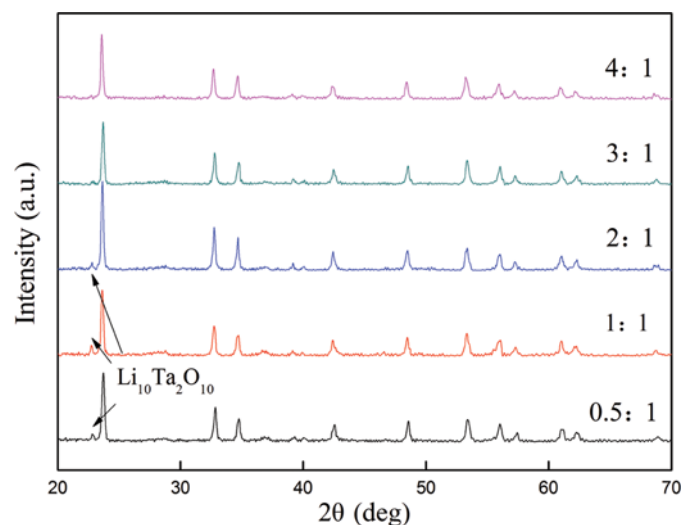


FIGURE 2.—The XRD patterns of the powder sintered at 700°C with different urea/ $(\text{Li}_2\text{CO}_3 + \text{Ta}_2\text{O}_5)$ mass ratios of 0.5:1, 1:1, 2:1, 3:1, and 4:1, respectively.

fades. While the LiTaO_3 single phase can be clearly obtained. This result indicates that under the premise of 6 h of reaction time, the calcination temperature of raw powder should be higher than 700°C . Compared with the traditional endothermic solid-state route or other synthetic methods of LiTaO_3 phase [6–12], our method has the shortest reaction time (6 h). However, this reaction time is still much longer compared with the time of the conventional solution combustion route (a few minutes). As discussed below in the thermogravimetry analysis, the formation of LiTaO_3 phase only takes a short time. Nevertheless, obviously our method still retains the shortcoming of solid-state reactions (nonuniform). To compensate such shortcoming, enough calcination time and proper temperature are used to help the diffusion between Li-rich phase and Li-lean phase. It should be stressed that the chosen temperatures ($500\text{--}800^\circ\text{C}$) are much lower than the traditional calcination temperature (1250°C) of Li and Nb complexes. The longer sintering time cannot influence the analysis of the chemical reaction. The time only serves to obtain pure powder. From the above analysis, 700°C (the mass ratio is 4:1, the calcination time is 6 h) is possibly the lowest calcination temperature to show a good crystallinity and purity of the powder.

Figure 2 shows the XRD patterns of different initial compositions (urea/ $[\text{Li}_2\text{CO}_3 + \text{Ta}_2\text{O}_5]$) under constant heat treatment temperature (700°C) during the same period of time (6 h). One can easily point out that unless the mass ratio is higher than 3:1, the Li-rich phase still exists. From our XRD patterns, no noticeable difference can be pointed out between 3:1 and 4:1 samples. Based on this result, we choose the mass ratio of 3:1 for economical reaction conditions. Furthermore, the reduction of FWHP (full width at half peak) could also be observed from the XRD patterns, which reveals the direct proportion between the enlargement of particle size and the increase of heating temperature. Namely, the crystallinity of samples increases with temperature.

Considering the volatilization of Li_2O , if the highest treatment temperature (800°C) could still maintain the stoichiometric ratio, other samples are confirmed to be stoichiometric. That's the reason to choose LiTaO_3 powder sintered at 800°C with the mass ratio of 3:1 to investigate the Li/Ta composition. Figure 3 shows the Raman spectra of the as-prepared sample. In previous works [22, 23], Raman spectrum has been particularly demonstrated as a function of the stoichiometry. Like the case of most of polycrystalline powder, compared with their single-crystal counterparts, the Raman spectra of these samples may lack some peaks. In accordance with previous works [23, 24], the missing 90 cm^{-1} peak may be regarded as a corroboration of the perfect stoichiometric ratio. Furthermore, the most important peak is the phonon at 140 cm^{-1} , which is very sensitive to the composition (Li/Ta), and can be written as a function of FWHP (Γ) [24],

$$C_{\text{Li}} = 51.45 - 0.2945\Gamma, \quad (1)$$

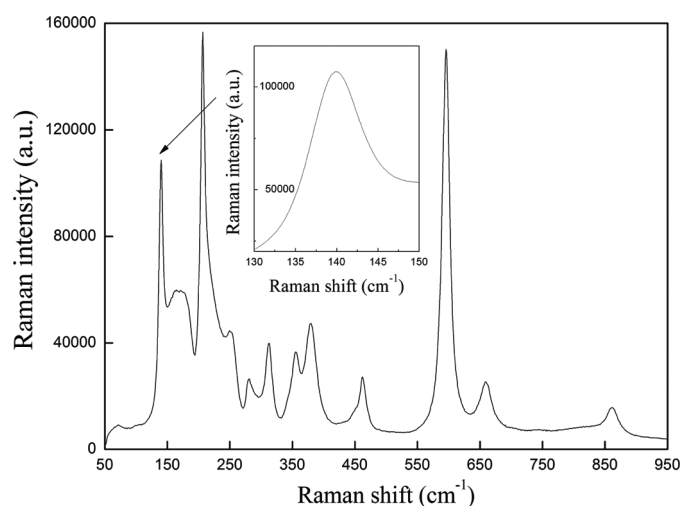


FIGURE 3.—The Raman spectra of the SLT sintered at 800°C with the ratio of 3:1.

