

## Infrared Reflectance Spectra of Doped BaTi<sub>4</sub>O<sub>9</sub>\*†

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Dielectric ceramics such as BaTi<sub>4</sub>O<sub>9</sub> have been widely used as microwave resonators in communication systems. In order to study the effect of doping on dielectric properties, infrared reflection spectra of BaTi<sub>4</sub>O<sub>9</sub> doped with Mn, Sn, Zr, Ca, Sr, and Pb were studied from 20 to 6000 cm<sup>-1</sup> at temperatures ranging from 15 to 297 K. The reflectance data was converted to the dielectric data using Kramers-Kronig analysis. The dielectric parameters  $k$ ,  $Q$ , and  $\tau_k$  calculated from the reflectance data were in agreement with resonant cavity measurements at 4 GHz. © 1991 Academic Press, Inc.

### I. Introduction

Infrared reflectance spectra of several electronic ceramics of technological importance such as quartz, BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, etc. have been studied (1-4). These investigations have shown that reflectance data can

be converted to dielectric data by the Kramers-Kronig analysis or by the classical dispersion theory, and that the optically active lattice modes can be identified.

Dielectric ceramics such as BaTi<sub>4</sub>O<sub>9</sub> have been widely used as dielectric resonators in the cellular telephone industry (5). Such applications require a high dielectric constant  $k = 35$  to 40, a high quality factor  $Q > 5000$  at 4 GHz, and a temperature coefficient of dielectric constant  $\tau_k (= 1/k \delta k / \delta T) < 20$  ppm/°C (6). The objective of this research was to obtain quantitative dielectric data for BaTi<sub>4</sub>O<sub>9</sub> from the infrared reflectance spectra, as well as to examine the effects of doping on the infrared spectra and dielectric properties.

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## II. Experimental Procedure

Samples of  $\text{BaTi}_4\text{O}_9$  doped with Mn, Sn, and Zr on the Ti-site and with Ca, Sr, and Pb on the Ba-site were prepared by solid state calcination and sintering of their respective carbonates and oxides. The solid solubilities of the dopants in  $\text{BaTi}_4\text{O}_9$  were confirmed by transmission electron microscopy and energy dispersive spectroscopy (7). The dielectric properties were measured by a resonant cavity technique at 4 GHz. The details of the processing and dielectric characterization of doped  $\text{BaTi}_4\text{O}_9$  are being published elsewhere (7).

Infrared reflection spectra were obtained with a Fourier transform infrared spectrometer (Model DA-3, Bomem Inc., Quebec, Canada) from 20 to 6000  $\text{cm}^{-1}$  between the temperatures of 15 to 297 K.  $\text{BaTi}_4\text{O}_9$  samples polished to a finish of 1  $\mu\text{m}$  were set in a vacuum chamber evacuated to  $10^{-4}$  Torr, and the reflectivities were measured relative to the reflectance of an evaporated gold mirror. The spectra were recorded at the resolutions of 1–4  $\text{cm}^{-1}$  at wavenumbers of 20–675  $\text{cm}^{-1}$  and at a resolution of 10  $\text{cm}^{-1}$  at wavenumbers greater than 675  $\text{cm}^{-1}$ . The incident angle of radiation was 11°.

The reflectance data was transformed to dielectric data by the Kramers–Kronig (K–K) analysis (8). The K–K relation for reflectivity  $R$  can be described as

$$\theta(\nu_0) = \frac{\nu_0}{\pi} \int_0^\infty \frac{\ln [R(\nu)/R(\nu_0)] d\nu}{\nu_0^2 - \nu^2}, \quad (1)$$

where  $\theta$  is the associated phase angle and  $\nu$  is the frequency in  $\text{cm}^{-1}$ . The index of refraction  $n$ , the index of absorption  $\kappa$ , the real and the imaginary parts of the dielectric constant  $\epsilon'$  and  $\epsilon''$ , and the quality factor  $Q$  can then be obtained from the relations

$$n = \frac{1 - R}{1 - 2\sqrt{R} \cos \theta + R} \quad (2)$$

$$\kappa = \frac{2\sqrt{R} \sin \theta}{1 - 2\sqrt{R} \cos \theta + R} \quad (3)$$

$$\epsilon' = n^2 - \kappa^2 \quad (4)$$

$$\epsilon'' = 2n\kappa \quad (5)$$

$$Q = \frac{\epsilon'}{\epsilon''}. \quad (6)$$

The integral in Eq. (1) was evaluated by representing  $\ln R(\nu)$  by straight-line segments between data points and using the trapezoidal rule to calculate the area under the straight-line segments (9). The reflectivity was assumed constant from 30  $\text{cm}^{-1}$  to 0 and from 6000  $\text{cm}^{-1}$  to  $\infty$ . Each peak in the plot of  $\epsilon''(\nu)$  computed from the K–K analysis corresponds to the frequency of a transverse-optic mode (3).

