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Influence of CaO and CuO on Barium Zinc Tantalate (BZT) Dielectric Properties

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Abstract

The structure and dielectric properties of Barium Zinc Tantalate (BZT) doped by copper oxide (CuO) and calcium oxide (CaO) with a variety of values of mol% doping from 0, 0.1, 0.25, 0.5, 1.0, 1.5 and 2.5 were prepared using a solid state method. A small amount of doping elements increased the relative density. The dielectric constant (ε_r) value of the BZT significantly improved with the addition of the CuO and CaO for the specimens sintered at 1250°C and it could be explained by the increase of the relative density. The tan δ of the CuO and CaO doped with BZT ceramics is lower than pure BZT ceramics, and decreases as the CuO and CaO content increases. Minimum return loss (dB) shown that the best results are produced when it is doped with 0.25 mol% CaO and 0.5 mol% for CuO sintered at 1250°C.

1. Introduction

Barium zinc tantalate (BZT) ceramics is one of the best candidates for dielectric resonator (DR) with high dielectric constant (ε_r > 25), low dielectric loss (tan δ) and also it can operate at high *f* (> 10GHz). DR was made by ceramic and able to resonate at the frequency of the carrier signal to allow that signal to be efficiently separated from other signals in the microwave band, and this frequency is called the resonance frequency (*f*) [1]. Although BZT can produce excellent dielectric properties, the BZT can be expensive to produce. This is due to the high sintering temperature (1500 -1550°C) [2] and long soaking times needed to get the desired properties. Several researches have reported that the dielectric properties of BZT can be increased by adding the dopants such as $BaZrO_3$ [3], Al_2O_3 [4], ZrO [5], TiO_2 [6], SnO_2 [7], and $BaWO_4$ [8] to reduce the sintering temperature and improve the dielectric properties. By adding the ZrO and $BaZrO_3$ the ordering of the crystal structure is transformed from 1:2 to 1:1 and the dielectric properties increased. Desu et al. (1985) point out that the high dielectric property value of BZT ceramics is related to the crystallographic distortion which has a connection with the evaporation of ZnO.

The effect on the dopant such as TiO and Al_2O_3 added to the BZT does not disturb the original structure of the BZT. It is because the size of Ti^{2+} and Al^{3+} ions are too small to disturb the BZT structure and to replace the Zn vacancy [9]. However, the addition of large amount (> 1.5 mol %) of these dopants can decrease the density and dielectric properties. Several dopants were added with varying valencies, ionic size and concentrations and the variations in densification, and microwave dielectric properties studied. It is found that the dielectric properties increase when the ionic radii of the dopant is close to that of the B-site ions (Zn or Ta). The dielectric properties increase when the ionic radii of the dopant is close to that of Zn (0.74 Å) or to that of Ta (0.64 Å). An amount of 0.5 mol% of Mg, Ni, Cr, In, Ga, Sn, Zr, Ce, Mn, and Sb improves the dielectric properties. On the other hand, when the amount of dopant was increased to 1 mol%, the

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dielectric properties were found to increase only for Cr, Ga, Zr, Ce, and Sn. The highest dielectric properties were found for doping with Zr, Cr and Ce.

However, the effect of CuO and CaO-doped BZT has yet to be reported. Therefore, in this research, the phase structure, relative density, microstructure and dielectric properties of CuO and CaO doped BZT ceramics are investigated.

