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# Microwave dielectric properties of $Ba_xLa_4Ti_{3+x}O_{12+3x}$ ($x = 0.0$–$1.0$) ceramics

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**Abstract**

In the $BaO$–$La_2O_3$–$TiO_2$ system, the $Ba_nLa_4Ti_{3+n}O_{12+3n}$ homologous compounds exist on the tie line $BaTiO_3$–$La_4Ti_3O_{12}$ besides tungstenbronze-type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth) solid solutions. There are four kinds of compounds in the homologous series: $n = 0$, $La_4Ti_3O_{12}$; $n = 1$, $BaLa_4Ti_4O_{15}$; $n = 2$, $Ba_2La_4Ti_5O_{18}$; $n = 4$, $Ba_4La_4Ti_7O_{24}$. These compounds have the layered hexagonal perovskite-like structure, which has a common sub-structure in the crystal structure. These compounds have been investigated in our previous studies. In this study, we have investigated the phase relation and the microwave dielectric properties of $Ba_xLa_4Ti_{3+x}O_{12+3x}$ ceramics in the range of $x$ between 0.2 and 1.0. With the increase in $x$, the dielectric constant $\varepsilon_r$ locates around 45, the quality factor $Q \times f$ shows over 80,000 GHz at $x = 0.2$ and the minimum value of 30,000 GHz at $x = 0.9$, and the temperature coefficients of resonant frequency $\tau_f$ is improved from −17 to −12 ppm/°C. At $x = 0.2$, the ceramic composition obtained has dielectric constant $\varepsilon_r = 42$, the temperature coefficient of the resonant frequency $\tau_f = -17$ ppm/°C and a high $Q \times f$ of 86,000 GHz.


*Keywords:* Dielectric properties; $BaTi0_3$ and titanates; Composites; X-ray methods

## 1. Introduction

Microwave dielectric ceramics are used in telecommunication mobile equipment as a resonance element, and they have contributed greatly to the downsizing.[1–4] The important properties required for a microwave dielectric ceramic are as follows: a high dielectric constant $\varepsilon_r$, a high quality factor $Q \times f$ and a low temperature coefficient of resonant frequency $\tau_f$. Especially, the microwave dielectric ceramics used in the base stations of mobile phones are required to have a high $Q \times f$ value more than 30,000 GHz to withstand high electric loads. But for the new digital systems, still higher $Q \times f$-value materials are required. Generally, the $Ba(Mg_{1/3}Ta_{2/3})O_3$ systems have a very high $Q \times f$ value of over 100,000 GHz, while the cost is very high because of the content of Ta element. Generally, in microwave materials, the $Q \times f$ value lowers as much as in the case of materials whose dielectric constant is high. Therefore, conventional microwave dielectric ceramics for base stations have relatively low dielectric constants.

In the $BaO$–$La_2O_3$–$TiO_2$ system as shown in Fig. 1, the $Ba_nLa_4Ti_{3+n}O_{12+3n}$ homologous compounds exist on the tie line $BaTiO_3$–$La_4Ti_3O_{12}$ beside tungstenbronze-type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth) solid solutions. $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions[5,6] exist on the tie line connecting the $BaTiO_3$ and $R_2Ti_3O_9$ compositions in the $TiO_2$-rich region of the $BaO$–$R_2O_3$–$TiO_2$ ternary system. Many extensive studies[7–14] of this compound have been carried out. There are four compounds on the tie line connecting the $BaTiO_3$ and $La_4Ti_3O_{12}$ compositions: $n = 0$, $La_4Ti_3O_{12}$; $n = 1$, $BaLa_4Ti_4O_{15}$; $n = 2$, $Ba_2La_4Ti_5O_{18}$; $n = 4$, $Ba_4La_4Ti_7O_{24}$ and are indicated in Fig. 1. These compounds have the layered hexagonal perovskite-like structure, which has a common sub-structure in the crystal structure.[15,16] And these compounds have been investigated in our previous studies except $n = 0$ compounds.[17] This $La_4Ti_3O_{12}$ ($n = 0$) compound decomposes to $La_2TiO_5$ and $La_2Ti_2O_7$ at 1450 °C, as shown in Fig. 2.[19] We have already found good properties in $n = 1$ compounds that is $BaLa_4Ti_4O_{15}$ as a candidate for a material for the base station.[18]

In this study, we have investigated the phase relation and the microwave dielectric properties between $n = 0$ and $n = 1$ $Ba_nLa_4Ti_{3+n}O_{12+3n}$ homologous compounds, that is $Ba_xLa_4Ti_{3+x}O_{12+3x}$ in the range of $x = 0.0$–$1.0$ as shown in Fig. 1.