## III. Results and Discussion

### 1. Infrared Reflectance Spectroscopy

The infrared reflectance spectrum of undoped  $\text{BaTi}_4\text{O}_9$  at 297 K, along with the computed  $\epsilon'$  and  $\epsilon''$  as a function of frequency are shown in Figs. 1 (a)–(c). Figure 1 (d) shows the  $\epsilon''(\nu)$  plot obtained for  $\text{BaTi}_4\text{O}_9$  at 17 K. The major change in the spectrum at the lower temperature is the considerable narrowing of bands, making the shoulders on peaks clearly discernable. Twenty-one infrared bands can be readily identified, and the prominent peaks are labeled in Fig. 1.  $\text{BaTi}_4\text{O}_9$  crystallizes in the  $Pm\bar{m}n$  space group, with two molecules per unit cell (10). The correlation tables predict that 33 infrared modes (13  $B_{1u}$  + 7  $B_{2u}$  + 13  $B_{3u}$ ) and 42 Raman modes (14  $A_g$  + 6  $B_{1g}$  + 14  $B_{2g}$  + 8  $B_{3g}$ ) are allowed (11). Due to the presence of center of symmetry in the space group, the Raman and infrared bands are mutually excluded. This appears to be the case upon comparing the infrared data in Fig. 1 with the published Raman data (12). Twenty-one of the thirty-three allowed infrared modes are observed. It is difficult to assign these modes to specific motions of atoms without a detailed normal coordinate analysis. How-

