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Microstructure and Microwave Dielectric Properties of Ni-doped $(Zr_{0.8}Sn_{0.2})TiO_4$ Ceramics

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The effects of NiO addition on the microstructure and microwave dielectric properties of $(Zr_{0.8}Sn_{0.2})TiO_4$ (ZST) were investigated. With the NiO addition, a higher density of ZST ceramics than 95% of the theoretical values has been obtained in the sintering temperature range of 1400 to 1500°C. Energy dispersive X-ray spectrometry (EDS) analysis of sintered specimen shows the presence of second phase at grain boundaries, which is considered to be $NiTiO_3$. Dielectric constant of the specimen is found to increase linearly with density. Q-values and TC_f decrease with increasing NiO content. The variation of dielectric properties with NiO content is discussed in terms of the second phase. The ZST ceramics with 0.25 wt% NiO showed ε_r=38, Q=7000 at 7 GHz and TC_f=-0.5 ppm/°C, comparable with the values obtained by the previous investigations.

Key words : ZST, Second phase, $NiTiO_3$, Q-value

I. Introduction

Zirconium tin titanate (ZST) ceramics, a solid solution of ZrO_2, TiO_2 and SnO_2, has reasonably good microwave properties: i. e. a high dielectric constant (ε_r), a high Q-factor and zero temperature coefficient of resonant frequency (TC_f) in SHF band. However, it has been found that ZST powders do not readily sinter by solid state reactions. Therefore, sintering aids, such as ZnO, have been invariably added to achieve good densification at temperature range of 1200 to 1400°C. According to previous works,[1-4] microwave dielectric properties of ZST are affected by the composition, microstructure and other phases present. Therefore, it has been known to be important to select proper additives, their quantities and processing conditions to improve microwave dielectric properties. There are a number of publications and patents which report on the efficacy of a variety of sintering aids and dopants which are employed to enhance sinterability, reduce densification temperature, and improve Q values.[5,6]

The addition of MnO_2 with ZnO has been reported to enhance the sinterability, reduce densification temperature, and improve Q values.[7] Recently, there has also been a report that the addition of WO_3 with ZnO and prolonged sintering could improve the Q of ZST.[8] However, a significant deterioration in Q value is caused by addition of Fe_2O_3 with ZnO. But the deterioration was somewhat suppressed by the addition of NiO with Fe_2O_3.[5] These additives, however, have led to the degradation of Q-factor due to the segregation of Fe_2O_3, NiO and ZnO into grain boundaries.

There have also been reports on the effects of combined addition of La_2O_3-ZnO[9] and NiO-CdO[10] on the sintering behavior and dielectric properties of ZST. When NiO was added with CdO, grain size increased linearly with NiO content. It was thus concluded that Ni acts as a grain growth enhancer. This is contrary to the conclusions made by other investigators.[5]

Addition of ZnO with other dopants may be assumed to cause significant deviation from the properties of materials without ZnO. Difficulties are therefore encountered in attempting to separate the effects of dopants on the dielectric behavior of ZST with dopants from the influence of ZnO.

The work reported herein was undertaken in an attempt to clarify the effects of the addition of NiO and microstructural features on the microwave dielectric properties of ZST. An interpretation of the role of grain boundary phase in determining dielectric properties is attempted. An understanding of these effects is clearly of importance to the development of materials with improved dielectric properties.

II. Experimental Procedure

ZST ceramics studied were prepared by conventional solid state synthesis from the oxides of >99% purity. Oxide compounds of 50 mol% TiO_2, 40 mol% ZrO_2 and 10 mol% SnO_2 with 0.25~2.0 wt% NiO addition were mixed for 24 hr in nylon jar with zirconia ball, then dried and calcined at 1150°C for 5 hr. After remilling, the powder was dried and pressed into discs and sintered at 1300~1500°C for 4 hr in air.

