Journal of the European Ceramic Society 21 (2001) 1735–1738
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Dielectric characterisation of ceramics from the TiO_2–TeO_2 system

M. Udovic *, M. Valant, D. Suvorov

"Jozef Stefan" Institute, Jamova 39, 1000 Ljubljana, Slovenia

Received 4 September 2000; received in revised form 5 October 2000; accepted 15 October 2000

Abstract

Compositions from TiO_2–TeO_2 tie line were characterised using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and dilatometry. Results show that the only binary compound existing on the tie line is $TiTe_3O_8$. Single-phase $TiTe_3O_8$ was synthesised at 700°C in air and sintered at 720°C to ~95% of theoretical density. Such ceramics exhibit a relative permittivity of 50, a $Q\times f$-value of 30,600 GHz and a temperature coefficient of resonant frequency (τ_f) of +133 ppm/°C, measured at ~5 GHz. The concentration of structural defects in the $TiTe_3O_8$ grains is negligible which makes the dielectric properties of $TiTe_3O_8$ ceramics insensitive to variations in the heat-treatment conditions. The $TiTe_3O_8$ compound is chemically compatible with TeO_2, which displays a negative temperature coefficient of resonant frequency (a relative permittivity of 19.3, a $Q\times f$-value of 30,000 GHz and a temperature coefficient of resonant frequency of −119 ppm/°C for TeO_2 ceramics with ~ 20% porosity) and can be used for compensation of the temperature coefficient of resonant frequency of the $TiTe_3O_8$ compound. Ceramics from the $TiTe_3O_8$–TeO_2 subsystem can be sintered to >97% of theoretical density at temperatures as low as 670°C, which together with the fact that the ceramics exhibit a highly tunable τ_f, relative permittivity around 30 and a $Q\times f$-value of ~22,000 GHz suggests a potential for use in LTCC technology. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; LTCC; TiO_2

1. Introduction

Pure tellurium dioxide is well known as a network-former in the glass industry, although pure tellurium dioxide does not form glass, even at high cooling rates.[1] Tellurium glasses exhibit a high refractive index and good optical transmission in the IR region, have interesting semiconducting properties and can be prepared at low temperatures.[2,3] In contrast to glasses, tellurium-based oxide ceramics have not yet been seriously considered for use in electronics. Most tellurium-based oxide materials can be synthesised and sintered at temperatures below 900°C, which makes them potential candidates for use in low-temperature-cofired-ceramics (LTCC) technology. Other requirements for LTCC materials, in terms of their electrical properties, are high relative permittivity (κ'), high Q-value and a temperature coefficient of resonant frequency (τ_f) tunable around zero. For ceramic processing the most important oxidation states of tellurium are Te^{+4} and Te^{+6}, where Te^{+4} possesses a lone electron pair. In some cases, when the thermodynamic conditions are fulfilled, an oxidation from Te^{+4} to Te^{+6} occurs in air. However, pure TeO_2 never oxidises in air to the +6 oxidation state.[4]

The highly temperature stable, tetragonal TeO_2 modification (space group $P4_12_12$), can be considered as a superstructure of rutile,[4,5] with a duplicated c axis and unit-cell parameters of $a = 4.796$ Å and $c = 7.626$ Å. The Te–O coordination polyhedra correspond to a heavily distorted quadratic bipyramid and the distances between the tellurium and oxygen ions are 2×1.91 Å, 2×2.09 Å and 2×2.89 Å. Like TeO_2, the rutile also TiO_2 crystallises in the tetragonal crystal system[5,6] (space group P4/mnm) with unit-cell parameters of $a = 4.594$ Å and $c = 2{,}959$ Å and a Ti ion coordinated with 6 oxygens.