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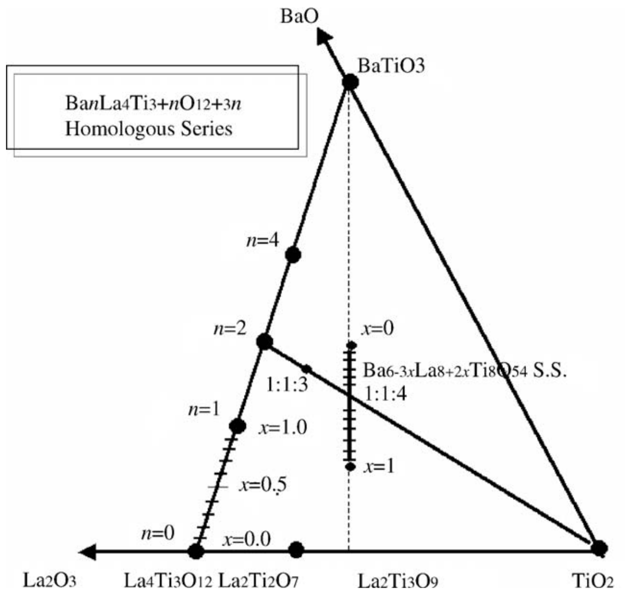


Fig. 1. $BaO–La_2O_3–TiO_2$ ternary system.

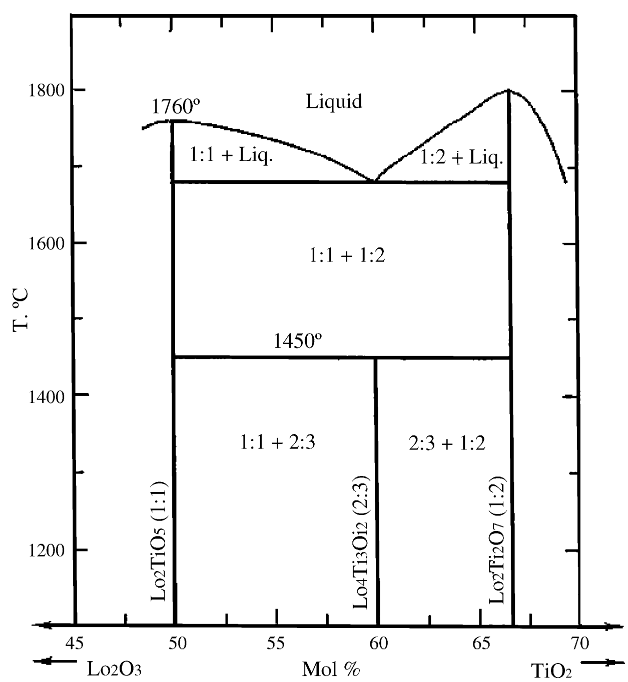


Fig. 2. $La_2O_3–TiO_2$ binary system.

## 2. Experimental

High-purity (99.9%) $BaCO_3$, $La_2O_3$ and $TiO_2$ powders were used as starting materials to prepare $Ba_xLa_4Ti_{3+x}O_{12+3x}$ with $x$ varying from 0.0 to 1.0. The powder mixtures were ball-milled in a polyethylene jar with zirconia balls and distilled water for 12 h, then dried and calcined at 1200 °C for 4 h in air. The calcined powders were ball-milled, dried and mixed with PVA as a binder. The powders were sieved and pressed into discs with a thickness of 6 mm and a diameter of 12 mm at 100 MPa. The discs were sintered at temperatures from 1500 to 1600 °C for 4 h in air. The crystalline phases of the sintered specimens were identified by X-ray powder diffraction (XRPD). The polished surface was observed by scanning ion microscopy (SIM). The dielectric constant $\varepsilon_r$, unloaded $Q$-values and temperature coefficients of the resonant frequency $\tau_f$ between 20 and 80 °C were measured using a pair of parallel conducting Ag plates on the $TE_{011}$ mode using Hakki and Coleman's method.[20,21]

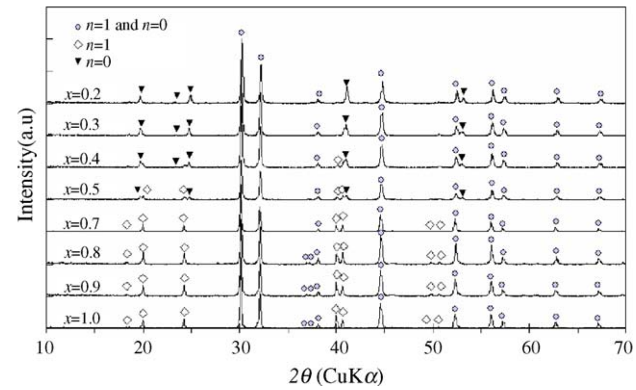


Fig. 3. X-ray powder diffraction patterns of $Ba_xLa_4Ti_{3+x}O_{12+3x}$.

