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Influence of sintering atmosphere on the microstructure and electrical properties of $BaTiO_3$-based X8R materials

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The effect of sintering atmosphere on the microstructure and capacity-temperature characteristics (TCC) of Yb-Mg and Yb-Mn substituted $BaTiO_3$ was investigated. The XRD and SEM results indicated the suppression of the solubilities of the acceptor ions when firing under reducing conditions. Mn was confirmed to promote the grain growth of $Yb_2Ti_2O_7$ while Mg could suppress the grain growth of this second phase. The X8R specification (−55 to 150°C, $\Delta C/C = \pm 15\%$ or less) could be satisfied by firing under proper conditions for the two compositions. It is suggested that the change of the solubilities of the acceptor ions, as well as the valence states of the Mn ions would affect the TCC behavior of the core-shell-structured $BaTiO_3$ materials. *© 2006 Springer Science + Business Media, Inc.*

1. Introduction

X7R multi-layer ceramic capacitors (MLCCs) are widely used for miniaturization of electronic components because of their temperature-stable dielectric behavior(−55 to 125°C, $\Delta C/C = \pm 15\%$ or less). In recent years, MLCCs have come into use for automotive applications, such as the engine electronic control unit (ECU), anti-lock brake system (ABS), and programmed fuel injection (PGMFI). As these systems work under harsh conditions, MLCCs that can only meet the X7R characteristic are not good enough to be used. Therefore, MLCCs satisfying EIA X8R specification (−55 to 125°C, $\Delta C/C = \pm 15\%$ or less) for automotive applications have been paid much attention recently [1–3].

$BaTiO_3$-MgO-Re_2O_3 (Re represents rare earth elements) and $BaTiO_3$-MnO-Re_2O_3 system were both heavily investigated due to their temperature-stable properties [4–8]. Medium ionic radius rare earth elements, such as Y, Dy and Ho, were confirmed to be very useful to improve lifetime performance of the non-reducible dielectric compositions [9, 10]. Therefore, they were often used in X7R Ni-MLCCs. However, as the Curie point (T_C) of pure $BaTiO_3$ is close to 130°C, it is extremely difficult to satisfy the R characteristic of the capacity-temperature characteristic ($\Delta C/C = \pm 15\%$ or less) in the region higher than that. Jung and co-workers studied the effect of the rare earth elements in $BaTiO_3$-$MgCO_3$-MnO_2-Re_2O_3 system [1]. They suggested that smaller ionic radius rare earth elements, such as Yb and Lu, were effective dopants to meet the X8R characterization, compared with medium and larger ionic radius ones, owing to that they could shift the Curie temperature to high temperature side. Sato *et al*. also confirmed that smaller ionic radius rare earth elements, such as Sc, Er, Tm, Yb, and Lu were indispensable for X8R Ni-MLCCs, at the same time, they also suggested that medium ionic rare earth elements, such as Y, Dy, Ho, Tb, Gd and Eu be added to the temperature-stable dielectric composition to improve the IR and IR lifetime of the MLCCs [2, 3]. However, few researches have been focused on the effect of sintering atmosphere on the X8R materials.

Of all the smaller ionic radius rare earth elements mentioned above, Yb is preferred to make X8R materials, owing to that it has large effect on improvement of the capacity-temperature characteristics and it is inexpensive compared with the other elements, such as Lu and Sc etc. In this paper, we report the effect of sintering conditions on the microstructure and dielectric properties of Yb-Mg and Yb-Mn substituted $BaTiO_3$. The possible mechanisms were also discussed.