X-ray diffractometer was used to identify the cry-

stalline phases in sintered discs. Microstructure of specimens were studied using TEM and SEM. TEM specimen was cut from disc, mechanically ground, and ion milled using argon. Composition analysis was carried out by EDS system attached in both SEM and TEM. Rigaku D/max-RC was used for the X-ray measurements and Akashi SR50 SEM and Philips CM30TEM microscopes were used to examine the specimens. The density of the sintered specimens were measured by the water immersion technique. The average grain size was determined by measuring the mean linear intercept of the grains.[11]

The dielectric properties in the microwave frequency range were measured by a dielectric post resonator technique, suggested by Hakki-Coleman[12] and Courtney.[13] A cylindrical resonator is placed between two parallel silver plates. The specimens were polished to such a size that the resonant frequency of this mode fell within the frequency range 7~8 GHz. The particular mode chosen for these measurements is the TE_{011} mode. The Q-factors reported in this article have all been normalized to a frequency of 7 GHz, assuming the empirical relationship $Q \times f_o$=constant.

III. Results and Discussion

XRD patterns of ZST as a function of NiO content are shown in Fig. 1. The major phase could be indexed in terms of an orthorhombic unit cell of ZST. We could not detect any changes in lattice parameters due to the addition of NiO. However, a minor amount of a Ni-rich second phase was detected in heavily doped specimens as designated by asterisk. In order to verify the presence of second phase, SEM. TEM studies and EDS were carried out on sintered specimens. Figure 2 shows the result of X-ray microanalysis of the specimens with 1.0 and 2.0 wt% NiO contents. EDS spectrum revealed the presence of a second phase at the grain boundaries (spot B and spot D in Fig. 2). However, we could not detect any Ni in the grains (spot A and spot C in Fig. 2). As can be seen in the figure, the grain boundary region was rich in Ni and Ti with small amount of Zr and Sn.

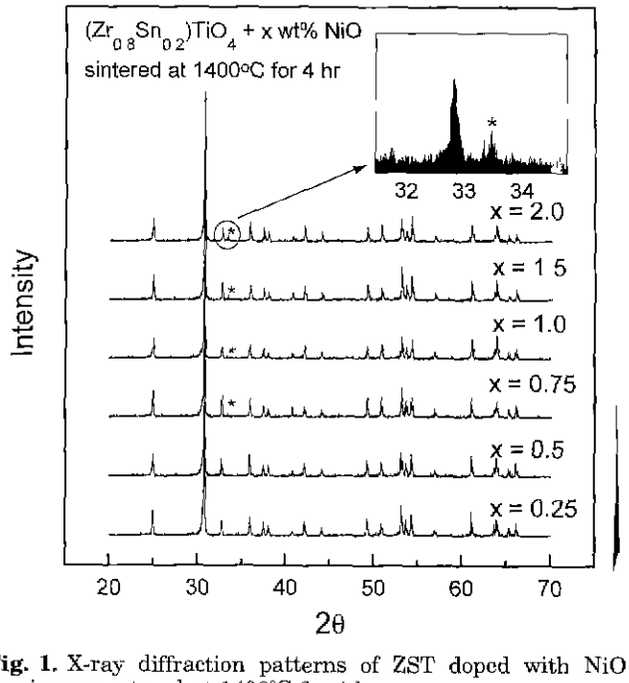

Fig. 1. X-ray diffraction patterns of ZST doped with NiO specimens sintered at 1400°C for 4 hr.

Figure 3(a) is the bright field image of the second phase. The inset shows selected area diffraction pattern (SADP) taken from the same area. The ring pattern observed in the SADP indicates the formation of polycrystalline phase at the grain boundaries. EDS shows that major components in the second phase are Ni and Ti (Fig. 3(b)). The amount of Zr and Sn in this phase is negligible. Thus, the second phase, verified by EDS, is considered to be in the form of nickel titanate, $NiTiO_3$. However, we do not rule out the possibility of the presence of other compounds, such as Ni_2TiO_4. But the atomic percents of Ni and Ti in EDS spectrum indicate that the phase is more likely to be $NiTiO_3$.

