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Control of dispersion frequency of $BaTiO_3$-based ceramics applicable to thin absorber for millimeter electromagnetic wave

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Abstract

Elements such as B, Li and Na were doped to barium titanate, $BaTiO_3$ in order to control dielectric dispersion. Addition of 3 mol% Li_2O lowered the dispersion at frequency of 0.53 MHz, while addition of 3 mol% B_2O_3 or Na_2O did not affect dispersion frequency. $BaTiO_3$ doped with 0.3 mol% Li_2O showed dielectric dispersion at around 2.5 GHz. An electromagnetic (EM) wave absorber using the doped $BaTiO_3$ plate was tried to produce for millimeter frequency range. A matching layer of 0.5 mm thick ceramic plate with relative permittivity 21 was attached to it to suppress reflection of incident EM wave due to the discontinuity at the boundary between the $BaTiO_3$ and air. The obtained EM wave absorber had reflectivity of −45 dB at 31 GHz and −25 dB at 95 GHz, respectively.

Keywords: Ferroelectrics; $BaTiO_3$ and titanates; Dielectric properties; Powder-solid state reactions; Electromagnetic wave absorber

1. Introduction

In order to perform testing of antennas or radar systems in anechoic rooms, the electromagnetic (EM) wave absorber were developed for the first time, which were composed of a pyramidal shaped foamed plastics dispersed with carbon powder.[1,2] Further, the ferrite EM wave absorber was newly developed for shutting out ghost images on the television display by the suppression of EM wave reflection from the obstacles such as buildings etc. surrounding a receiving antenna. A lot of materials for EM wave absorbers have been developed such as M-type hexagonal ferrite, λ/4-type absorber with ITO resistive film, plastics dispersed with silicon carbide.[3,4]

Ceramic EM wave absorbers were also developed for the use of outdoor circumstances which had fire-proof and weather-proof characteristics, but all of which operated at frequency as low as microwave frequency.[5,6] A ceramic absorber composed of titanite, which has a relative permittivity of 35, was developed for the use of millimeter wave frequency range.

Ferroelectric ceramics have particular potential as thin electromagnetic (EM) wave absorbers due to the large relative permittivity, usually larger than 1000, and large dielectric loss compared with ordinary ceramics. If the dielectric dispersion frequency is controlled suitably, EM wave absorbers which operate at arbitrary frequency can be realized. $BaTiO_3$ is one of the ferroelectric ceramics which has been tried to apply for thin EM wave absorber material.[5,6] Because of the restraint that $BaTiO_3$ has dielectric dispersion is limited at around few GHz, there were some attempts to change the dispersion frequency of $BaTiO_3$ by adding SrO or CaO.[7,8] However, the range was small for these additives. In this paper we report the effects of addition of light dopants such as B, Li and Na to $BaTiO_3$ on the dielectric dispersion with a view to enlarge the frequency shift range.

2. Experimental

A flow chart of synthesizing, forming and sintering processes for doping B, Li and Na for $BaTiO_3$ is shown in Fig. 1. Additives such as B_2O_3, Li_2CO_3, and $C_3H_4(OH)(COONa)_3$ are commercially available. A plate of $BaTiO_3$ doped with 0.3 mol% Li_2O was prepared. Thickness of the plate was 0.2 mm since the large permittivity is able to shorten the wavelength. A ceramic plate with thickness of 0.5 mm and relative permittivity of 21 was attached to the $BaTiO_3$ plate in order to suppress reflection of the incident EM wave. Complex relative permittivity was measured using three different apparatus: an impedance analyzer

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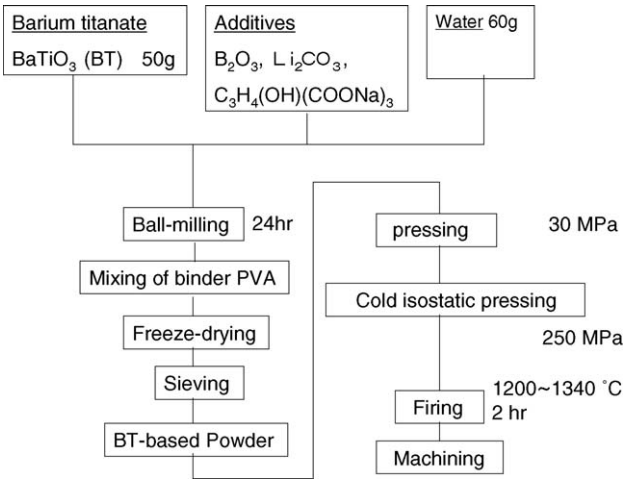

Fig. 1. Flow chart of synthesizing, forming and firing processes for $BaTiO_3$-based powders doped with B, Li and Na.

