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Aqueous synthesis and sintering of zirconium titanate powders for microwave components

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Abstract

Zirconium titanate (ZT–$ZrTiO_4$) is a well-known ferroelectric material commonly used as a dielectric in microwave devices due to its high permittivity at microwave frequencies. Reactive precursors of ZT in form of nanopowders have been prepared in a very simple way by hydrolysis of an aqueous solution of $TiCl_4$ and $ZrOCl_2$ using ammonia. ZT single-phase powder has been obtained by high temperature reaction during calcination at 1200°C. α-PbO_2-type structure was stabilised by air quenching to room temperature. Sinterability was investigated by constant heating-rate and isothermal sintering. High-density ceramics were obtained by firing performed at different temperatures and prototypes of substrates for microwave devices were prepared.

Keywords: $BaTiO_3$ and titanates; Dielectric properties; Powder-chemical preparation; Substrates

1. Introduction

Zirconium Titanate (ZT–$ZrTiO_4$) is commonly used as a dielectric in microwave devices due to its high permittivity at microwave frequencies.[1–4]

The traditional preparation of ZT ceramics is based on the solid-state reaction between TiO_2 and ZrO_2 powders at high temperatures. In order to improve the functional properties of the ceramics, expensive and energy consuming post-reaction treatments are generally needed. Chemical methods based on the coprecipitation of reactive precursors were developed to prepare high purity powders and to lower the cost of the post-reaction treatments. The main features of the preparation methods of ZT powders were described by Navio et al.[5] Controlled hydrolysis of alkoxides[3] and sol–gel syntheses[6–8] were investigated to obtain fine particles.

In the present work reactive precursors of ZT have been prepared in a simple way by controlled hydrolysis by ammonia of an aqueous solution of $TiCl_4$ and $ZrOCl_2$. ZT single-phase powder has been obtained by solid state reaction during calcination.

Sinterability has been investigated by high-temperature dilatometry. Prototypes of substrates for microwave applications of the required grain size were prepared.

2. Experimental

An aqueous solution containing Ti(IV) and Zr(IV) in the ratio 1:1, corresponding to 0.1 mol l^{-1} of ZT, was prepared by addition of the required amount of $ZrOCl_2$ (Strem Chemicals, hydrate form, 27.15 wt.% Zr) to a $TiCl_4$ (Acros — 99.9%) solution and stabilised by 140 ml l^{-1} of fuming HCl. Coprecipitation of hydroxo-polymers of Ti and Zr was performed at 20°C under stirring at 120 rpm into a pyrex batch reactor by dropping the Ti–Zr solution at the rate of 0.3 ml/s in an excess of ammonia solution (Fluka, 25%). In order to eliminate ammonia, the precipitate was washed[9] by dis-

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tilled water in the ratio of 50 ml per 1 g of precipitate. The last two washing treatments were carried out by a high-speed turbine mixer (IKA Ultraturrax 50, S50TT-W40TT tool, 2′ at 6000 rpm) to improve the effectiveness of washing. Water was removed by vacuum filtration on a black-ribbon filtering paper.

Residual water and chloride ions were removed by a specific washing in the conditions described above using a 0.2 M solution of butylamine (Aldrich 99.5%) in ethanol (Fluka, absolute 99.8%, denaturated with 4.8% isopropanol). Two further ethanol washing treatments were performed. The precipitate was then dried at 80°C, sieved at 80 mesh and calcined.

During calcination at 1200°C for 4 h (heating rate 5°C min^{-1}), solid-state reaction leading to formation of ZT takes place. Air quenching allows the stabilisation at room temperature of ZT phase characterised by α-PbO_2 type structure.[10,11] On the contrary, if cooled down at slow cooling rates, ZT phase decomposes in the range 1100–1150°C leading to formation of ZrO_2 and $ZrTi_2O_6$, the stable phase at low-temperature.[11]

3. Results and discussion

The powder of reactive precursors was characterised by very high specific surface areas (Micromeritics ASAP 2010, 370±20 m^2 g^{-1}), corresponding to spherical particles with diameter of 3.2 nm. At SEM investigation (Philips 515) agglomerates of nanoparticles were observed. The high value obtained can also be explained by mesoporosity inside particles due to water elimination during drying.

After calcination at 1200°C, powder morphology was characterised by round particles of size ranging from 200 to 500 nm. As shown in Fig. 1, diffuse necking phenomena among the particles are present. Accordingly, specific surface area of about 3 m^2 g^{-1} was measured.

Single-phase orthorombic $ZrTiO_4$ (Card 34-0415 PDF, S.G. Pnab n.60) was identified by XRD. Powder pattern reported in Fig. 2 (lattice parameters: a= 0.5035, b=0.5487 and c= 0.4801 nm) was collected by a Philips PW1710 diffractometer.