To confirm the above analysis, $NiTiO_3$ ceramics was prepared by sintering for 2 hr in the temperature range of 1330~1400°C. The formation of $NiTiO_3$ was confirmed by XRD (Fig. 4). The major peak at 33.2° matches that designated by asterisk in Fig. 1. Dielectric constant (ε_r) and Q-value of $NiTiO_3$ were measured to be about 12 and 3,500 at 7 GHz, respectively. Both ε_r and Q of $NiTiO_3$ are lower than the measured values for ZST. These values will be referred later when dielectric properties of ZST are discussed. In summary, XRD, SEM and TEM studies suggest that Ni prefers to react with Ti in ZST bodies and form a second phase at grain boundaries. The presence of minor amounts of this phase at grain boundaries in ZST is expected to affect the microwave dielectric properties of ZST ceramics.

The effect of NiO addition on microstructure was investigated by SEM. The increase of average grain size with NiO content was clearly noticeable. We could not find any evidence of abnormal grain growth in our specimens, although abnormal grain growth have been observed in ZnO doped specimens.[14]

The variation of grain size and density with the NiO content and sintering temperature are shown in Fig. 5. The average grain size increases with NiO content and sintering temperature. This could be attributed to the presence of Ni-rich second phase at grain boundaries. Thus, it is thought that Ni ions are working as grain growth enhancers.

The relative density steadily increased with increasing temperature from 1300 to 1500°C, as shown in Fig. 5. The density of ceramics sintered above 1350°C ranged between 93% and 98% of the theoretical density, except for specimens with low NiO content. However, the densities of sintered specimens do not show significant variation with increasing NiO content.