where C_{Li} is the molar concentration of Li ions and Γ is the half width of Raman band at 140 cm^{-1} . In Fig. 3, the Raman absorption band at 140 cm^{-1} is very obvious, and the band's half width (Γ) is 5.2 cm^{-1} (which means the C_{Li} is 49.92 mol%). It should be noticed that the present Li/Ta ratio extremely approaches stoichiometric ratio. Therefore, the ratio strongly confirms the fact that the obtained LiTaO_3 powder is stoichiometric. From above, Raman spectra afford us a convenient method to quantify the composition of LiTaO_3 . As this is the highest calcination temperature among our samples, its great value of C_{Li} strongly ensures that all products are stoichiometric. And all samples could well keep their initial components.

The SEM images of LiTaO_3 powder under different thermal treatment temperatures of 600°C , 650°C , 700°C , and 800°C are shown in Fig. 4. It can be clearly observed that the powder of 650°C is well-crystallized with 500 nm in diameter. The average particle size rises with the calcination temperature, which agrees well with the XRD and the thermo gravimetric-differential thermal analysis (TG-DTA) results and indicates the aggregation of the synthesized powder. Figure 4 also shows that the shape of powder is thin flakes. Using Pauling's third rule and law of Bravais, the morphology depends on the crystallographic origin of the material for single crystals [25]. According to previous work [18] and Fig. 1, we can deduce that the growth rate of (012) plane is the slowest, so the (012) plane becomes the most mighty face to influence the morphology of the LiTaO_3 crystal grain.

The TG-DTA measurement is used to investigate the thermal reaction of the raw mixture. In Fig. 5, one can find that there are two stages in the whole weight loss curve. The first stage ($130\text{--}190^\circ\text{C}$) generates a sharp weight loss of about 25%. After that, the second stage is from 336°C to 500°C , along with a weight loss of 8% of the total mass. Corresponding to the mass curve, there are two noticeable thermal peaks at 133.6°C and 336°C .

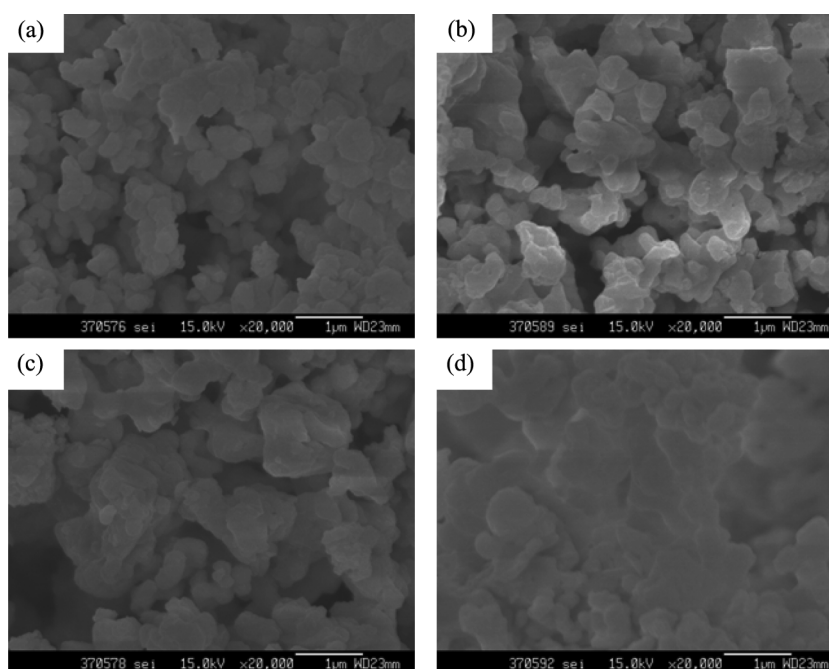
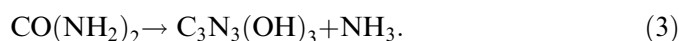
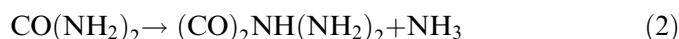


FIGURE 4.—The micrographs of the LiTaO_3 powder sintered at different temperatures (a) 600°C, (b) 650°C, (c) 700°C, and (d) 800°C, respectively.

