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Zirconium Titanate Microwave Dielectrics Prepared via Polymeric Precursor Route

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Abstract

Zirconium titanate based materials are widely used as dielectric resonators in telecommunications. The performance of the devices depends on compositional and microstructural features. The polymeric precursor route enables the preparation of fine zirconium titanate powders at low processing temperatures. $ZrTiO_4$ *powders containing different amount of Hf (0·5% and 40 ppm) were prepared and sintered without additives at 1600°C. The resulting materials were single-phase and had densities 96–98% theoretical. The dielectric* Q *value at 5 GHz was 5640 and the relative permittivity 36. The presence of Hf does not significantly affect the microwave dielectric response. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

Zirconium titanate-based thin films are highly promising for large scale integration applications. Interest in these materials has grown because of their high resistivity and high dielectric constant which provides a high charge storage capacity. Moreover, the excellent temperature stability of microwave properties makes these materials particularly suitable for producing dielectric resonators in telecommunication systems.[1–3] Several different advanced applications have recently been proposed for these materials: as refractory and electronic fibres,[4] as a matrix in composites for high temperature corrosive environments,[5] as a refractory oxide in RAINBOW actuator materials.[6]

In this paper results are presented for the production and the microwave dielectric property of dense zirconium titanate bodies. Preparation was achieved without sintering additives by means of a polymeric precursor methodology (previously reported[7]) based on the Pechini process.[8] The presence of sintering additives seriously degrades the dielectric properties of the material, due to the formation of second phases at grain boundaries.[9] The quality factors of the ceramics are dramatically reduced when yttria is present.[10,11] The damaging effect of trivalent ions is well known and it is thought to be due to the diffusion of such +3 cations into the primary grains.[12,13]

Although our actual approach to the chemical process concerns the production of ceramics in bulk form, the method is also applicable for the preparation of thin films by deposition of the polymeric precursors. Compared to the conventional sol–gel routes,[14] the production of thin films via polymeric precursors is particularly attractive because it does not requires controlled atmosphere during preparation or deposition.

2 Experimental

Zirconium titanate oxide powders of atomic composition (Zr/Ti) close to 1/1 were obtained by thermal decomposition of polymeric precursors.

The starting materials were titanium (IV) butoxide ($Ti(OBut)_4$, Aldrich 99%) and zirconium oxychloride octahydrate. In order to define the role of Hf on the microwave dielectric properties, two $ZrOCl_2{\cdot}8H_2O$ compounds were used (Aldrich, 98%, 0·5% Hf) and (Aldrich, 99·9%, 40 ppm Hf).

Details of the preparation process are reported elsewhere.[7]

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The crystallisation process of the amorphous powder was monitored by high temperature XRD; specimens were prepared by pressing 0·5 g of powder in a 20 mm die. Spectra were collected in the 2θ range 20–45 at 500, 600, 650, 670, 690 and 720°C; samples were finally air cooled to room temperature.

Complementary differential thermal analysis was performed (Pt crucible, sample weight 60 mg) using the following condition: heating rate 10°C/min, peak temperature 1200°C, air flow 80 cc min^{-1}.

After calcining the precursor at 1200°C (heating rate 120°C/h^{-1}, furnace cooling to room temperature), batches of approximately 1·5 g of each powder were gently ground in a mortar and then uniaxially pressed into pellets (12 mm diameter) at 100 MPa. Green bodies were then sintered on Pt foil at 1600°C for 4 h in static air (heating and cooling rate 300°C h^{-1}).

The densities of sintered materials were measured using a He pycnometer. Microstructures of the as-sintered samples were studied by optical and scanning electron microscope. Compositional analyses were determined by energy dispersive spectroscopy.

XRD measurements were performed on dense bodies, spectra were collected in the range $2\theta =$ 20–80°.

Microwave dielectric measurements were performed on disks of 11 mm diameter and 4 mm thickness. The measurements were carried out at room temperature with a network analyser and a sweep oscillator. The permittivity of the samples was measured by placing them between two large polished copper plates (Hakki and Coleman method[15]). For dielectric losses, samples was supported onto a quartz disk in the middle of a circular copper cavity such that its diameter and length were at least 3–4 times the diameter and length of the samples. The system was previously calibrated using standard specimens. Relative permittivity and dielectric loss were calculated from the resonant frequency and peak width of the TE_{011} resonant mode.[16]

3 Results and Discussion

3.1 Crystallisation

Differential Thermal Analysis (DTA) of the amorphous powders at 500–1200°C revealed, on heating, only one sharp exothermic peak around 700°C. Figure 1 shows the 650–750°C region of the DTA spectrum, and the single peak.

