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Synthesis of $MgTa_2O_6$ nano-powders by citrate sol–gel method

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ABSTRACT

A sol–gel processing was used to synthesize $MgTa_2O_6$ nano-powders at a low temperature using Ta_2O_5 as starting materials. The decomposition of precursors, and the crystal structure and microstructure of the $MgTa_2O_6$ powders were characterized by DTA/TG, XRD and SEM techniques. The effects of the amount of citrate acid and pH values on the stability of sol–gel solution and microstructure of $MgTa_2O_6$ nano-powders were investigated. XRD and TG/DTA results show that the $MgTa_2O_6$ nano-powders can be synthesized at 900 °C, and non-stoichiometric ratio of Mg to Ta was required to form the single $MgTa_2O_6$ phase. The average particle sizes of $MgTa_2O_6$ powders range from 25 nm to 100 nm with different CA/Ta and pH values.

1. Introduction

With the rapid progress of mobile and satellite communication systems such as cellular phones, and global positioning systems, the dielectric ceramics with high Q values have been paid much attention for their applications in microwave resonators, filters, microstrip antennas and wave guides in the past decade [1]. Recently, the binary niobate and tantalate compounds with general formula AB_2O_6 (where A = Ca, Mg, Zn, Co, Ni, Cu, Mn and B = Nb, Ta) were found to be promising candidates for application in microwave devices [2,3]. Among these compounds, $MgTa_2O_6$ exhibits excellent microwave dielectric properties: $Q \times f = 59{,}600$ GHz, $\varepsilon_r = 30.3$ and $\tau_f = 30$ ppm/°C [2–4]. However, the sintering temperature is too high (1550 °C) for $MgTa_2O_6$ ceramics prepared by traditional solid-state route. Therefore, many researchers have focused their interesting on the low-fired microwave dielectric ceramics. Huang et al. investigated the dielectric properties of $MgTa_2O_6$ ceramics with CuO addition prepared by traditional solid-state method, and found that 0.5 wt% addition of CuO can effectively reduce the sintering temperature of $MgTa_2O_6$ ceramics from 1550 °C to 1400 °C [5]. In general, the wet chemical preparation routes have been found to be a more effective method to lower the sintering temperature of ceramics because it is possible to produce very pure, homogeneous, and extremely fine powders with good sintering properties by those techniques [6–8]. For example, Kavian and Saidi synthesized $BaTiO_3$ nano-powders by sol–gel process at a low temperature of 800 °C [9], and Ravi and co-workers prepared $MgTa_2O_6$ powders by co-precipitation method at 550 °C [10,11]. However, other wet chemical methods, especially sol–gel processes to synthesize $MgTa_2O_6$ ceramic powders have not been reported in the literature, therefore, we reporter an improved citrate sol–gel method to synthesize $MgTa_2O_6$ nano-powders, and the effects of pH value on the crystal structure and microstructure of $MgTa_2O_6$ powders were investigated in this study.

2. Experimental

An improved sol–gel method was used to synthesize the $MgTa_2O_6$ nano-powders in this work, and high purity Ta_2O_5 powders, HF (40%), $Mg(NO_3)_2$ and ammonia were used as raw materials, and citric acid monohydrate (CA) was used as a chelating agent and reaction medium. The key step of this process for preparing the $MgTa_2O_6$ nano-powder is to obtain the Ta^{5+} solution. Firstly, Ta_2O_5 was dissolved in HF (40%) to form a transparent solution, and in order to remove the F^- from the solution, ammonia (28%) was added, and then white $Ta(OH)_5$ precipitation can be obtained. After being washed with deionized water for three times and dried, the $Ta(OH)_5$ was dissolved in different amount of citric acid to form the Ta-citric solution, and the molar ratios of Ta^{5+} to citric acid ranged from 1:1 to 1:5. Then, $Mg(NO_3)_2$ which mole number is half of that of Ta^{5+} was dissolved in deionized water, and added to this solution. The solution containing Ta^{5+} and Mg^{2+} was stirred and heated at 80 °C to form citrate gels, and then precursors were obtained by heating these gels at 120 °C. Finally, $MgTa_2O_6$ powders can be obtained by heating the polymeric precursor at 700–1000 °C.