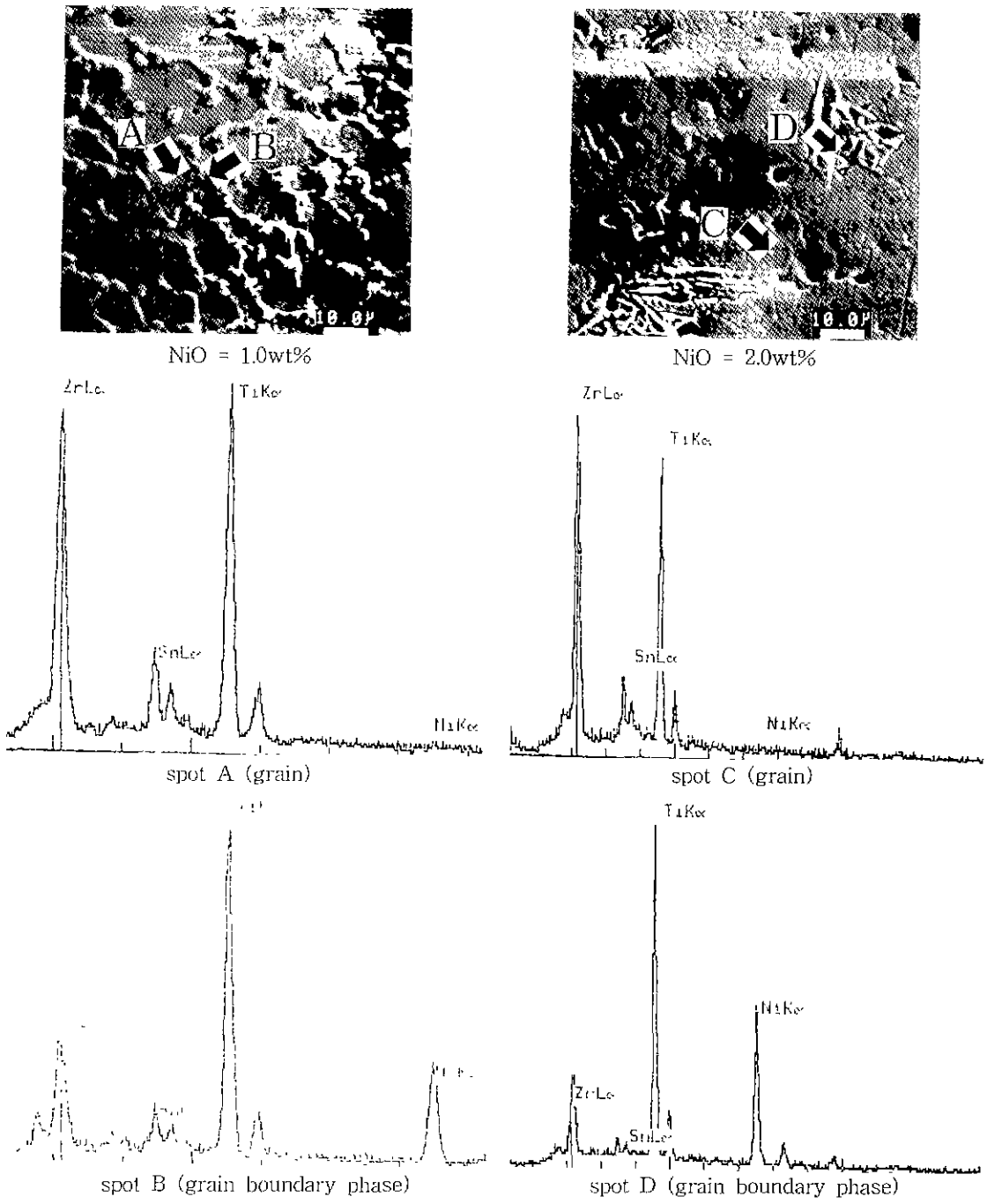

Fig. 2. SEM EDS of grain and grain boundary phases in ZST specimens with 1.0 and 2.0 wt% NiO sintered at 1450°C for 4 hr.

The variation of dielectric constant (ε_r) with NiO content and sintering temperature is illustrated in Fig. 6(a). It has been noticed that the variation of ε_r with NiO is very similar to the variation of density with NiO for all sintering temperature. Figure 7 shows the dielectric constant (ε_r) of the specimens as a function of percentage theoretical density. ε_r is increased linearly with increasing density as expected.

The variation of the quality factor (Q-factor) with additive content is shown in Fig. 6(b). The Q-factors are normalized values to a frequency of 7 GHz. There is a slight decrease in Q with increasing additive content. This result is attributed to the presence of second phase at grain boundaries which is in the form of $NiTiO_3$. Q-factor of $NiTiO_3$ was about 3,500 as previously described and the presence of minor amounts of this phase at grain boundaries in ZST is thought to lead to a reduction in Q, due simply to the additive effects of the introduction of an amount of a more lossy dielectrics.

Formation of the second phase could also affect the

Fig. 3. (a) TEM bright field image of grain boundary phase in powder sample of ZST with 1.0 wt% NiO sintered at 1450°C for 4 hr.

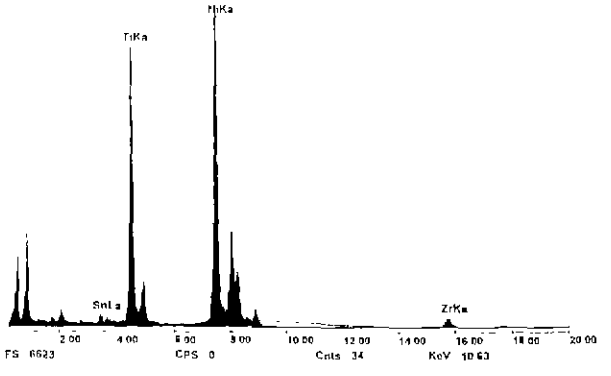

Fig. 3. (b) TEM EDS of grain boundary phase in powder sample of ZST with 1.0 wt% NiO sintered at 1450°C for 4 hr.

