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Citrate solution combustion derived $Ba_2Ti_9O_{20}$ ceramics

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Abstract

A citrate solution combustion process was adopted to synthesize $Ba_2Ti_9O_{20}$ phase. The precursor powders with small particle size of ∼100 nm and homogeneous distribution of multiphasic particles could be obtained by combustion of a citrate complex solution. The molar ratio of nitrate to citrate in the initial complex solutions had an obvious effect on the phase compositions and organic residuals of the precursor powders. However, those precursor powders all could be easily sintered into single phase $Ba_2Ti_9O_{20}$ ceramics at 1250 °C for 4 h. The densities and dielectric constants of the ceramics depended on the molar ratio of nitrate to citrate in the initial complex solutions used for forming the precursor powders. The relations between the preparation conditions and properties were discussed.

Keywords: Barium titanate; Powders-chemical preparation; Sintering; Dielectric property

1. Introduction

Single phase $Ba_2Ti_9O_{20}$ ceramic possesses an excellent combination of low dielectric loss, moderate dielectric constant and small temperature coefficient of the dielectric constant.[1–3] It is therefore a significant material for microwave dielectric resonators applied to microwave telecommunication and satellite broadcasting. Many studies showed single phase $Ba_2Ti_9O_{20}$ required a severe and inconvenient processing conditions.[4–10] Current studies show that sol–gel technique, especially citrate and EDTA gel,[11–13] demonstrates a good way to obtain high reactive precursors for single phase $Ba_2Ti_9O_{20}$ ceramics. However, a calcining process is mandatory before sintering for the sake of $Ba_2Ti_9O_{20}$ ceramic.[11,12]

Recently, combustion synthesis by metal complex solution has been developed based on the complex gel route. The method utilizes the in-built exothermicity of combustion of the reaction system to synthesize the ultrafine ceramic precursor powders, and it has been used for the synthesis of nanosized barium titanate powder, $BaTi_4O_9$ and $Pb_xBa_{1-x}Ti_4O_9$ ceramic precursor powders.[14,15] Also it has proved to be effective for obtaining metal oxides with fine particles.

In this work, citrate solution combustion was used to synthesize the precursor powders for a single phase $Ba_2Ti_9O_{20}$ ceramic. In addition, the effect of the ratio of nitrate:citrate in the solutions on the precursor powders and ceramics was investigated and discussed.

2. Experimental procedure

Butyl titanate, barium nitrate and citric acid with analytical grade purity were used as starting materials. In order to prepare citrate complex solution, titanyl nitrate solution was prepared according to the following reactions:

$$Ti(OC_4H_9)_4 + 3H_2O \rightarrow TiO(OH)_2 + 4C_4H_9OH \quad (1)$$

$$TiO(OH)_2 + 2HNO_3 \rightarrow TiO(NO_3)_2 + 2H_2O \quad (2)$$

The Ti ion concentration in the titanyl nitrate solution was determined by gravimetry with hydrolyzing, filtrating and calcining.

The mixed citrate complex solutions were prepared by titanyl nitrate solution and barium nitrate in a Ba:Ti molar ratio of 2:9, the nitrate:citrate molar ratio in the solution was adjusted by adding a designed amount of citric acid. During the preparation of the mixed citrate complex solution, pH value was kept to be 6. The samples studied in this work are listed in Table 1.

The mixed citrate complex solutions in beaker were heated on an electrical furnace until complete combustion. The resulting powders were used as the precursor powders for $Ba_2Ti_9O_{20}$ ceramics. With increasing the nitrate to citrate molar ratio in the mixed solution, the combustion reaction became more drastic and the combustion time became shorter.

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Table 1
The specification of the samples studied in this work

Sample number	Nitrate:citrate molar ratio	Remark
S1	1.82	Mixed citrate complex solution
S2	5	Mixed citrate complex solution
S3	10	Mixed citrate complex solution
PS1		Combusted product of S1
PS2		Combusted product of S2
PS3		Combusted product of S3
CS1		Sintered body by PS1 powders at 1250 °C for 4 h
CS2		Sintered body by PS2 powders at 1250 °C for 4 h
CS3		Sintered body by PS3 powders at 1250 °C for 4 h

The precursor powders were mixed with 5 wt.% PVA solution and compacted in a steel die at 12 MPa. The pellets were sintered at a rate of 10 °C/min to 1250 °C, soaked for 4 h in air, and cooled in furnace.

The phase in the precursor powders and sintered bodies were identified by X-ray powder diffractometer with Cu Kα (XRD, D/MAX-rA). Differential thermal analysis (DTA, CRY-2) and thermogravimetry (TG, WRT-3P) with a heating rate of 10 °C/min in air were used to analyze thermal behaviors of the precursor powders. Fourier transform infrared spectroscopy (Nicolet-Avatar 360) was used to characterize structural groups in the samples. Transmission electron microscopy (TEM, JEOL 200CX) was employed to investigate morphology and particle size of the precursor powders.

The densities of the disc-shaped specimens were determined by Archimedes method. The dielectric properties of the ceramics were measured at room temperature using an impedance analyzer (HP4914A) at frequencies of 100 MHz.

3. Results and discussion

After the mixed citrate complex solution combusted, the resulting powders had crystalline phases depending on the nitrate to citrate molar ratio as shown in Fig. 1.When the ratio increases, the XRD pattern changed from amorphous character to well-crystallized one.

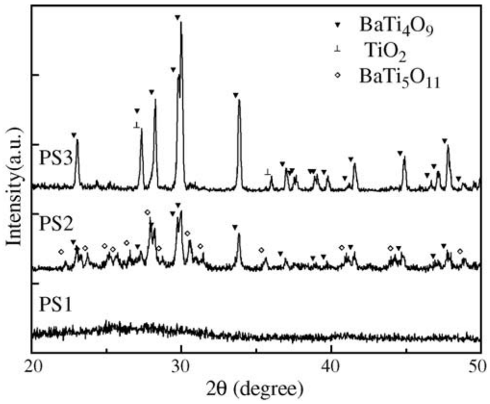

Fig. 1. XRD patterns of the precursor powders derived from combustion from S1, S2 and S3 solution.

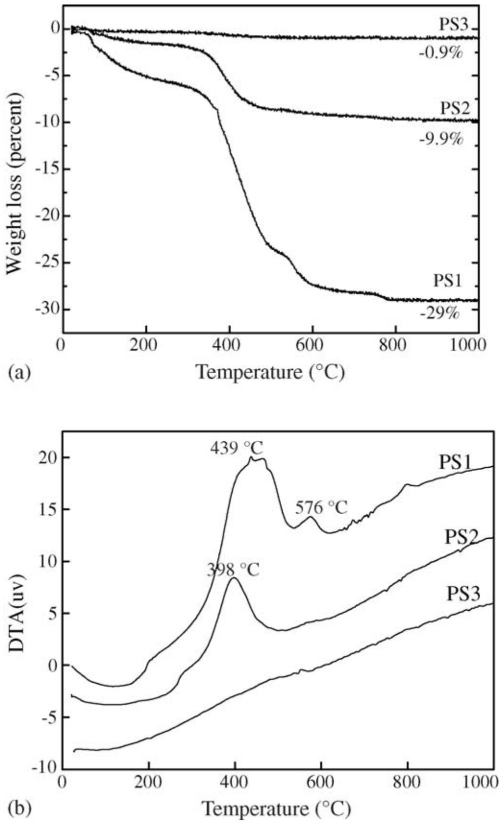

Fig. 2. (a) TG curves for the precursor powders derived from combustion from S1, S2 and S3 solution. (b) DTA curves for the precursor powders derived from combustion from S1, S2 and S3 solution.

The thermal evolution (Fig. 2) of the precursor powders showed that Sample PS1 had a large weight loss of 29% in TG, and a big exothermic peak at ~400 °C in DTA; while Sample PS3 had only a weight loss of 0.9% in TG, and no exothermic peak in DTA. This indicates that Sample PS1 has much more organic residuals than Sample PS3, it can be proven by their IR spectra (Fig. 3) in which there were strong absorption bands at

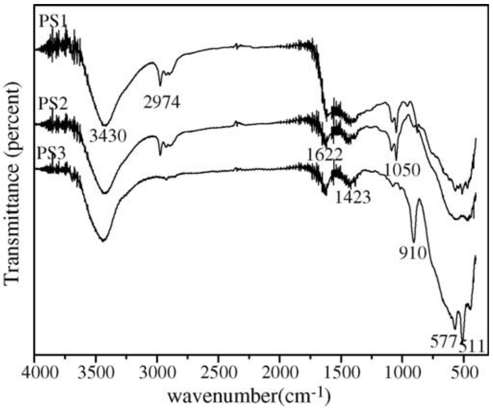

Fig. 3. FTIR spectra of the precursor powders derived from combustion from S1, S2 and S3 solution.

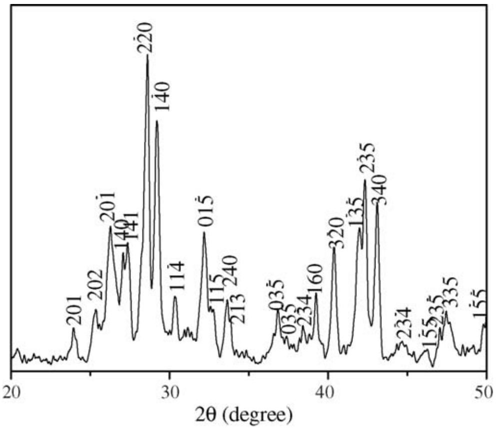

Fig. 4. XRD pattern of the ceramic sintered at 1250 °C for 4 h for CS1, CS2 and CS3.