Only one compound on the TiO_2–TeO_2 tie line is thermodynamically stable in air: $TiTe_3O_8$ with the tellurium in the +4 oxidation state.[7] Many authors[4,6–9] have already reported on the synthesis of the $TiTe_3O_8$ compound with a cubic unit cell, prepared from oxides at 700°C in air. Yamaguchi et al.[10] have reported on the synthesis of another hexagonal modification prepared from amorphous precipitates which is irreversibly converted to the cubic modification at 520–570°C. Maeda et al.[9] have reported microwave-dielectric properties of

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* Corresponding author. Tel.: +386-1-477-3762; fax: +386-1-426-3126.
E-mail address: marko.udovic@ijs.si (M. Udovic).

PII: S0955-2219(01)00105-4

some tellurium ceramics: a relative permittivity of 36, a $Q{\times}f$ of 10,200 GHz and a temperature coefficient of relative permittivity (τ_ϵ) of −220 ppm/°C, measured at 4 GHz, were reported for cubic $TiTe_3O_8$ ceramics with 12% porosity.

The aim of the present study is to characterise the dielectric properties of the compositions from the TiO_2–TeO_2 tie line. In addition, a study of the influence of the processing parameters on the dielectric properties of single-phase $TiTe_3O_8$ ceramics was performed. Because TeO_2 displays a negative temperature coefficient of resonant frequency and is chemically compatible with the $TiTe_3O_8$ compound we attempted to compensate the positive temperature coefficient of $TiTe_3O_8$ by an addition of TeO_2 and to determine its influence on the relative permittivity and $Q{\times}f$-value.

2. Experimental

Ceramic samples have been prepared from reagent-grade TeO_2 (Alfa Aesar, 99.999%, lot I15J04) and TiO_2 (Johnson Matthey 99%, lot D17H27) via a solid-state-reaction method. The powders were weighed in different molar ratios, mixed in alcohol, dried and calcined for 80 h at 620–700°C with intermediate crushing until phase equilibrium was achieved. X-ray diffraction analysis (XRD) using a Philips PW 1710 X-ray powder diffractometer and CuK_α radiation was used to monitor the degree of calcination. After the calcination the samples were milled for one hour in a planetary ball mill at 200 rpm using 3 mm ϕ zirconia balls. An analysis revealed a mean particle size below 1 μm measured by granulometer (Cilas 8050). Powders were isostatically pressed into pellets and sintered in air. For the investigation of possible solid solubilities, unit-cell parameters were determined from XRD patterns using LCLSQ[11] software. Microstructural analyses were performed on a scanning electron microscope (SEM) (Jeol 5800 equipped with LINK ISIS X-ray spectrometer). Investigations of structural defects have been carried out on a transmission electron microscope (TEM) (Jeol 2000 FX). The sintering curves were recorded with a dilatometer (Bähr).

Electrical properties were measured by a reflection-resonant-cavity method at ~5 GHz with a HP 8719C network analyzer. The temperature dependence of resonant frequency was determined in the temperature range between 20 and 60°C.

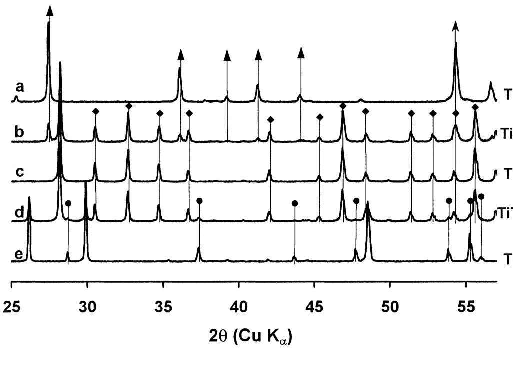

Fig. 1. XRD patterns of various samples on the TiO_2–TeO_2 tie line.

3. Results

3.1. Characterisation of $TiTe_3O_8$

A single-phase $TiTe_3O_8$ compound was synthesised by solid-state reaction in air. (Fig. 1c) The determined unit-cell parameter (a = 10.953 Å) corresponds well to the literature data.[8]

To prevent the possible evaporation of TeO_2, samples were sintered in a closed aluminum crucible together with TeO_2 powder. TeO_2 powder was placed in a separate aluminum crucible to increase the partial pressure of TeO_2 and to suppress the evaporation from $TiTe_3O_8$. Obtained weight losses were in the range of 0.3 wt.%. A typical microstructure of a ceramic sintered at 720°C for 5 h, is shown in Fig. 2.