The decomposition and crystallization behavior of the polymeric precursor with CA/Ta = 2:1 (molar ratio of citric acid to Ta^{5+}) were analyzed by thermogravimetry and differential thermal analysis (TG/DTA, DIAMOND 6300, USA) at a heating rate of 5 °C/min. The phase identification of the synthesized powders was investigated by X-ray diffraction (XRD, D/max 2200VPC, Japan) using CuKα radiation with a scan speed of 8°/min. The microstructures of the synthesized powders were studied by scanning electron microscopy (SEM, Camscan, MX2600, England).

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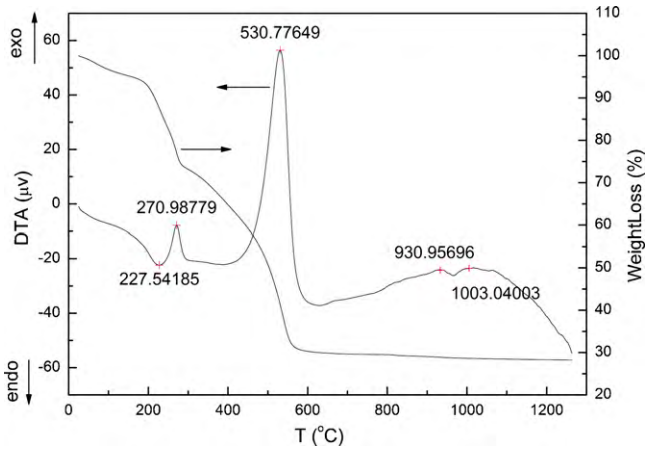

Fig. 1. The DTA and TG curves of $MgTa_2O_6$ polymeric precursors heated by 5 °C/min.

3. Results and discussion

The DTA and TG curves of $MgTa_2O_6$ polymeric precursor with CA/Ta = 2:1 were shown in Fig. 1. A sharp endothermic peak can be observed at 270.98 °C, which corresponds to the 24.9% weight loss, and this endothermic peak is mainly caused by the decomposition of structure water in the xerogels and the vaporization of the remnants organic acid. With increasing temperature, a sharp and strong exothermic peak is observed at 530.77 °C, which correspond to a rapid weight loss about 69.4% in TG curve, and this exothermic peak is attributed to the dehydration and decarbonation reaction, the thermal decomposition of the whole organic elements and the oxidation of partial metallic ions. The broad exothermic peak observed between 930 °C and 1030 °C is considered to be the result of the crystallization of $MgTa_2O_6$. Therefore, the reaction mechanism from precursor to product revealed by DTA and TG curves can be considered as that the polymeric precursor with Mg^{2+} and Ta^{5+} undergoes a process of dehydration, decarbonation and crystallization. Those above results indicate that $MgTa_2O_6$ crystalline phase can be synthesized at a temperature around 950 °C by citrate sol–gel process.

Fig. 2 shows the XRD patterns of $MgTa_2O_6$ polymeric precursors heated at different temperatures for 2 h in air. It can be seen that the polymeric precursor is still amorphous and noncrystalline as the calcination temperature is below 750 °C, and with increasing

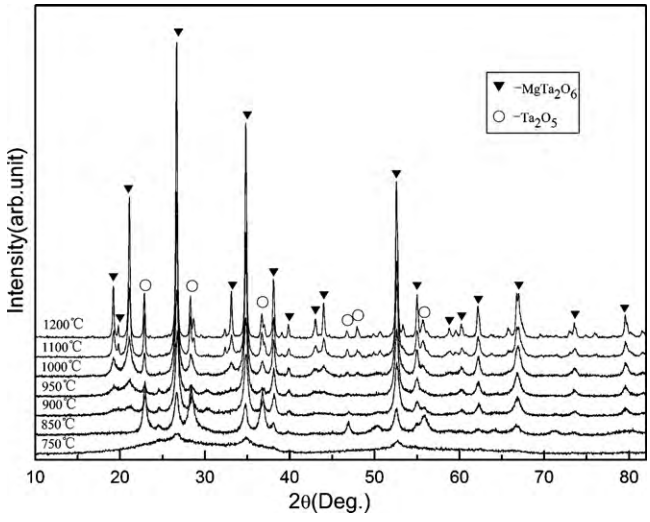

Fig. 2. The XRD patterns of $MgTa_2O_6$ precursors heated at different temperature for 2 h in air.

