Distribution of Calcium Ion in the Crystal of $MgTiO_3$-$CaTiO_3$ System

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Synopsis. The crystal of 0.96 $MgTiO_3$–0.04 $CaTiO_3$ was grown by a TSFZ method. The distribution of $CaTiO_3$ in the crystal was analyzed by SEM and EPMA. The results obtained suggest that the change of dielectric properties of $MgTiO_3$ by adding $CaTiO_3$ results from the independent distribution of $CaTiO_3$ in $MgTiO_3$.

Some dielectric materials have been studied up to date to develope high-quality filters of microwave resonator. From the characteristics of practical filters, the following three dielectric properties are required for materials: (i) high dielectric constant, (ii) high dielectric Q value, and (iii) low temperature coefficient ($=\eta_f$) of resonant frequency.[1] There exsist, for example, systems of BaO–TiO_2, $MgTiO_3$–$CaTiO_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$–$Ba(Zn_{1/3}Ta_{2/3})O_3$ *etc.*[2-4] which satisfy such requirements.

In the system of $MgTiO_3$–$CaTiO_3$, to add a slight amount of $CaTiO_3$ into $MgTiO_3$ betters the temperature coefficient η_f of $MgTiO_3$.[2] The purposes of the present report are to study the crystal growth of $(Mg_{0.96}Ca_{0.04})TiO_3$ by a travelling solvent floating zone method and to study the detailed phase diagram of the system of $MgTiO_3$–$CaTiO_3$ just near both end-members in order to make clear an effect of adding $CaTiO_3$ on the dielectric properties, especially on the coefficient η_f, of $MgTiO_3$–$CaTiO_3$ system.

Starting materials were MgO, $CaCO_3$ (99% purity), and TiO_2 (99.5% purity). They were weighed at the molar ratio of Mg : Ca : Ti=0.96 : 0.04 : 1, sufficiently mixed in acetone for 2 h, and fired at 1200 °C for 12 h. After the compound obtained was remixed in acetone for 2 h, it was pressed into a cylindrical rod of 10 mm in diameter and 100 mm in length under the hydrostatic pressure of 1 t/cm². The rod was sintered at 1400 °C in oxygen gas for 2 h; this rod was used as a feed of the crystal growth. An apparatus used for the crystal growth was the ellipsoidal image furnace (Nippon Electric Co.) whose heater source was a halogen lamp of 1.5 kW located at one focus position. The sintered rod was set up at the other focus position of the furnace where the light emitted from the halogen lamp focuses. The crystal was grown under the following conditions: the seed and feed were counter-rotated at the rate of 35 cm^{-1}, the growth rate was 2 mm/h, and the flow rate of air was 5 l/min. The dimension of the crystal obtained was 10 mm in diameter and 50 mm in length. The chemical analysis of the middle part of the crystal indicates Mg=19.1, Ca=1.20, and Ti=39.7 in wt%, which agrees with the composition of the starting material, that is, Mg=19.3, Ca=1.33, and Ti=39.6 in wt%.

The microscopic analysis in the middle part of the crystal was performed by the scanning electron microscope (SEM) and by the electron probe microanalyzer (EPMA). Figure 1 shows the result of qualitative analysis by SEM, together with the variation of intensities of the characteristic X-rays of both Mg and Ca ions along a straight line a. As seen from the figure, there exsist two domains; one is a light enclosed domain and the other is a dark dominant domain. The content of Mg is large outside of the light domain, while inside of the light domain, its content is very small. The behaviors of Ca is quite opposite to that of Mg: the content is extremely small outside of the light domain but large inside. On contrary to Mg and Ca, the content of Ti changes little over both the domains.

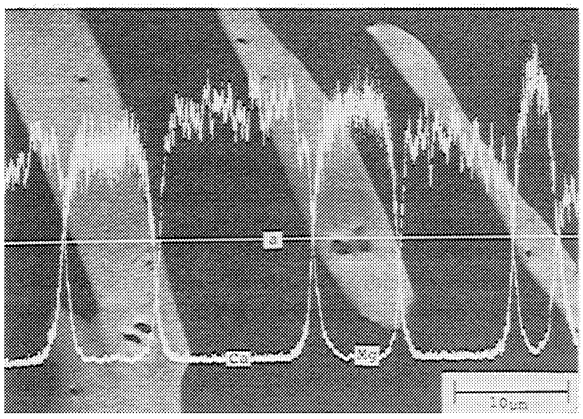

Fig. 1. Composition image of SEM for the middle part of the crystal $(Mg_{0.96}Ca_{0.04})TiO_3$. Lines denoted by Mg and Ca respectively show the results of the line analysis of Mg and Ca contents along a line a.

TABLE 1. EPMA ANALYSIS OF THE CRYSTAL

	Mg(wt %)	Ca(wt %)	Ti(wt %)	O(wt %)
Dark domain	20.15	0.06	40.85	40.53
Light domain	0.29	29.77	34.81	32.81

In order to determine the compositions of both the domains, the distribution of Mg, Ca, Ti, and O was quantitatively analyzed by EPMA; the results are summarized in Table 1. Two kinds of product could be observed as predicted from the phase diagram reported by Rouf *et al.*,[5] the products being roughly expressed by $MgTiO_3$ and $CaTiO_3$, respectively. $MgTiO_3$ occupies dominant part of the crystal corresponding to the dark domain in Fig. 1, while $CaTiO_3$ is a little interpersed as inclusions along the growth direction, corresponding to the light domain in Fig. 1. Table 1 shows that $CaTiO_3$ is solved into $MgTiO_3$ by 0.2 wt% ($=C_1$), while $MgTiO_3$ also into $CaTiO_3$ by 1.4 wt% ($=C_2$). This suggests that there exsist solid solutions just near both the end-members of the system $MgTiO_3$–$CaTiO_3$, which are not shown in the diagram reported by Rouf *et al.*[5] The result that $C_2 \gg C_1$ is reasonable since Mg ions more easily substitute Ca ions than Ca ions do Mg ions because of $r_{Ca} > r_{Mg}$, where r

indicates a radius. The result of powdered X-ray diffraction shows that both solid solutions have same crystal structures and lattice constants as $MgTiO_3$ (ilmenite type) and $CaTiO_3$ (perovskite type), respectively. The physical properties of the solid solution are, therefore, almost same as the original materials, $MgTiO_3$ and $CaTiO_3$.

As mentioned above, the temperature coefficient η_f changes by adding $CaTiO_3$ by about 4—6 mol% into $MgTiO_3$. In practice, the η_f of the crystal is −38 ppm/deg although it contains oxygen defects, the absolute value of the η_f being smaller than that (η_f= −60 ppm/deg) of $MgTiO_3$ reported by Courtney.[3] Thus, the experimental results lead us the conclusion that the change of the coefficient η_f does not result from forming solid solution such as $(Mg,Ca)TiO_3$ whose temperature coefficient η_f is nearly equal to zero, but from the independent distribution of $CaTiO_3$ and $MgTiO_3$ whose coefficients η_f have mutually opposite sign.[2]

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