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$Ba_{0.6}Sr_{0.4}TiO_3$ and $BaZr_{0.3}Ti_{0.7}O_3$ thick films as tunable microwave dielectrics

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Abstract

Thick films have been investigated for application in frequency and phase agile microwave devices. Since $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) and $BaZr_{0.3}Ti_{0.7}O_3$ (BZT) bulk ceramics exhibit high tunability ($\tau = (\varepsilon(0) - \varepsilon(E_{max}))/\varepsilon(0)$) near room temperature, both compositions have been chosen for preparation of screen printed thick films. Low frequency dielectric properties have been characterized using metal-insulator-metal capacitor structures in a temperature range of −120 °C to +160 °C. Measurements of the bias dependent permittivity show a hysteresis effect in both materials in the whole investigated temperature range. BZT thick films exhibit a more diffuse phase transition than BST and therefore a lower temperature dependence. Permittivity, dielectric loss and tunability have also been determined at microwave frequencies from 4 to 90 GHz. Temperature and frequency dependence of the dielectric losses and tunability of both materials have been compared.

Keywords: $BaTiO_3$ and titanates; Dielectric properties; Films; Grain size; Porosity

1. Introduction

The rapidly growing communication market demands for powerful and low cost microwave systems e.g. fast band switching for multimedia services with high data transmitting rates or electronically steerable antennas in automobiles for collision radars. Band switching and tunability can be achieved with tunable microwave components like varactors, filters, oscillators and phase shifters currently based on PIN diodes, GaAs Schottky diodes or ferromagnetics. In contrast to the above-mentioned, ferroelectric components offer the advantage of continuous, quick and low power tunability up to the highest GHz frequencies. Furthermore, ferroelectric ceramics enable a high cost reduction by integration. The tunability of ferroelectrics is based on the nonlinearity of the internal electrical polarization steerable by an external electrostatic field.

For room temperature applications, main research focuses on BST material systems deposited as thin films.[1,2] In comparison to bulk ceramics mechanical stress in films leads to lowered dielectric constants, necessary for impedance matching with conventional components. In addition there is only one broad phase transition which leads to low temperature dependence of the dielectric properties in the operating temperature range of −50 °C to +120 °C.

As BST layers show very high dielectric losses in the microwave region, numerous investigations aim at the reduction of losses. No significant improvement has been achieved up to now.[3] Thus a profound knowledge of dielectric behavior of BST is necessary in order to optimize the material under the boundary conditions of low permittivity, low loss and high tunability. Especially thick films offer the possibility to study the influence of grain size, material substitutions and doping from lowest frequencies up to 90 GHz.[4,5] In this work $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) and $BaZr_{0.3}Ti_{0.7}O_3$ (BZT) thick films have been investigated.

2. Material preparation and experimental methods

BST and BZT powders have been prepared by the mixed oxide route. Stoichiometric portions of $BaCO_3$, $SrCO_3$, TiO_2 and ZrO_2 have been mixed and calcinated

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at 1050 °C for BST and at 1250 °C for BZT. BST powder showed a mean grain size of $D_{50} = 0.17$ μm and BZT a value of 0.3 μm after milling. The powders have been processed into pastes, which have been screen printed on alumina substrates. While the BST thick films have been sintered at 1200 °C, BZT has been sintered at 1080 °C to prevent a reaction with Al_2O_3 substrate.

The dielectric material has been sandwiched between a platinum bottom electrode and a gold top electrode. This capacitor structure has been investigated in a frequency range of 100 mHz to 100 kHz (LF) using an ALPHA-H dielectric analyzer while the temperature has been varied between −120 °C and +160 °C. Microwave characterization at 4–12 GHz (HF) has been carried out using a HP 8510B network analyzer by measuring coplanar waveguide resonators structured on the top of the BST and BZT thick film, as described in.[6] The high frequency material parameters of the thick films have been calculated from the effective permittivity and the quality factor $Q = 1/\tan\delta$ by using conformal mapping methods as described in.[7,8] At frequencies of 30 and 90 GHz an open resonator [9] has been used to obtain the material parameters. These measurements have been performed at the Institut für Materialforschung I (IMF I, Research Center Karlsruhe).