High-temperature behaviour was investigated on green ceramics prepared by isostatic pressing (200 MPa; green density 60% theoretical). By using a Setaram SetSys 24 thermomechanical analyzer, constant heating rate sintering tests were carried out at 5°C min^{-1} to get information on the shrinkage behaviour and the maximum sintering rate, corresponding to 1490°C. Density of ceramics was measured by Archimede's method. Average grain size was estimated by the intercept method.

Tests of isothermal sintering were performed at 1450 and 1530°C. Sintering processes were complete after 4 and 2 h respectively, reaching 92.9 and 98.8% of theoretical density (5.084 g cm^{-3}).

Sintering performed at 1700°C for 2 h (heating rate 10°C min^{-1} up to 1350°C and 5°C min^{-1} up to 1700°C; air quenching) gave rise to very high density ceramics (99.8% theoretical) characterised by average grain size of about 11 μm. Microstructure after thermal etching at 1350°C for 15 min followed by air quenching is shown in Fig. 3.

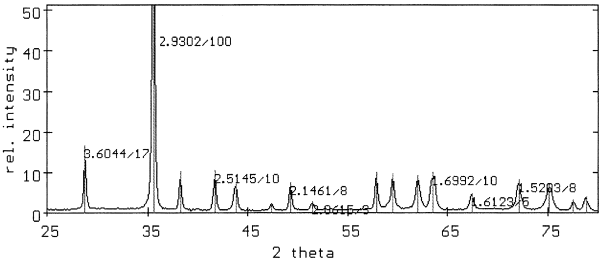

Fig. 2. XRD pattern of orthorhombic $ZrTiO_4$ (Card 34-0415 PDF, S.G. Pnab n.60).

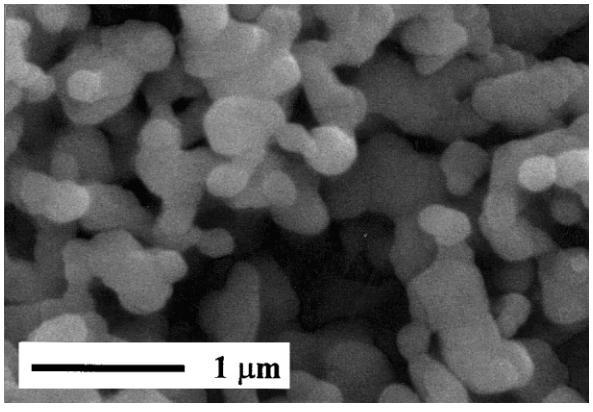

Fig. 1. Morphology of ZT powder prepared by calcination at 1200°C of reactive precursors obtained by aqueous synthesis.

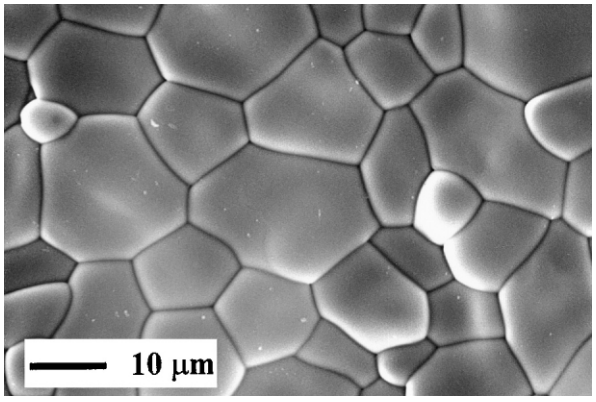

Fig. 3. Microstructure of a ZT ceramic sintered at 1700°C (99.8% theoretical density). Thermal etching at 1350°C for 15 min followed by air quenching.

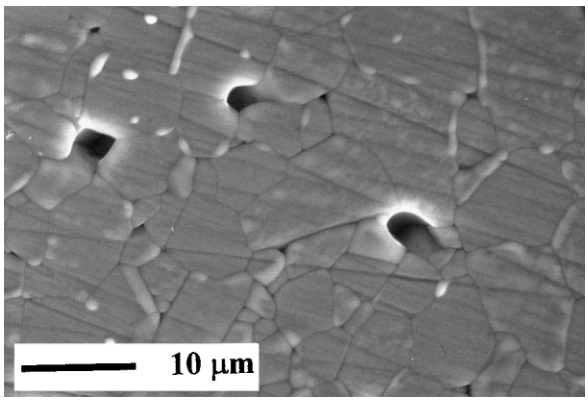

Fig. 4. Microstructure of a ZT substrate sintered at 1550°C (99.6% theoretical density). Thermal etching at 1300°C for 35 min followed by air quenching.