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TABLE I Compositions of samples (mole%)

	$BaTiO_3$	Yb_2O_3	$BaSiO_3$	$MgCO_3$	MnO_2
comp.MG	100	1.5	1.0	1.5	–
comp.MN	100	1.5	1.0	–	1.5
comp.MG1	100	2.5	1.0	1.5	–

2. Experimental procedure

Submicrometer size hydrothermal $BaTiO_3$ powders and reagent grade Yb_2O_3, $MgCO_3$ and MnO_2 were used as starting materials. $BaSiO_3$ was used as a sintering aid. In order to determine the effect of Mg and Mn on the microstructure and dielectric properties of the $BaTiO_3$-based ceramics, additives were added according to Table I. The three compositions were abbreviated to comp.MG, comp.MN, and comp.MG1, respectively. The mixed powders were ball-mixed in deionized water for 20 h. The prepared ceramic powders were pressed in disk form (10 mm in diameter by 1 mm thick) by mixing ceramic powder with 3 wt% of PVA binder. After debindering, the disks were fired at 1270°C for 2 h under oxidizing conditions (air), under reducing conditions controlled by H_2, N_2 and O_2, or under reducing conditions controlled by H_2, N_2 and O_2 with a subsequent annealing at 1000°C under conditions controlled by N_2 and O_2, the resulting samples were denoted as air-fired samples, reducing-fired samples and re-oxidized samples, respectively.

In/Ga alloy was applied on both sides of the as-fired samples after firing to obtain the contact electrodes. Dielectric measurements of the samples were performed by using a LCR meter (YY2812) auto-controlled by computer at 1 kHz and 1.0 V rms in the temperature range from −55 to 150°C. Insulation Resistance was measured at room temperature on a megohmmeter (HM2672A) at 100 V DC.

Microstructure of the $BaTiO_3$-based ceramics was observed using a S-530 scanning electron microscope (SEM). The X-ray diffraction (XRD) analyses were carried out using a Philips X'Pert diffractometer over the range of $2\theta = 20$–$70°$ with Cukα radiation.

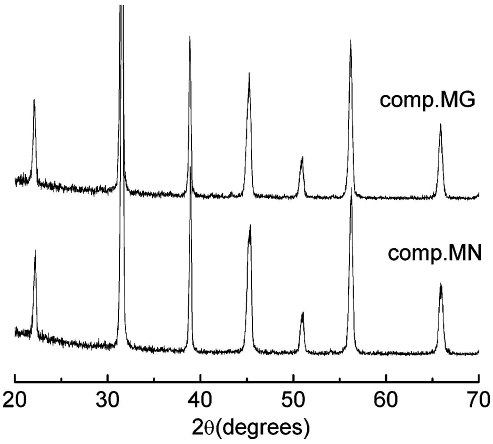

Figure 1 XRD patterns of air-fired comp.MG and comp.MN.

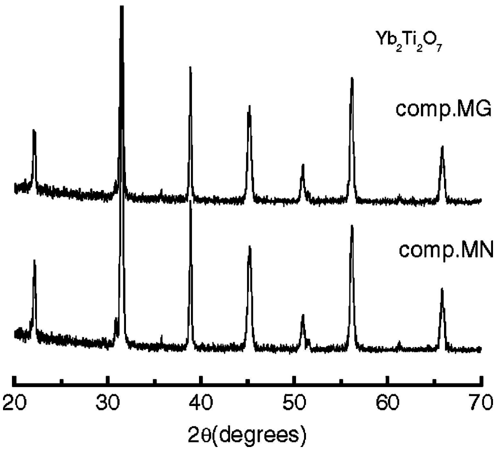

Figure 2 XRD patterns of re-oxidized comp.MG and comp.MN.

3. Results and discussion

The X-ray diffraction patterns of the air-fired samples of comp.MG and comp.MN in Fig. 1 show a clear single perovskite phase. This indicates that the solubility limit of the Yb in $BaTiO_3$ in air is more than 3 mole%. The crystal structures of the two samples were both pseudo cubic, as evidenced by the overlapping of the (200) and (002) peaks in the range of $2\theta = 44$–$46°$. This observation coincided with Molokhia *et al.* who confirmed that the room temperature structure of $BaTiO_3$ would transform from tetragonal to cubic with the increase of doping amount of Yb [11].

