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Short communication

Enhanced microwave-assisted sintering of X7R ceramic dielectrics for use in multilayer capacitors

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Abstract

A hybrid furnace, allowing the simultaneous application of microwave (2.45 GHz) and radiant energy, has been used to investigate the sintering of a commercial X7R powder commonly used in multilayer capacitors. Samples were processed at temperatures in the range 1060–1120 °C. Enhanced sintering has been observed in the form of accelerated densification when a microwave field is applied. At 1090 °C for example, 99.4% dense material was obtained by microwave-assisted heating but only 96.9% density was reached by conventional heating. The relative permittivity of the microwave sintered material was ~2200, typically 10%, higher than for conventionally sintering. The Curie temperature was lower by 5 °C in the microwave heated samples.

Keywords: A. Microwave processing; E. Capacitor; $BaTiO_3$; Dielectric

1. Introduction

1.1. Microwave-enhanced sintering of ceramics

Microwave heating offers greater flexibility than conventional heating in the thermal treatment of materials. Depositing energy in the centre of the material enables rapid heating with the generation of uniform temperature profiles, offering fine grained/uniform microstructures, faster production rates, and high controllability. The microwave heating of materials has been reviewed by a number of authors including Clark and Sutton [1] and Binner and Vaidhyanathan [2]. There is evidence to suggest that the interaction of microwaves with some materials gives rise to effects not explained by the simple thermal evolution of the material. These athermal microwave effects include the reduction in the required processing temperature, an increase in the processing rate or an improvement in the material properties [3–5].

The development of microwave heating techniques brought exciting opportunities for the processing of ceramics. Over a decade ago, Wroe and Rowley [4] used a microwave-assisted furnace to monitor the sintering of partially stabilised zirconia. They demonstrated that the sintering temperature was reduced by approximately 80–100 °C. Other authors [5–8] have reported that microwave sintering leads to microstructural enhancement, such as reduced or more uniform grain size. Bokhan et al. [5] noted that barium titanate ceramic sintered using microwaves had grain sizes approximately half the size of those in samples sintered by conventional means. Research into athermal effects has been reviewed by several authors [9–11]. Recently, Binner et al. [12–14] provided convincing evidence for the existence of a microwave effect in a variety of materials.

1.2. Microwave-assisted (hybrid) heating

Despite the advantages of microwave processing, there exists the potential problem that large thermal gradients may develop during heating, and the resulting stresses may lead to cracking or weakening of the material. Such temperature gradient problems can be overcome by maintaining the environment temperature at that of the sample through the simultaneous application of microwave and conventional heating. This is the basis of microwave-assisted heating, which was which pioneered at EA Technology [15] and has led to the

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development of several hybrid furnaces combining microwave heating and electrical resistance or gas heating.

1.3. Microwave-assisted sintering of electronic ceramics

A number of workers have investigated the sintering of barium titanate based ceramics in a microwave field [16–23]. Humphrey and Anderson [16] were amongst the first groups to employ microwave processing. Cherradi et al. [17] sintered $BaTiO_3$ by microwaves with the aid of LiF sintering aid. Derling and Abicht [18] indicated that microwave sintering of barium titanate doped with Cu leads to accelerated shrinkage, and that the average grain size could be controlled by the heating rate, whilst Bai and Kim [19] sintered $BaTiO_3$ thick films. Thakur et al. [20] were able to sinter $BaTiO_3$ at 1450 °C in 25 min compared to 4 h by radiant heating. Yasuoka et al. [21] demonstrated the benefit of a liquid phase in the microwave enhanced sintering of $BaTiO_3$. Takahashi et al. [22] showed that reducing the domain size in microwave sintered $BaTiO_3$ enhanced the piezoelectric d_{33} coefficient. In $BaTiO_3$ prepared with zirconium ($BaZr_{0.1}Ti_{0.9}O_3$) high density, fine grain ceramics can be produced by microwave sintering in a quarter of the time by conventional sintering [23]. Whilst the diffusion of Zr appears to enhance processing, it may also be responsible for the degradation of electrical properties at high temperature [23]. The present study focuses on the use of microwave-assisted technology to sinter a typical commercial X7R dielectric powder intended for multilayer capacitor applications.

