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Correlation of the phonon characteristics and microwave dielectric properties of the $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials

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Abstract

The $Ba(Mg_{1/3}Ta_{2/3})O_3$, BMT, materials possess the highest quality factor ($Q \times f$) in microwave frequency regime among the microwave dielectric materials and can potentially be used for high frequency communication application. To understand the mechanism that determines microwave dielectric properties of the BMT materials, spectroscopic techniques including Raman and Fourier transform infrared (FTIR) analyses are used for investigating the phonon characteristics of the materials. The Raman-shift ($\Delta\omega_{0j}$) of the Raman peaks and the resonance frequency (ω_{0j}) of the FTIR peaks vary insignificantly among the samples, which correlate very well with the phenomenon that the *K*-values for these materials are similar with one another. In contrast, the full-width-at-half-maximum (FWHM) of the Raman peaks and the damping coefficient (γ_j) of the FTIR peaks vary markedly among the samples. The high-*Q* materials possess sharpest vibrational modes, viz., smallest FWHM value for Raman peaks and smallest γ_j value for FTIR peaks and vice versa. The intimate relationship between the phonon characteristics and the fine structure of the materials is confirmed.

Keyword: Dielectric properties; Raman; FTIR spectroscopies

1. Introduction

Complex perovskite compounds with the chemical formula $Ba(B'_{1/3}B''_{2/3})O_3$, where B′ is Zn, Mg, Ni, or Mn and B″ is Nb or Ta, exhibit ultra-low dielectric losses at microwave frequencies[1] when the materials possess B′–B″ 1:2 ordered arrangement with a structural symmetry described by the $P\bar{3}m1$ (D^3_{3d}) space group.[2]

Since the dielectric properties in microwave range follow mainly from ionic polarization, the phonon vibration spectra of $Ba(B'_{1/3}B''_{2/3})O_3$ have been of particular interest. Tamura et al.[3] first analyzed the vibration of 1:2 ordered $Ba(Zn_{1/3}Ta_{2/3})O_3$ normal modes, and Siny et al.[4] investigated the Raman spectra of several complex perovskites, proposing the existence of short-range 1:1 order in $Ba(Mg_{1/3}Ta_{2/3})O_3$. Recently, Chia et al.[5] and Chen et al.[6] studied the Raman and FTIR phonons in $Ba(Mg_{1/3}Ta_{2/3})O_3$, concluding that ionic sizes and the quality of 1:2 ordered structure are two important parameters that impact the vibrational characteristics of the materials. They thus determined the dielectric properties in the microwave region based on the observation of simple perovskite *Pm*3*m* structures.

This study investigates the Raman and FTIR spectra of $Ba(Mg_{1/3}Ta_{2/3})O_3$, and their relationship with microwave properties. Phonon properties are analyzed and correlated with microwave dielectric properties.

2. Experimental procedure

BMT ceramic samples were prepared by a conventional mixed oxide process. These samples were sintered at 1600 °C for 2–200 h in air and were then cooled at different rates (Table 1). The microwave dielectric properties were measured by the TE011 resonant cavity method using an HP 8722 network analyzer, near 6 GHz. Far-infrared and midinfrared reflectance spectra were obtained at room temperature using a Bruker IFS 66v FTIR spectrometer. The modulated light beam from the spectrometer was focused onto either the sample or an Au reference mirror, and the reflected beam was directed onto a 4.2 K bolometer detector ~40–600 cm^{-1} and a B-doped Si photoconductor ~450–4000 cm^{-1}. The different sources, beam splitters,

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Table 1
The processing conditions for preparing the $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials, the corresponding microwave dielectric properties and the related characteristics of the $A_{1g}(O)$ Raman mode

	Processing at 1600 °C		Microwave properties		$A_{1g}(O)$ mode	
	Sintering time (h)	Cooling rate (°C/h)	K	$Q \times f$ (GHz)	Raman-shift (cm^{-1})	FWHM (cm^{-1})
A	200	2	22.2	248,000	797.00	14.55
B	20	20	22.3	205,700	797.15	14.62
C	2	200	25.5	182,600	797.20	15.16

and detectors used in these studies provided substantial spectral overlap, and the reflectance mismatch between adjacent spectral ranges was less than 1%. The optical properties were calculated from a Kramers–Kronig analysis of the reflectance data.[7] These transformations were performed by extrapolating the reflectance at both low and high frequencies. The low-frequency extensions were determined by using the Lorentz model. In the meantime, Raman measurements were taken at room temperature, and the signals were recorded by a DILOR XY-800 triple-grating Raman spectrometer, equipped with a liquid-nitrogen-cooled CCD. The 10 mW output of the 514.5 nm line of an Ar ion laser was used as the excitation source. The obtained Raman spectra exhibited a resolution approximately 0.5 cm^{-1}.