Fig. 2 shows the XRD patterns of the re-oxidized samples of comp.MG and comp.MN. Also the crystal structures of the doped $BaTiO_3$ ceramics were considered as pseudo cubic. However, a second phase, identified as pyrochlore-type $Yb_2Ti_2O_7$, was detected for both of the re-oxidized samples, confirming that the solubility limit of Yb in $BaTiO_3$ in the reducing atmosphere was less than 3 mole%. The extra Yb_2O_3 beyond the solubility limit may react with TiO_2 to form the $Yb_2Ti_2O_7$ phase. As Yb^{3+} occupies Ti-site in $BaTiO_3$ as a electron acceptor [10], this phenomenon can be interpreted by the model proposed by Bheemineni *et al.* who suggested that acceptor solubilities in $BaTiO_3$ could be strongly depressed when sintered in highly reducing atmospheres [12]. The solubility suppression was attributed to a mass-action interaction between the processes that generate vacancies, those that result from the compensation of acceptor centers, and those that result form reduction. They also suggested that the normal solubility could be restored by subsequent anneals in air.

Fig. 3 illustrates the SEM photos of the air-fired samples of comp.MG and comp.MN. It can be seen that the two samples had the similar microstructures. The SEM indicated a uniform morphology consisted of fine, rounded grains, with no evidence of any secondary, intergranular phase(s). The mean grain sizes of the two sample were all as fine as 0.4 μm. This indicates that there was little difference between the microstructures of the Mg- and Mn-doped $BaTiO_3$ ceramics fired in air.

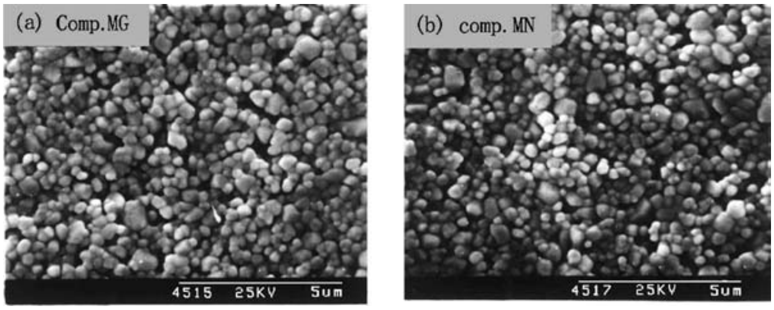

Figure 3 SEM micrographs of air-fired samples (a) comp.MG and (b) comp.MN.

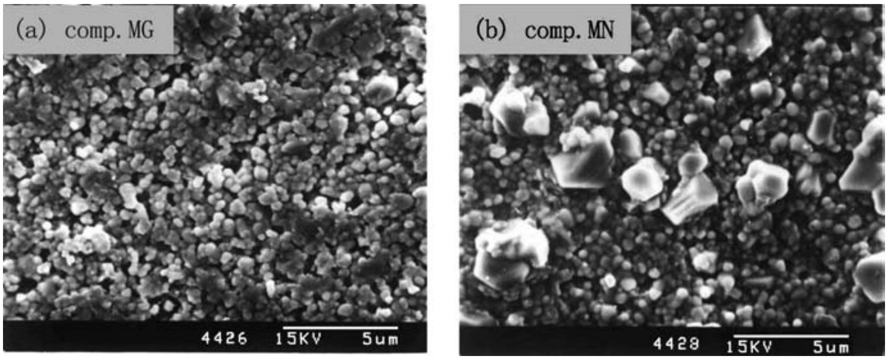

Figure 4 SEM micrographs of reducing-fired samples (a) comp.MG and (b) comp.MN.