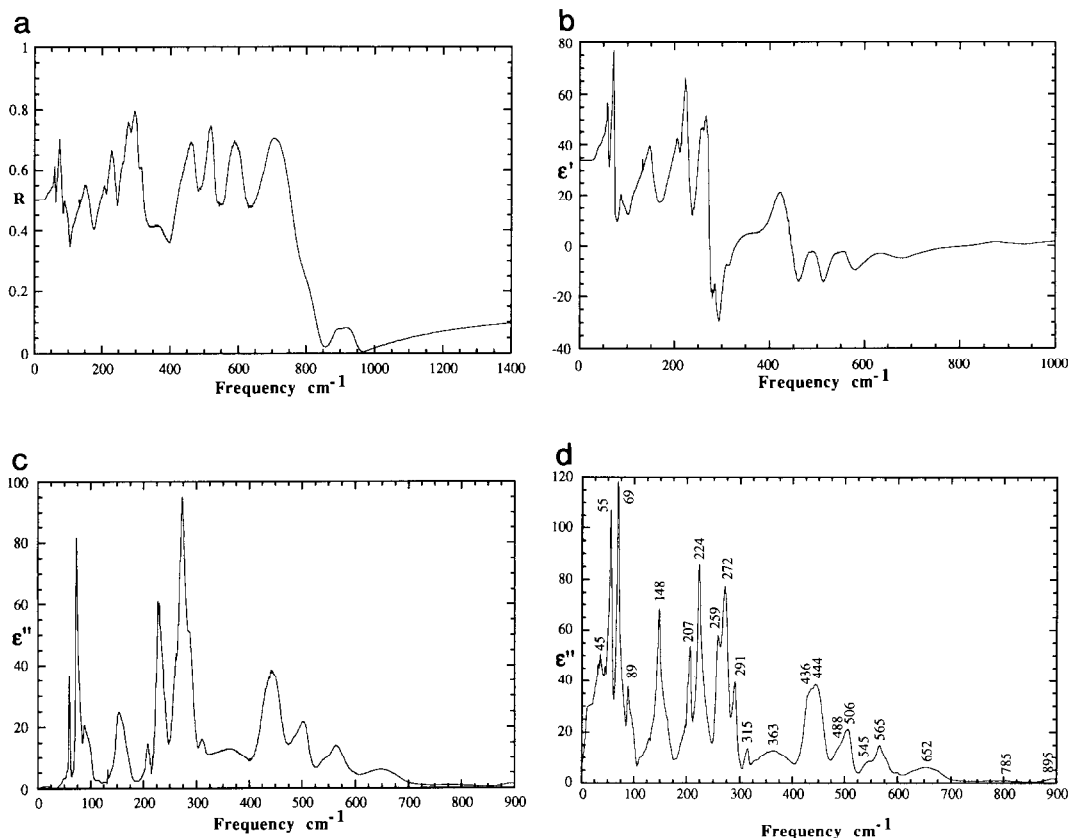


FIG. 1. (a) Infrared reflectance of undoped BaTi<sub>4</sub>O<sub>9</sub> at 297 K. (b) Real,  $\epsilon'$ , and (c) Imaginary,  $\epsilon''$ , parts of the dielectric constant for undoped BaTi<sub>4</sub>O<sub>9</sub> at 297 K. (d) Imaginary part of dielectric constant for undoped BaTi<sub>4</sub>O<sub>9</sub> at 17 K.

ever, based on previous infrared and Raman spectra of titanates and zirconates (13–16), some broad generalizations can be made. All titanates exhibit bands in the 700–900  $\text{cm}^{-1}$  region and can be assigned to asymmetric stretch of the Ti–O–Ti unit. Low frequency bands, below 300  $\text{cm}^{-1}$ , which appear to be the most prominent in the infrared and Raman spectra of titanates, are expected to have motions involving both the Ti–O and Ba···O groups, with both stretching and bending components. Mid-frequency bands between 300–700  $\text{cm}^{-1}$  are expected to primarily involve the Ti–O unit.

Infrared reflectance spectra were also col-

lected for BaTi<sub>4</sub>O<sub>9</sub> samples doped with Mn, Sn, and Zr at the Ti-site and Ca, Sr, and Pb at the Ba-site. The  $\epsilon''(\nu)$  plots at 297 K for the Zr and Pb doped samples are shown in Figs. 2 (a) and (b), respectively. The general appearance of the spectra remain unchanged upon doping, which is not unexpected considering that doping levels were kept below  $\sim 10$  mole% to prevent phase segregation. The most structurally sensitive infrared band to doping is a broad band at 363  $\text{cm}^{-1}$ , which shifts to 375  $\text{cm}^{-1}$  upon doping with Pb (10 mole%) and 350  $\text{cm}^{-1}$  upon doping with Zr (6 mole%), as shown in Figs. 3 (a) and (b). The shift of this band,

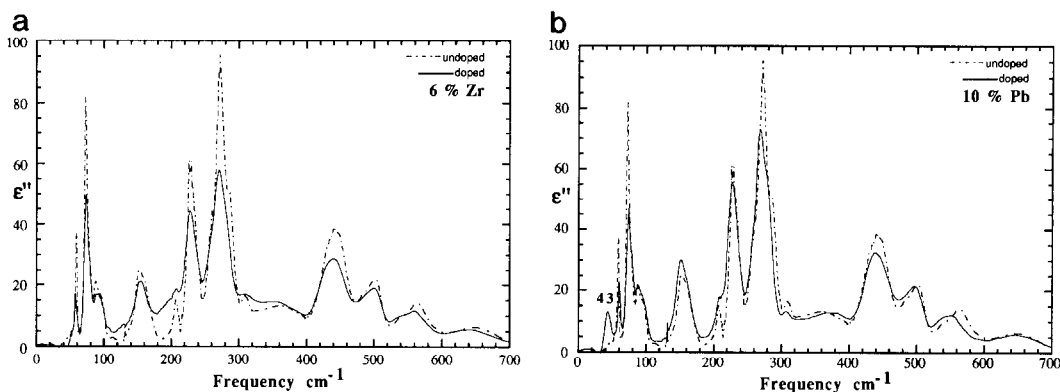


FIG. 2.  $\epsilon''(\nu)$  for  $\text{BaTi}_4\text{O}_9$  doped with (a) 6 mole% Zr and (b) 10 mole% Pb.