## 3. Results and discussion

In the composition range between $x = 0$ and $x = 1$ in $Ba_xLa_4Ti_{3+x}O_{12+3x}$, the $La_4Ti_3O_{12}$ ($x = 0.0$) compound was excluded in this study because of its difficult sintering. Though the densities of the samples with $x = 0.2–1.0$ were almost constant at 6.1 g/cm$^3$, the sample with $x = 0.0$ was at a lower density of 4.6 g/cm$^3$ as shown in Fig. 4. As it was not able to obtain

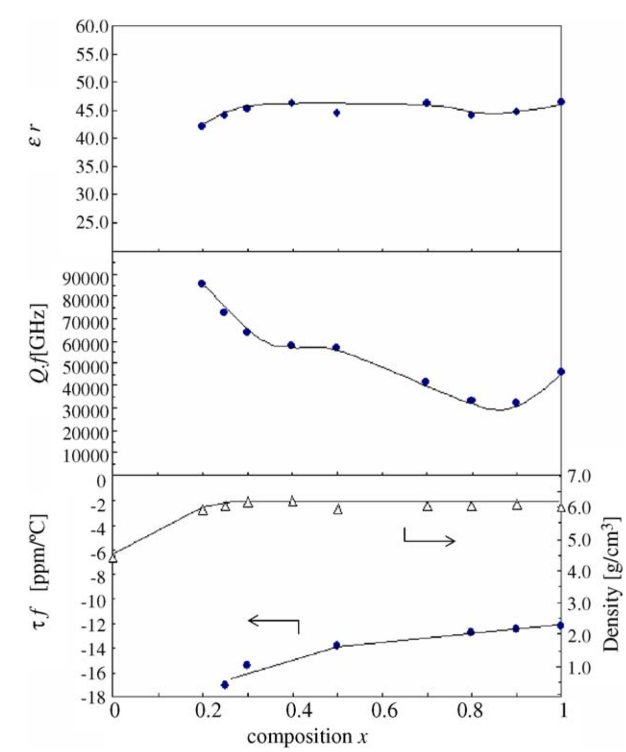


Fig. 4. Microwave dielectric properties of $Ba_xLa_4Ti_{3+x}O_{12+3x}$ as a function of $x$.

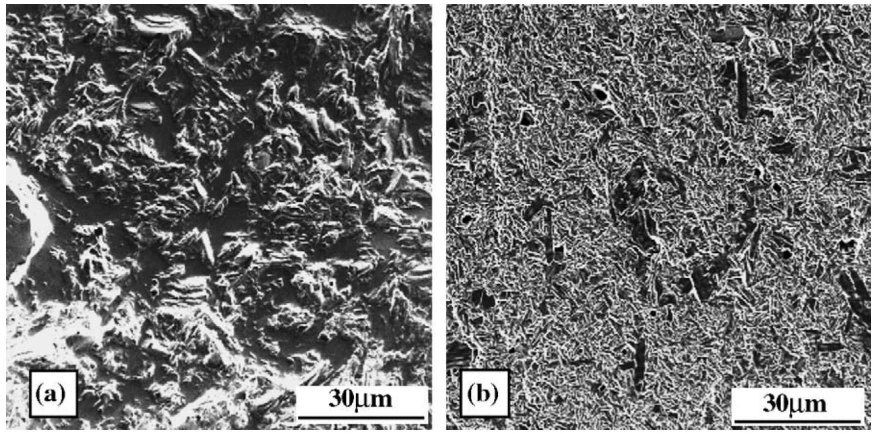


Fig. 5. Images of SIM (Scanning Ion Microscopy) with (a) $x = 0.7$ and (b) $x = 0.4$ composition.

high-density ceramics, we could not measure the dielectric properties. The difficulty in sintering comes from its decomposition into two phases at temperatures above 1450 °C from the $La_2O_3$–$TiO_2$ binary phase diagram as shown in Fig. 2.[19]

In the composition range $x = 1.0$–$0.0$ of $Ba_xLa_4Ti_{3+x}O_{12+3x}$, the precipitated phases were homologous $Ba_nLa_4Ti_{3+n}O_{12+3n}$ compounds with $n = 1$ and $n = 0$ identified based on XRPD patterns as shown in Fig. 3. Diffraction peaks of the homologous compound with $n = 1$ and $n = 0$ are shown by diamond and reversed solid triangle, respectively. The diffraction peaks denoted by solid circles are from similar *d*-spacing in both homologous compounds. In the composition range of $x = 1.0$–$0.7$ and $x = 0.3$–$0.2$, the homologous compounds with $n = 1$ and $n = 0$ are observed, respectively. And in the intermediate composition range $x = 0.5$–$0.4$, two phases with $n = 1$ and $n = 0$ are co-observed.

