Materials Chemistry and Physics 119 (2010) 118–122

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Phase transition and dielectric properties of $BaTiO_3$ ceramics containing 10 mol% $BaGeO_3$

Roberto Köferstein*, Lothar Jäger, Mandy Zenkner, Stefan G. Ebbinghaus

Institut für Chemie/Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes Strasse 2, D-06120 Halle, Germany

ARTICLE INFO

Article history:
Received 3 April 2009
Received in revised form 17 August 2009
Accepted 20 August 2009

Keywords:
Ceramics
Differential thermal analysis (DTA)
Dielectric properties
Phase transitions

ABSTRACT

Dielectric properties and the cubic ⇆ tetragonal phase transition temperature of dense $BaTiO_3$ ceramics containing 10 mol% $BaGeO_3$, sintered between 840 and 1350 °C, have been investigated. The ceramic bodies were prepared from a nano-sized $BaTi_{0.9}/Ge_{0.1}O_3$ powder consisting of both $BaTiO_3$ and $BaGeO_3$ phases. The addition of $BaGeO_3$ leads to a reduction and broadening of the permittivity maximum, and to a small downshift of the paraelectric ⇆ ferroelectric phase transition temperature, compared to a pure $BaTiO_3$ ceramic. Lower sintering temperatures and thus small grain sizes of the ceramics cause an additional reduction of the maximum permittivity down to 2800. Both DTA and dilatometric measurements reveal also a downshifting of the phase transition temperature, as well as a decrease of the latent heat.

1. Introduction

Barium titanate ($BaTiO_3$) is one of the most frequently used ceramic materials in electronic devices due to its outstanding dielectric properties. Both, very fine-grained $BaTiO_3$ powders or sintering additives allow to reduce the sintering temperature. Sintering aids can influence not only the sintering temperature but also the dielectric/electrical properties of the final ceramics [1,2]. Yang [3] investigated the influence of CuO/BaO addition on the dielectric characteristic of $BaTiO_3$ ceramics. The effect of the sintering aid SiO_2 on the dielectric properties of $BaTiO_3$- or $BaTiO_3$-based ceramics was examined by Freidenfelds et al. [4] and Lee et al. [5], respectively. Freidenfelds [4] reported that the addition of SiO_2 to $BaTiO_3$ decreases the dielectric permittivity. The dependency of the dielectric permittivity on glass-like additive of $BaTiO_3$ ceramics was investigated by Jeon et al. [1].

The addition of germanates, like lead germanate, is used in industrial applications to produce heterophasic ceramic bodies [6,7]. Recently, we have investigated the influence of $BaGeO_3$ on the sintering behaviour and properties of fine- and coarse-grained $BaTiO_3$ powder compacts [8,9]. $BaGeO_3$ can be used as a sintering aid to reduce the sintering temperature of $BaTiO_3$ ceramics below 1000 °C. Guha and Kolar [10] studied the $BaTiO_3$–$BaGeO_3$ system and they determined a eutectic composition of 68 mol% $BaGeO_3$ with a melting temperature of about 1120 ± 5 °C. The authors did not observe any shifting of the cubic ⇆ tetragonal phase transition temperature of $BaTiO_3$ (Curie temperature) by addition of $BaGeO_3$, in agreement with the investigations by Plessner and West [11]. Plessner and West noticed only a reduction of the sharpness of the permittivity maximum. In contrast, Pulvari [12] and Baxter et al. [13] found a small decrease in the Curie temperature with the addition of GeO_2. Consequently, the knowledge about the effect of sintering additives on the dielectric properties of $BaTiO_3$-based ceramics is important for potential technical applications.

The purpose of this study is to investigate the effects of the sintering additive $BaGeO_3$ on the dielectric characteristic of barium titanate ceramics. The influence of the sintering regimes and grain sizes has also been investigated. Additionally, the cubic ⇆ tetragonal phase transition has also been studied by dilatometric and DTA measurements.

