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Microwave dielectric loss of thermally stressed MgTiO3 via TEM observation

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Abstract The influence of cooling rate on the dielectric loss of MgTiO3 ceramics at microwave frequencies via thermal stress and TEM was investigated. The specimens were cooled down with 1, 5, 30 °C/min and air-quenching from the sintering temperature of 1,350 °C. As the cooling rate increased, Q·f value decreased due to an increase of the crystallographic strain. The line defects such as dislocations increased with an increase of cooling rate except the specimen cooled down at 1 °C/min, which showed no dislocation. This result revealed that the line defects contribute to the deterioration of dielectric losses.

Keywords Dielectric loss · MgTiO3 · Thermal strain · Cooling rate · Dislocation

1 Introduction

Generally the mechanisms of dielectric loss are strongly associated with microstructural factors such as lattice defects (vacancies, dislocations, impurities), second phases, porosity and other processing related defects. Some of them also related to the quality of the raw materials and consequently to the powder preparation methods [1–4].

In case of microwave materials, thermal stress is also a major contributor to limit the service life of many components and devices. Thermal stress can lead to mechanical as well as to functional failures [5], and this stress is a significant factor affecting the dielectric loss of the materials. It was reported that dielectric loss was affected by internal stress in the film-substrate interface, and the decrease in dielectric loss was correlated well with the reduction of strain in the thin films [6, 7]. And the layered structure of $Mg_{0.93}Ca_{0.07}TiO3$ -(Ca $_{0.3}$ $Li_{0.14}Sm_{0.42}$) TiO3 system was investigated for Q·f value dependence on the variation of applied stress [8].

In our previous study [9], $MgTiO_3$ specimens with very high Q·f value were prepared, and the effect of thermal stress on dielectric loss of the $MgTiO_3$ specimens was studied according to various cooling rates after sintering. As the cooling rate increased, density, grain size, dielectric constant and temperature coefficient of resonant frequency of the $MgTiO_3$ specimens did not change significantly. The relative density of the all specimens was 97% of the theoretical value. However, the crystallographic strain [10, 11] increased, which was calculated with the full width at half maximum (FWHM) of the X-ray diffraction patterns of the MgTiO3 specimens, according to the decrease of Q·f values. From this result, we could find out the strain dependence on the deterioration of the dielectric loss.

In our following study [12], it was confirmed that the decrease of Q·f values with an increase of the cooling rate in the $MgTiO_3$ specimens was attributed to the thermally

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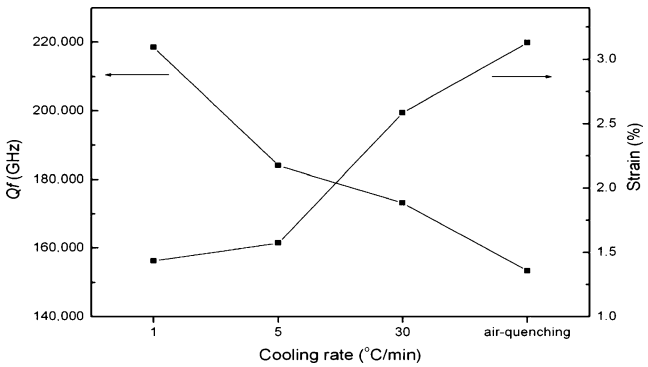

Fig. 1 Measured Q·f versus strain of $MgTiO_3$ specimens sintered at 1,350 °C for 3 h as a function of cooling rate

induced strain and lattice anharmonicity via far-infrared reflectivity spectra.

As a continuous study, TEM observation was carried out to determine structural disorders which were closely correlated with dielectric losses when the $MgTiO_3$ specimens were cooled down from the sintering temperature of 1,350 °C.

2 Experimental procedure

$MgTiO_3$ ceramics were prepared by the conventional solid-state reaction with high-purity reagents, MgO and

