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The effect of $BaTiO_3$ particle shape on complex permittivity of $0.98MgTiO_3–0.02BaTiO_3$ composite powders at GHz frequencies

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ABSTRACT

The effect of $BaTiO_3$ particle shape on the properties of $0.98MgTiO_3–0.02BaTiO_3$ composite powders was characterized and analyzed using an indirectly coupled open-ended coaxial cavity resonator at gigahertz frequencies. Elongated micrometre sized $BaTiO_3$ particles were found to have a significantly stronger effect on permittivity when compared to composite powders having micro and nano sized spherical $BaTiO_3$ particles. Inclusion permittivities and dielectric loss tangents of composite powders increased from that of pure $MgTiO_3$ powder, 13.3 and 4.6×10^{-3}, up to 15.7 and 1.7×10^{-2} with needle shaped $BaTiO_3$ particles, respectively. The presented results give valuable information for tailoring the properties of dielectrics which can be utilized in the vast field of electronic component manufacturing.

1. Introduction

Dielectric powdery substances are used in the extensive field of RF and electronics applications, for example, in polymer-ceramic composites and inks for printed electronics applications. These composites may consist of several different powdery parts as well as coatings which together determine both the mechanical and the electrical properties of the final product. Thus, by utilizing different dielectric materials, final products can be tailored to achieve desired properties, such as mechanical flexibility or dielectric losses, permittivity and capacitance in a certain frequency range. In particular, in specific narrowband filter applications a strict permittivity value is required without a compromise in frequency response as a function of operation temperature [1–4]. Therefore, the temperature coefficient can also be one of the limiting factors in the choice of volume ratio of the powdery materials [5–7]. In addition to the dielectric properties and molecular ratios of the materials used, the effective permittivity of composites can also be affected by different particle shapes and sizes. Using, for example, spherical, ellipsoidal, flake or needle shaped nano- and micrometre sized particles, the effect of a surrounding electric field varies, thus changing the total permittivity of the component [8–11]. Yet, the properties of powders and the influence of their particle shape in practice are poorly known, especially at high frequencies.

In this paper, the effect of $BaTiO_3$ particle shape on dielectric properties of $0.98MgTiO_3–0.02BaTiO_3$ composite powders was characterized for the first time in powdery format using an indirectly coupled coaxial cavity resonator.

2. Experimental

Dielectric characterization of pure $MgTiO_3$ and $0.98MgTiO_3–0.02BaTiO_3$ composite powders was done by using an open-ended coaxial resonator. A comprehensive and detailed description aboutthe characterization method has been presented in journal paper previously reported by Tuhkala et al. [12]. The method was proved to be accurate for the characterization of magnesium and calcium titanate composite powders with varying molar ratios [13]. In the present experiment different sizes and shapes of $BaTiO_3$ particles were dosed into $MgTiO_3$, which is commonly used as the dielectric powder in composite applications, to form $0.98MgTiO_3–0.02BaTiO_3$ composite powders [14]. The $MgTiO_3$ was a commercial dielectric powder from Alfa Aesar (99%, +325 mesh, formula weight 120.21 g/mol). Needle shaped micrometre size $BaTiO_3$ particles (formula weight 233.2 g/mol, density 5.47 g/cm^3) were prepared in the Jožef Stefan Institute, Slovenia. These particles were formed under hydrothermal conditions at + 240 °C from sodium titanate belts in an alkaline (C_{NaOH} = 0.07 mol/l) water solution of barium

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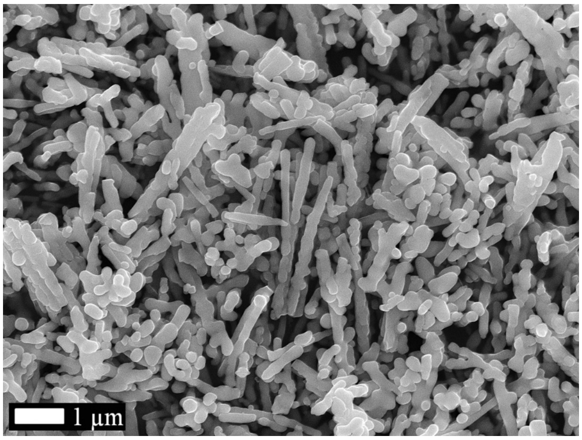

Fig. 1. SEM figure of elongated $BaTiO_3$ particles.

acetate. These elongated $BaTiO_3$ particles had average thickness and length of 270 nm and 2 μm, respectively (Fig. 1).