The microstructure of the thick films has been investigated by scanning electron microscopy (SEM). The pictures show well sintered samples with a mean grain size of 300 nm (see Fig. 1) and a porosity of approximately 30% determined by computer analysis of SEM pictures of polished samples.

3. Results and discussion

The measurements of the permittivity as a function of temperature show a very diffuse phase transition of both materials (see Fig. 2). BST has a broad maximum of the permittivity with a value of $\epsilon_{max} = 230$ at $T_{max} = -25$ °C, i.e. small grains and porosity lead to a shift of T_{max} of about −35 °C to lower temperatures compared to bulk ceramics.[10] This noticeably lower value of permittivity, compared with the reported ones of other groups ($\epsilon = 603$,[11] $\epsilon = 1250$ [12]) can be explained by presumably higher porosity and smaller grains.[13] In $BaZr_{0.3}Ti_{0.7}O_3$ a maximum permittivity of $\epsilon_{max} = 500$ can be found at $T_{max} = -50$ °C, thus T_{max} remains the same in both thick films and bulk ceramics, only the diffusivity is enhanced like in BST. The drastically reduced permittivity compared to BZT bulk measurements,[14] can also be ascribed to high porosity and small grains.

The dielectric loss in both materials shows a similar dependence on the temperature. There is a strong increase in $\tan\delta$ at $T < T_{max}$, while for $T > T_{max}$ $\tan\delta$ remains under $<1\%$.[15] Temperature dependent impedance spectra show a strong increase in the dielectric loss with decreasing frequency especially at high temperatures (Fig. 3). This behavior can be described by a Maxwell–Wagner mechanism.

The dependency of permittivity on quasi-static electrical fields is shown in Fig. 4. The electrical field has been varied between zero and $\pm E_{max}$ at different temperatures to investigate the hysteresis effects in these

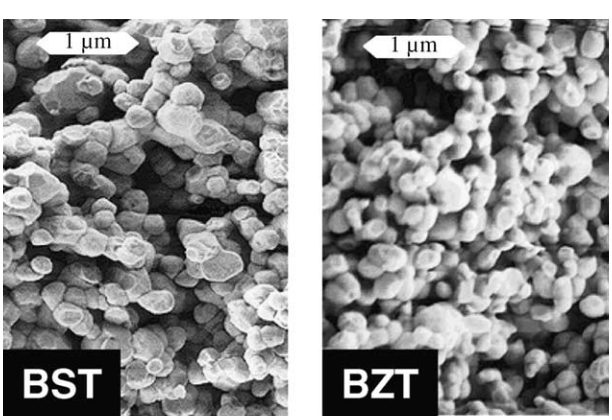

Fig. 1. Cross section of the BST thick film (left) and the BZT thick film (right). Both samples show a homogenous structure with a mean grain size of 300 nm.

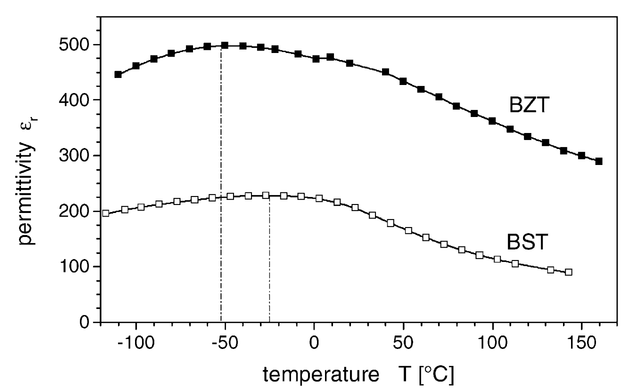

Fig. 2. Diffuse phase transition of BST and BZT thick films measured at 1 kHz.

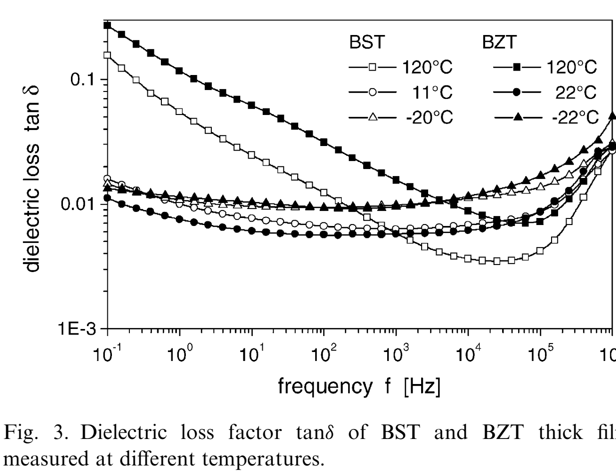

Fig. 3. Dielectric loss factor $\tan\delta$ of BST and BZT thick films measured at different temperatures.