2. Experimental

2.1. Material preparation

The preparation of a fine-grained $BaTi_{0.9}/Ge_{0.1}O_3$ powder and its characterization have been described elsewhere [8]. Briefly, a $[Ba(HOC_2H_4OH)_4][Ti_{0.9}Ge_{0.1}(OC_2H_4O)_3]$ complex precursor was prepared by reaction of $Ba(OH)_2{\cdot}8H_2O$, $Ti(O^iC_3H_7)_4$ and $Ge(OC_2H_5)_4$ in 1,2-ethanediol. The resulting precursor was calcined by the following thermal treatment: heating to 550 °C with a heating rate of 10 K min^{-1}, slow heating with 1 K min^{-1} to 730 °C, dwelling time 30 min and followed by cooling at 10 K min^{-1}. After calcination the resulting nm-sized $BaTi_{0.9}/Ge_{0.1}O_3$ powder has a specific surface area of S_{BET} = 16.9 m^2 g^{-1} ($d_{av.}$ = 61 nm) and mainly consists of a mixture of both $BaTiO_3$ and $BaGeO_3$ (denoted as: $BaTi_{0.9}/Ge_{0.1}O_3$). Chemical analyses (described in [8]) indicated a Ba/Ti ratio of 1.117 (calcd. 1.111) and a Ba/(Ti + Ge) ratio of 0.999 (calcd. 1.000). The preparation of the $BaTiO_3$ powder is similar to the preparation mentioned above [8,14]. The Ba/Ti ratio is 1.004 and the specific surface area is S_{BET} = 15.0 m^2 g^{-1} ($d_{av.}$ = 66 nm). Detailed investigations of both the $BaTi_{0.9}/Ge_{0.1}O_3$ and $BaTiO_3$ powders are described elsewhere [8,9].

* Corresponding author. Tel.: +49 345 5525630; fax: +49 345 5527028.
E-mail address: roberto.koeferstein@chemie.uni-halle.de (R. Köferstein).

0254-0584/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2009.08.026

The powders were milled in propan-2-ol and pressed to disks (green density: 2.8–2.9 g cm^{-3}) as described in [15] and sintered at various temperatures and sinter regimes.

2.2. Analytical methods

X-ray powder diffraction (XRD) patterns were recorded on a *STOE* STADI MP diffractometer at 25 °C using CoKα_1 radiation. Dilatometric investigations (thermal expansion) were performed in a TMA 402 unit from *Netzsch*. The determination of the complex relative permittivity was achieved using an Impedance Analyzer 4192 Alf from *Hewlett Packard* in a temperature range between 14 and 140 °C and frequencies from 1 to 1000 kHz. As electrode material aluminium was deposited by evaporation, the samples were slowly heated to 140 °C, held for 3 h and then cooled down. Differential thermoanalytic (DTA) measurements were done using a STA 429 from *Netzsch* (Pt crucible, flowing air (30 ml min^{-1})). Scanning electron microscope images were recorded with a *Philips* XL30 ESEM (Environmental Scanning Electron Microscope).

3. Results and discussion

In Refs. [8,9] we have recently reported on the preparation and characterization of a nm-sized $BaTiO_3$ powder and resulting ceramic bodies containing 10 mol% $BaGeO_3$ ($BaTi_{0.9}/Ge_{0.1}O_3$). The ceramic bodies were obtained after conventional sintering (heating up to a certain temperature (rate 10 K min^{-1}), dwell for 1 h, and then cooling down with 10 K min^{-1}), as well as a 2-step sintering process (heating to a higher temperature (T_1, rate 10 K min^{-1}), then cooled (30 K min^{-1}) and held 50 h at a lower temperature (T_2)). SEM images of these ceramic bodies are shown in Fig. 1 (see also [8]). Grain sizes were determined on the basis of these images by lineal intercept technique [16]. $BaTi_{0.9}/Ge_{0.1}O_3$ ceramics show a heterogeneous grain size distribution. An overview of the ceramic bodies is given in Table 1. The relative densities of $BaTi_{0.9}/Ge_{0.1}O_3$ ceramic bodies (**1a**–**1e**) were related to the theoretical value of 5.85 g cm^{-3} [8] and of the $BaTiO_3$ ceramic body (**2**) to 6.02 g cm^{-3} [17]. As seen in Table 1 the addition of $BaGeO_3$ leads to a considerable reduction of the sintering temperature of $BaTiO_3$. As reported by Guha and Kolar [10], both $BaGeO_3$ and $BaTiO_3$ form solid solutions only up to a $BaGeO_3$ content of 1.8 mol% and they found a melting point of the eutectic at 1120 °C. The $BaTi_{0.9}/Ge_{0.1}O_3$ ceramic **1a** consists of tetragonal $BaTiO_3$, small amounts of orthorhombic $BaGeO_3$ and $Ba_2TiGe_2O_8$. Moreover, the grains in sample **1a** are surrounded by a solidified eutectic melt, as a result of liquid phase sintering (see Fig. 1a) [8]. Whereas samples **1b**–**1e** consist of tetragonal $BaTiO_3$ and hexagonal $BaGeO_3$ (see Ref. [9]) and they were obtained after solid state sintering. Results of dielectric measurements are shown in Fig. 2. The following data are related to the measurements of 1 kHz and collected from the cooling curve. Sample **2** ($BaTiO_3$) shows a sharp maximum of the relative permittivity (ε_r) at 128.4 ± 0.3 °C in agreement with earlier investigations [18–22]. The maximum of permittivity can be considered as a good

