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Effect of annealing on microstructure of CuO-doped $(Zr_{0.8}Sn_{0.2})TiO_4$

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ABSTRACT

Zirconium tin titanate ceramics, and specifically the $(Zr_{0.8}Sn_{0.2})TiO_4$ (ZST) are the preferred materials for use in resonators or filters working at microwave frequency. However, the problem with these materials is their high sintering temperature which is as high as 1550 °C. In this research, the influence of different amounts of CuO additions on the densification and microstructure evaluations of ZST ceramics modified with 1 wt% ZnO has been studied in two different states: before and after annealing. Results showed that annealing process at 1250 °C resulted in some changes in density, grain size and shape due to the rearrangement of liquid phase and its reactivation, but no secondary phase was detected. Also, variations in lattice parameters during annealing compared to those of as-sintered specimens suggested the possibility of disorder–order transformation during long time high temperature heat treatment process.

1. Introduction

Owing to their high quality factor, high dielectric constant, and low temperature coefficient of resonant frequency, zirconium tin titanate materials are good candidates for applications in microwave domain [1,2]. $(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics, referred to as ZST, have been proved to be among the most popular dielectric resonator materials. This composition offers high value of quality factor and dielectric constant near 37. In addition, its temperature coefficient of resonant frequency is almost zero [3,4]. However, due to their high sintering temperature, it is difficult to reach a fully densified ZST ceramics which is critical in final properties [5]. Using sintering aids as flux formers is a method to reduce the sintering temperature and to keep the microwave properties in a desired range by adding a combination of two or more oxides such as ZnO, La_2O_3, NiO, Fe_2O_3, B_2O_3, Bi_2O_3, and V_2O_5 [5–7]. In all cases, the temperature of liquid phase formation determines the sintering temperature [5,6]. Moreover, Pamu et al. [6] reported that in doped ZST ceramics, quality factor is affected by grain morphology.

Not only bulk ceramics, but also thin films of ZST have found various applications as memory and gate dielectrics [3]. Chemical vapor deposition (CVD), sol–gel, RF magnetron sputtering, and pulsed laser ablation are the most common methods for preparation of ZST thin films [3,4,6]. In addition, the effect of heat treatment as a further process on microstructure of some thin films is reported [1–3]. Yang et al. [3] reported that ZST polycrystalline structure can be obtained by sol–gel method, followed by an annealing process at temperatures higher than 450 °C. Hsu [1] proved that increase in time and temperature of annealing results in higher crystallinity of ZnO-doped ZST thin films prepared by RF magnetron sputtering. It is also reported that at low annealing temperature of 250 °C, preferred growth of grains occurs and this process yields smoother surfaces [2]. However, it is hard to find the effect of annealing on bulk specimens prepared by solid state reactions, using additives as sintering aids.

This paper reports on a study of phases and microstructures of CuO-doped ZST ceramics, formerly modified with 1 wt% ZnO, at two different states: before and after annealing. Structural characteristics of the samples at these states are compared and the effect of annealing process on CuO-doped samples is found. Since CuO forms a liquid phase at 1070 °C, which acts as a flux former and improves the sinterability [8], variations of density, microstructure, and phase evolution of $(Zr_{0.8}Sn_{0.2})TiO_4$ samples are studied as a function of CuO addition.

2. Experimental

2.1. Sample preparation

$(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics were prepared by solid state reactions from pure oxides of ZrO_2, SnO_2 and TiO_2 (purity >99.9%, Merck Co.). The starting materials were mixed according to the desired stoichiometry. The oxides powders were milled in distilled water for 3 h. Mixtures were dried and calcined at 1100 °C for 3 h. Then 1 wt% ZnO and different amounts of CuO (1, 1.5, 2 and 2.5 wt%) as sintering aids, were added to calcined powder and remilled for 1 h. After drying the mixtures, 4 wt% PVA was added as a binder. Pellets of 10 mm diameter and 5.3 ± 0.3 mm thickness were pressed by uniaxial pressure of $2\,T/cm^2$. Samples were sintered at 1250 °C for 3 h.