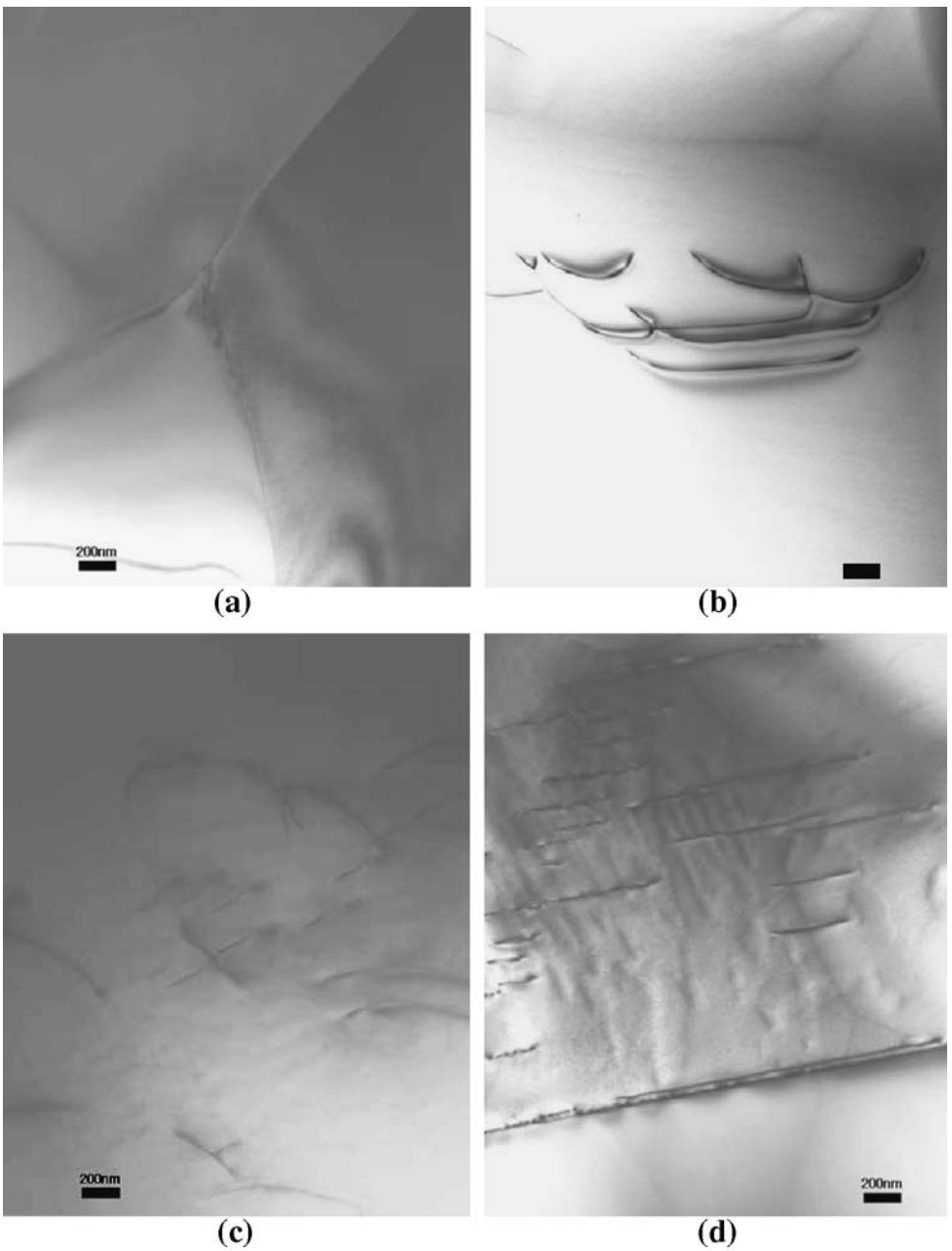

Fig. 2 TEM images of $MgTiO_3$ specimens sintered at 1,350 °C for 3 h and then cooled down with (**a**) 1 °C/min (**b**) 5 °C/min, (**c**) 30 °C/min and (**d**) air quenching

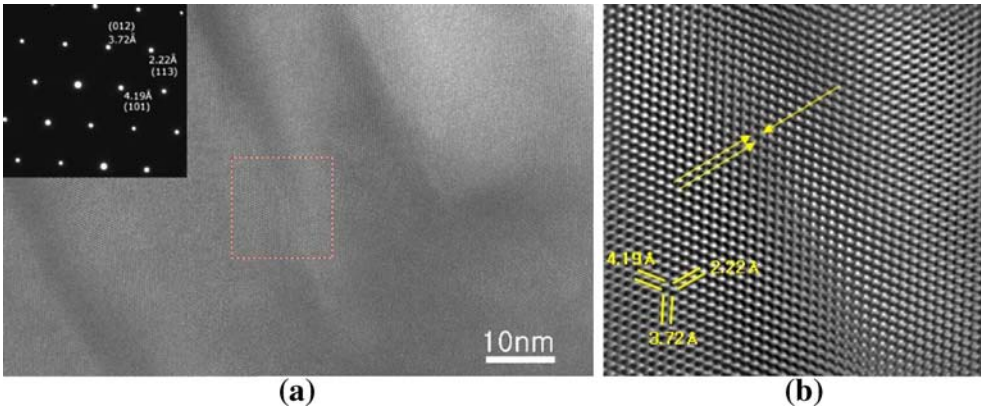

Fig. 3 Transmission Electron Micrograph of MgTiO3 specimens sintered at 1,350 °C for 3 h and then cooled down at 5 °C/min; (**a**) HRTEM image of dislocation of the specimen and SADP on the zone axis of $[12\bar{1}]$, and (**b**) Filtered image of the selected part of (**a**)