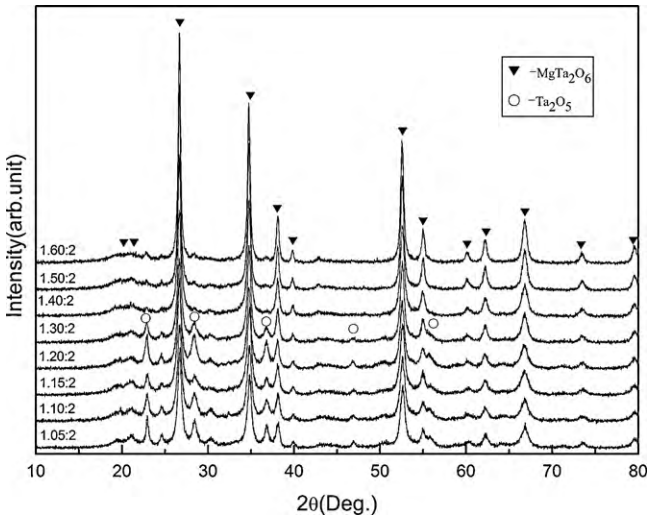

Fig. 3. The XRD patterns of $MgTa_2O_6$ polymeric precursors with different amounts of MgO heated at 900 °C.

the calcination temperature from 750 °C to 850 °C, the diffraction peaks of the main crystal phase appear, and the diffraction peaks of $MgTa_2O_6$ can be observed at 900 °C. However, the secondary phase of Ta_2O_5 (marked as '*') exists at this temperature, and it can be observed until the calcination temperature increased to 1200 °C. Therefore, the above results indicate that the single $MgTa_2O_6$ phase can not obtained with stoichiometric compositions by this processing. Ferrari et al. had also reported this phenomenon in preparing $MgTa_2O_6$ ceramics by solid-state route. In order to obtain the single $MgTa_2O_6$ phase powders, different amounts of $Mg(NO_3)_2$ were used in this work, and Fig. 3 shows the XRD patterns of $MgTa_2O_6$ polymeric precursors with different amounts of $Mg(NO_3)_2$ heated at 900°C for 2 h in air. The intensity of Ta_2O_5 diffraction peaks decreased with increasing values of Mg/Ta (mol) from 1:2 to 1.3:2, and all the diffraction peaks of Ta_2O_5 disappear as the ratio of Mg to Ta is 1.40:2. Therefore, an excess of 40% mole percentage for $Mg(NO_3)_2$ compared with every 2 mol $Ta(OH)_5$ was required to form the single $MgTa_2O_6$ phase. In addition, it needs 1200 °C to synthesize $MgTa_2O_6$ ceramic powders by solid-state route. Therefore, it can be concluded that the synthesis temperature of $MgTa_2O_6$ powders can be remarkably reduced.

For sol–gel processing, it is very important to form chelate complex between citric acid and metal cation, therefore, different molar ratios of citric acid to Ta^{5+}(CA/Ta) in sol–gel processing was investigated in this work. Fig. 4 shows the SEM photographs of $MgTa_2O_6$ powders with different CA/Ta values calcined at 900 °C. The average particle size decreases from 50 nm (Fig. 4(a)) to 25 nm (Fig. 4(b)) with increasing CA/Ta values from 1:1 to 2:1, and the particle size ranges between 25 nm and 30 nm for the samples with the CA/Ta values of 3:1 and 5:1 (Fig. 4(c) and (d)). This result indicates that the citric acid and metal cation may be chelated more completely as the ratio of CA/Ta is larger than 2:1. Therefore, the optimal ratio of CA/Ta is 2:1 in this sol–gel processing.