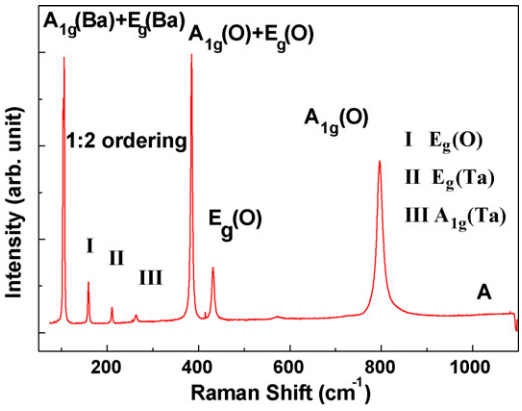

Fig. 2. Typical Raman spectra of the $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials.

3. Results and discussion

The effect of the processing parameters on the microwave dielectric properties of the BMT materials is summarized in Table 1, indicating that the longer soaking time, in conjunction with slower cooling rate, leads to materials with higher $Q \times f$-value, whereas the processing parameters seem to result in insignificant effect on the K-value of the samples. The crystal structures of these materials were examined using X-ray diffraction (XRD) technique to confirm that all the three samples are pure perovskite materials with $P\underline{3}m1$ structure. Detailed analysis using Rietvelt analysis on these XRD patterns indicates that the samples possessing larger ordering parameters show larger $Q \times f$-values, as shown in Fig. 1 (curves a). Moreover, the dielectric constants (K) of the samples are intimately related to the *cell volume*, although the change in K-values among the samples is very modest. The larger *cell volume* (or larger *lattice parameter*) leads to larger K-value (Fig. 1, curves b), sample C.

While it is clear that the increase in ordering parameters is the main factor improving the $Q \times f$-values of the materials, what is the genuine mechanism for such a correlation needs more detailed studies. The Raman and FTIR spectroscopies of these materials are thus investigated. Typical Raman spectra of these BMT materials are shown in Fig. 2, indicating that the Raman peaks are very sharp, a characteristic for the high Q materials. Among the major Raman peaks, the $A_{1g}(O)$ mode at 796 cm^{-1} varies more markedly among the samples. The characteristics of this Raman resonance peak are closely related with the microwave dielectric properties of the materials. As shown in Table 1, the shift of Raman peak is largest for the samples with largest dielectric constant ($K_C = 25.5$, sample C) and is smallest for those with smallest K-value ($K_A = 22.2$, sample A). However, the change is very modest.

In contrast, Table 1 illustrates that the width of the Raman peak (full-width-at-half-maximum, FWHM) is narrowest ($(FWHM)_A = 14.55\ cm^{-1}$) for sample A, which possesses highest quality factor ($(Q=f)_A = 248{,}000$), and is broadest ($(FWHM)_C = 15.16\ cm^{-1}$) for sample C, which has lowest

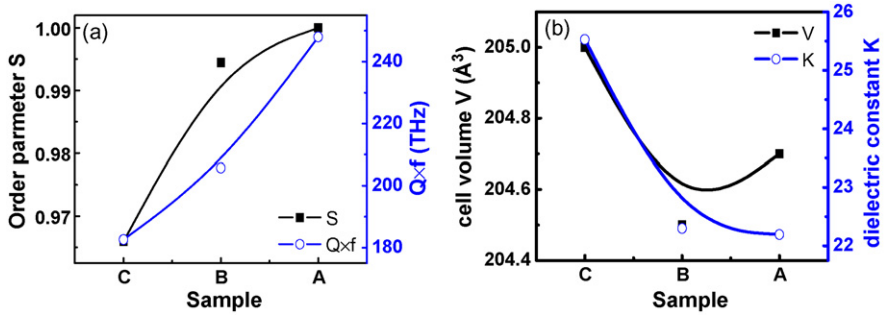

Fig. 1. The (a) ordering parameter vs. quality factor and (b) cell volume vs. dielectric constant of three $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials.