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Non-reducible $BaTiO_3$-based dielectric ceramics for Ni-MLCC synthesized by soft chemical method

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Abstract

In order to meet the demand on the miniaturization and manufacturing cost reduction of multilayer ceramic capacitors, a nano-$BaTiO_3$-based non-reducible dielectric material through a soft chemical route has been developed. The particle size was decreased down to the level of 30 nm and the dielectric medium could be co-fired with Ni-electrodes under a $N_2 + H_2$ reducing atmosphere. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and volume shrinkage have been employed to detect the sintering behavior and microstructure evolution including grain growth, pore formation and body densification. After a sintering process at 1200 °C for 2 h, the dielectric constant was 8800, the dissipation factor was less than 2%, the insulation resistance was about 10^{12}–10^{13} Ω cm, and the temperature coefficients of capacitance were less than 22% and −82% at −30 °C and 85 °C, respectively. The material is anticipated to be used for the Ni-multilayer ceramic capacitors (MLCC) with thin dielectric layers with a Y5V specification in the Electron Industries Association standard.

Keywords: Nano-$BaTiO_3$-based; Non-reducible; Ni-MLCC

1. Introduction

$BaTiO_3$-based multilayer ceramic capacitors (MLCC) are widely used components in electrical devices and circuits. Previously, the alloy of palladium and silver were served as internal electrode in MLCC. However, the price of palladium is too high, which causes a serious pressure for the MLCC production, especially when the number of dielectric layers rapidly increases today [1]. To seek cheap metals to substitute the traditional Pt/Ag electrode is needed. Nickel is a promising candidate, large effort has been devoted to realize Ni electrode in MLCC, and substantial progress has been achieved [2,3]. In another aspects, the increasing of dielectric layer number requires diminish of the layer thickness, in turn, the particle size of the powders used for the dielectric ceramic layers in MLCC. Mechanical milling appears no longer suitable method to obtain powders with hoped fineness. Search to develop various chemical techniques to synthesize thinner powders are actively conducted in the past years [4]. In this report we present recent result of our work for synthesis of nm-sized non-reducible $BaTiO_3$-based ceramic powders by a chemical coprecipitation method and their use to $BaTiO_3$-based dielectric for Ni-MLCC with Y5V specification. According to this item of Electron Industries Association (EIA) standard the temperature coefficient of capacitance must be within +22% or −82% of the value at 25 °C from −30 °C to +85 °C [5].

2. Experimental procedure

2.1. Sample preparation

The basic composition of the samples are $[(Ba_{1-x}Ca_x)O]_m[(Ti_{1-y}Zr_y)O_2]$, where $x = 0.05$–0.1, $y = 0.08$–0.12, $m = 1.02$–1.05. The additives include Mn, Mg, Sr, Fe, Y, RE, totaling less than 4 mol% of the formulation. The

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starting solutions of the constituents were mainely prepared from nitrates with commercially guaranteed purity (90%–99%) and distiled water as the solvent, while the solution of titanium was made of oxalate. Coprecipitation was carried out under conditions of stirring the mixture solution at room temperature and adjusting the pH value (9–10) by adding ammonia into the solution. After 200 °C drying the precipitates were calcined at 850 °C for 2 h and powder with light green color was obtained. Then, the powder was compacted into pellets and coated with Ni electrode. Sintering of the pellets was carried out in H_2/N_2 atmosphere at temperature of 1200 °C for 2 h with a heating rate of 300 °C/h.

2.2. Characterization

X-ray diffraction (XRD) analysis has been done to determine the phase composition. The X-ray machine used was Rigaku Dmax-RB diffractometer with rotational anode. The radiation used was Kα of Cu, and the working voltage, current and scanning rate were 40 kV, 80 mA and 4°/min, respectively. The phase composition of the powder was identified by comparison of interplanar spacings with $BaTiO_3$ perovskite given by the JCPDS cards.

The particle morphology of the powder was characterized with transmission electron microscope (TEM 400). The grain size of specimens sintered at 1200 °C was examined by scanning electron microscope (SEM S250).

Thermal analysis including TG and DSC was done on the equipment NETZSCH STA 409C, where the temperature covered was from room temperature to 950 °C.

Dielectric constant and dielectric loss were measured over a temperature range from −55 °C to +125 °C at 1 kHz using a RCL apparatus (LCR Databridge 2810A). The insulation resistance of the samples was measured with a ZC36 high resistance meter.

3. Results and discussion

3.1. Phase structure analysis of calcined non-reducible $BaTiO_3$-based powders

Fig. 1 is a X-ray diffraction spectrum of powder sample calcined at 850 °C. The spectrum is well matched with $BaTiO_3$ perovskite structure. The strongest diffraction peak in Fig. 1 was identified as (1 1 0) of the $BaTiO_3$ phase. Split of diffraction peaks was observed, indicating the coexistence of tetragonal phase. Comparing to the cubic $BaTiO_3$ the distorted tetragonal $BaTiO_3$ has a longer *c* axis and a shorter *a* axis.