High temperature XRD measurements provided information on the kinetics of the crystallisation of the amorphous oxide powders (Fig. 2). Below 650°C the sample was amorphous, but the main reflections of the zirconium titanate phase[17] were clearly visible above 670°C. The XRD spectra

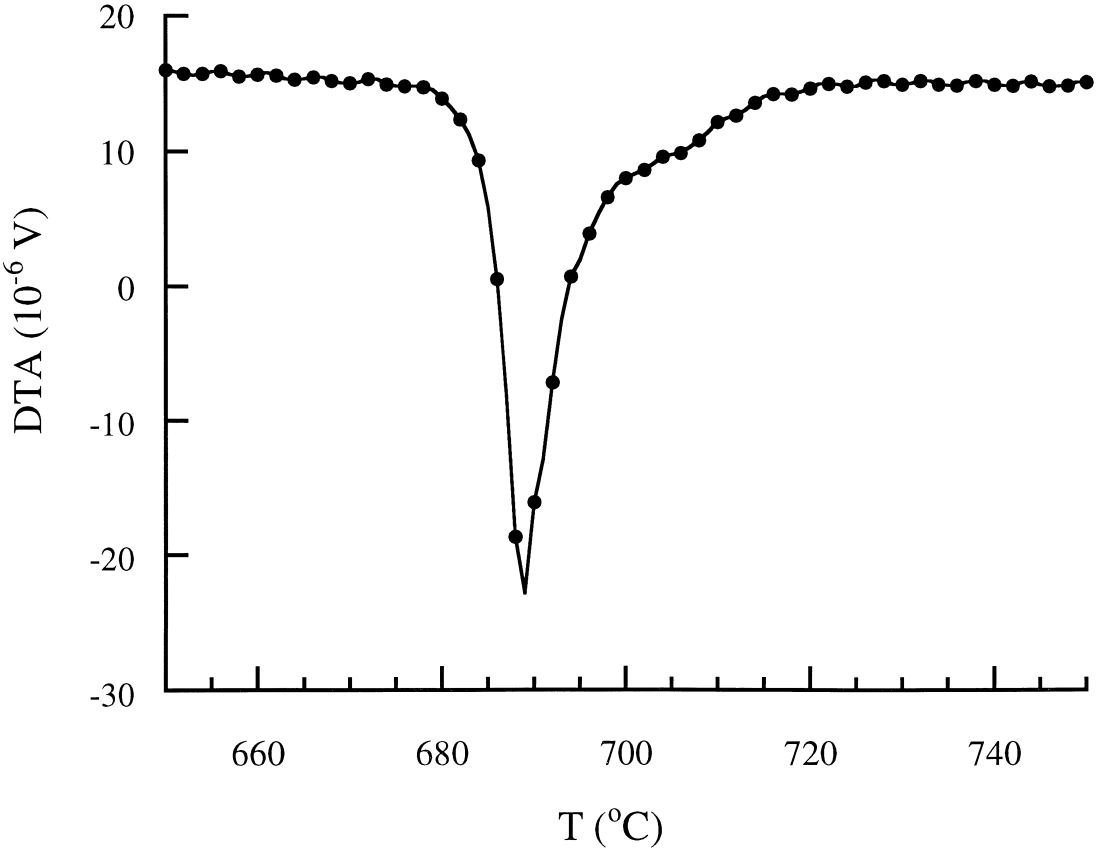

Fig. 1. DTA spectrum obtained on heating the amorphous powder in the region 650–750°C.

