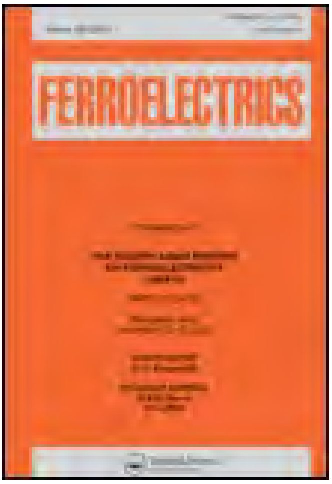

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Dense Composition with High Q on the Complex Perovskite Compounds

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Dense Composition with High *Q* on the Complex Perovskite Compounds

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It is clarified in previous paper that high Q depends on high symmetry instead of ordering. The compositions of complex perovskite with high Q were found at composition shifted from ideal one by Koga et al.*, Kugimiya, and Surendran* et al. *These data can be summarized as based on Kugimiya's results. The composition located on the tie-line* $Ba(Mg_{1/3}Ta_{2/3})O_3$ *to* $BaTa_{4/5}O_3$ *with chemical formula* $Ba_{1+\alpha}(Mg_{1/3}Ta_{2/3+4\alpha/5}V_{alpha/5})O_{3+3\alpha}$ *. The structure has no defects on A- and O-sites, and the vacancies of* $V_{\alpha/5}$ *with neutrality in the* B-*site. The density becomes high by resolving of* $BaTa_{4/5}O_3$*, because Mg ions are substituted by Ta ions with high weight.*

Keywords Microwave dielectrics; Complex perovskite; Quality factor; High *Q*, High symmetry; Ordering

Introduction

Recently, the usage of radio frequency (RF) for microwave communication is expanding to high frequency because of the shortage of frequency area, and request of high speed and high data transfer rate. As microwave dielectrics are expected to have high quality factor *Q* (high *Q*) based on those background, we will clarify the origin of high *Q* that is one of three important properties [1, 2] in RF technology. *Q* is inverse of dielectric losses tanδ, other properties are dielectric constant ε_r and temperature coefficients of resonant frequency τ_f. The ε_r is expected to be small for higher frequency millimeterwave region, because of reducing the delay time of electronic signal transmission and improvement of accuracy for production. The τ_f is expected to be near zero ppm/°C for receiving the RF signals in all places in the world. The *Q* is affected by intrinsic factors such as crystal structure and by extrinsic factors such as grain growth, impurity, and so on.

We presented about origin of high *Q* for microwave complex perovskite in a previous paper [3]. Authors concluded that the high symmetry brings high *Q* instead of ordering comparing some cases as follows: As if ordering ratio of $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) is high of about 80%, *Q* values are distributed from low to high *Q* [4, 5]. Disordered BZT ceramics

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with high density obtained for short sintering time by spark plasma sintering (SPS) showed high *Q* [6]. $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) with order-disorder transition showed high *Q* at disorder form sintered over the transition temperature. And, the disordered BZN with high *Q* annealed at lower temperature changed to order structure without improvement of *Q* [7].

In this study, we add more informations about complex perovskite with high *Q* as follows: in the complex perovskite compounds, the composition with high *Q* is deviated from ideal one. The composition locates on the $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT)-$BaTa_{4/5}O_3$ tie line presented by Kugimiya [8], which is composed by completed perfect crystal structure without oxygen defects. Moreover, the higher density is obtained with the substitution of Ta for Mg. In the case of BZT presented by Koga et al. [5, 9], the composition with high *Q* also deviated from pure BZT. Surendran and Sebastian et al. [10], also presented Ba and Mg defect composition in BMT. Those results after Koga and Sebastian's group are explained by Kugimiya's result [8].

Experimental

Synthesis methods of each compound are referred to previous papers as follows: BZT samples are synthesized by Koga et al. [4, 5] using solid state reaction (SSR) in container covered tightly with the lid at 1400°C, 100 hours after decomposition of binder at 500°C, 2 hours. Synthesized compositions for BZT are shown by alphabets A to S on three lines ① to ③ in Fig. 1. Precipitated phases are identified by X-ray powder diffraction (XRPD). Point A is pure BZT composition. The ordering ratios are obtained by Rietveld method [11].