The $TiTe_3O_8$ ceramics exhibit ~5% porosity and a grain size of 2–5 μm. Microwave-dielectric properties of these ceramics, measured at ~5 GHz, are a $Q{\times}f$-value of 30,600 GHz, relative permittivity of 50 and a temperature coefficient of resonant frequency of +133 ppm/°C. The $Q{\times}f$ value and the relative permittivity of these ceramics are much higher than previously reported due to a significant reduction in the porosity.

Additional investigations have been undertaken to examine whether any further improvement in the dielectric properties can be obtained by an adjustment of the processing parameters. Different thermally induced effects like stresses, precipitates and structural

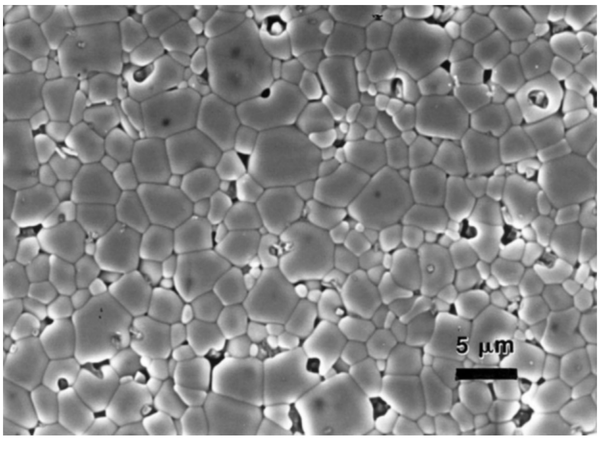

Fig. 2. Typical SEM image of the microstructure of a $TiTe_3O_8$ ceramic sintered at 720°C/5 h. The sample was thermally etched for 10 min at 710°C.

defects which can appear with the change in cooling rate, dwell time and sintering temperature, might have an influence on the dielectric properties of the ceramic. Investigations showed that neither a variation in the dwell time (5–15 h) nor the cooling rate (10–0.3°C/min) have an influence on the dielectric properties. Moreover, even variations in the sintering temperature in the range 720–750°C did not influence the dielectric properties. The only significant influence was observed when the sintering temperature was decreased too far for the successful densification of ceramics.

The apparent insensitivity of the $TiTe_3O_8$ ceramics to the firing conditions can be rationalised by the result of the TEM investigations, performed on a sample sintered at 720°C/5 h and cooled at 10°C/min. The TEM study (Fig. 3) revealed the presence of no structural defects such as inclusions, twins, precipitates, etc., which can be influenced by heat treatment conditions and subsequently reflected in the dielectric properties. Because of the regular structure of the $TiTe_3O_8$ compound further improvement in the dielectric properties of the $TiTe_3O_8$ ceramics can be expected only as a result of porosity elimination.

3.2. Characterisation of the $TiTe_3O_8$–TeO_2 tie line

Tellurium and oxygen ions have a small difference in their electro-negativity (3.50 for oxygen and 2.01 for tellurium, according to Allred-Rochow), therefore, covalent bonding contributes significantly and hinders the sintering of pure TeO_2. The sintering of milled, pure TeO_2 at 640°C for 15 h resulted in ceramics with ~20% porosity. Dielectric measurements, performed on such ceramics revealed a relative permittivity of 19.3 and a $Q\times f$ value of 30,000 GHz at ~4 GHz. Pure TeO_2 exhibits a negative temperature coefficient of resonant frequency (−119 ppm/°C), therefore, it can be used to compensate for the positive temperature coefficient of $TiTe_3O_8$. In accordance with the literature data,[7] our XRD and SEM analyses confirmed the chemical compatibility of $TiTe_3O_8$ and TeO_2 (Figs. 1d and 4a) which is also important for the successful compensation of the temperature dependence of resonant frequency.