which should primarily involve the Ti–O bond, to lower frequencies upon substitution of Ti with Zr can be due to both a mass effect involving the heavier Zr atom as well as a decreased bond order of the Zr–O bond. Comparison of perovskite titanates and zirconates show that, in general, the Zr–O stretch occurs at a lower frequency than the Ti–O stretch (16). In the case of substitutions at the Ba-site by Pb, the  $363\text{ cm}^{-1}$  band exhibits an increase in frequency. A new band is also observed at  $43\text{ cm}^{-1}$  upon Pb doping (Fig. 2 (b)), which we assign to the Pb···O stretch. This band is distinct from the  $45\text{ cm}^{-1}$  band, which is only observed in  $\text{BaTi}_4\text{O}_9$  at temperatures of 17K. The band due to Ba···O stretch cannot be unambiguously identified, but since the new band at  $43\text{ cm}^{-1}$  is the lowest in frequency, it is reasonable to assume that the Ba···O mode appears at a higher frequency. This would indicate a weaker “covalent” interaction between Pb and O which should lead to an increased bond order for the Ti–O bond. This may help explain the upward shift in frequency upon Pb doping. The presence of the lone pair in PbII as compared to a closed shell for BaII may also be important, as evidenced by the role played by these electrons in the attractive interactions between structural layers in  $\alpha$  and  $\beta$  PbO (17). In the case

of  $\text{BaTi}_4\text{O}_9$  doped with Ca (5 mole%), the  $363\text{ cm}^{-1}$  band appears to be considerably broadened with the presence of two bands at  $345$  and  $369\text{ cm}^{-1}$  (Fig. 3 (c)). In analogy with the Zr and Pb doping, this would suggest that Ca may be doping at both the Ba and Ti sites. The possibility of Ca substituting for both Ba and Ti has been previously reported (18).

The  $\text{BaTi}_4\text{O}_9$  samples doped with Sr (6 mole%), Mn (3 mole%), and Sn (6 mole%) do not have any perturbation on the  $363\text{ cm}^{-1}$  band. Electron microscopy of these samples does not show the presence of a second phase, suggesting that substitutional doping may indeed be occurring. It is unclear at present why there is no shift of this band upon doping with these elements.

## 2. Dielectric Parameters: Measured and Calculated

The dielectric parameters  $k$ ,  $Q$ , and  $\tau_k$  calculated from the K–K analysis of infrared reflectance are compared with those obtained from direct dielectric measurements at GHz frequencies in Table I. The calculated dielectric constants are lower than the measured values by a difference of about four. The calculated  $Q$  was lower than the measured values by a factor of two. However, the trends in  $Q$  as function of doping