The SEM photos of the re-oxidized samples of comp.MG and comp.MN are shown in Fig. 4. For comp.MG, only fine grained $BaTiO_3$ was observed by the observation of SEM, there was no second phase. While for comp.MN, two kinds of grains were observed, the rounded and fine grains were $BaTiO_3$, while the second phase which had huge grain size was ascribed to be pyrochlore-type $Yb_2Ti_2O_7$, as $Yb_2Ti_2O_7$ was confirmed to exist in the re-oxidized sample by XRD and $Yb_2Ti_2O_7$ was suggested to have much more coarse grain size than $BaTiO_3$ by Sato *et al.* [2, 3]. This indicates that Mn could promote the growth of this pyrochlore-type $Yb_2Ti_2O_7$ grains, while Mg could suppress the grain growth of this second phase. However, both Mn and Mn did not show much effect on the growth of the $BaTiO_3$ grains. For each of the two compositions, the mean grain size of $BaTiO_3$ grains of the re-oxidized samples was about 0.5 μm, which was greater than that of the air-fired ones, this can be explained by the model proposed by Yan, who suggested that oxygen lattice diffusion controls the pore mobility [13]. As lower oxygen partial pressure would increase the oxygen vacancy concentration in $BaTiO_3$, thus the low oxygen pressure in the reducing atmosphere promoted the grain growth of $BaTiO_3$. Because $Yb_2Ti_2O_7$ phase has huge grain size, it is detrimental for the reliability of MLCCs, especially when the dielectric layers are made thinner. Therefore, too large Mn amount will not be acceptable if the $BaTiO_3$-$MgCO_3$-MnO_2-Yb_2O_3 system is adopted for the dielectric materials of MLCCs, judging from above discussion.

Fig. 5 illustrates the temperature dependence of capacitance change of comp.MG sintered in the three processing atmospheres (the capacitance change, $\Delta C/C$ equals to $(C-C_{rt})/C_{rt}$, where C and C_{rt} represent the capacitance value at measuring temperature and at room temperature, respectively). As shown in Fig. 5, comp.MG fired in the reducing atmosphere resulted in a sharp dielectric peak at Curie point around 127°C, and a broad peak at lower temperature around 45°C. For the re-oxidized sample, we can see a little decrease of the high temperature peak value and a little increase of the low temperature peak value, the $\Delta C/C$-T curve was a little flattered by the re-oxidation treatment, especially at low temperatures. At the same time, it can be seen that the air-fired sample indicated two sharp peaks at about 127°C and 35°C, respectively.

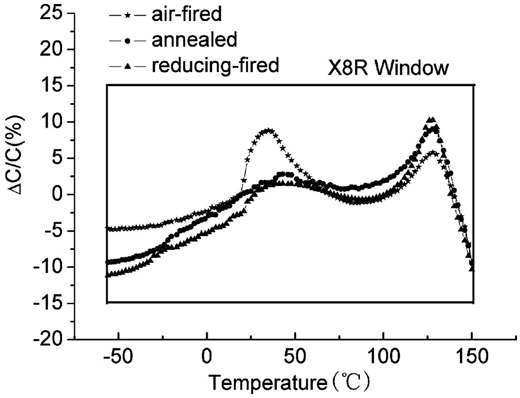

Figure 5 Temperature dependence of capacitance change of comp.MG fired under different conditions.

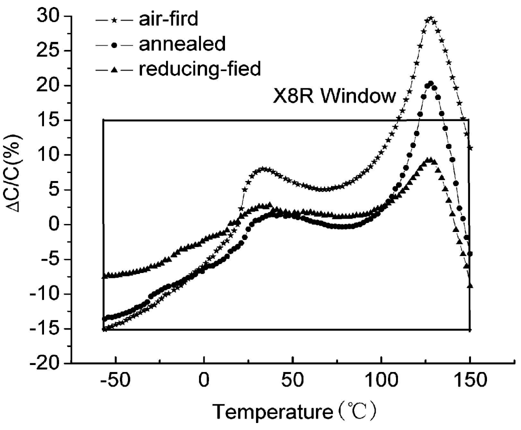

Figure 6 Temperature dependence of capacitance change of comp.MN fired under different conditions.