As some diffraction peaks in the diffraction spectrum of powder sample from the same precipitates but calcined at 750 °C (Fig. 2) could be attributed to perovskite structure, the starting temperature of the generation of $BaTiO_3$ should be lower than 750 °C, though the amount of it left uncertain.

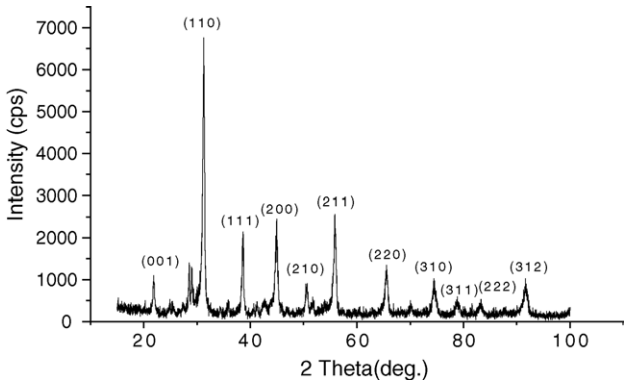

Fig. 1. XRD pattern of a powder sample calcined at 850 °C for 2 h.

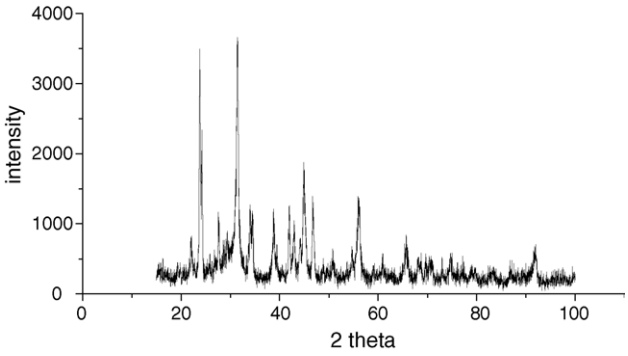

Fig. 2. XRD pattern of a powder sample calcined at 750 °C for 2 h.

The thermal analysis results are shown in Fig. 3. A series of exothermic peaks in the interval of 250 °C to 500 °C including the prominent peak at 498 °C should be corresponding to the decomposition of the compounds such as hydroxides and oxalates formed during chemical synthesis. These low temperature phases exsist until the temperature rised to above 750 °C. The endothermic peak appeared at 800 °C in the DSC curve provides a symbol of the completion of the $BaTiO_3$ phase formation. This

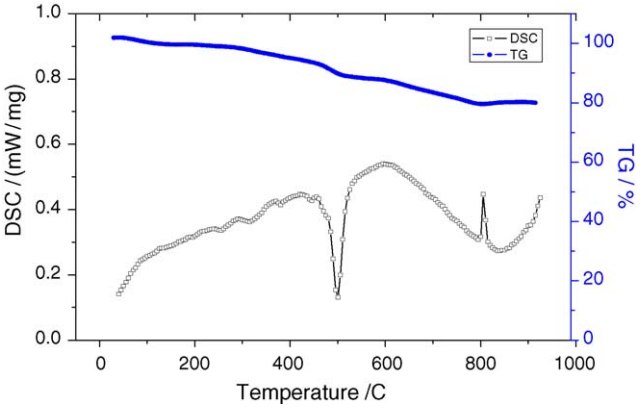

Fig. 3. TG and DSC curves of precipitate.

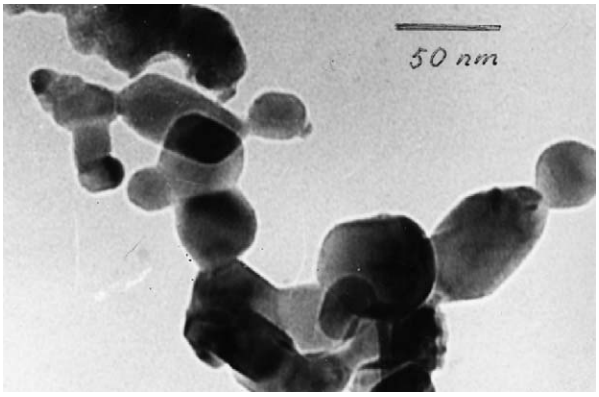

Fig. 4. TEM, 850 °C/2 h calcined.

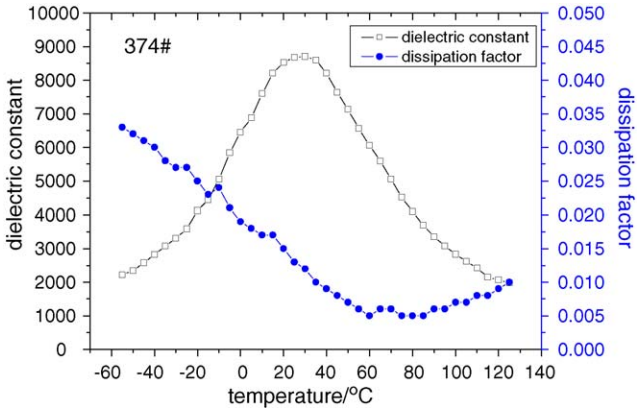

Fig. 6. Dielectric constant and dielectric loss versus temperature at 1 kHz.

temperature is about 200 °C lower than the temperature for mechanically milled powders. This is because the wet chemical method enables a sufficient homogeneous mixing between different components, benefiting atomic diffusion and the formation of $BaTiO_3$ as a new phase.