BMT samples are synthesized by master-batch method for composition precise control about 0.05 % by Kugimiya [8]. The compositions designed are mixed using four cornered compositions which are prepared previously by the raw materials more than 99.9%. The mixtures are calcined after ball milling in alcohol. BMT ceramics with cylinder shape are sintered at 1600°C, 20 hours in air.

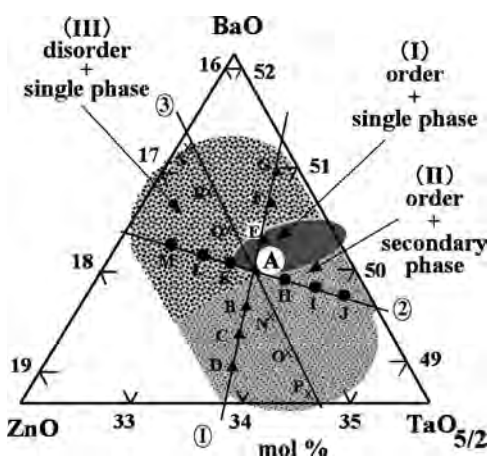

Figure 1. BaO-ZnO-$TaO_{5/2}$ partial ternary system in the vicinity of BZT. Synthesized compositions are shown by alphabets A to S. A point is pure BZT. Three areas are shown as (I) for order/single phase, (II) for order/secondary phase, (III) for disorder/single phase. (See Color Plate I)

The nonstoichiometric compositions based on $Ba(Mg_{1/3-x}Ta_{2/3})O_3$ and $Ba_{1-x}(Mg_{1/3}Ta_{2/3})O_3$ are presented by the conventional solid-state ceramic route by Surendran and Sebastian et al. [10].

The crystalline phases are characterized by the method reported in the previous papers [6, 7, 9]. Densities of these compounds are measured by Archimedes method. Microwave dielectric properties are measured using Hakki and Colman method [12, 13].

Results and Discussion

Koga et al. [5, 9] presented following three areas in the vicinity of BZT. These areas are shown in Fig. 1 which is arranged according to Kugimiya' results explained later [8].

(1) Ordering area with BZT single phase
(2) Ordering area with secondary phase $BaTi_2O_6$
(3) Disordering area with BZT single phase

Here, ordering resulted by long sintering time of 100 hours is identified by XRPD.

The 1st area (I) is composed with a single phase of BZT with ordering structure, and high *Qf*. Compositions E and K show ∼ 50% higher *Qf* than pure BZT composition A. The composition K is located on the boundary area (I) which has a minor secondary phase revealed by SEM figures as reported in previous paper [4]. Although the densities of the composition E and A are same, the ordering ratio of E is lower than that of A. The 2nd one (II) is ordered BZT with secondary phase $BaTa_2O_6$ included Zn. The ordering ratio of compounds located in this area is high about 70 to 80% as shown in Fig. 2(a). Although the structure is order, *Qf* values decrease according to far from pure BMT as shown in Fig. 2(c). The composition of the ordered BMT compounds should be located on Ta_2O_5 rich side, which is precipitated with secondary phase as a eutectic phase diagram system. The 3rd area (III) is precipitated single BZT solid solutions with disordered structure. The *Qf* values are degraded according to degraded ordering ratio and lowered density as shown in Fig. 2(b). The lower density comes from existents of many pores due to hard sintering. The single phase in this area is originated by solid solution accompanying defects in *B*- and O-sites, which introduce degradation of *Qf*.