In order to get an average grain size below 10 μm, high density ZT substrates were prepared. Green ceramics (disks of 40 mm diameter; thickness 0.7 and 1.4 mm) were shaped at 15 MPa by uniaxial pressing, sealed into polyethylene bags and isostatically pressed at 200 MPa. Firing performed at 1550°C for 2 h (heating rate 10°C min^{-1} up to 1350°C and 5°C min^{-1} up to 1550°C; cooling rate 5°C min^{-1} down to 1350°C, furnace cooling to room temperature) gave rise to ceramics of 99.6% of theoretical density and average grain size of about 6 μm (Fig. 4). The presence of a secondary phase, observed after thermal etching, can be related to segregation of impurities and their diffusion at the surface of the ceramic. If thermal etching is performed at higher temperatures, i.e. 1350°C, formation of secondary phase is not observed (Fig. 3), probably due to the solubility into the bulk of the ceramic.

Adhesion of conductive patterns was checked by a pull-test carried out on Au electrodes 4.7 μm thick (area 0.8×0.8 mm) electrolytically grown onto a 0.3 μm NiCr/Pt/Au film previously deposed by RF sputtering. Pull-tests performed on wires welded onto the patterns gave an average value of 2.34 kg mm^{-2}.

Dielectric losses and permittivity were measured on a portion of a substrate (Au electrodes realised by evaporation) at low frequencies (1–10 MHz) by impedance spectroscopy (Solartron, SI 1260). Permittivity and loss-factor resulted respectively $\varepsilon_r = 42$ and $\tan\delta = 4\ 10^{-3}$.

The high value of loss-factor can be ascribed to the presence of impurities in the raw materials and to the effects of the electrodes.

In order to obtain loss-factors at GHz frequencies in agreement with industrial requirements (Q factor $= 1/\tan\delta > 4000$; 30–80), electronic grade reagents must be used.

4. Conclusions

Aqueous processing represents an easy way to prepare reactive precursors of ZT from low-cost raw materials. High-density ZT substrates with average grain size below 10 μm were prepared. Permittivity measured at 10 MHz is in agreement with industrial requirements for substrates, usually in the range 30–80 at GHz frequencies.

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References

1. Lynch, R. W. and Morosin, B., Thermal expansion, compressibility, and polymorphism in hafnium and zirconium titanate. *J. Am. Ceram. Soc.*, 1972, **55**, 409–413.
2. Wolfram, G. and Göbel, E., Existence range, structural and dielectric properties of $Zr_xTi_ySn_zO_4$ ceramics $(x+y+z=2)$. *Mater. Res. Bull.*, 1981, **16**, 1455–1463.
3. Hirano, S., Hayashi, T. and Hattori, A., Chemical processing and microwave characteristics of $(Zr,Sn)TiO_4$ microwave dielectrics. *J. Am. Ceram. Soc.*, 1991, **74**, 1320–1324.
4. Buchanan, R.C., *Ceramic Materials for Electronics*. Dekker, New York, 1986 pp. 154.
5. Navio, J. A., Macias, M. and Sanchez-Soto, P. J., Of the influence of chemical processing in the crystallization behaviour of zirconium titanate materials. *J. Mater. Sci. Lett.*, 1992, **11**, 1570–1572.
6. Navio, J. A., Marchena, F. J., Macias, M., Sanchez-Soto, P. J. and Pichat, P., Formation of zirconium titanate powder from a sol–gel prepared reactive precursor. *J. Mater. Sci.*, 1992, **27**, 2463–2467.
7. Renoult, O., Boilot, J. P., Chaput, F., Papiernik, R., Hubert-Pfalzgraf, L. G. and Lejeune, M., Sol–gel powders for microwave dielectric resonators. In *Ceramics Today — Tomorrow' Ceramics*, ed. P. Vincenzini. Elsevier Science Publishers, London, New York, 1991, pp. 1991–1997.
8. Bianco, A., Gusmano, G., Freer, R. and Smith, P., Zirconium titanate microwave dielectrics prepared via polymeric precursor route. *J. Eur. Ceram. Soc.*, 1998, **19**, 959–963.
9. Duran, P., Villegas, M., Fernandez, J. F., Capel, F. and Moure, C., Theoretically dense and nanostructured ceramics by pressureless sintering of nanosized Y–TZP powders. *Mater. Sci. Eng.*, 1997, **A232**, 168–176.
10. Newnham, R. E., Crystal structure of $ZrTiO_4$. *J. Am. Ceram. Soc.*, 1967, **50**, 216.
11. McHale, A. E. and Roth, R. S., Low-temperature phase relationships in the system ZrO_2–TiO_2. *J. Am. Ceram. Soc.*, 1986, **69**, 827–832.