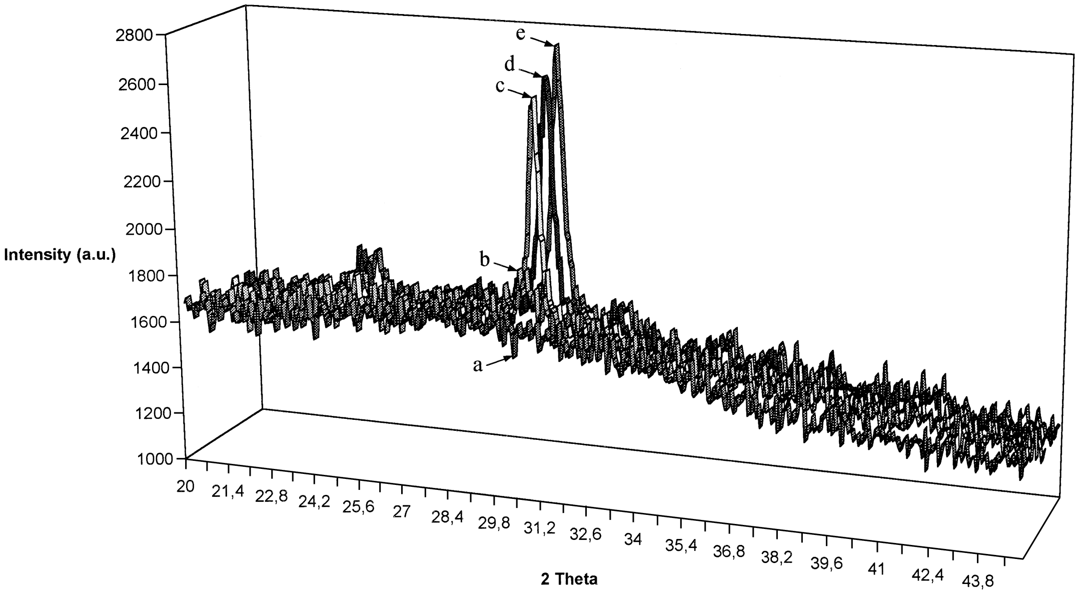

Fig. 2. High temperature XRD spectra for precursor powder collected at (a) 600°C; (b) 650°C; (c) 670°C, (d) 690°C and (e) 720°C.

collected after air cooling to room temperature (e.g. Fig. 3), show that the powder which had been heated to 720°C, was single-phase $ZrTiO_4$ (orthorombic, P*bcn* 60, disordered form) (JCPDS 34-415). In a recent phase diagram of the system TiO_2–ZrO_2,[18] it was indicated for Zr/Ti = 1:1, that both baddeleyite and zirconium titanate solid solution are expected at room temperature. We checked for the presence of the monoclinic form of zirconia (JCPDS 37-1484) but none was detected (Fig. 3). This confirms the interpretation of previous investigators concerning the crystallisation at low temperature of the metastable, high-temperature form of zirconium titanate. The former only occurs for such chemically prepared powders; the single phase field being much wider (35–75% mol TiO_2) than the equilibrium region at high temperature.[19]

Furthermore, the presence of different amounts of Hf in the precursors (0.5% and 40 ppm) does not seem to significantly affect the crystallisation process of the material.

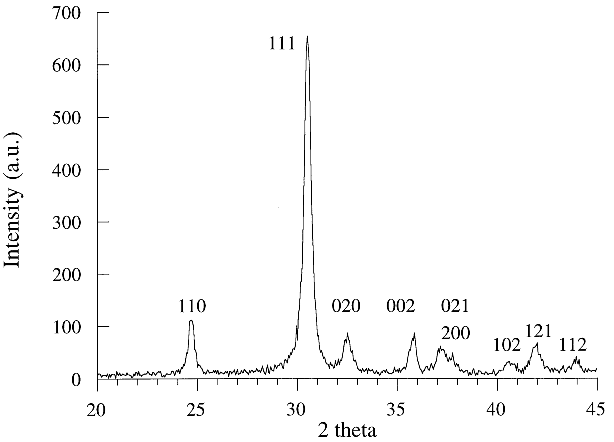

Fig. 3. Room temperature XRD spectrum for $ZrTiO_4$ powder after heating to 720°C and air cooling to room temperature.

3.2 Densification and microstructures

The two polymeric precursors were calcinated at 1200°C and furnace cooled to room temperature. The cooling rate across the temperature range of the order-disordered transition (1100–1190°C)[20] was $13°C\,min^{-1}$. XRD spectra of the powders were comparable with those obtained at low temperatures (Fig. 3); thereby confirming low temperature phase formation. Further results on phase development in zirconium titanate are presented elsewhere.[7]

Powders were pressed to form green bodies of 65% theoretical; after sintering dense bodies of 96–98% theoretical were obtained. The surface and the interiors of all the specimens were uniformly pale yellow. The absence of dark zones indicated that no reduction of the material (with formation of electronic defects) had occurred.

Microstructural analysis revealed that the grain size of the samples ranged from 10 and 20 μm. A typical microstructure of an as-sintered sample is shown in Fig. 4. SEM micrographs of as-sintered samples showed few pores at grain boundaries or triple points; craks or microcraks were not observed (Fig. 5).

EDS analysis showed that sample compositions were homogeneous with no distinction between the grains and the grain boundaries, and no evidence of segregation of the main components (Ti or Zr) or the primary impurity (Hf).