2. Experimental procedure

2.1. Furnace design

The hybrid furnace used in this study allows the simultaneous application of microwave and conventional heat; each source can be independently controlled. The furnace is shown schematically in Fig. 1. The microwave component consists of a multimode 2.45 GHz cavity powdered by a 1.2 kW magnetron. The conventional component consists of six electrical radiant heating elements (total 6 kW). The platinum/rhodium thermocouples are encased in metal sheathes and designed such that they do not interact with the microwave field. One thermocouple was used to monitor the ambient temperature of the furnace. Another thermocouple was placed approximately 5 mm from the sample surface and monitored the temperature of the ceramic sample being processed. The thermocouples were linked to two Eurotherm 818P controllers.

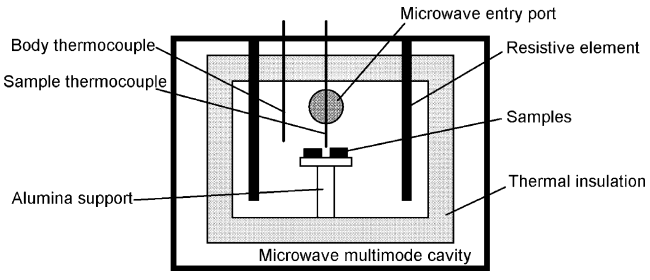

Fig. 1. Microwave-assisted furnace used for sintering experiments.

2.2. Sample preparation

The samples used in this study were prepared from a commercial barium titanate based powder supplied by the Ferro Corporation. The powder conformed to the X7R EIA specification [24] for capacitor dielectrics (maximum of ±15% variation in relative permittivity between −55 °C and +125 °C), and had an average particle size of 1.1 μm. With conventional processing conditions it is usually sintered at temperatures of 1090–1100 °C for 3 h, yielding a room temperature relative permittivity of ∼2200. The as-received powder was first wet milled with propan-2-ol, and then with a small amount of polyethylene glycol (PEG) binder. The resulting powder was dried, crushed and sieved. Disc shaped pellets, approximately 4.5 mm thick and 13 mm in diameter were prepared by uniaxially pressing the powder in a hardened steel die using a pressure of 130 MPa. The resulting pellets had a relative density of approximately 50–55%.

2.3. Sintering experiments

Pairs of X7R samples were sintered on an alumina support in the centre of the furnace. In each experiment, the sample temperature was controlled by the radiant heating elements and the microwave power was kept constant. The sintering temperatures were 1060 °C, 1080 °C, 1090 °C, 1100 °C and 1120 °C; the heating and cooling rates were 400 °C/h, with samples held at the peak temperature for 90 min. For each sintering temperature, one run was performed using conventional heating only, and a second run performed using both conventional heating and a nominal 600 W of microwave power. For each pair of runs the thermal cycles were identical. A further set of experiments was performed to investigate the effect of the applied microwave power (200–800 W) on the sintering of X7R samples. The hold temperature was 1080 °C in this series of experiments.

2.4. Specimen characterisation

For microstructural analysis the specimens were ground on 1200 grade SiC, then polished down to 0.25 μm diamond paste, followed by OPS (colloidal silica suspension), and examined using a Philips XL30 FEG scanning electron microscope. The densities of the sintered samples were determined by the Archimedes method, involving immersion in deionised water. Electrical characterisation focussed on relative permittivity as a function of temperature. A Hewlett Packard 4284A Impedance Analyser was used to determine the capacitance and resistance from 30 to 150 °C as a function of frequency (1 kHz, 10 kHz, 100 kHz).