ferroelectric materials. In both BST and BZT small hysteresis have been found at each temperature. This suggests the existence of ferroelectricity over the investigated temperature range of −120 °C to +160 °C, although the material should be in the paraelectric phase at temperatures higher than −30 °C. Another explanation could be, that existing localized charges at grain boundaries or defects are moved and trapped in new positions under the influence of biasing electrical fields applied to the sample and thus show up as a hysteresis effect.[16] This is in accordance with increasing dielectric losses at low frequencies (see Fig. 3) and can be explained in consequence of excitation of localized, hardly reorientable polarizations and conduction mechanisms.[17] Moreover, the enhancement of dielectric losses with temperature pointing out a thermal activation, gives rise to an explanation on the basis of localized charges, which can be reoriented the more easily the higher the temperature is. Additionally there are theoretical considerations which predict a suppression of ferroelectricity in isolated $BaTiO_3$ spheres of about 300 nm diameter.[18] This is a further hint that ferroelectric polarization effects might be dominated by charge accumulation at discontinuous interfaces within the BST and BZT thick films, consisting of numerous grain boundaries.

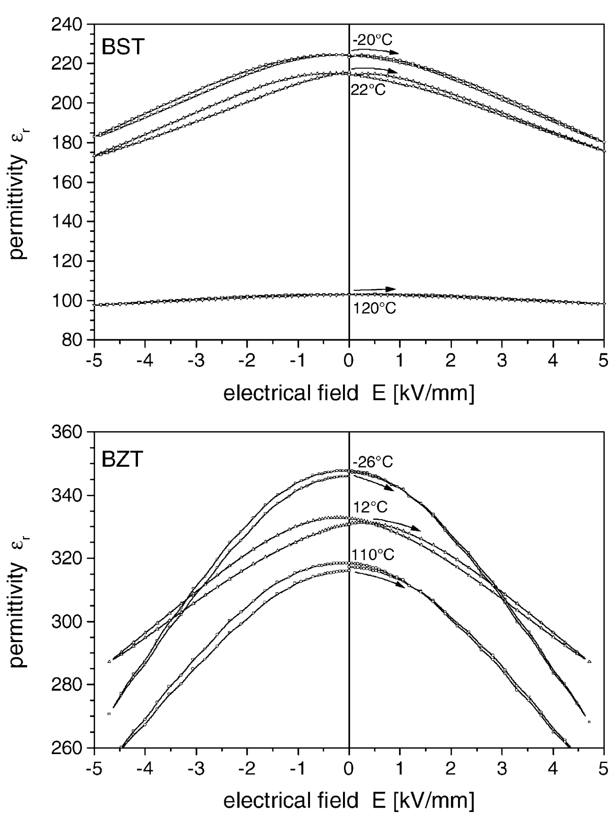

Fig. 4. Hysteresis measurement on BST (top) and BZT (bottom) thick films at 1 kHz. A bias voltage sequence {0 V,. . ., +40 V,. . .,−40 V,. . .,0 V} has been applied at different temperatures.

The tunability of BST and BZT thick films in the low frequency range (see Fig. 5) can be used to estimate the HF tunability. BZT shows a higher tunability than BST. Better performance of BZT at higher temperatures is due to the very diffuse ferroelectric phase transition in $BaZr_{0.3}Ti_{0.7}O_3$ ceramics. This results in a two times higher tunability of BZT at 120 °C compared to BST.

Ngo et al. report a tunability of 17% at RT and an applied field of 2 kV/mm for electrophoretic deposited BST thick films.[11] This is twice the tunability of here presented BST thick films at the same temperature and electrical field. This can be due to the higher permittivity of the electrophoretic deposited thick films. The higher tunability described in [11] is accompanied with higher dielectric loss.