Fig. 4 shows the microwave dielectric properties as a function of composition *x*. The dielectric constants $\varepsilon_r$ in the whole composition range showed excellent values of 42–45. The $\varepsilon_r$ is usually desired more than 40 for the miniaturization of base station. Moreover, the quality factor $Q \times f$ of 86,000 GHz for $x = 0.2$ was the highest value reported among the dielectrics with high $\varepsilon_r$ more than 40 in our knowledge in the world. The $\varepsilon_r$ is a little lower of 42 due to lower density because of its difficult sintering described above, and $\tau_f$ is near −17 within −20 to +20 ppm/°C of suitable values for applications. In the range of $x = 0.3$–$0.2$, the $Q \times f$ increases from 60,000 to 85,000 GHz. So, the $Q \times f$ value could be extrapolated to $x = 0$, that is, $n = 0$ homologous $La_4Ti_3O_{12}$ phase to be 125,000 GHz. If ceramics with $x = 0.0$ composition has been synthesized, it is expected that the microwave materials which has high $Q \times f$ product more than 100,000 GHz without expensive Ta element will be put to practical use.

In another region of $x = 0.7$–$1.0$, they are composed with $n = 1$ homologous compound as shown in XRPD of Fig. 3 and in the SIM image of Fig. 5a without secondary phases. These results reveal formation of solid solutions with $n = 1$. The microwave dielectric properties are stable for $\varepsilon_r$ values to be in the vicinity of 45, for $Q \times f$ values to be varied between 30,000 and 60,000GHz and for $\tau_f$ values to be in the range of −14 to −12 ppm/°C. The compounds with $x = 0.5$–$0.7$ also have excellent microwave dielectric properties of $\varepsilon_r = 45$ and $Q \times f$ product larger than 40,000 GHz for base station dielectrics like the $n = 1$ homologous compound with 46,000 GHz in a previous paper.[17] The $Q \times f$ curve has the minimum value of 30,000 GHz at $x = 0.9$. The reason might be stacking fault of $(Ba,La)O_3$ packing layer due to formation of solid solutions. At just $x = 1.0$, it is considered that $Q \times f$ becomes a great value of 46,000 GHz due to dissolution of stacking fault.

In the range of $x = 0.3$–$0.5$, two phases with $n = 0$ and $n = 1$ coexist in XRPD patterns as shown in Fig. 3, and also in the image of SIM with $x = 0.4$ as shown in Fig. 5b. The SIM image is composed by two phases with different contrast. The dark phase is confirmed to be $La_4Ti_3O_{12}$ from the result of the XRPD. The $Q \times f$ product of 58,000 GHz and $\varepsilon_r$ of 45 are almost constant, because the $Q \times f$ and $\varepsilon_r$ values of the end members of $n = 0$ and $n = 1$ solid solutions may be same.

## 4. Conclusions

We have clarified following knowledge for microwave dielectrics properties of $Ba_xLa_4Ti_{3+x}O_{12+3x}$ ($x = 0.0$–$1.0$) ceramics.

There are two single-phase regions in the ceramics: (a) $n = 0$ homologous $Ba_nLa_4Ti_{3+n}O_{12+3n}$ compound in the range of $x = 0.0$–$0.3$, and (b) $n = 1$ in the range of $x = 0.5$–$1.0$. In the intermediate composition range $x = 0.5$–$0.3$, the two phases are coexisting.

The ceramics have high dielectric constants $\varepsilon_r$ in the whole composition range with values 42–45 and are useful for miniaturization of base stations.

There are three excellent candidates for base station dielectrics applications: (1) for $x = 0.2$ having highest $Q \times f$ product of 86,000 GHz with high $\varepsilon_r$ of 42 and $\tau_f$ of −17 ppm/°C; (2) for $x = 0.35$–$0.5$ showing good compositional stability with $Q \times f$ product of 60,000 GHz with high $\varepsilon_r$ of 45 and $\tau_f$ of −15 to −16 ppm/°C. (3) The third candidates in the range of $x = 0.5$–$0.7$ also show good dielectric properties with $Q \times f = 60,000$–$40,000$ GHz, $\varepsilon_r = 45$ and $\tau_f \sim -14$ to −12.5 ppm/°C.

If a ceramics with $n = 0$ composition can be synthesized overcoming the difficulty of sintering, then it may be possible to realize a super microwave dielectrics with high $Q \times f$ product more than 100,000 GHz.

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