Substituting the values of 2θ and the width of half height of the strongest diffraction peak of XRD spectrum into Sherrer equation, the average particle diameter was obtained. It is 30 nm for the powder calcined at 850 °C for 2 h.

The XRD data of the ceramics of non-reducible $BaTiO_3$-based dielectric obtained after 1200 °C sintering show that the diffraction peaks become much sharper. It means upon the increase of temperature, the grain size in the samples has been increased.

3.2. Microstructure

A TEM photograph of the non-reducible $BaTiO_3$-based powder calcined at 850 °C for 2 h is shown in Fig. 4. The distribution of particle size is uniform and mainly situated in the vicinity of 50 nm. This result demonstrates that the chemical precipitation method offers advantage in a much smaller particle size, and therefore a lower sintering temperature.

Fig. 5 is a fracture morphology picture of a ceramic sample after 1200 °C sintering for 2 h. The measured grain size in the sample is about 3–4 μm, which is smaller than usually observed in similar samples with the same dielectric properties but made by solid state milling method. So, there is the possibility to obtain a finer grain size of ceramic from the nm-scaled powders and to lower the sintering temperature. The grains in Fig. 5 have a rather round shape, hence a lower density of the ceramic. A higher sintering temperature will lead to more dense material and improve the dielectric properties, but the grain size would increase rapidly at the same time [6].

3.3. Dielectric properties

The temperature dependence of the dielectric constant and dielectric loss at 1 kHz for the sample sintered at 1200 °C for 2 h are shown in Fig. 6. The dielectric constant of this sample is 8800 and the dielectric loss is 0.015 at room temperature. The shift of Curie temperature from about 120 °C to 30 °C shows a significant role played by the additives in these samples. The temperature coefficient of capacitance (TCC) of the non-reducible $BaTiO_3$-based

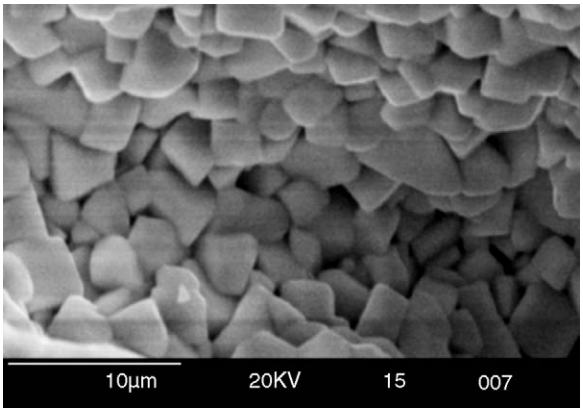

Fig. 5. SEM, 1200 °C/2 h sintered.

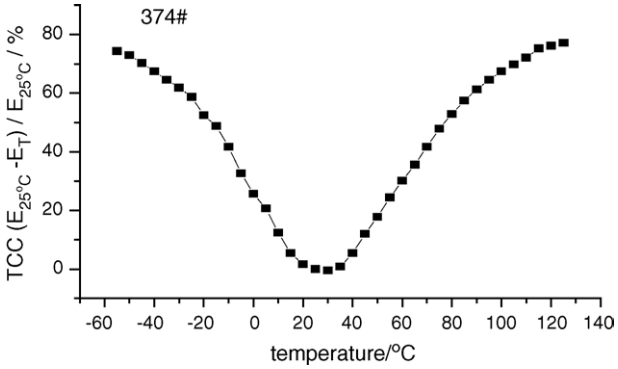

Fig. 7. TCC vs. temperature at 1 kHz.

samples calculated from the formula

$$\mathrm{TCC} = \frac{100(C_T - C_{25\,^\circ C})}{C_{25\,^\circ C}}$$

are ploted in Fig. 7. The TCC are less than (+22 to −82)% in the interval −30 °C to 80 °C, satisfy Y5V TCC specification of EIA standard of capacitors.

The insulate resistance of the samples measured by high resistance meter are higher than 10^{12} Ω cm.

4. Conclusions

Non-reducible $BaTiO_3$-based dielectric ceramics were obtained from powders with perovskite structure, which were about 50 nm in particle size and were synthesized with chemical method. These ceramics have low firing temperature (1200 °C), high dielectric constant (8800) and quite uniform microstructure with grain size of 3–4 μm. In addition, the temperature coefficients of capactiance fulfill Y5V specification of EIA standard. This study confirmed that the simple and low cost chemical route, namely coprecipitation in aqueous solution is an appropriate method for preparing high property nm-scaled dielectric materials applicable to Ni internal electrode multilayer capacitors.

Acknowledgements

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