4194A at frequency range of 100 Hz–1 MHz, an impedance analyzer 4291B at 2 MHz–1.8 GHz, with test fixture 16192A for sub miniature device measurement, and HVS dielectric spectrometer above 33 GHz.[9] In millimeter wave frequency, it was only possible to obtain the correct value of relative permittivity by measuring the transmission coefficient S_{21} for a very thin sample of thickness 0.2 mm. The EM wave absorption characteristic, i.e. reflectivity, was measured by free space method.[9] XRD patterns were recorded from sintered and powdered samples to obtain crystal lattice parameters.

3. Result

Fig. 2 shows the SEM photographs of pure and $BaTiO_3$ added with 3 mol% Li_2O, B_2O_3 and Na_2O, which were sintered at 1270, 1250, 1200 and 1340 °C, respectively.

Complex relative permittivity ε' and ε'' of pure and Li_2O added $BaTiO_3$ is shown in Fig. 3 as a function of frequency. $BaTiO_3$ added with 3 mol% Li_2O showed a dispersion at a frequency of 0.52 MHz. In the case of 0.3 mol% Li_2O doped $BaTiO_3$, the dielectric dispersion was observed at around 2.5 GHz. On the other hand, addition of B_2O_3 or Na_2O did not cause such a phenomenon.

XRD curves of $BaTiO_3$ added with 0, 0.3, 1 and 3 mol% Li_2O are shown in Fig. 4. Pure $BaTiO_3$ exhibits two clear peaks of (0 0 2) and (2 0 0) planes, which correspond to ferroelectric

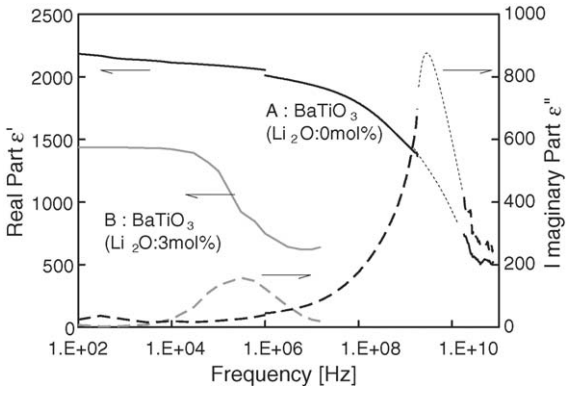

Fig. 3. Relative permittivity ε' and ε'' of pure and added $BaTiO_3$ with 3 mol% Li_2O as a function of frequency.

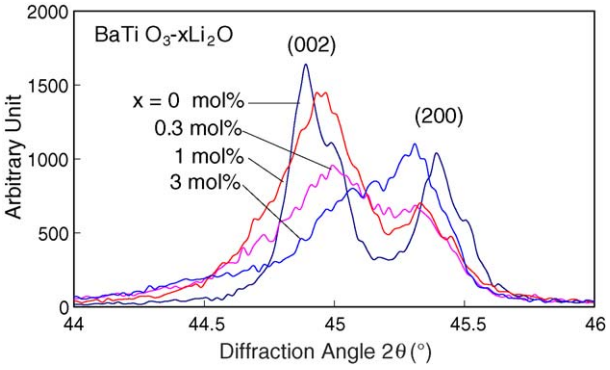

Fig. 4. XRD (0 0 2) and (2 0 0) reflection peaks of $BaTiO_3$ added with Li_2O.

tetragonal crystal phase. With increasing Li_2O, the two peaks approached each other and finally degenerated into a single (2 0 0) peak. The $BaTiO_3$ added with B_2O_3 or Na_2O has two clear peaks similar to that of pure $BaTiO_3$, as shown in Fig. 5.

Fig. 6 shows the temperature dependence of the relative permittivity of pure and doped $BaTiO_3$ with Li, B and Na. Phase transition characteristics were clearly observed for the case of B-and Na-doped $BaTiO_3$, and the transition temperature, Tc, shifted from that of pure $BaTiO_3$. On the other hand, Li-doped $BaTiO_3$ exhibited a weak broad peak.