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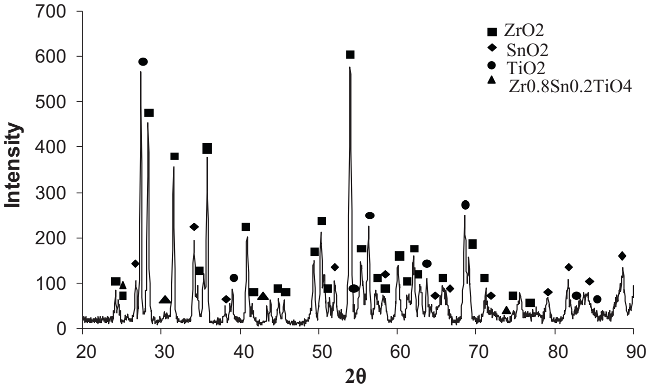

Fig. 1. X-ray diffraction pattern of calcined powder.

In order to investigate the effect of annealing on microstructure properties of ZST ceramics, similar samples were annealed after the sintering step, for 12 h at 1250 °C.

2.2. Characterization procedure

The bulk densities of the pellets were measured by Archimedes method. X-ray diffraction analysis was performed to study the structure and to identify the phase compositions by using copper target X-ray tube (Philips MPD Xpert, $\lambda_{CuK\alpha} = 1.5418$ Å). Microstructural examination of the sintered and annealed specimens was performed by scanning electron microscopy (Philips XL30) equipped with energy dispersive spectroscopy (EDS).

3. Results and discussion

Primary calcination step in preparation of ZST ceramics by conventional solid state method is suggested as it offers the opportunity of pre-reaction of precursors. X-ray diffraction pattern of calcined powder is shown in Fig. 1. It is observed that after calcination at 1100 °C, as received oxides, ZrO_2, SnO_2 and TiO_2 (rutile phase) still exist. A few weak peaks of ZST are also identified which show that it has not been formed completely. While these results are in good agreement with those of Houivet et al. [9], the existence of ZrO_2 and SnO_2 at 1100 °C is in contrast to Huang et al. [10].

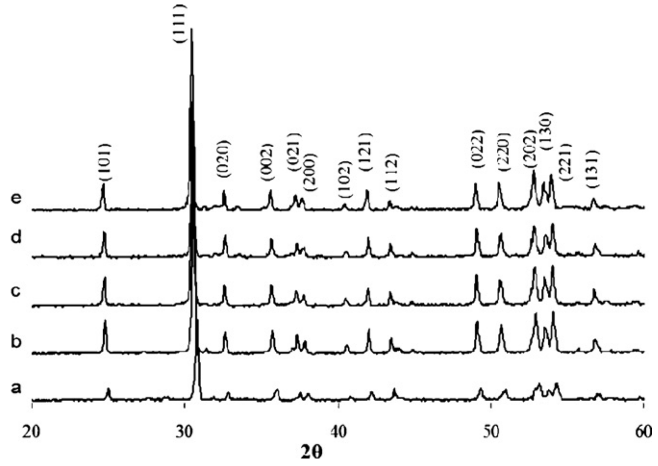

Fig. 2. X-ray diffraction patterns of as-sintered samples: (a)1 wt% ZnO, (b) 1 wt% ZnO + 1 wt% CuO, (c) 1 wt% ZnO + 1.5 wt% CuO, (d) 1 wt% ZnO + 2 wt% CuO, and (e) 1 wt% ZnO + 2.5 wt% CuO.

X-ray diffraction patterns of sintered samples with different amounts of CuO from 0 to 2.5 wt% are shown in Fig. 2a–e, respectively. It can be seen that all samples exhibit an orthorhombic-type structure which corresponds to $(Zr_{0.8}Sn_{0.2})TiO_4$. Although ZnO, as the primary additive, is well known to form boundary phases such as Zn_2TiO_4, no second phase containing Cu^{2+} and Zn^{2+} was detected at these levels of ZnO and CuO due to the fact that the detection of a minor phase by XRD is extremely difficult [11]. As the ionic radius of Cu^{2+}(0.73 Å) is close to those of Zr^{4+} (0.72 Å), Sn^{4+} (0.69 Å) and Ti^{4+} (0.605 Å), Cu^{2+} ions can substitute for tetravalent elements of ZST ceramics [12]. In addition, since the total charges of two copper ions equal tetra, no charge distortion would occur during their entrance into the structure.