The unit-cell parameters of TeO_2 and $TiTe_3O_8$ phases in ceramics along the TeO_2–$TiTe_3O_8$ tie line showed no variations with the composition. This suggests a negligible solid solubility of both compounds. These results are expected since the Te^{+4} ion with a stereoactive lone electron pair possesses a much larger ionic radius (0.97 Å for coordination number 6) than the Ti^{+4} ion (0.605 Å for coordination number 6), therefore, isovalent substitution is not very probable.

The sintering curve shows that ceramics with the composition 0.9 $TiTe_3O_8$–0.1 TeO_2 start to sinter at temperatures around 600°C. Ceramics fired at 670°C were highly dense with an estimated porosity of less than 3%. Microwave-dielectric characteristics of the compositions from the $TiTe_3O_8$–TeO_2 tie line are shown in Fig. 5.

The pure $TiTe_3O_8$ compound exhibits a τ_f of +133 ppm/°C. When the amount of TeO_2 compound in the system is increased the τ_f is reduced to +24 ppm/°C for the ceramic with a composition of 0.2 $TiTe_3O_8$–0.8 TeO_2 and finally to −19 ppm/°C for 0.1 $TiTe_3O_8$–0.9 TeO_2. It is to be expected that the τ_f can be fully suppressed at approximately 0.15 $TiTe_3O_8$–0.85 TeO_2.

The relative permittivity of single-phase $TiTe_3O_8$ ceramics with ~5% porosity was determined to be 50 and to decrease with an increase in the concentration of the TeO_2 phase. The 0.2 $TiTe_3O_8$–0.8 TeO_2 sample exhibits a relative permittivity of 34 and the 0.1 $TiTe_3O_8$–0.9 TeO_2 sample has a relative permittivity of

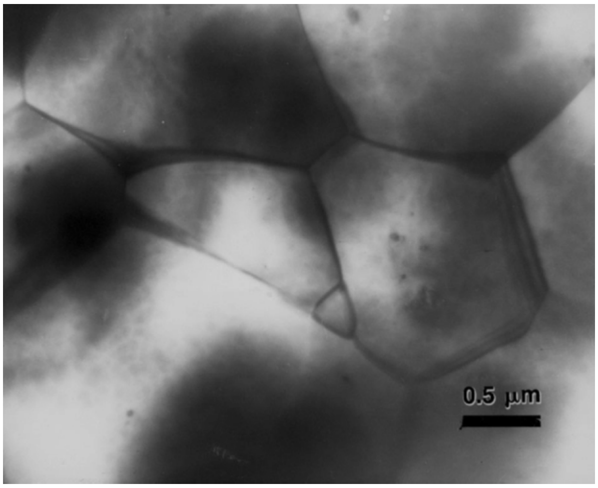

Fig. 3. Typical TEM image of a $TiTe_3O_8$ ceramic sintered at 720°C/5 h and cooled at 10°C/min. Micrograph reveals no main structural defects.

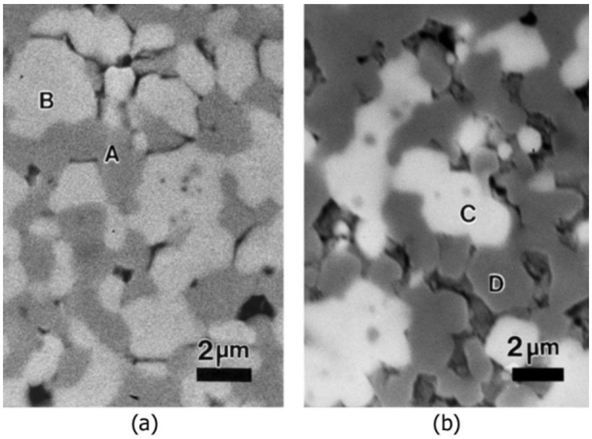

Fig. 4. (a) Typical back-scattered electron (BSE) image of a two-phase (Phase A: $TiTe_3O_8$; Phase B: TeO_2) dense ceramic with the composition 0.80 $TiTe_3O_8$–0.2 TeO_2. (b) Typical BSE image of two-phase (Phase C: $TiTe_3O_8$; Phase D: TiO_2) ceramic with the composition 0.6 TiO_2–0.4 TeO_2.

