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Barium titanate characterization by differential scanning calorimetry

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Abstract

Differential scanning calorimetry (DSC) was used to characterize barium titanate formed after decomposition of barium titanyl oxalate. Three different methods of the oxalate precipitation reaction were used to prepare barium titanyl oxalate which after calcinations result in barium titanates with different barium to titanium ratio (A/B). It appears that two factors have effect on Curie temperature: barium to titanium ratio and mechanical stress introduced by milling.

Keywords: $BaTiO_3$ and titanates; Ferroelectric properties; Capacitors

1. Introduction

Barium titanate is the most widely used dielectric material for applications in multi layer capacitors (MLC). The ferroelectric nature of barium titanate related to its tetragonal crystal structure results in a high dielectric constant that makes it attractive to use in MLC's. Above the so-called Curie temperature, the change in crystal structure from tetragonal to cubic, for pure barium titanate at about 130 °C, the dielectric constant drops down strongly.

The most common application of pure barium titanate in MLC's is in X7R capacitors. This means that by doping and tailored crystallite size the capacity of the device is stable within ± 15% from −55 to 125 °C. This stability is achieved by so-called core-shell structure, in which the size of the pure barium titanate core is responsible for the level of dielectric constant obtained and the high temperature behavior.[1] Important powder properties in this are crystallite size and lattice distortion, which can be expressed, in the so-called tetragonality. This is either defined as crystal axis ratio or simple peak ratios of the tetragonal barium titanate as measured by XRD. The Curie temperature is determined commonly by measuring the change in permittivity of sintered products.

Differential scanning calorimetry (DSC) opens the possibility to measure the energy of the tetragonal to cubic transition; it can give the amount of tetragonality as well as the Curie temperature on the as prepared powder. The influence of the barium to titanium ratio as well as the mechanical lattice distortion, introduced by milling, on the Curie temperature and tetragonality are shown. These results initiated the development of dielectric material for high temperature (>125 °C) application.

2. Experimental procedure

For the preparation of the precursor barium titanyl oxalate (BTO) three different oxalate precipitation methods have been followed:

A. Standard Clabaugh precipitation method at temperatures >50 °C by addition of a mixture of barium chloride and titanium oxychloride to oxalic acid. The barium titanate formed after calcination has a Ba/Ti = 0.996 as measured by XRF.
B. Formation of barium titanyl oxalate by adding barium carbonate to a mixture of titanium oxychloride and oxalic acid as described by Walter Symes.[2] Depending on washing conditions the A/B can be controlled between 0.996 and 1.001
C. Precipitation of barium titanyl oxalate in extreme high concentrations and low temperature. It was prepared by adding solid barium salts to a concentrated solution of oxalic acid in hydrous titanium tetrachloride.

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Table 1
Temperature curve Naber 60

Step	Temperature °C	Duration (min)
1	25–400	120
2	400	60
3	400–1050	120
4	1050	240
5	1050–25	120

The Ferro production site in Uden supplied BTO type A, R&D Ferro Penn Yan NY supplied BTO type B and the Ferro site in South Plainfield NJ supplied BTO type C. The barium titanyl oxalates are calcined in a Naber 60 box kiln. Table 1 shows the applied curve.

The first characterization of the calcined samples was on Curie temperature with use of DSC measurements. The heat of transition of the tetragonal to cubic transition was measured with use of a Netzsch Jupiter 449 (Netzsch-Gerätebau GmbH, Wittselbacherstrasse 42, D-95100 Selb Bavaria) TGA-DSC analyzer. The DSC measurement was performed with a ramp of 10 K/min from 25 to 200 °C in a gas flow of 30-ml/min air. A DSC(/TG) HIGH RG4 sample carrier was used and closed platinum crucibles of type DSC/TG pan Pt–Rh. As reference one crucible was filled with aluminum oxide. After the measurement was completed the result was analyzed with Netzsch Proteus software.

To compare tetragonal properties of barium titanate samples and XRD date have been provided by Dr. Joe Capurso, R&D group Ferro Electronic Materials Systems in Penn Yan NY.

XRD was measured with a Philips 3020 Diffractometer with an 1830 Generator and a 3710 MPD Control. It was run at 35 kV, 35 mA. The scan is from 44.00 to 46.50 degrees 2-theta, with 0.01 degree step size and 5 s dwell per step.

For the XRF sample preparation $BaTiO_3$ was dissolved in a lithium borate flux, with subsequent formation of clear disks for XRF measurement. The XRF equipment used was a PAnalytical PW2400 sequential spectrometer.

To investigate the effect of milling on the transition energy and temperature barium titanate type B was milled with 5 mm Yttrium stabilized zirconia balls in a ball mill.

Some of the milled powder are processed to discs and sintered at 1300 °C. After sintering the discs are metallized and the permittivity was measured.

3. Results and discussion

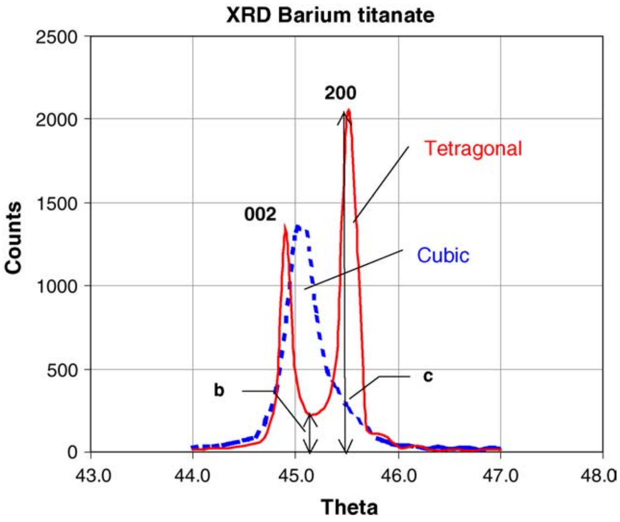

Fig. 1. Example of XRD curves tetragonal and cubic barium titanate.

One of the difficulties in quantification the tetragonality of barium titanate is the interpretation of the XRD measurement of 200 and 002 peaks. Theoretically 100% tetragonal barium titanate has two separate peaks between theta 44° and 47° (Fig. 1). Complete cubic barium titanate shows just one peak. A mixture of tetragonal and cubic barium titanate will show all intermediate forms between one and two peaks. There are different ways to express the tetragonality most of them comparing the relative peak height of the 002 and 200 peak. To compare the DSC measurement with XRD the ratio between minimum between two peaks (*b*) and maximum (*c*) was used. Fig. 2 shows for different types of barium titanate the relation between XRD (*b*/*c*) and heat of transition ($\Delta H_{t\rightarrow c}$). The tested samples barium titanate are made by: standard solid state reaction between barium carbonate and titanium dioxide (SSBT), standard Clabaugh oxalate precipitation (Oxalate), reaction between titanium isobutoxide and barium hydroxide at temperature <100 °C (Alkoxide) and reaction of unknown barium and titanium precursors followed by calcination (sol–gel). Most of the barium titanate powders are commercially available. As expected the heat of transition as measured with DSC is related to the tetragonality. However for highly agglomerated materials as barium titanate formed from standard Clabaugh formed oxalate (type A) the transition energy is higher than expected. This observation is consistent to the results of Li et al.[3]

It was observed that it is possible to use the heat of transition as a measure for the percentage of tetragonal barium titanate.

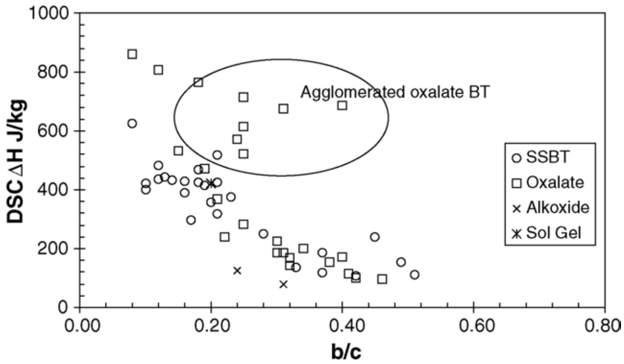

Fig. 2. Relation tetragonality expressed as *b*/*c* ratio compared to heat of transition tetragonal to cubic barium titanate.

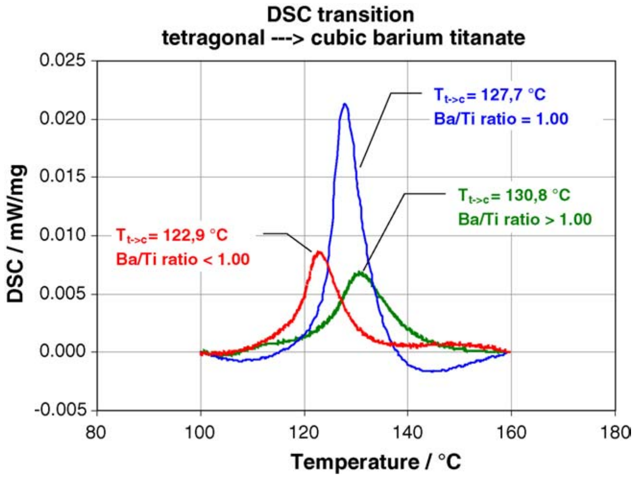

Fig. 3. Effect of *A*/*B* on Curie temperature for type C barium titanate.

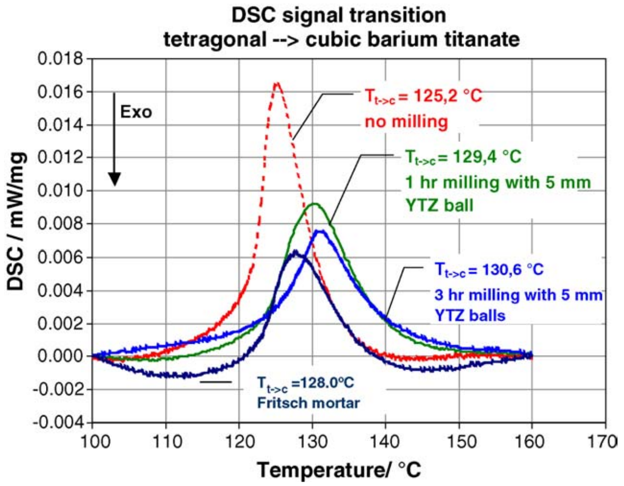

Fig. 5. Effect of milling on Curie temperature.

Within the scope of developing a new dielectric material for high temperature applications it was decided to look inside the group of oxalate barium titanate for one with a Curie temperature greater than 130 °C. Initially there was some indication that the Curie temperature and tetragonality was related to the barium to titanium ratio (*A*/*B*). Some samples from type C indicate that there is a relation between *A*/*B* and Curie temperature with a maximum at *A*/*B* >1 (Fig. 3). This is in agreement with DS Filimonov (CDS). The DSC measurement of the Curie temperature was confirmed by measuring the Curie temperature of sintered pure barium titanate. After milling with 2 mm yttrium stabilized zirconia balls to a mean particle size of 0.7 μm the barium titanated was processed to discs and the capacity change as function of the temperature was measured (Fig. 4). The measured Curietemperature difference of the fired ceramics does not differs significantly from the data obtained by DSC on the respective powders.

The increase of the Curie temperature of just 5 degrees gave the possibility to start the development of a X8R material.[5]

It was already found that milling has an influence on tetragonality as measured with XRD, but so far we did not know the influence of milling on Curie temperature. It was found that mechanical distortion of the barium titanate agglomerates has two effects: decrease of tetragonality and increase of the Curie temperature. Fig. 5 shows the effect of desagglomeration in a Fritsch agate mortar and milling with 5 mm balls.

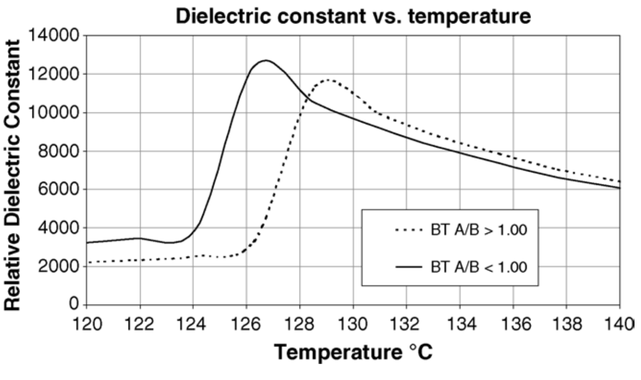

Fig. 4. Dielectric constant change discs with BME X7R formulation.

4. Conclusion

Heat of transition measurement is a very useful tool for the characterization of barium titanate. It opens the possibility to measure not only the tetragonality but also the transition temperature. The measurement is fast (measuring time 20 min) and simple. It makes it also possible to measure the transition temperature on conducting samples as shown by Kishi et al.[6]

We did see the influence of mechanical energy on both tetragonality and Curie temperature. The influence of milling on the tetragonality was noticed earlier but the effect on Curie temperature was not seen before.

It opens the possibility to start the development of a new dielectric material for high temperature (>125 °C) applications.

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References

1. Liu, X., Cheng, S. and Randall, C. A., The core-shell structure in ultrafine X7R dielectric ceramics. *J. Korean Phys. Soc.* Febrary 1998, **32**, S312–S315.

2. Symes, W. J and Wilson, J., *Method of Making Barium Titanate*. US patent 5783165,21-7-1998.
3. Li, X. and Shih, W., Size effect in barium titanate particles and clusters. *J. Am. Ceram. Soc.* 1997 **80**(11), 2844–2852.
5. Koebrugge, G., Albertsen, K., Coppens, W. and Derks, W., *BME X8R for automotive applications*. at ISIEM 2004.
6. Kishi, H. C., Base metal electrode multilayer ceramic capacitors; past, present and future perspectives, *Jpn. J. Appl. Phys.* 2003 **42**, 1–15.