2974 (C–H) and 1050 cm^{-1} (C–O) for Sample PS1, at 910, 577 and 511 cm^{-1} (titanate) for Sample PS3.

The nitrate to citrate molar ratio in the mixed solutions has a remarkable effect on the phase compositions and thermal behaviors of the precursor powders. This is mainly because the increase in nitrate to citrate molar ratio in the solution enhances oxidation ability, and consequently the combustion reaction occurs easily and drastically. The more completely combustion reaction goes, the less organic residuals remain in the precursor. Sample PS1 existing as amorphous phase can be attributed to having more organic residuals due to incomplete combustion.

When the three precursor powders were sintered at 1250 °C for 4 h, the sintered body all showed to have a XRD pattern of well-developed and pure $Ba_2Ti_9O_{20}$ phase (Fig. 4). Such a lower sintering temperature can lead to the formation of single phase $Ba_2Ti_9O_{20}$ ceramic, it may result from: (a) During the combustion process, the release of extensive gaseous by-products and the instantaneous reactions all inhibit the growth and agglomeration of the particles in the precursor powders. As a result, the particles have a round shape with 100 nm particle size (Fig. 5). Such fine particles are very reactive and favorable to accelerate further solid reactions upon heating. (b) Although the precursor powders have a few phases like $BaTi_4O_9$, $BaTi_5O_{11}$ and TiO_2 (Fig. 1), the basic Ti–O octahedral units and close oxygen packing density in these titanates are similar to those in $Ba_2Ti_9O_{20}$.[16] Such similarity in unit structure could favor the conversion to a thermodynamically stable phase, $Ba_2Ti_9O_{20}$, during sintering.[16] (c) Since the multiphasic particles are derived from the citrate complex solution combustion, these fine multiphasic particles should be homogeneously distributed in the precursor powders. Such homogeneous distribution facilitates kinetically the formation of $Ba_2Ti_9O_{20}$.

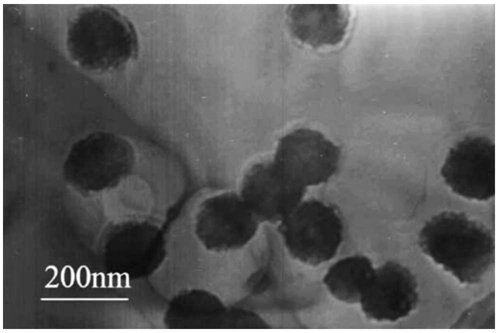

Fig. 5. TEM micrograph of the precursor powders derived from combustion from S1, S2 and S3 solution.

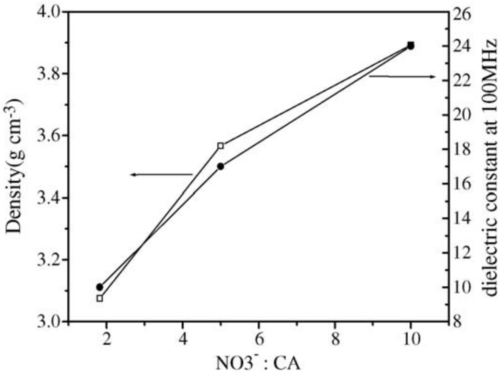

Fig. 6. Densities and dielectric constants of the ceramics vary with NO_3:CA molar ratio in the initial complex solutions used for forming the precursor powders.

Fig. 6 shows the density of the ceramics relates to the formation condition of the precursor powders. The citrate complex solution with higher NO_3:CA molar ratio results in the precursor powders with less organic residuals, and the derived ceramic has higher density due to less porosity which is usually caused by decomposition of organic residuals. The dielectric constant of the ceramic becomes small with decreasing the density as a usual way. The dielectric losses are about 2×10^{-3} at 100 MHz, the value does not show enough low, and it could result from the low density of these ceramics. It is suggested that further densification could give better dielectric properties, and the work is being done.

4. Conclusions

Single-phase $Ba_2Ti_9O_{20}$ ceramic could be easily prepared by sintering precursor powders directly at 1250 °C for 4 h due to the high reactivity and good homogeneous distribution of fine multiphasic particles in the precursor powders derived from citrate solution combustion. The present work shows that the change in nitrate to citrate molar ratio in the initial complex solutions has a significant influence on the properties of the resulting ceramic. The relatively high nitrate to citrate molar ratio is needed in order to realize a complete combustion. As a result, a dense sintered body can be formed. The dielectric constant is 24 and loss tangent is 2×10^{-3} at 100 MHz for the $Ba_2Ti_9O_{20}$ ceramic.

Acknowledgments

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