There was a drastic increase of the low temperature peak value, and a significant decrease of the high temperature peak value, therefore, the capacity-temperature characteristics (TCC) performance was significantly improved. Comp.MG satisfied the X8R specification, which is encircled by a broad rectangular line in Fig. 5, when fired in the different conditions. As this composition was compatible for both air and the reducing atmosphere, hence, it can be concluded that the $BaTiO_3$-$MgCO_3$-Yb_2O_3 system was suitable for both precious metal electrode (PME) and base metal electrode (BME).

The ΔC/C-T curves of comp.MN sintered in the three processing atmospheres are shown in Fig. 6. It can be seen that there were also two peaks in each of the curves. The ΔC/C-T curves of the reducing-fired comp.MG and comp.MN were similar to each other, as indicted in Figs 5 and 6. However, the re-oxidized comp.MN showed a dramatic increase of the high temperature peak value, a little decrease of the low temperature peak value, and much lower value of $(\Delta C/C)_{-55^\circ C}$, compared with the reducing-fired sample. Moreover, the air-fired case showed the highest temperature peak value as well as the lowest $(\Delta C/C)_{-55^\circ C}$ value, the low temperature peak was shifted to even higher temperature. For the air-fired and re-oxidized case, the $(\Delta C/C)_{130^\circ C}$ value was shifted out of the X8R specification for comp.MN.

For both of comp.MG and comp.MN, the air-fired samples had insulation resistances (IR) higher than 10^{12} Ω, dielectric constant at room temperature around 1600 and dielectric loss less than 1.5%. The re-oxidized samples had comparable IR and dielectric loss values to those of the air-fired samples, and dielectric constants about 2000.

Several models have been developed to explain the TCC of the $BaTiO_3$-based ceramics. Kishi *et al.* confirmed that core-shell structure could form in $BaTiO_3$-MgO-Re_2O_3 system [4]. The core-shell structure is considered to be a state of the inhomogeneous grains, in which the unreacted grain core is pure $BaTiO_3$, whereas the grain shell consists of reacted $BaTiO_3$ severely doped with additives. The grain cores are responsible for the ΔC/C values around the Curie point, while the grain shells are related to the low temperature ΔC/C values, the volume fractions of grain cores and grain shells determines the TCC behavior of the core-shell-structured $BaTiO_3$ ceramics. Hwang and coworkers suggested that a second phase, such as $Er_2Ti_2O_7$ could contribute to the improvement of TCC, especially at low temperatures [5]. Li *et al.* suggested that Mn ions could cause some paraelectric compositions in $BaTiO_3$-based ceramics, thus lowering the dielectric constant of the system and improve the TCC at low temperatures [14]. Yang *et al.* suggested that MgO could shift the dielectric constant-temperature curve of the $BaTiO_3$-Y_2O_3-MgO system toward lower temperature, so the $(\Delta C/C)_{-55^\circ C}$ moved upward, while the $(\Delta C/C)_{125^\circ C}$ moved downward [6].

To clarify the effect of $Yb_2Ti_2O_7$ on the TCC behavior, comp.MG1 was sintered in the reducing atmosphere. This composition had greater Yb content and thus apparently would cause more $Yb_2Ti_2O_7$ in the ceramics. The resulting ΔC/C-T curve showed only one peak at about 50°C (not shown), this indicates that too much Yb would cause collapse of the core-shell structure in the system. As the ΔC/C-T curve of comp.MG1 was quite different from those of comp.MG and comp.MN. Therefore, it can be concluded that predominately the core-shell structure, rather than the $Yb_2Ti_2O_7$, determined the TCC behavior. Hence, the influence of the second phase of $Yb_2Ti_2O_7$ on the TCC behavior was not considered in the following discussion.