Measured lattice parameters, c and a, of the doped $BaTiO_3$ are listed in Table 1. $BaTiO_3$ added with 3 mol% B_2O_3 or Na_2O has a ratio $c/a = 1.009$, which is close to the value, 1.010, for pure $BaTiO_3$.

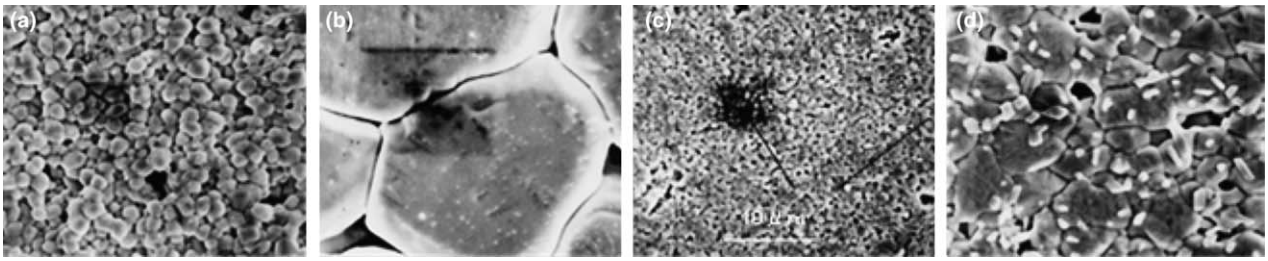

Fig. 2. SEM photographs of pure and doped $BaTiO_3$ with Li, B and Na. Values in the bracket show sintering temperatures: (a) pure $BaTiO_3$ (1270 °C); (b) Li (1250 °C); (c) B (1200 °C); (d) Na (1340 °C).

Table 1
Lattice parameters of $BaTiO_3$ added with Li_2O, B_2O_3 and Na_2O

Added element	Adding rate (mol%)	*c*/2 (nm)	*a*/2 (nm)	*c*/*a*	Firing temperature (°C)
Li	0	0.20186	0.1998	1.010	1270
	0.3	0.20131	0.1994	1.009	1297
	1	0.20152	0.1999	1.008	1346
	3	0.20122	0.2000	1.006	1250
B	3	0.20169	0.1998	1.009	1200
Na	3	0.20177	0.2000	1.009	1340

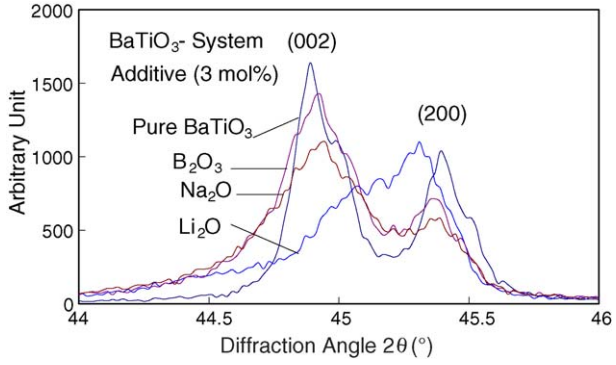

Fig. 5. XRD peaks of $BaTiO_3$ added with 3 mol% Li_2O, B_2O_3 and Na_2O.

It was found that the ratio *c*/*a* decreased with increasing Li contents. $BaTiO_3$ added with 0.3 mol% Li_2O was selected as an EM wave absorber for millimeter wave range.

A thin quarter wavelength EM absorber, which operates at 30 and 90 GHz could be fabricated by using 0.2 mm $BaTiO_3$ because the relative permittivity of $BaTiO_3$ is roughly 400 and the wavelength in $BaTiO_3$ may be shortened 1/20 as large as that in air. A plate of the $BaTiO_3$ system showed reflectivity as high as 97% because of the large relative permittivity beyond 2000. It was effective to reduce the reflection by using a low-loss matching dielectric layer with relative permittivity 21, which was nearly equal to the square root of that of $BaTiO_3$ when the minimum reflection of incident EM wave on the surface of the $BaTiO_3$ was occurred. The EM wave absorption characteristics of the fabricated absorber are shown in Fig. 6. The absorber showed reflectivity of −45 dB at 32 GHz and −25 dB at 95 GHz, respectively.