2. Materials and Methods

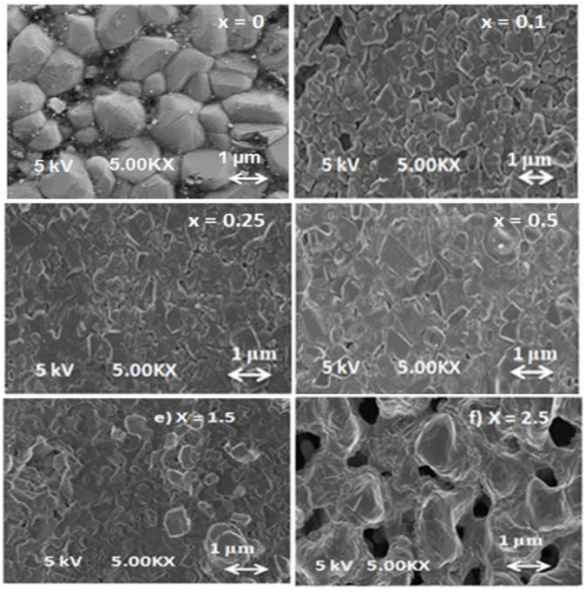
Pure BZT ceramics were doped with 0.1-2.5 mol% of CaO and CuO, and prepared using the conventional solid state reaction method respectively. High purity of raw materials $BaCO_3$ (> 99%, Merck, Darmstadt, Germany), ZnO(> 99%, Merck, Darmstadt, Germany) and Ta_2O_5(>99% Aldrich Chemical Co.) were weighted and mixed stoichiometrically with a zirconia ball for 3 hours and calcined at 1150°C for 1 hour. The calcination temperature was optimized based on the XRD analysis and surface morphology [10]. After re-milling with CaO and CuO additive, the powders were dried and pressed into disc-shaped pellets with a diameter of 15 mm and 1 mm thickness at 125 Mpa and sintered at 1200-1300°C for 4 hours respectively.

The crystal structure of the sintered pellets was studied by using an X-ray diffraction (XRD) using Bruker D8 Advance with CuKα radiation (40kV, 30mA) a diffracted beam monochromator and a step scan mode with the step size of 0.1° and scan in the range of 10°-90° of 2θ°. The density was measured based on the Archimedes method. For the dielectric properties, the analysis was conducted using the HP4219B RF Impendence Analyzer (1MHz-1GHz). The selected samples will be measured for the actual antenna application using HP8720D Network Analyzer (50MHz-20GHz) to find the resonance frequency.

3. Results and Discussion

The SEM micrographs of the BZT + *x*CuO and BZT + *x*CaO ceramics with 0.0 mol% ≤ *x* ≤ 2.5 mol% at 1250°C and 4 hours soaking time are shown in Fig. 1(a)(b). It can be seen obviously that the grain size is greatly influenced by the addition of CuO and CaO. The level of porosity for the doped BZT, then became lower when the CuO and CaO were added respectively and the grain size were denser and formed a more compacted and dense structure. This observation in the porosity and level of sintering from the FESEM seems to be parallel with the observation from the density analysis. The results further reveal that a small amount of CuO and CaO gives an effect on the size reduction, acts as a good grain growth inhibitor and leads to the grains being well-formed.

Fig. 2 shows the relative density of the BZT + xCuO and BZT + xCaO ceramics with 0.0 mol% ≤ x ≤ 2.5 mol%. The relative density of the specimens sintered at 1200°C, 1250°C and 1300°C had slightly increased with the addition of CuO but significantly decreased when the CuO content increased for temperatures of 1200°C and 1300°C. Meanwhile, for the specimen that sintered at 1250°C, the highest density was at 8.68 g/cm3 when x = 0.25 mol% and decreased when there was further addition of CuO. The relative density of the specimens sintered at 1250°C had slightly increased with the addition of CaO but significantly decreased when the CaO content increased. Based on these results, it is revealed that a small amount of CuO and CaO addition can increase the density of the BZT at low sintering temperature compared with the theoretical density, 7.90 g/cm3 that sintered at temperature more than 1450°C.