Spherical shaped $BaTiO_3$ particles were supplied by Alfa Aesar (99.7%, Metal basis, formula weight 233.19 g/mol, density 5.85 g/cm^3) and Sachtleben (P23757, formula weight 233 g/mol, density 5.78 g/cm^3). The crystal structures of the powder particles were determined using X-ray diffraction and pattern matching (Discover D8, Bruker AXS) between 2θ angles of 20–70°. In the case of $BaTiO_3$ powders, crystal phases were also investigated using TOPAS 4.2. software (Bruker AXS) and Rietveld refinement. In the refinement powders were assumed to have tetragonal and also a very small amount of cubic phases. For the tetragonal structure the Z—coordinate of Ti and O atoms were refined, thus allowing for distortion of the tetragonal structure and enabling better fitting. Particle densities of $MgTiO_3$ and $BaTiO_3$ powder particles were measured using Archimede's method, a pycnometer (Gay-Lussac BlauBrand®, Brand Gmbh + Co., KG, Germany) and clean de-ionized water. Densities of composite powder particles were calculated using the densities and molar ratios of magnesium and barium titanate powders. Specific surface areas (SSA) were analyzed using the BET-method based on nitrogen gas adsorption on particles at the temperature of liquid nitrogen (ASAP™ 2020, Micromeritics Instrument Corporation, U.S.A.). Nanoparticle sizes were analyzed using a laser diffraction based method (Beckman Coulter LS 13 320). It should be noted that agglomerates, especially with non-coated nanometre sized particles, may affect the determined particle sizes. Master samples (5 g) were prepared using a precision balance (Precisa XB 620 M) and thorough dry mixing in geometric series in order to obtain well-homogenized powder composite mixtures. The master samples were preserved for one week in a silica filled desiccator to avoid moisture adsorption. The dielectric characterization was done at room temperature (+21 °C) and a relative humidity of 16%.

The characterization of pure $MgTiO_3$ and $0.98MgTiO_3$–$0.02BaTiO_3$ composite powders were done using six different volume fractions between 10 and 50% of theoretical density which filled the sample cavity (1.092 cm^3). In order to get homogenous filling of the cavity vibration and compression were used during the filling process. Frequency responses, i.e., resonance frequency (f_r) and quality factor (Q), of an empty (f_r = 4.55 GHz, Q = 1200) and sample filled resonator were measured using a vector network analyzer (Rohde and Schwartz ZVB 20 GHz) and −35 dB coupling strength.

Inclusion permittivities of $MgTiO_3$ and $0.98MgTiO_3$–$0.02BaTiO_3$ composite powders were determined using the measurement results of effective permittivities and the mixing equations of Bruggeman symmetric (Eq. (1)) and Looyenga (Eq. (2)). These equations had previously been found to have good correlation in the characterization of dielectric properties of particles reported by Tuhkala et al., Conger et al. and Nelson et al. [12,13,15–18].

$$\frac{\varepsilon_i - \varepsilon_{eff}}{\varepsilon_i + 2\varepsilon_{eff}} f + \frac{\varepsilon_e - \varepsilon_{eff}}{\varepsilon_e + 2\varepsilon_{eff}} (1 - f) = 0 \quad (1)$$

${\varepsilon_{eff}}^{1/3} = (1 - f){\varepsilon_e}^{1/3} + f{\varepsilon_i}^{1/3}$,(2)where ε_{eff},ε_e, ε_i are the effective permittivity of the medium, permittivities of the matrix (e.g., air, ε_r = 1.00059) and inclusion respectively, and f is the volume fraction of the inclusions. Inclusion permittivities were determined at volume fraction 0.43 where the mixing equations define the same theoretical effective permittivity. In addition, a certain compaction level (f > 0.25) was required in order to get comparable

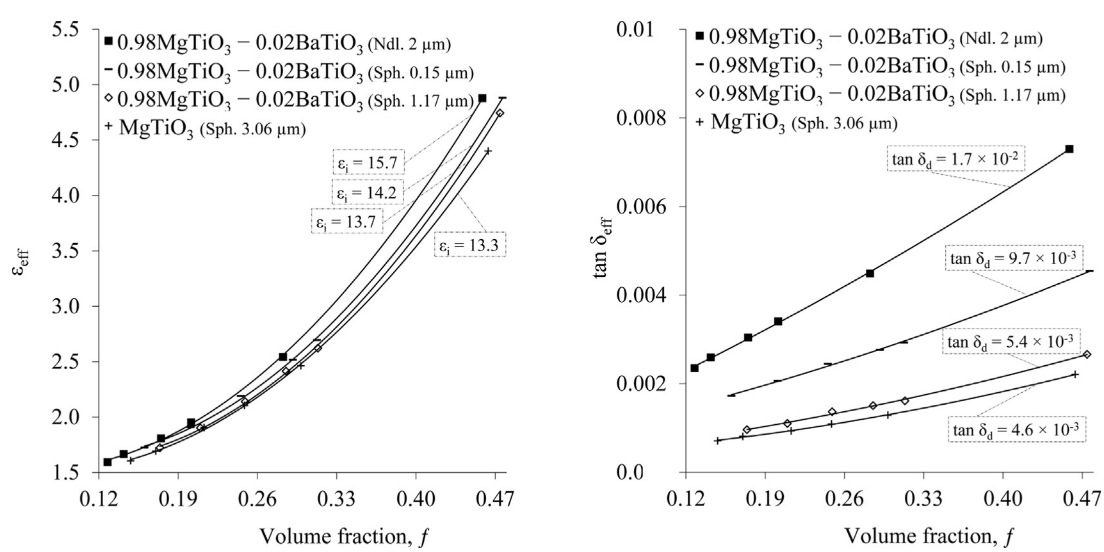

Fig. 2. Effective permittivity and loss tangent values of composite and $MgTiO_3$ powders as a function of volume fraction. Determined dielectric values of inclusions are presented as inserts. Sizes and shapes of $BaTiO_3$ particles are in brackets. Resonance frequencies of the measurements were within the range of 2.2–3.7 GHz.