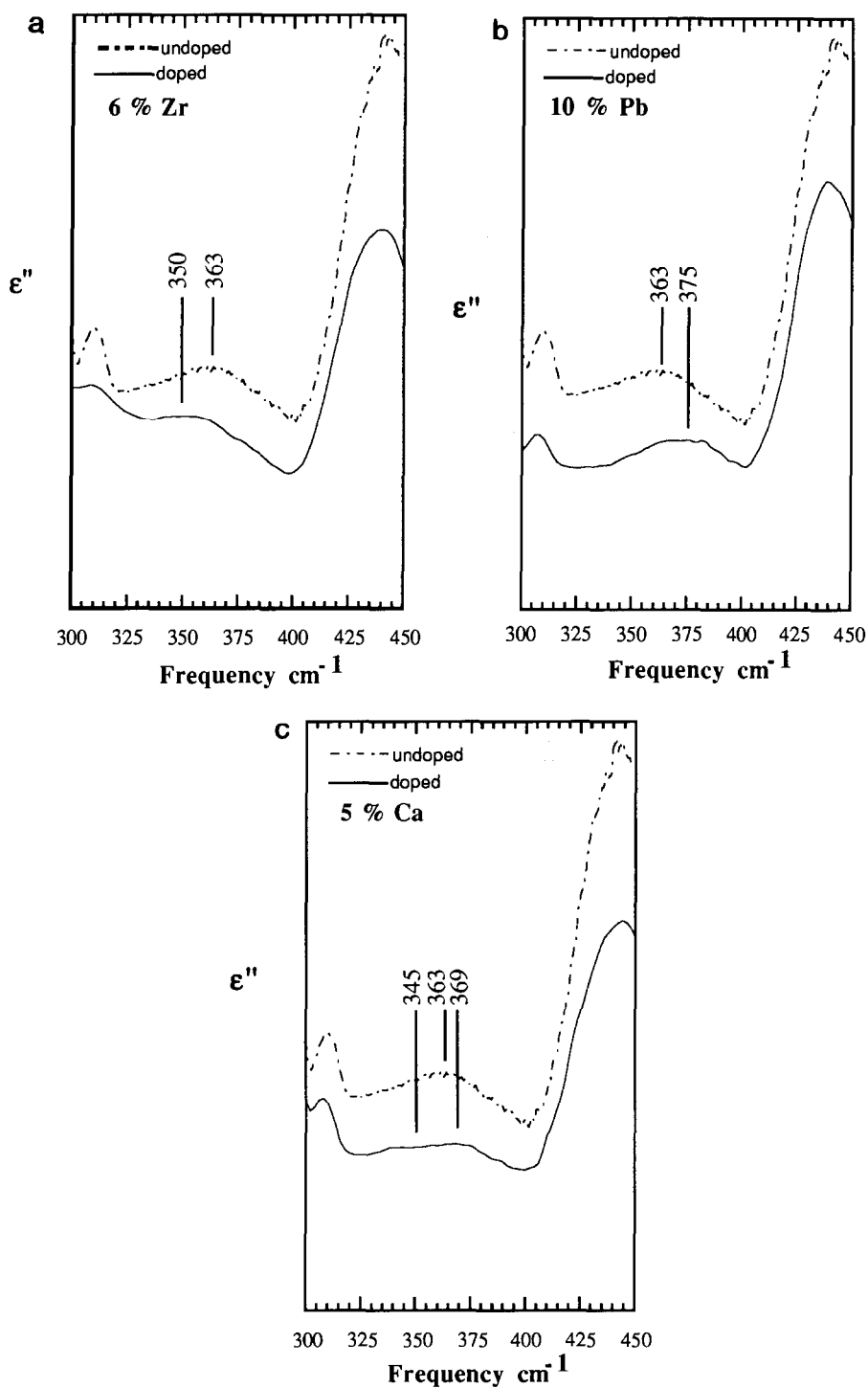


FIG. 3. The effect of doping on the 370  $\text{cm}^{-1}$  infrared active mode: (a) 6 mole% Zr, (b) 10 mole% Pb, and (c) 5 mole% Ca.

TABLE I  
COMPARISON OF DIELECTRIC PROPERTIES CALCULATED FROM INFRARED  
REFLECTANCE AND MEASURED AT 4 GHz

mole%	$k$ mea	$k$ calc	$Q$ mea	$Q$ calc	$\tau_k$ mea (ppm/°C)	$\tau_k$ calc (ppm/°C)
0	36.96	33.97	5675	2930	-49.6	-192.3
4 Sn	36.22	33.59	1684	965		
6 Zr	37.28	32.84	7575	3260		
5 Ca	38.12	33.39	7100	3045		
2 Sr	38.17	33.26	6156	2860		
10 Pb	30.18	34.02	600	469		

with various elements (Fig. 4) are similar for both the direct measurement and that computed from the infrared reflectance data. The origin of the difference in the absolute values of  $k$  and  $Q$  obtained by these two methods is not understood, however, it could be the result of an error in the measurement of reflectance due to factors such as scattering from porosity and scratches on the ceramic samples.

The calculated and measured  $\tau_k$  were -192.3 and -49.6 ppm/°C, respectively. The errors in  $\tau_k$  are likely to be an artifact of an error in the measurement of temperature. Additional errors could have arisen from the fact that the measured  $\tau_k$  was obtained from  $\tau_f$  (the temperature coefficient of resonant frequency) and  $\alpha$  (7) (the coefficient of linear thermal expansion), whereas the calculated

$\tau_k$  was obtained from the variation of  $k$  with temperature.

The variants of  $k$  and  $Q$  (calculated) with frequency from 1–225 GHz are illustrated in Figs. 5 (a) and (b). The value of  $k$  is almost constant, whereas the variation of  $Q$  with frequency  $f$  can be described by the equation

$$Q = f^{1.0096} = 1.45 \times 10^{13}. \quad (7)$$

In the frequency range 1–10 GHz an empirical relationship  $f \times Q = \text{constant}$  has been previously reported (1, 19). The dispersion of  $k$  and  $Q$  with frequency has been modeled by a single-relaxation (single-resonance) model (20). The single-relaxation model is described by the Lorentz oscillator model (20),

$$\epsilon'(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau^2} \quad (8)$$

$$\epsilon''(\omega) = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2}, \quad (9)$$

where  $\epsilon'$  and  $\epsilon''$  are the real and imaginary parts of the complex dielectric constant,  $\omega = 2\pi f$  is the frequency,  $\epsilon_0$  is the static dielectric constant for  $\omega = 0$ ,  $\epsilon_\infty = n^2$  is the dielectric constant for  $\omega = \infty$ , and  $\tau$  is called the relaxation time. A maximum in  $\epsilon''(\omega)$  occurs when the frequency of the applied field equals  $1/\tau$ . At microwave frequencies ( $f < 300$  GHz or  $f < 10$  cm<sup>-1</sup>)  $\omega\tau \ll 1$  and