The XRD spectra of the sintered pellets were indexed against the α-PbO_2 polytype of $ZrTiO_4$ (JCPDS 34-415). Except for line broadening the spectra are not significantly different from those of the corresponding powders calcined at 1200°C and furnace cooled. Interpretation of such spectra have been discussed elsewhere.[7]

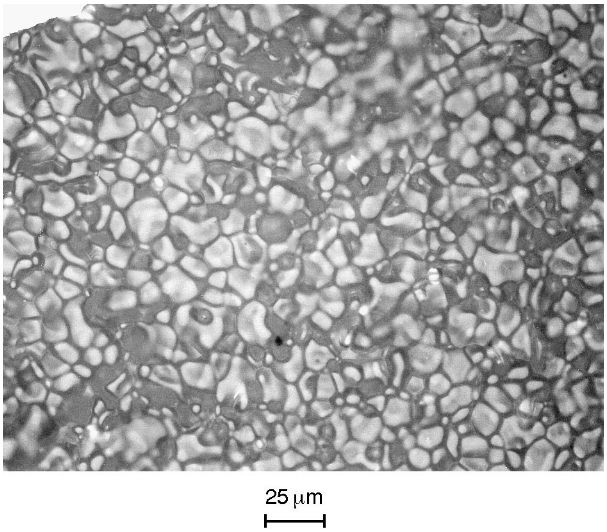

Fig. 4. Optical micrograph of $ZrTiO_4$ as-sintered pellet.

3.3 Microwave dielectric properties

The samples show good dielectric properties (Q, ε_r) at microwave frequencies (Table 1). Dielectric data are also given in terms of the frequency independent parameter $Q \times f_0$, which is used as a *figure of merit* for the comparison of loss properties.

The $Q \times f_0$ values for $ZrTiO_4$ are in excellent agreement with data reported for $ZrTiO_4$ ceramics prepared via different chemical routes by Hirano *et al.*[21] and Christoffersen *et al.*[22] To our knowledge, the present data are the first results for the microwave dielectric properties of dense $ZrTiO_4$ bodies prepared by polymeric precursor method. This processing route is thus a good alternative and yields material with excellent functional properties. The results (Table 1) showed that the presence of small amounts of Hf, dissolved in the zirconium titanate solid solution, did not cause any detectable variation of the microwave dielectric response of the material. Moreover, it shows the potential of producing samples with reproducible functional characteristics.

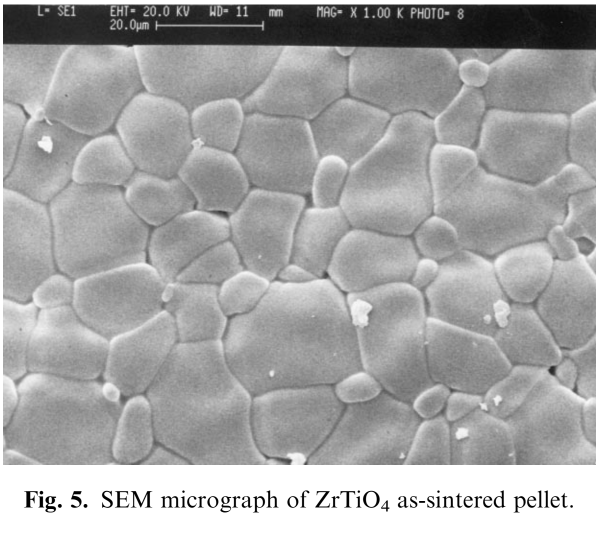

Fig. 5. SEM micrograph of $ZrTiO_4$ as-sintered pellet.

Table 1. Relative permittivity (ε_r) and dielectric quality factor (Q) of additive-free $ZrTiO_4$ ceramics at microwave frequencies

Hf[a]	f_0 *(GHz)*	Q	Q×f_0	ε_r
0·5%	5.267	5640	29 705	36
40 ppm	4·950	6000	29 700	35

[a] Amount in the Zr precursor.

Since the dielectric Q value is particularly sensitive to cation ordering and compositional homogeneity the result in Table 1 in terms of $Q \times f_0$ suggest also that: (i) different amounts of Hf do not influence the kinetics of ordering and (ii) the material is homogeneous (this is in agreement with the microanalysis results noted above). Since the ε_r values depend on several factors (including second phases, cation ordering, density and grain size) comparison with literature data is not easy. However, published ε_r data for zirconium titanate ceramics at 2–10 GHz range predominantly from 35 to 46.[21–23]

4 Conclusions

The kinetics of crystallisation of amorphous zirconium titanate oxide powder prepared via polymeric precursors was followed by high temperature XRD. Complete crystallisation was achieved by 700°C. Samples were single-phase zirconium titanate (orthorhombic, α-PbO_2 polytype).

Powders were calcined, pressed and sintered without additives at 1600°C (heating and cooling rate $300°C\,h^{-1}$). Densities were approximately 96–98% theoretical. Dense bodies showed good microwave dielectric properties (Q, ε_r) in excellent agreement with data reported for other chemically processed materials. Finally, the presence of Hf did not cause any detectable degradation of the microwave dielectric properties of the ceramics.

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