TiO_2 . They were batched according to the desired compositions and then mixed in ethanol with ZrO_2 balls for 24 h. After drying, the mixed powders were calcined at 1,200 °C for 2 h. The prepared powders were pressed uniaxially at 20 MPa to the pellets with 12 mm in diameter and 5∼6 mm in thickness and cold—isostatically pressed at 138 MPa. These pellets were sintered at 1,350 °C for 3 h in air with a heating rate of 5 °C/min and then cooled down with various cooling rates of 1, 5, 30 °C/min and air quenching.

X-ray diffraction (XRD, Cu Kα radiation, Model Rint/Dmax 2500, Rigaku, Japan) analysis was carried out on powders of the sintered specimens for identification of crystalline phase and estimation of the amount of thermally induced strain. Microwave dielectric properties were measured by the post resonant method (Hakki–Coleman method) with TE011 mode [13].

In this work, the specimens for TEM observation were prepared by mechanical grinding to a thickness of 100 μm, dimpling to a thickness of less than 10 μm and ion-beam milling for electron transparency. Then the microstructures were observed in a transmission electron microscope using JEM-4010 model (JEOL Ltd., Tokyo, Japan) with the point resolution of 0.15 nm operated at 400 kV.

3 Results and discussion

The Q·f value decreases significantly as the cooling rate increases as shown in Fig. 1. The strain calculated from FWHM (full width half maximum) data of X-ray diffraction increased as cooling rate increased. During the cooling process after sintering, generally the thermal contraction was occurred from the intrinsic thermal expansion coefficient of material and this contraction was induced, that could be assumed the thermal strain. The amount of strain calculated from the broadening of X-ray diffraction line was reported in reference [9].

Figure 2 is the TEM images of $MgTiO_3$ sintered at 1,350 °C for 3 h and then cooled down with various rates of 1, 5, 30 °C/min and air-quenching. It shows the tendency of an increase of defects (i.e. dislocations) with increasing cooling rate, and also shows the single phase without APB (anti-phase boundary) revealing close distance ordering.

Figure 3(a) shows the HRTEM (High-Resolution TEM) micrograph of $MgTiO_3$ specimen sintered at 1,350 °C for 3 h and then cooled down at 5 °C/min. The upper-left portion of the Fig. 3(a) shows lattice indices of the SADP (Selected Area Diffraction Pattern) of $MgTiO_3$ with $[12\bar{1}]$ zone axis. Any diffraction patterns for super lattices are not shown in Fig. 3(a) of SADP with $[12\bar{1}]$ zone axis.

Figure 3(b) shows the filtered image which was obtained from the inverse FFT (Fast Fourier Transformation) cleared other diffractions except basic lattice diffraction of FFT of the marking area of Fig. 3(a). According to the investigation of the filtered image, mismatched dislocations was confirmed as indicated by arrows in Fig. 3(b).

Figure 3(b) also shows the lattice indices from the diffraction patterns and distances between faces. At $[12\bar{1}]$ zone axis, distances between faces of (012), (113) and (101) are 3.72, 2.22 and 4.19 Å, respectively. These results agree well with the indices of JCPDS #06-0494 of MgTiO3 (3.7030 Å(012), 2.2180 Å(113) and 4.1800 Å(101)).

These results could be confirmed that the single phase of the MgTiO3 specimen was identified without order–disorder transformation or superlattice, and as the cooling rate increased, the dislocations in the grain also increased. Finally more TEM work for determination of the dislocation concentration with cooling rate change is needed in the near future.

4 Conclusion

As the cooling rate increased, Q·f value decreased due to an increase of the crystallographic strain. The line defects such

as dislocations increased without order–disorder transformation or superlattice, as the cooling rate increased. This result revealed that the thermally induced strain and the line defects such as dislocations mainly contribute to the deterioration of dielectric losses.

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