The first endothermic peak around 133.6°C is ascribed to the dehydration and thaw of added urea, which is the beginning of weight loss. From the endothermic peak to the first inflection point (190°C) of the big exothermic and the mass curve, the trend may be ascribed to the decomposition of urea into biuret and cyanuric acid [18],



The second peak centered at 336°C is due to the exothermic decomposition of organic components.

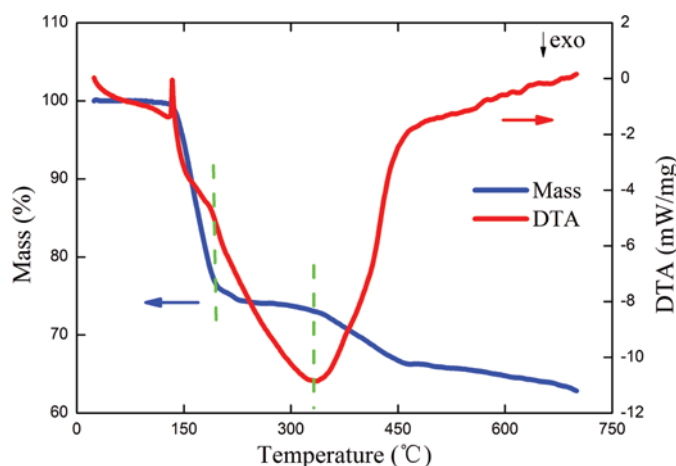


FIGURE 5.—The TG-DTA curve obtained from the raw mixture heated in air for 3 h.

Investigating the infrared spectra [25] of the urea and the Li_2CO_3 mixture in various temperatures, one can observe the NH_2 bond, the $\text{C}=\text{O}$ bond, and the $\text{Li}-\text{N}$ bond. It means that the added urea reacts with lithium carbonate below 200°C. From 200°C to 350°C, these bonds do not change much. Then along with the increasing temperature to 400°C, the NH_2 bond disappears. The $\text{C}=\text{O}$ and the $\text{Li}-\text{N}$ bonds shift further. But the pure Li_2CO_3 sample does not change in the whole temperature range from 100°C to 400°C [25]. The analysis of infrared spectra perfectly fits the DTA curve in Fig. 5. Around 190°C, lithium carbonate reacts with urea and produces intermediate compounds. Meanwhile, a large amount of small molecules like NH_3 , H_2O , CO_x , etc. come from the urea and penetrate into the Li_2CO_3 and the Ta_2O_5 . These gases lower the reaction temperature by reducing the bonding energy, improving the porosity and enhancing the interface reaction greatly [25]. After this period (133–190°C), there is no evident weight loss until 336°C. Then the solid-state reaction between lithium and tantalum cation takes place under the exothermic peak of organic compounds. At the same time, CO_2 is released during the second stage of weight loss. From the above, we can now come to the conclusion that there is a match between the fuel combustion temperature and the carbonate dissociation temperature. After the chemical reactions which end at about 476°C, there is still small-scale exothermic phenomenon for the nucleation of LiTaO_3 crystallite. It can also be easily verified by XRD data in Fig. 1 that the higher temperature contributes to the crystallization.

In general, urea is not a solvent but a fuel and an inducer to reduce reaction temperature. It takes part in

the reaction, improves the porosity, and greatly enhances the interface reaction. But the urea is far less than its potent role in the conventional solution combustion, namely the solid-state grain-to-grain reaction needs much more energy than the molecular-scale reaction. The total exothermic energy of urea decomposition has to match the absorbed heat of solid-phase reaction. The lack of urea will result in incomplete reaction, but too much fuel will also generate undesired phase (which refers to the phase diagram of Li_2O - Ta_2O_5 binary system). Therefore, proper urea content is strictly required. From the point of view of energy saving and the requirement of extremely high pure and uniform product in industrial manufacture and scientific research, the mass ratio (urea/ $[\text{Li}_2\text{CO}_3 + \text{Ta}_2\text{O}_5]$) of 3:1 under 700°C is chosen.

CONCLUSIONS

The above works demonstrate that solid-state combustion method could afford us a remarkable way to synthesize stoichiometric high-purity SLT powder. The Li/Ta mole ratio in the obtained LiTaO_3 powder is extremely close to stoichiometry. It should be noted that this method is also helpful to improve the quality of crystals and polycrystalline device. Our result presents a novel approach to further comprehend the various performance of SLT.

Using a simple method, we successfully synthesize pure LiTaO_3 powder at a constant temperature (700°C) over a relatively short period of time (6 h), with the mass ratio of 3:1 (urea to $\text{Li}_2\text{CO}_3 + \text{Ta}_2\text{O}_5$). The urea makes the generation of SLT single phase easier. Such consequence indicates that the solid-state combustion is a practical one-step approach to synthesize stoichiometric LiTaO_3 powder and a promising method to prepare many kinds of oxide ceramics. This method has potential advantages in industrial production and material science.

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