(a)BZT + *x*CuO

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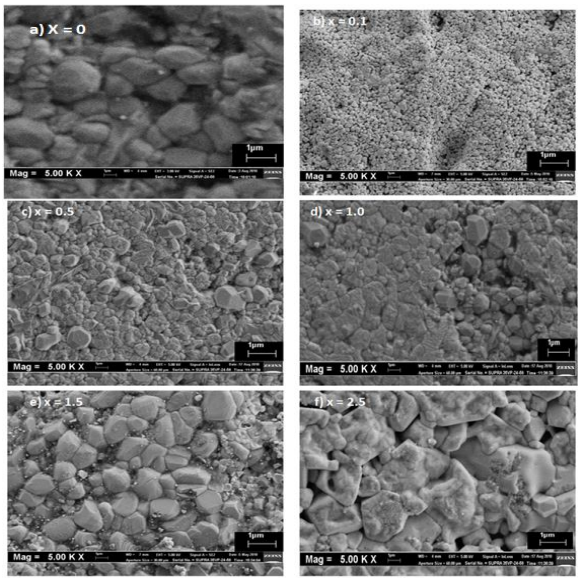

(b) BZT + *x*CaO

Figure 1(a)(b): SEM micrograph of BZT + xCuO and BZT + xCaO for different mol %. a x = 0, b x = 0.1, c x = 0.5, d x = 1.0, e x = 1.5, f x = 2.5 sintered at 1250°C for 4 hours

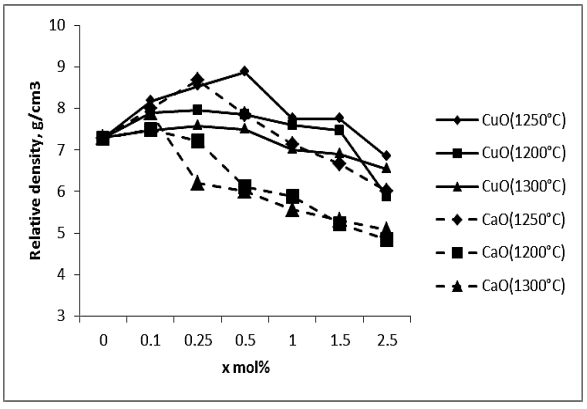

Figure 2: Variation of the relative density with CuO and CaO for BZT ceramics sintered at BZT ceramics sintered at various sintering

Fig. 3 illustrates the variation of the ε_r of BZT + *x*CuO and BZT + *x*CaO ceramics with 0.0 mol% $\leq x \leq$ 2.5 mol%. The relationship between ε_r values of BZT + *x*CuO and BZT + *x*CaO and sintering temperatures presents a trend similar to that between the densities and SEM micrographs, since a higher density means a lower porosity. A maximum ε_r of 72.5 was achieved for 0.5 mol% CuO and 70.25 at 0.25 mol% CaO that sintered at 1250°C. Uniform grain morphologies also contribute to the maximum dielectric properties for each specimen prepared with different CuO and CaO contents due to a reduction in the lattice imperfection [11]. The ε_r decreased when the amount of CuO and CaO increased due to the liquid phase tends to agglomerate at the grain boundary and lower the density and deteriorate the ε_r.

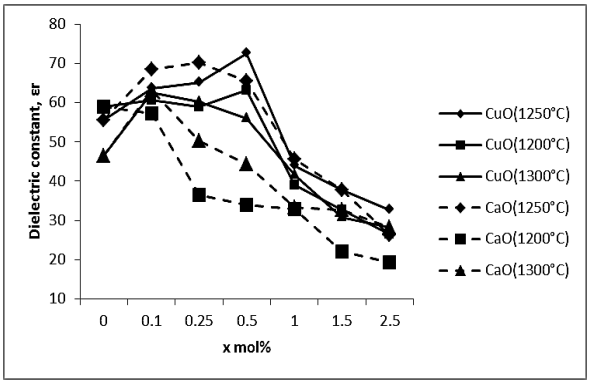

Figure 3: Variation of the ε_r with CuO and CaO for various sintering temperatures for 4 hours temperatures for 4 hours

Fig. 4 shows the variation of tan δ of BZT doped with 0.1 to 2.5 mol% of CuO and CaO respectively. The tan δ value was about 0.025 and decreased with the addition of CuO, and it illustrated a minimum value when x = 0.5 mol% while for CaO, the lowest tan δ was when BZT doped with 0.25 mol% CaO where the value was 0.03 for specimens that sintered at 1250°C. The low value of the tan δ could be explained by the increased relative density. The specimen exhibited the lowest tan δ value when the grain growth was completed. Meanwhile, the increasing of tan δ value at temperature 1200°C due to low density that leads to porosity occurred. For specimens that sintered at 1300°C, the tan δ values were higher compared to 1250°C because the electron hopping that occurred at high sintering temperature [12].