Shifts in peak positions of samples with different amounts of CuO indicate the changes in lattice parameters. These parameters were calculated by using the four peaks of (1 0 1), (1 1 1), (0 2 2), and (2 2 0). Table 1 lists the variations of the lattice parameters as a function of additive content. As can be seen, in doped samples, c_0-length value is larger for higher CuO addition. As it is known, above 1400 °C, Zr^{4+} and Ti^{4+} cations distribute randomly within $ZrTiO_4$ structure [13], and it has been proved that addition of Sn^{4+} stabilizes this disordered structure [14]. Furthermore, different additives can

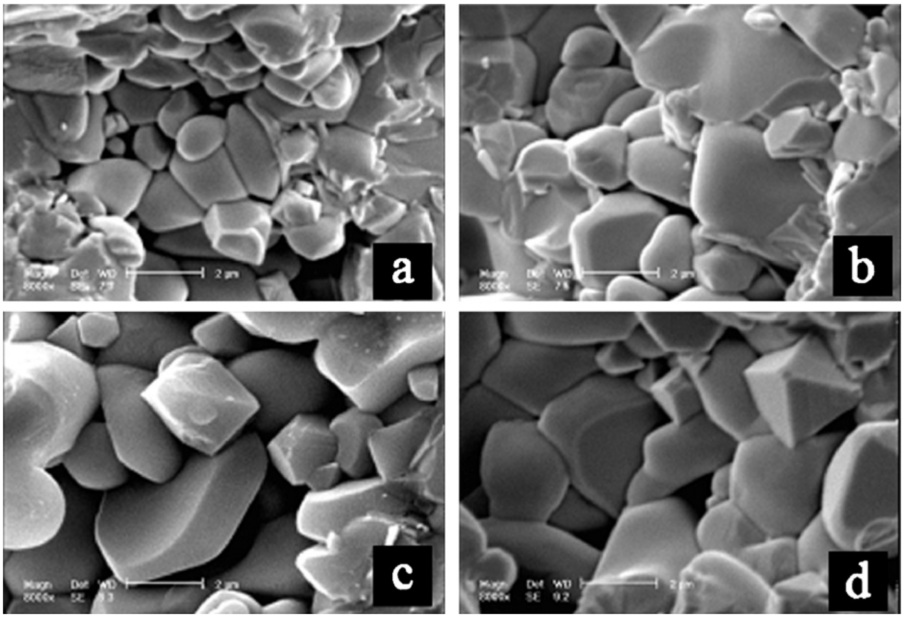

Fig. 3. SEM micrographs of as-sintered samples: (a) 1 wt% ZnO + 1 wt% CuO, (b) 1 wt% ZnO + 1.5 wt% CuO, (c) 1 wt% ZnO + 2 wt% CuO, and (d) 1 wt% ZnO + 2.5 wt% CuO.

Table 1
Lattice parameters, lattice volume and density of as-sintered samples with different amounts of CuO.

Sample	a_0 (Å)	b_0 (Å)	c_0 (Å)	V_0 (Å^3)	ρ (g/cm^3)
1 wt% ZnO	4.683	5.008	5.474	128.379	3.668
1 wt% ZnO + 1 wt% CuO	4.752	5.049	5.467	131.169	4.369
1 wt% ZnO + 1.5 wt% CuO	4.764	5.053	5.473	131.749	4.487
1 wt% ZnO + 2 wt% CuO	4.765	5.033	5.499	131.878	4.781
1 wt% ZnO + 2.5 wt% CuO	4.770	5.018	5.542	132.649	4.667

Table 2
Lattice parameters, lattice volume and density of annealed samples with different amounts of CuO.

Sample	a_0 (Å)	b_0 (Å)	c_0 (Å)	V (Å^3)	ρ (g/cm^3)	$\lvert\Delta d/d\rvert$
1 wt% ZnO	4.757	5.033	5.510	131.920	3.832	1.3143
1 wt% ZnO + 1 wt% CuO	4.727	5.021	5.480	130.065	4.491	0.9039
1 wt% ZnO + 1.5 wt% CuO	4.759	5.049	5.456	131.100	4.576	0.5701
1 wt% ZnO + 2 wt% CuO	4.785	5.057	5.468	132.311	4.843	0.4624
1 wt% ZnO + 2.5 wt% CuO	4.752	5.029	5.492	131.260	4.710	0.4576

affect disorder–order transformation in ZST. It has been shown that the changes in structure from disordered to ordered state, are accompanied by reduction in unit cell volume and c_0 length [15]. Since these two parameters have been increased with CuO addition (Table 1), it can be concluded that CuO addition might not accelerate the disorder–order transformation.