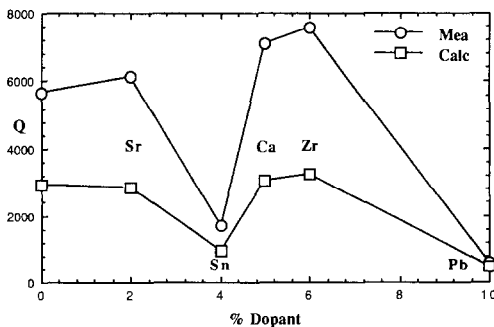


FIG. 4. The effect of doping on  $Q$ .

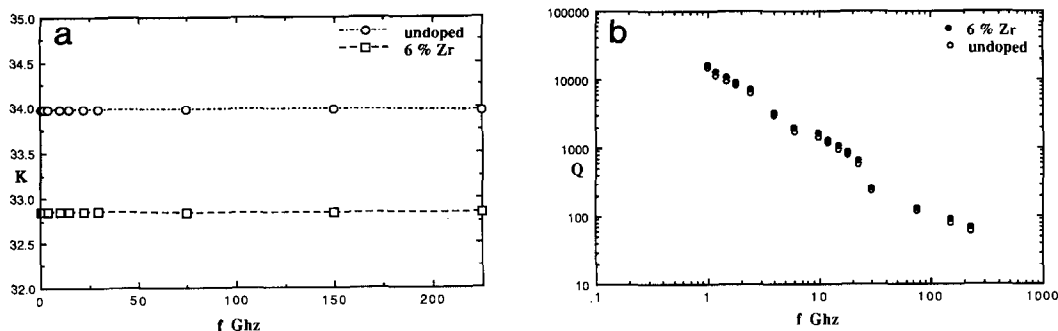


FIG. 5. The variation of (a)  $k$  and (b)  $Q$  as a function of frequency; values calculated from K-K analysis of reflectance data.

hence  $\omega^2\tau^2 \ll 1$ . Equations (8) and (9) are thus reduced to

$$\varepsilon'(\omega) = \varepsilon_0 \quad (10)$$

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty)\omega\tau. \quad (11)$$

From Eqs. (10) and (11) at microwave frequencies,  $Q$  is given by

$$Q = \frac{\varepsilon'}{\varepsilon''} = \frac{\varepsilon_0}{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}. \quad (12)$$

Substituting the values of  $\varepsilon_0 = 36.96$  and  $\varepsilon_\infty = 5.05$  (Fig. 1 (b)) and expressing  $\omega$  as  $2\pi f$  we have

$$Q \times f = \frac{0.18}{\tau}. \quad (13)$$

Since  $\tau$  is the relaxation time for the single-relaxation model and is a constant, Eq. (13) can be rewritten as

$$Q \times f = \text{constant}. \quad (14)$$

It is thus shown that the empirical relation  $Q \times f = \text{constant}$  (Eq. (7)) which was arrived upon from the data calculated from infrared reflectance can be explained by the single-relaxation model. By comparing Eqs. (7) and (13) the value of  $\tau$  is determined as  $1.27 \times 10^{-14}$  sec. Relaxation times of the order of  $10^{-13}$  sec have been reported (20). Also,  $2\pi\nu_0 = 1/\tau$ , where  $\nu_0$  is the frequency of relaxation and is calculated to be 420

$\text{cm}^{-1}$ . In this frequency range, infrared active modes involving Ti-O motion are observed.

#### IV. Conclusions

The nature of the reflectance spectra for the doped and the undoped samples was similar, although the magnitude of reflectance for the doped samples was slightly lower. For undoped BaTi<sub>4</sub>O<sub>9</sub>, 21 infrared lattice modes were observed from the  $\varepsilon''(\nu)$  plot. The  $\varepsilon''(\nu)$  dispersion for samples doped with Pb, Zr, and Ca show that the  $363 \text{ cm}^{-1}$  (Ti-O) mode shifts to a higher frequency upon doping at the Ba-site and a lower frequency upon doping at the Ti-site. At 4 GHz the trends in dielectric parameters calculated from infrared reflectance were in good agreement with the dielectric properties measured using a resonant cavity technique. This suggests that infrared reflectance spectroscopy could be used as an alternative to resonant cavity methods for the characterization of dielectric ceramics.

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