The percentage of bandwidth (%BW) value of BZT + *x*CuO and BZT + *x*CaO ceramics with 0.0 mol% $\leq x \leq$ 2.5 mol% is illustrated in Fig. 5. The function of the BW is to determine the strength of the transmitter and receiver of the signal wave that has been produced.

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If the percent of BW becomes wider, this means that the material can be used for high frequency applications. % of BW was influenced by the ε_r [17]. When the ε_r decreased, the % BW also decreased. The strength of the signal of the DR depends on the % BW. Thus, when the % BW for DR increases, more services can be conducted in the range of that frequency.

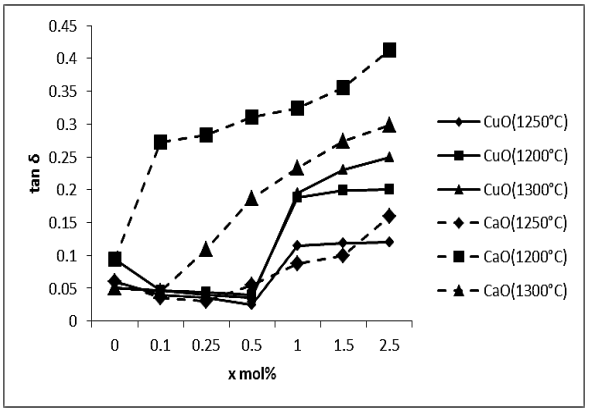

Figure 4: Variation of the tan δ with CuO and CaO for BZT ceramics sintered at various for BZT ceramics sintered at various sintering

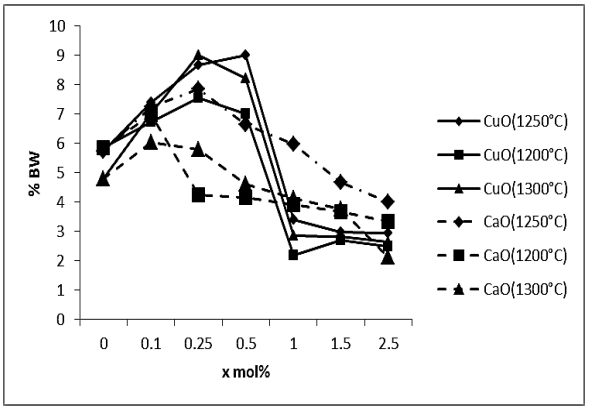

Figure 5: Variation of the % BWwith CuO and CaO sintering temperatures for 4 hours temperatures for 4 hours

Conclusion

Microstructure and microwave dielectric properties of BZT + *x*CuO and BZT + *x*CaO ceramics with 0.0 mol%≤ $x \leq$ 2.5 mol% were investigated. The signature of the CuO and CaO doping were also observed in the grain size lowering of the BZT ceramics, which is one of the factors in the variation of the dielectric properties. On the other hand, the relative density increased and grain growth occurred when a small amount of CuO and CaO were added. Therefore, the increased relative density and grain size could be responsible for the improvement of the dielectric properties. The ε_r and %BW values of the BZT were significantly increased with the addition of CuO and CaO. The increased ε_r value could be related to the increased relative density and grain size. Meanwhile, the tan δ of doped BZT ceramics is lower than that of pure BZT ceramics and decreases as the CuO and CaO content increases. As a conclusion, by doping the BZT with CuO and CaO respectively, the multiphase DR ceramics fabricated in this research can be manufactured with high dielectric properties, as compared to the pure BZT.

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