3. Results and discussion

Fig. 2 shows sample densities as a function of sintering temperature. The presence of Bi and Nb in the X7R powder

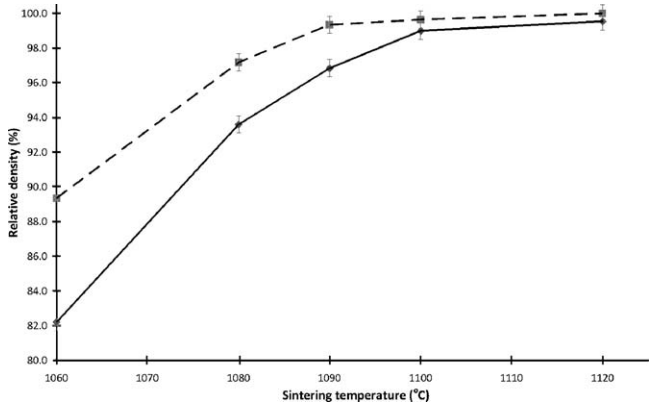

Fig. 2. Density of X7R specimens as a function of temperature after conventional sintering (solid line) and microwave-assisted sintering (broken line).

enables effective sintering in the vicinity of 1090 °C. The enhancement of densification by microwave-assisted sintering is clearly demonstrated, particularly at the lower sintering temperatures. At the highest sintering temperatures both sets of data approach 100% relative density. When a sintering temperature of 1090 °C was used, the conventionally processed samples reached a density of 96.9%. However, by microwave-assisted sintering a relative density of 99.4% was achieved. In general, microwave-assisted sintering lowered the effective sintering temperature by al least 20 °C. A further benefit is that by the use of microwave-assisted techniques the sintering time to achieve full density has been reduced by approximately 50%; instead of the expected 3 h, 90 min is adequate.

Microstructural analysis showed the grain size was typically 1–2 μm, with no significant different between specimens produced by conventional or microwave-assisted heating. All samples exhibited core-shell structures. Earlier TEM studies of a range of X7R dielectrics confirmed that the cores are essentially pure $BaTiO_3$, containing ferroelectric domains, whilst the dopant species are concentrated in the rims [25].

The effect of applied microwave power for sintering at 1080 °C is shown in Fig. 3. It is evident that specimen density scales linearly with applied microwave power. In reality, power levels greater than 800 W will not be any more advantageous in terms of enhanced densification than the use of 800 W

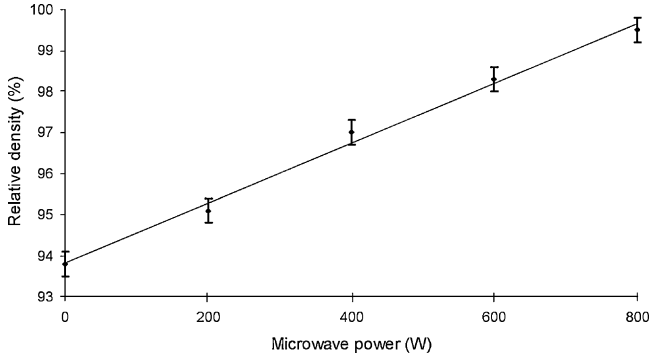

Fig. 3. Density of X7R specimens sintered at 1080 °C as a function of applied microwave power.

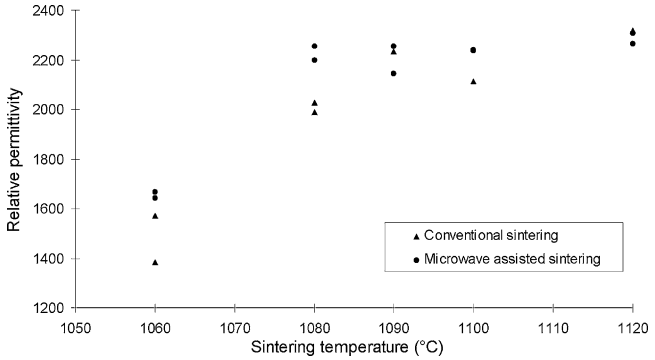

Fig. 4. Room temperature relative permittivity (at 1 kHz) of X7R specimens sintered by conventional and microwave-assisted techniques.

microwave power. The small size of the specimens in comparison to the furnace body, precludes accurate determination the of microwave energy dissipated by the sample under different sintering conditions.