Density values as a function of CuO content are also seen in Table 1. Since increasing the CuO content leads to higher densities, it can be concluded that CuO has improved the densification of ZST samples effectively and performed as a flux former at 1250 °C. Moreover, while the density has an increasing trend up to 2 wt% CuO, it is decreased slightly by higher weight percent of CuO.

Fig. 3a–d shows SEM micrographs of the typical specimens. Grains are faceted in all samples and by increasing CuO content, they become more faceted and slightly larger. The range of grain size for all samples was 1–3 μm and addition of CuO increased the number of larger grains, and volume percentage of smaller grains decreased.

Fig. 4 shows X-ray diffraction patterns of annealed samples for different amounts of CuO addition. Similar to as-sintered samples, annealed ones show the orthorhombic-type structure which corresponds to $(Zr_{0.8}Sn_{0.2})TiO_4$. Phase identification of these samples did not detect secondary phases containing Cu or Zn ions, and no changes were observed in comparison with as-sintered samples. During annealing, copper oxide has more time to form grain boundary phases and operate as a flux former. In addition, it might not been activated completely during the primary sintering, and

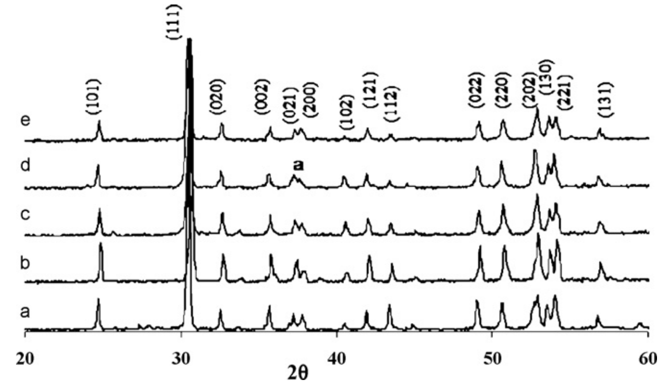

Fig. 4. X-ray diffraction patterns of annealed samples: (a) 1 wt% ZnO, (b) 1 wt% ZnO + 1 wt% CuO, (c) 1 wt% ZnO + 1.5 wt% CuO, (d) 1 wt% ZnO + 2 wt% CuO and (e) 1 wt% ZnO + 2.5 wt% CuO.