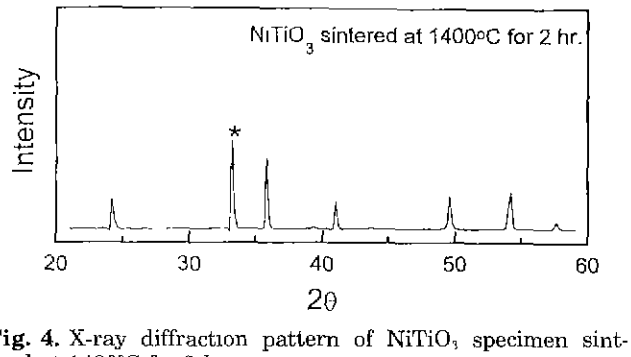

Fig. 4. X-ray diffraction pattern of $NiTiO_3$ specimen sintered at 1400°C for 2 hr.

stoichiometry of major ZST phase. Since NiO is added to ZST, the actual composition of ZST could be Ti-deficient due to the loss of Ti ions to the second phase at grain boundaries and as a result, Q of ZST could degrade to a lower value.

An attempt is made to find a correlation between Q-values and grain size or density by plotting Q-values as

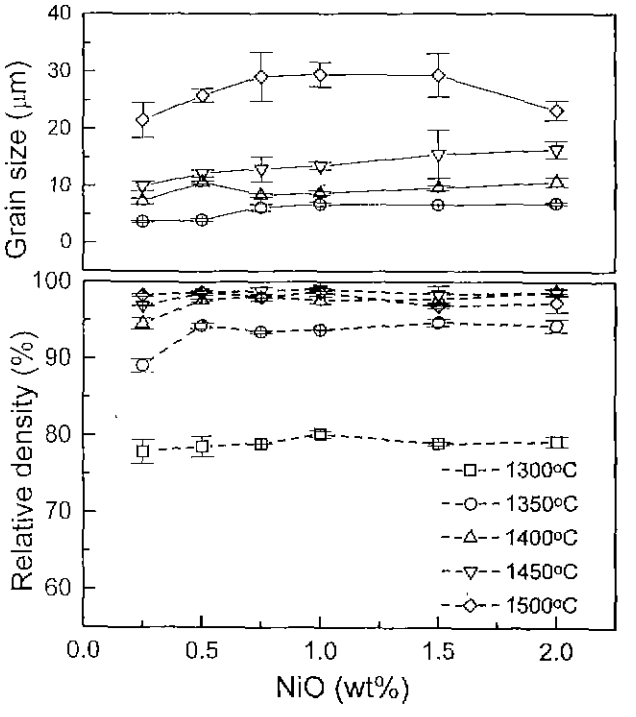

Fig. 5. Grain size and relative density as a function of NiO additives for ZST specimens sintered at various temperatures.