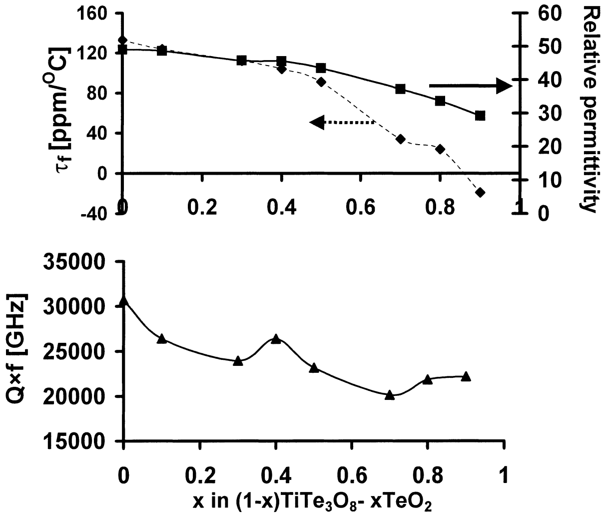

Fig. 5. Microwave dielectric properties of compositions from the $TiTe_3O_8$–TeO_2 tie line.

29. The $Q\times f$-value decreases from 30,600 GHz for single-phase $TiTe_3O_8$ to 22,000 GHz for the composition 0.2 $TiTe_3O_8$–0.8 TeO_2 and remains the same for the 0.1 $TiTe_3O_8$–0.9 TeO_2 sample.

3.3. Characterisation of the $TiTe_3O_8$–TiO_2 tie line

SEM and XRD analyses of the 0.6 TiO_2–0.4 TeO_2 sample (Fig. 1b) confirmed the literature data[7] regarding the chemical compatibility of $TiTe_3O_8$ and TiO_2. Cell-parameter determination of the 0.6 TiO_2–0.4 TeO_2 sample indicates no changes in the unit-cell parameters, neither for the TiO_2 nor the $TiTe_3O_8$ phase, which again indicates a negligible solid solubility.

Fig. 4b shows a typical microstructure of ceramic with 0.6 TiO_2–0.4 TeO_2 composition. The ceramic sample with this composition exhibits a relative permittivity of 62, a $Q\times f$ value of 23,000 GHz and a τ_f of +260 ppm/K. Both phases, TiO_2 and $TiTe_3O_8$, possess positive temperature coefficients of resonant frequency, as a consequence the suppression of the temperature coefficient of resonant frequency is not possible.

4. Conclusions

$TiTe_3O_8$ is the only binary compound from the TiO_2–TeO_2 tie line which is stable in air. Any solid solubility between the compounds has not been detected and is also not very probable because of the large difference in the ionic radii of the titanium and tellurium ions. Single-phase $TiTe_3O_8$ ceramics with >95% theoretical density can be produced by sintering at 720°C in air. Measurements performed at ~5 GHz showed that such ceramics exhibit a relative permittivity of 50, a $Q\times f$-value of 30,600 GHz and a positive temperature coefficient of resonant frequency of +133 ppm/°C. The temperature coefficient of resonant frequency of the $TiTe_3O_8$ compound can be compensated by the addition of ~85 mol% TeO_2.

TeO_2 at ~4 GHz displays a relative permittivity of 19.3, a $Q\times f$-value of 30,000 GHz and a temperature coefficient of resonant frequency of −119 ppm/°C. Ceramics with a composition 0.15 $TiTe_3O_8$–0.85 TeO_2, measured at ~5 GHz, exhibit a temperature coefficient of resonant frequency relative around 0, a permittivity ~30 and a $Q\times f$-value of 22,000 GHz.

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