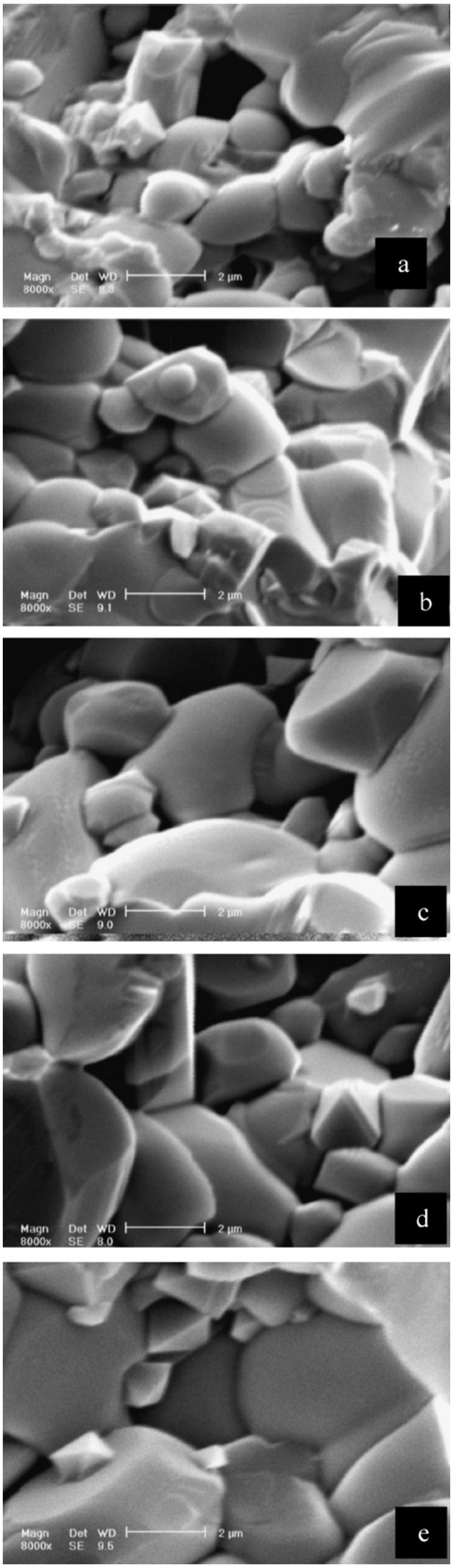

Fig. 5. SEM micrographs of annealed samples: (a) 1 wt% ZnO, (b) 1 wt% ZnO + 1 wt% CuO, (c) 1 wt% ZnO + 1.5 wt% CuO, (d) 1 wt% ZnO + 2 wt% CuO and (e) 1 wt% ZnO + 2.5 wt% CuO.

annealing could improve it. Therefore, it can be concluded that the amount of the boundary phase would probably increase during annealing because of the long time high temperature process, but also, in this case, the amount of phase is not enough to be identified by XRD.

Table 2 includes lattice parameters, density and relative change in diameter ($|\Delta d/d|$) of annealed samples. As can be seen, for all samples with CuO addition, annealing resulted in shrinkage across the diameter. The amount of shrinkage decreases as the weight percentage of CuO is increased. In addition, when the density values in Table 2 are compared with those in Table 1, it is found that annealing has led to higher density for every particular sample. The difference in shrinkage values and changes in density indicate that in specimens with lower amounts of CuO, reactivation of additive and its rearrangement plays more effective role in increasing the value of density.

Fig. 5 shows SEM micrographs of annealed samples with different amounts of CuO. These micrographs show that in annealed samples, grain size is in the range of 1–3 μm, like the as-sintered ones, but the grains in annealed samples are a little larger. Also, there are some grains which are larger than 3 μm. This growth shows the improvement of diffusion during annealing process. In all samples, grains were neither spherical nor faceted. By increasing the amount of CuO, some grains with regular shape appeared which can be easily seen in 2 and 2.5 wt% CuO-doped samples. However, the number of these grains is very low in all samples.

Another important fact that should be discussed for annealed samples is the possibility of oxygen entrance to the structure. Oxygen vacancy, known as a common defect in ZST ceramics can increase dielectric losses, and different additives have dissimilar roles [10]. During the addition of CuO, Cu^{2+} performs neither as 3+ ions which their entrance and substitution with tetravalent ions in ZST increases oxygen vacancies nor like 5+ ions which can decrease the number of oxygen vacancies [10,15]. However, diffusion of oxygen from atmosphere because of high temperature and long time annealing is possible. Oxygen ionic radius (1.4 Å) is much larger than those of ZST cations. Its vacancy reduces the unitcell volume and entrance of this ion may increase this parameter. Comparison of lattice parameters and unitcell volume in two different states (Tables 1 and 2) shows that these parameters do not have regular changes in annealed samples. However, the trend of changes in unitcell volume is important. If the entrance of oxygen was the main process during annealing, this parameter should increase. But as measured values listed in Table 2, it has decreased for all doped samples except for the one with 2 wt% CuO. Reduction in unitcell volume indicates that another process may occur; cation ordering and changes in spatial charges are two processes which could be effective in lattice volume reduction. As this parameter has decreased in almost all doped samples, it can be concluded that cation ordering is more effective than oxygen entrance. However, it is not yet possible to prove that the transformation from the disordered structure to the ordered one has occurred or not. Although it is necessary to keep samples in high temperatures for long time to achieve the ordered structure [16], larger lattice volume in all samples than that of as-sintered undoped one makes it difficult to assure that the transformation has taken place completely.

4. Conclusions

The influence of CuO on ZST ceramics was investigated as a sintering aid in two different states. Addition of CuO led to an increase in grain size and density, and some changes in lattice parameters in both states. While rearrangement of liquid phase during annealing resulted in some changes in density, grain size and grain shape, no other new phases were detected. In addition, the variations in lattice parameters during annealing compared to those of as-sintered specimens suggested the possibility of disorder–order transformation during long time high temperature heat treatment process.

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