The influences of the sintering atmosphere on the two compositions were quite different, as indicates that there were different mechanisms by which the sintering conditions affect the TCC behavior. The firing atmosphere could affect the valence of Mn ions and the solubilities of the acceptor ions [7, 8, 14], such as Mn^{2+}, Mn^{3+}, Mg^{2+} and Yb^{3+}. As each of the ΔC/C-T curves of comp.MG and comp.MN showed two peaks in the temperature range of 30–140°C, we suggest that the core-shell structure formed in the two compositions. Hence, the difference between the TCC of the as-fired samples can be explained in terms of the core-shell structure as follows: For comp.MG, as Mg^{2+} and Yb^{3+} ions both had constant valences, firing atmosphere only affected the solubilities of these acceptor ions. While sintering in air, almost all Mg^{2+} and Yb^{3+} ions were incorporated in the grain shells. However, when fired in reducing conditions, the solubilities of the acceptor ions was depressed, as evidenced by the second phase of $Yb_2Ti_2O_7$. Less acceptor ions were incorporated in the grain shells, therefore, the volume fraction of grain shells decreased while the fraction of the grain core increased. Thus, the values around the low temperature peak in the ΔC/C-T curve decreased pronouncedly, while the values around the Curie point increased significantly. The solubilities of the acceptor ions might be slightly recovered by re-oxidation; hence, the re-oxidized sample had lower ΔC/C value at the Curie point but higher ΔC/C values at low temperatures, compared with the reducing-fired one.

While for comp.MN, as the sintering atmosphere could affect the valence of the Mn ion, its influence on the ΔC/C-T curve was quite different from that for comp.MG. Mn ion acts as a divalent acceptor during firing in reducing conditions, like the Mg ion, therefore, the ΔC/C-T curve of reducing-fired comp.MN was quite similar to that of the reducing-fired comp.MG, as indicated by Figs 5 and 6. However, a portion of the doped Mn^{2+} ions could be oxidized to Mn^{3+} or Mn^{4+} by re-oxidation treatment [7, 8]. Thus for the re-oxidized case, the acceptor doped grain shells would had higher T_C than for the reducing-fired one, due to the decrease of distortion in the octahedral site induced by the smaller ionic size Mn^{3+} and Mn^{4+} ions [7, 8], or decrease of the concentration of oxygen vacancies [15]. As the T_C of the grain shells shifted to higher temperature, it is apparent that the ΔC/C values at high temperatures would increase while the values at low temperature would decrease. When the comp.MN sample was sintered in air, there must be even more Mn^{3+} and Mn^{4+} in the grain shells, and would result in even higher T_C of the grain shells. Therefore, it showed the highest ΔC/C values at high temperatures and the lowest ΔC/C values at low temperatures. Although the sintering conditions would also affect the solubilities of the acceptors in comp.MN, as suggested above, the effect of the valence change of the Mn ions seemed to be the major factor in determining the TCC behavior for this composition.

4. Conclusions

Effect of sintering atmosphere was observed to markedly affect the microstructure and dielectric properties of the Yb-Mg and Yb-Mn substituted $BaTiO_3$. The reducing conditions would depress the solubilities of the acceptor ions, as a result, a second phase of $Yb_2Ti_2O_7$ was confirmed to formed in the re-oxidized samples while no second phase was found in the air-fired ones. Mn was confirmed to promote the grain growth of $Yb_2Ti_2O_7$ while Mg could suppress the grain growth of this second phase. Mg-doped and Mn-doped samples showed different TCC behavior when sintered under oxidizing (air), reducing and re-oxidizing conditions. It is suggested that there were two different mechanisms by which the firing conditions could affect the TCC behavior of the Mg or Mn-doped $BaTiO_3$ ceramics. For $BaTiO_3$- Yb_2O_3-MgO system, it is suggested that the depression of acceptor solubilities in reducing conditions could affect the volume fraction of the grain shells in the core-shell structure, and would be responsible for the differences of the TCC behavior. While for Mn and Yb co-doped $BaTiO_3$ ceramics, the different valence state of Mn ions in the three processing atmospheres could affect the Curie point of the grain shells, and this would be the main factor in determining the TCC behavior of the composition.

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