In addition, the pH value also has a significantly influence on the formation of a stable sol–gel solution in the process, therefore, as CA/Ta = 2:1, different pH values in this sol–gel processing was also investigated. The results show that stable Mg–Ta precursor solutions can be obtained for all pH values from 2 to 9. Fig. 5 shows the SEM photographs of $MgTa_2O_6$ powders with different pH values calcined at 900 °C. It can be seen that the average particle size decreases from 100 nm (Fig. 5(a)) to 85 nm (Fig. 5(b)) with increasing pH values from 2 to 4, and more, the shape and size of grains are inhomogeneous for these two samples. The smallest particle size of

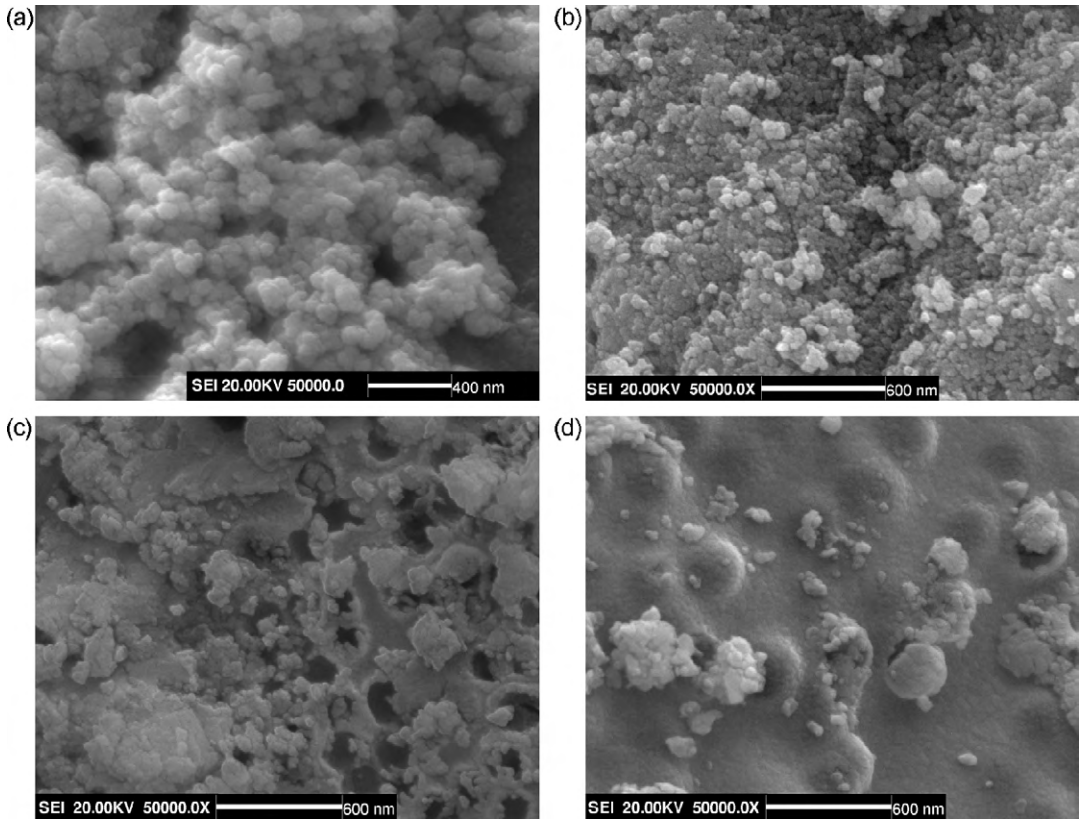

Fig. 4. The SEM photographs of $MgTa_2O_6$ powders with different CA/Ta values calcined at 900 °C. (a) CA/Ta = 1:1, (b) CA/Ta = 2:1, (c) CA/Ta = 3:1, (d) CA/Ta = 5:1.