Kugimiya [8] presented the highest *Qf* composition at Ta and Ba rich side in BMT system as shown in Fig. 3. Here, chemical formulae in the vicinity of BMT are cited as follows: the author presented three areas divided by following two lines as shown in

Table 1
Chemical formula for three areas divided by two lines: $\alpha = 5\gamma/4$ and $\alpha = \gamma/2$, here, α and γ are in $Mg_{1/3}\,Ba_\alpha\,Ta_\gamma\,O_{\alpha+5\gamma/2}$ and vacancies on the *A*, *B* and O sites. (after Kugimiya [8])

α	Chemical formula	Vacancy
$\alpha > 5\gamma/4$	$Ba_{1+\alpha}\,(Mg_{1/3}Ta_{2/3+\gamma}\,V_{\alpha-\gamma})O_{3+\alpha+5\gamma/2}\,V_{2\alpha-5\gamma/2}$	*B*-, O-: vacancy *A*-: fill
$\alpha = 5\gamma/4$	$Ba_{1+\alpha}\,(Mg_{1/3}Ta_{2/3+4\alpha/5}V_{\alpha/5})O_{3+3\alpha}$	*B*-: vacncy *A*-, O-: fill
$5\gamma/4 > \alpha > \gamma/2$	$Ba_{1+\alpha}\,V_{5\gamma/6-2\alpha/3}(Mg_{1/3}Ta_{2/3+\gamma}\,V_{\alpha/3-\gamma/6})\,O_{3+\alpha+5\gamma/2}$	*A*-, *B*-: vacncy O-: fill
$\alpha = \gamma/2$	$Ba_{1+\alpha}\,V_\alpha\,(Mg_{1/3}Ta_{2/3+\gamma})O_{3+6\alpha}$	*A*-: vacancy *B*-, O-: fill
$\alpha < \gamma/2$	$Ba_{1+\alpha}\,V_{\gamma-\alpha}\,(Mg_{1/3}Ta_{2/3+\gamma})O_{3+\alpha+5\gamma/2}\,V_{\gamma/2-\alpha}$	*A*-, O-: vacancy *B*-: fill

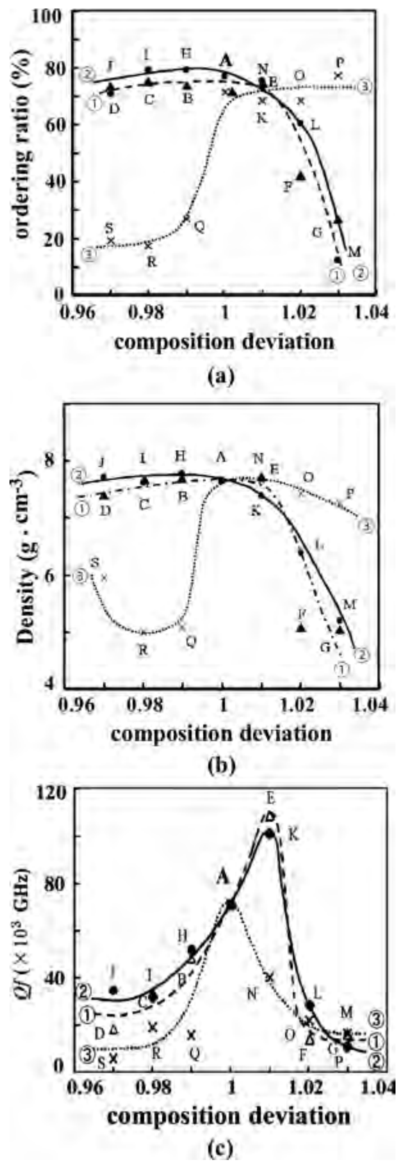

Figure 2. Ordering ratio (a), density (b) and Qf (c) as a function of composition deviation from pure BZT.

Table 1, and Fig. 3.

$$\alpha = 5\gamma/4$$
$$\alpha = \gamma/2$$

Here, α and γ are in Ba_α Ta_γ $O_{\alpha+5\gamma/2}$.

In the region $\alpha > 5\gamma/4$, the composition denoted by $Ba_{1+\alpha}$ $(Mg_{1/3}Ta_{2/3+\gamma}$ $V_{\alpha-\gamma})O_{3+\alpha+5\gamma/2}V_{2\alpha-5\gamma/2}$ has B- and O-site vacancies with holes and electrons. On the $\alpha = 5\gamma/4$ line, the compositions denoted by $Ba_{1+\alpha}$ $(Mg_{1/3}Ta_{2/3+4\alpha/5}V_{\alpha/5})O_{3+3\alpha}$ ideal ones without vacancies in A- and O-sites. B-site vacancy is neutrality without charge. The

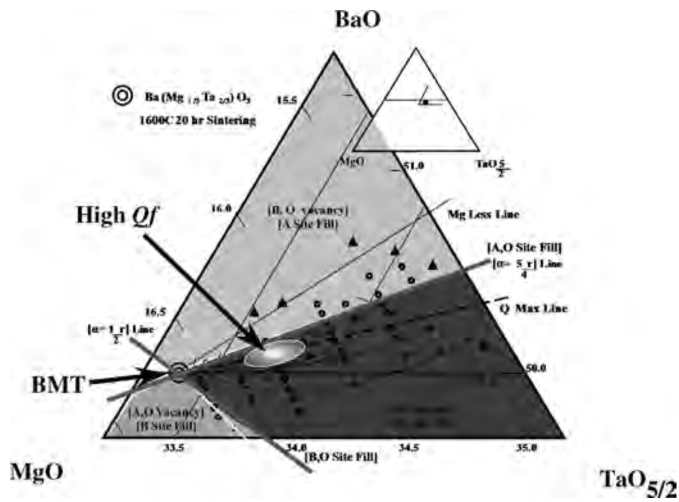

Figure 3. Partial BaO-MgO-$TaO_{5/2}$ ternary system in the vicinity of BMT (based on Kugimiya report [8]). On the tie line BMT-$BaTa_{4/5}O_3$, $Ba(Mg_{1/3-\alpha/3}Ta_{2/3+2\alpha/15}V_{\alpha/5})O_3$ solid solutions are formed with high density and high Q, on which A- and O- are filled, and B-site has vacancies without charge. Three areas as follows are divided by two lines:$\alpha = 5\gamma/4$ and $\alpha = \gamma/2$. 1st one is B- and O-site have vacancy though A-site is filled. 2nd one is A- and B-sites have vacancies though O-site is filled. 3rd one is A-and O-sites have vacancies, though B-site is filled. (See Color Plate II)

highest Qf composition locates near the line $\alpha = 5\gamma/4$ as shown in Fig. 3. The composition on the line is ideal for microwave dielectrics, because of no oxygen defects and high density due to substitution Ta for Mg. In the region $5\gamma/4 > \alpha > \gamma/2$, the composition denoted by $Ba_{1+\alpha}\ V_{5\gamma/6-2\alpha/3}(Mg_{1/3}Ta_{2/3+\gamma}\ V_{\alpha/3-\gamma/6})O_{3+\alpha+5\gamma/2}$ has defects in A- and B-sites filled with hole and electrons. At $\alpha = \gamma$ in this region, the composition denoted by $Ba_{1+\alpha}$

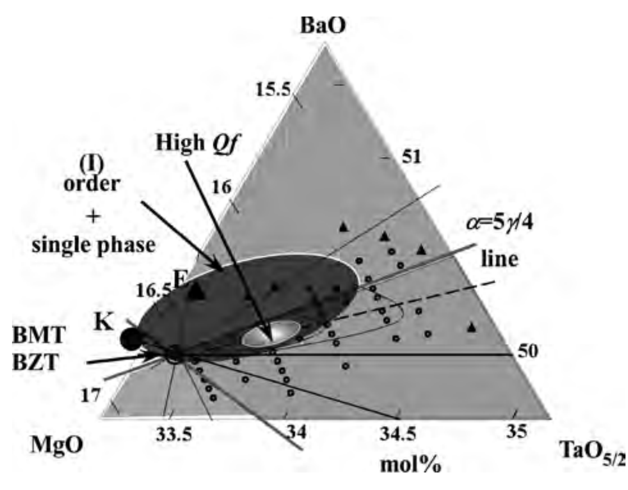

Figure 4. On the partial BaO-MgO-$TaO_{5/2}$ ternary system in the vicinity of BMT presented by Kugimiya[10], 1st area (I) with ordering and single phase presented by Koga et al.[5] is super imposed. (See Color Plate III)