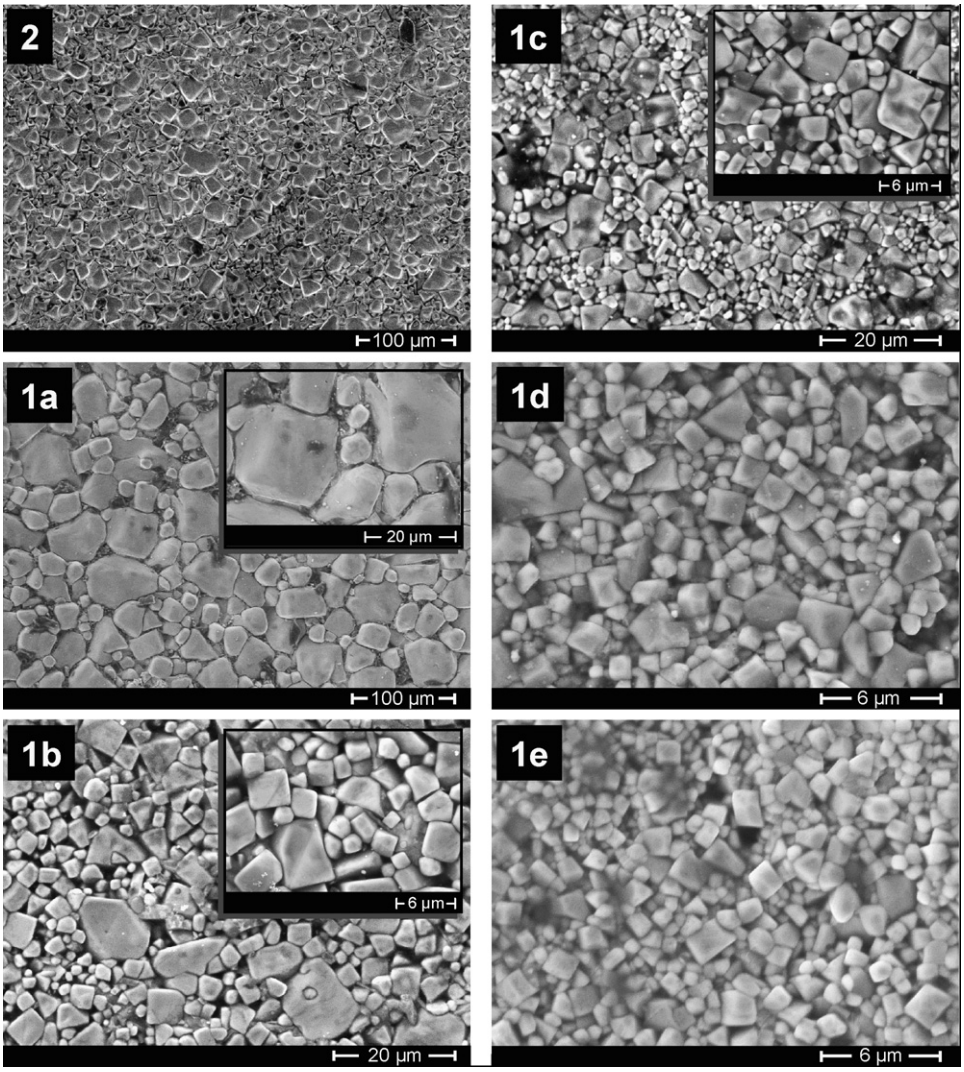

Fig. 1. SEM images of the surface of $BaTiO_3$ (**2**) and $BaTi_{0.9}/Ge_{0.1}O_3$ (**1a**–**1e**) ceramic bodies.