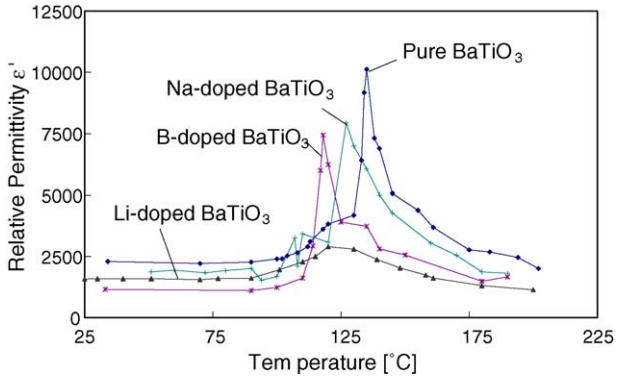

Fig. 6. Temperature dependence of relative permittivity of pure and doped $BaTiO_3$ with 3 mol% Li, B and Na.

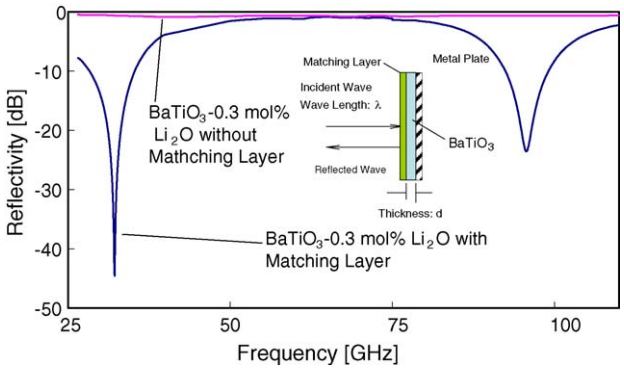

Fig. 7. EM wave absorption characteristics of $BaTiO_3$ added with 0.3 mol% Li_2O. Thickness of $BaTiO_3$ and matching layer are 0.2 and 0.5 mm, respectively.

4. Discussion

The reason why the new dielectric dispersion emerged only for Li doping is discussed below. Ionic radii of Ba^{2+}, Li^+, B^{3+}, and Na^+ ions are 0.14, 0.07, 0.02 and 0.10 nm, respectively.[10] Since the radius of Li^+ is far smaller than that of Ba^{2+}, the lattice parameter changed with increasing the Li doping: the *c*/*a* ratio decreased and approached to 1 at 3 mol% Li accompanied with the XRD peak shift and the degeneration into a single (2 0 0) peak. The parameter change indicates that the 3 mol% Li doping brought phase transition from tetragonal ferroelectric phase to cubic paraelectric phase. Temperature dependence of relative permittivity for the Li doped $BaTiO_3$ in Fig. 6 also indicates that the ferroelectricity was almost lost. The new dielectric dispersion at about 0.5 MHz may be due to the piezoelectric vibration of large crystal grains of about 20 μm as shown in Fig. 2, because Li-doped $BaTiO_3$ had much different microstructure compared with the others.

On the other hand, the ratio *c*/*a* is close to that of pure $BaTiO_3$ ceramics for $BaTiO_3$ doped with 3 mol% B or Na. Ionic radius of Na^+ resembles to that of Ba^{2+}. $BaTiO_3$ doped with 3 mol% B or Na still has ferroelectric spontaneous polarization and dielectric dispersion similar to that of the pure $BaTiO_3$. The doping of Na or B caused only a shift of Tc and no new dielectric dispersion (Fig. 7).

5. Conclusion

It has been demonstrated that the dielectric dispersion frequency is decreased from several GHz to few MHz for $BaTiO_3$ doped with 3 mol% Li_2O. It was interpreted that the ferroelectric

phase of $BaTiO_3$ was disappeared by the structural phase transition from tetragonal to cubic crystal phase by the Li doping and new dielectric dispersion appeared at around 0.5 MHz. It was confirmed that the Li-doped $BaTiO_3$ plate attached with suitable non-reflection matching layer operated as a thin EM wave absorber at microwave and millimeter wave frequency ranges. Further investigation is necessary to clarify that excellent EM wave absorbers are realized at different frequency ranges by accurate control of Li doping.

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