$V_{\alpha/6}(Mg_{1/3}Ta_{2/3+\alpha}\ V_{\alpha/6})O_{3+7\alpha/2}$ has same amount vacancies in both *A*- and *B*-sites filled with same holes and electrons. In the case of $\alpha = \gamma\ /2$, the composition denoted by $Ba_{1+\alpha}$ V_α $(Mg_{1/3}Ta_{2/3+\gamma})O_{3+6\alpha}$ has vacancies only in *A*-site with hole and excess electrons in *B*-site which introduce unstable. In the region $\alpha < \gamma\ /2$, the composition denoted by $Ba_{1+\alpha}$

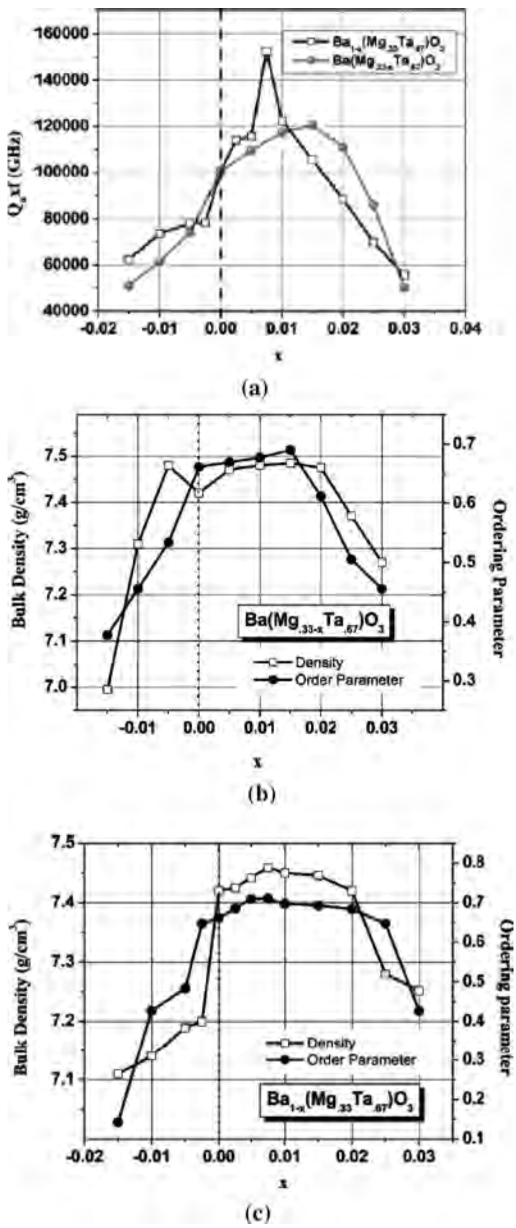

Figure 5. (a) *Qf* for $Ba(Mg_{1/3-x}Ta_{2/3})O_3$ and $Ba_{1-x}(Mg_{1/3}Ta_{2/3})O_3$ as a function of composition deviation (x), (b) Bulk density and ordering parameter for $Ba(Mg_{1/3-x}Ta_{2/3})O_3$ as a function of x, (c) Bulk density and ordering parameter for $Ba_{1-x}(Mg_{1/3}Ta_{2/3})O_3$ as a function of x. (after Surendran et al. [10]).

$V_{\gamma-\alpha}$ $(Mg_{1/3}Ta_{2/3+\gamma})O_{3+\alpha+5\gamma/2}V_{\gamma/2-\alpha}$ has holes in the both *A*- and O-sites with electrons, and excess electrons in B-site which brings unstable crystal structure.