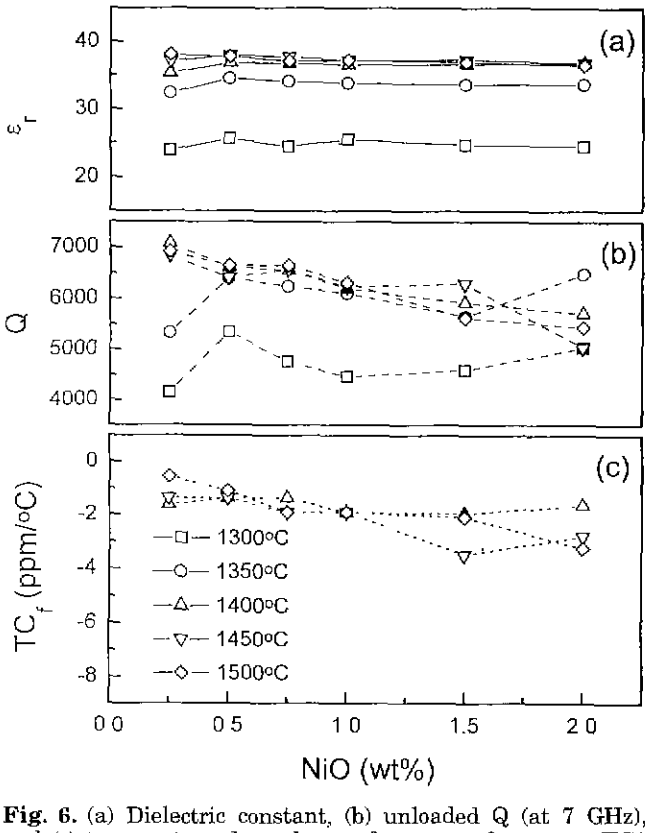

Fig. 6. (a) Dielectric constant, (b) unloaded Q (at 7 GHz), and (c) temperature dependence of resonant frequency (TC_f) as a function of NiO additives for ZST specimens sintered at various temperatures.

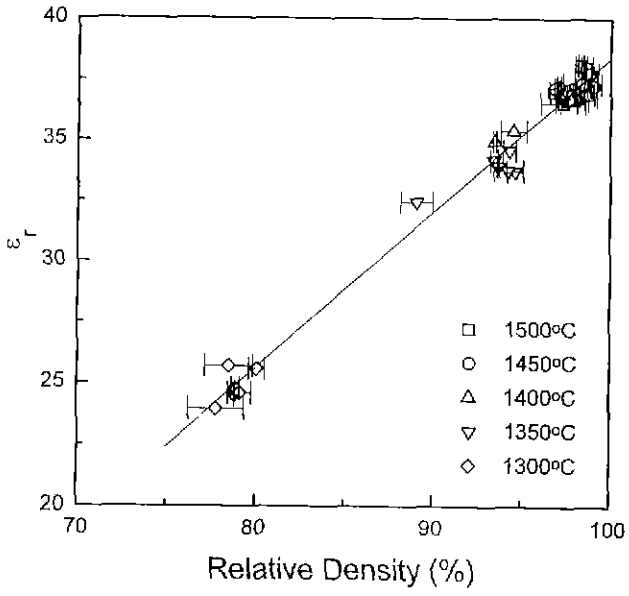

Fig. 7. Relative density dependence of dielectric constant for ZST specimens sintered at various temperatures.

a function of grain size or density for given compositions. However, we could not find any correlation between Q and grain size or density for specimens of 90% theoretical density. Thus it can be stated that grain size and density are not the major factor controlling the Q-values. Same conclusion has been made before by a previous investigator.[15]

Figure 6(c) gives the variation of the temperature coefficient of resonant frequency (TC_f) with NiO content. TC_f decreased from -0.5 to -3.4 ppm/°C with increasing NiO content from 0.25 to 2.0 wt%. This is thought as a result of formation of a boundary phase, $NiTiO_3$. TC_f of the $NiTiO_3$ was measured to be -15.8 ppm/°C.

IV. Conclusion

Ceramics of composition $(Zr_{0.8}Sn_{0.2})TiO_4$ doped with NiO were prepared. The densification of ZST ceramics has improved by the addition of NiO. A dense body of density above 95% theoretical has been obtained. A small amount of second phase was observed at grain boundaries whereas the grains were free of Ni ions. The major portion of the second phase is considered to be $NiTiO_3$. Q-values of ZST decreased with increasing NiO content. The presence of the second phase at grain boundaries is considered to lead to a slight degradation in Q due to the additive effects of the introduction of a small amount of a more lossy dielectrics, namely, $NiTiO_3$. TC_f decreased from -0.5 to -3.4 ppm/°C with increasing NiO content. This is thought as a result of formation of $NiTiO_3$ whose TC_f was measured to be -15.8 ppm/°C.

Acknowledgments

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