The frequency dependence of permittivity and losses of BST and BZT can be seen in Fig. 6. The strong decrease of BZT permittivity at frequencies higher than 100 kHz is accompanied with an increase of losses and indicates a relaxation lower than for BST. At 30 GHz no values for BZT could be determined with the open resonator method due to extremely high losses. This indicates the occurrence of the relaxation close to this

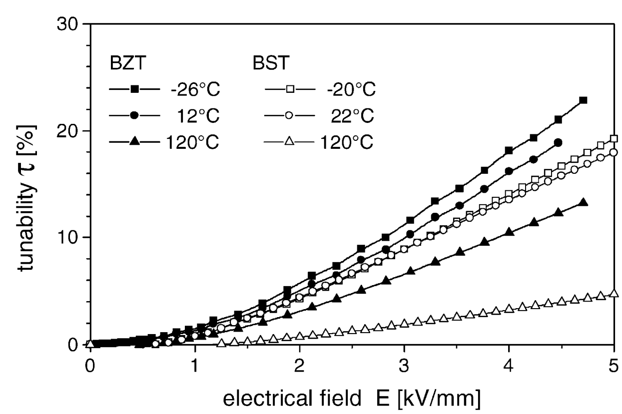

Fig. 5. Low frequency tunability of BST and BZT thick films at different temperatures measured at 1 kHz.

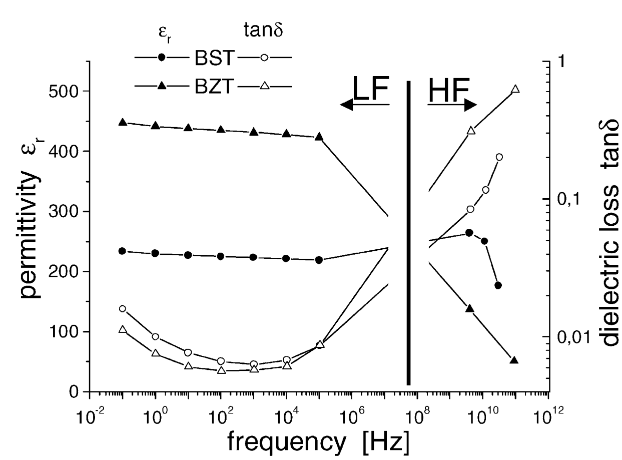

Fig. 6. BST and BZT frequency dependence of permittivity and losses at room temperature.

frequency. Similar problems can be found in BST at 90 GHz. For barium titanate a grain size dependent Debye relaxation has been observed at frequencies of about 100 MHz to 10 GHz.[19] As the grain size of both thick films is similar the lowered relaxation frequency of BZT could be due to the influence of zirconium which has two times the mass of titanium. The slightly higher permittivity for BST in the high frequency region in comparison to low frequencies can be explained by measurement inaccuracy in determining the film thickness of the different samples investigated at LF and HF. An influence of the relaxation on the tunability is observed. At 8 GHz tunability is about 6% for BST and 4% for BZT, respectively.

4. Conclusions

$Ba_{0.6}Sr_{0.4}TiO_3$ (BST) and $BaZr_{0.3}Ti_{0.7}O_3$ (BZT) thick films with grains of 300 nm diameter have been prepared and the dielectric properties have been characterized in a broad frequency range of 100 mHz to 90 GHz.

In LF region, temperature dependent measurements of permittivity show a diffuse phase transition in both materials. The increase in dielectric loss with decreasing frequency especially at high temperatures can be described by a Maxwell–Wagner mechanism. Together with the observed hysteresis at -120 °C to $+160$ °C, this is evidence for charge accumulation at discontinuous interfaces, which dominates ferroelectric polarization effects within the BST and BZT thick films.

A relaxation has been found at about 30 GHz for BZT and 90 GHz for BST. The difference in the relaxation frequencies is ascribed to the two times higher mass of zirconium in comparison to titanium.

Whereas BZT shows a higher tunability than BST at low frequencies, BST shows a better performance in the HF range, due to a higher relaxation frequency. To transfer the good properties of BZT to the HF range, the relaxation should be shifted to higher frequencies. This can be achieved by a further reduction of the grain size to nanoscale.

It has been shown that low permittivity and less temperature dependence can be achieved using porous thick films with a small grain size. Nevertheless, for application under 10 GHz they can not compete with the performance of PIN diodes. The further investigations and optimizations must aim at applications at higher frequencies, e.g. automotive radar at 24 and 77 GHz.

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