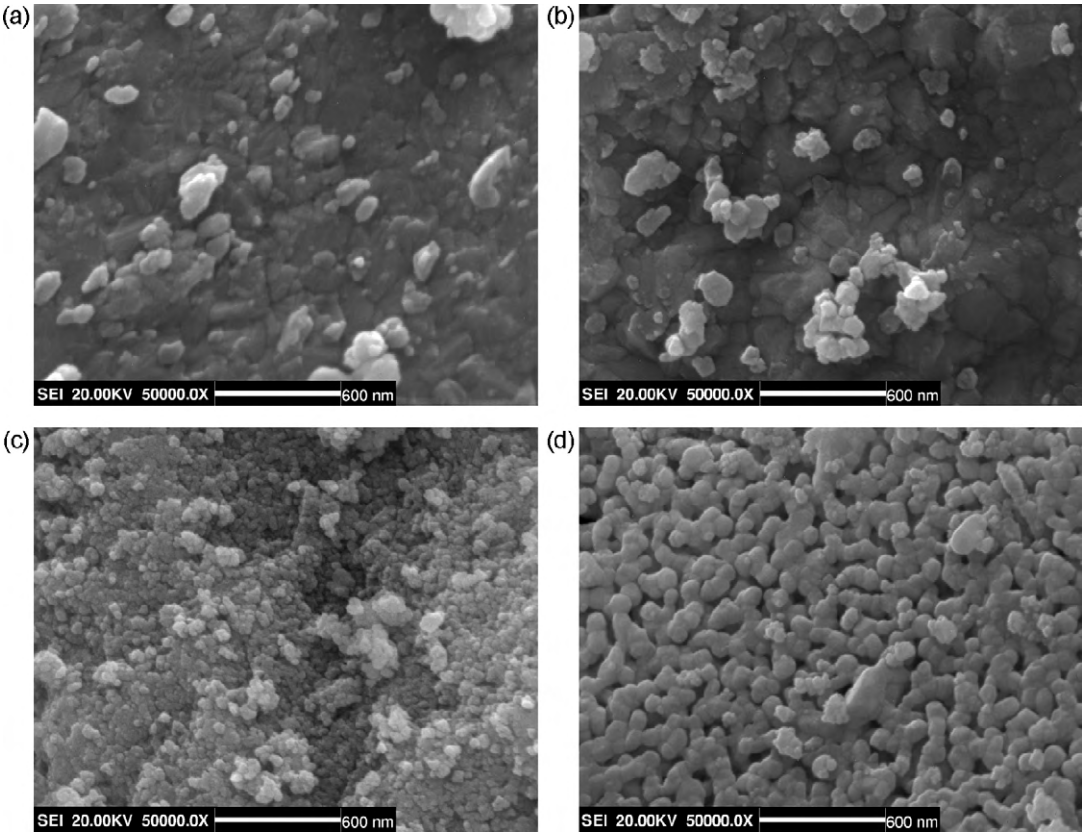

Fig. 5. The SEM photographs of $MgTa_2O_6$ powders with different pH values calcined at 900 °C. (a) pH = 2, (b) pH = 4, (c) pH = 7, and (d) pH = 9.

25 nm can be observed in the sample with pH = 7 (Fig. 5(c)), and then the particle size increases to 65 nm with pH = 9 (Fig. 5(d)). These results suggest that the optimal pH value is around 7 for preparing the $MgTa_2O_6$ powders in this sol–gel process. This is also consistent with that of our previous work in synthesizing $MgNb_2O_6$ powders by this method [12,13]. These phenomena can be explained by the effects of pH values on the stability of sol–gel. For solution with Ta^{5+}, stable citrate sol–gel may be more easily formed because that a neutral pH value can promote the complexation between metal ion and citric acid.

4. Conclusions

$MgTa_2O_6$ nano-powders were synthesized at a low temperature of 900 °C using Ta_2O_5 as the starting materials by citrate sol–gel method. XRD results reveal that a single phase of $MgTa_2O_6$ can not be synthesized with stoichiometric ratio of Mg to Ta by this processing, and an excess of 40% mole percentage for $Mg(NO_3)_2$ compared with every 2 mol $Ta(OH)_5$ was required to form a single phase of $MgTa_2O_6$. Both the amount of citrate acid and the pH value have a significant influence on sol–gel processing and the particle size. The citric acid and metal cation may be chelated more completely as the ratio of CA/Ta is larger than 2:1. A neutral pH value can also promote the complexation between metal ion and citric acid, resulting in smaller particle sizes. As CA/Ta = 2:1 and pH = 7, good homogeneity of $MgTa_2O_6$ nano-powders with an average grain size of 25 nm can be obtained by calcining the xerogels at 900 °C for 2 h.

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