Koga's data [5] are comparable with Kugimiya's BMT data [8]. The (I) area with highest *Qf* in Fig. 1 is superimposed with Kugimiya's area with high *Qf* as shown in Fig. 4, though the area is shift a little. The E composition in Fig. 1 will be comparable with the completed ideal crystal structure $Ba_{1+\alpha}$ $(Mg_{1/3}Ta_{2/3+4\alpha/5}V_{\alpha/5})O_{3+3\alpha}$ presented by Kugimiya [8]. The formula is rewrite as $Ba(Mg_{1/3-\alpha/3}Ta_{2/3+2\alpha/15}V_{\alpha/5})O_3$ solid solutions on the tie-line BMT-$BaTa_{4/5}TiO_3$. The crystal structure on the composition region is perfect without defects and with high density. BMT becomes high density by resolving of $BaTa_{4/5}O_3$, because Mg ions are substituted by Ta ions with high weight.

Slendran et al. [10] also presents compositions with high *Q* on the two kinds of magnesium and barium deficiency nonstoichiometric compositions on $Ba(Mg_{1/3-x}Ta_{2/3})O_3$ $[x = 0.015]$ and $Ba_{1-x}(Mg_{1/3}Ta_{2/3})O_3$ $[x = 0.0075]$ deviated from pure BMT composition as shown in Fig. 5(a). The microwave dielectric properties of $Ba_{0.9925}(Mg_{0.33}Ta_{0.67})O_3$ [$\varepsilon_r = 24.7$, $\tau_f = 1.2$ ppm/°C, $Qf = 152580$ GHz] and $Ba(Mg_{0.3183}Ta_{0.67})O_3$ [$\varepsilon_r = 25.1$, $\tau_f = 3.3$ ppm/°C and $Qf = 120500$ GHz] are found to be better than pure BMT [$\varepsilon_r = 24.2$, $\tau_f = 8$ ppm/°C and $Qf = 100500$ GHz]. The important difference from Kugimiya's results [8] is standing on the nonstoichiometry with barium or magnesium deficiency. We reconsider the Slendran's data [10] based on Kugimiya's results [8]. In the case of Mg-deficiency BMT, as the composition locates near the Kugimiya's area with high *Qf*, the composition of the main compound must be $Ba(Mg_{1/3-\alpha/3}Ta_{2/3+2\alpha/15}V_{\alpha/5})O_3$ solid solutions on the tie-line BMT-$BaTa_{4/5}TiO_3$. As shown in Fig. 5 (b), in the solid solution area the Mg deficiency are filled with Ta and create vacancies in B-site, so, the density and ordering ratio are maintained. On the other hand, the existing area of Ba-deficiency BMT is included in Koga's (II) area as shown in Fig. 1, which composes with ordered BMT and secondary phase. The ordered BMT will have near composition with high density and high *Qf* on the BMT-$BaTa_{4/5}TiO_3$ tie-line presented by Kugimiya [8]. The compound by Surendran et al. [10], may be located in eutectic phase diagram region accompanying with secondary phase. But, as amount of the secondary phases is small, the detection may be difficult. Though the density and ordering ratio are maintained high level as shown in Fig. 5(c), *Qf* values may be steeply degraded according to the secondary phase. The compound should be stoichiometric and completed, because microwave dielectrics with high *Q* usually should be no defects.

Conclusions

In previous study, we presented High symmetry beings High *Q* instead of Ordering. In this study, we added more information about complex perovskite with High *Q* as follows:

In the complex perovskite compounds, the composition with High *Q* is deviated from ideal complex perovskite compound. The composition locates on the BMT-$Ta_{4/5}O_3$ tie line presented by Kugimiya, which is made by completed perfect crystal structure without oxygen defects. Moreover, the higher density is obtained with the substitution of Ta for Mg.

In the case of BZT by presented by Koga et al. the composition with High *Q* also deviated from pure BZT. Sebastian's group also presented Ba and Mg defect compositions. Those results after Koga and Surendran group are explained by Kugimiya's result.

For microwave dielectrics with good properties, the crystal structure should be completed and have high dense crystal structure.

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