The room temperature relative permittivities of the sintered specimens are shown in Fig. 4. For temperatures of 1080 °C and above, the ceramics reach the anticipated relative permittivity of ∼2200. In the majority of cases, particularly for temperatures up to 1100 °C the enhancement of the room temperature relative permittivity by typically 10% is quite clear. In contrast for samples sintered at 1120 °C, both the microwave-assisted and conventionally processed samples exhibited very similar relative permittivities, because all the samples were close to 100% dense.

The temperature dependence of the relative permittivity for microwave assisted and conventional processing at 1080 °C is shown in Fig. 5. Both samples conform to X7R specification with less than 15% variation in relative permittivity in the temperature range up to 125 °C. The enhancement in the relative permittivity of the sample sintered with microwave assistance is consistent through the range up to the Curie temperature. In fact the Curie temperature in the microwave processed sample has been reduced by approximately 5 °C. Following the earlier work on microwave sintering of undoped $BaTiO_3$ [22] and the liquid phase sintering of $BaTiO_3$ [21] the most important finding of the present work is that microwave-assisted sintering yields superior electrical properties at lower

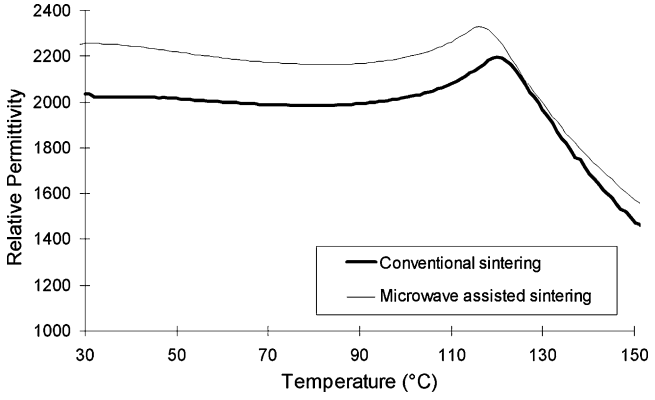

Fig. 5. Temperature dependence of the relative permittivity for X7R samples sintered at 1080 °C by conventional and microwave-assisted techniques.

temperatures and indeed in shorter processing times for the X7R type ceramics. There is clearly some form of athermal effect [11–13] in achieving such enhancement, but we have demonstrated the benefit of microwave-assisted techniques for processing low temperature, $BaTiO_3$-based ceramics intended for use in multilayer capacitors. Preliminary experiments on the sintering of X7R-type multilayer ceramic chips, containing standard 30%Pt/70%Al internal electrodes have been very encouraging. There is every reason to believe that such chips can be mass produced by microwave-assisted techniques. To utilise lower temperatures and base metal electrodes requires controlled atmosphere sintering [26].

4. Conclusions

The microwave-assisted sintering of X7R formulation dielectrics provided significant benefits over conventional radiant sintering techniques. At 1090 °C, microwave-assisted heating yielded 99.4% dense material whilst conventionally fired specimens were only 96.9% dense. Microwave-assisted sintering enables a reduction in processing temperature by typically 20 °C. In addition, the enhancement in densification is accompanied by an enhancement in the relative permittivity. Microwave-assisted samples exhibited relative permittivities of ∼2200, typically 10% higher than for samples conventionally processed samples; in addition the Curie temperature was lower by 5 °C in the microwave heated samples.

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