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Use of Raman spectroscopy to determine the site occupancy of dopants in BaTiO₃

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Chemical doping is one of the major methods by which the properties of BaTiO₃ are modified to induce various device characteristics. Doping strategies are generally separated into iso- and aliovalent (donors and acceptors) and into A- and B-site species within the perovskite structure. The A_{1g} octahedral breathing mode at $\sim 800\text{ cm}^{-1}$ in BaTiO₃ is Raman inactive for compositions with single B-site species. However, this mode becomes Raman active if more than one B-site species is present, including titanium vacancies, V_T^{'''}. Moreover, the relative intensity of the A_{1g} breathing mode is qualitatively related to the concentration of the species replacing Ti in the B-site. This article illustrates some clear cases where the A_{1g} octahedral breathing mode can be utilized to verify the site occupancy of dopants in BaTiO₃ when used in conjunction with more conventional indirect methods such as x-ray diffraction (Vegard's Law) and dielectric measurements as a function of temperature. © 2011 American Institute of Physics. [doi:10.1063/1.3592192]

I. INTRODUCTION

Ferroelectric barium titanate exhibits three successive structural phase transitions with increasing temperature: rhombohedral ($-100\text{ }^{\circ}\text{C}$) \rightarrow orthorhombic ($0\text{ }^{\circ}\text{C}$) \rightarrow tetragonal ($120\text{ }^{\circ}\text{C}$) \rightarrow cubic.¹ These phase transitions have been the subject of extensive investigations over many years, utilizing a wide range of techniques from dielectric measurements to high resolution neutron and x-ray diffraction. Characterization using vibrational spectroscopy is less common but nonetheless extensive literature exists with a preponderance of Raman spectroscopy data. For undoped tetragonal BaTiO₃ (BT) the mode assignments are well-known.² Fig. 1 illustrates typical spectra obtained on undoped BT ceramics between room temperature and $300\text{ }^{\circ}\text{C}$. For convenience, in-house spectra have been utilized but many similar spectra can be found in the literature and the reader is referred to Refs. 2–4 for greater insight into the detailed origins of the Raman modes. In brief, however, the room temperature tetragonal phase (Fig. 1) is characterized by sharp bands at ~ 170 and 306 cm^{-1} and asymmetric broader bands at 270 , 520 , and 720 cm^{-1} .² These latter three bands are also present but much broader and more symmetrical in the cubic para-electric phase. They were often attributed to second-order effects, however, more correctly, they relate to the disorder of Ti displacements in the octahedra.^{3,4} The band at 720 cm^{-1} is extremely broad and weak in the para-electric phase and is often considered unique to the tetragonal phase. The spectra are used as a reference point for comparison throughout the paper.

In each of the characteristic spectra of BaTiO₃ shown in Fig. 1, the region around $\sim 800\text{ cm}^{-1}$ does not exhibit evidence of any modes. However, in this region of reciprocal wavelength, an A_{1g} octahedral breathing mode occurs

which is Raman inactive for simple perovskites since the mode is symmetrical and does not result in a change in polarization.⁵ However, for complex perovskites and solid solutions with two or more B-site species, the A_{1g} becomes Raman active since the presence of dissimilar ions in the center of the octahedra creates asymmetry in the breathing-like mode. It is particularly intense and narrow for ordered complex perovskites but appears as a broad peak in disordered perovskite solid solutions. This has been experimentally shown in a comprehensive study of stoichiometric perovskite solid solutions by Zheng *et al.*⁶ which was principally aimed at understanding the relation between the short range cation order and quality factor in microwave dielectric ceramics. The A_{1g} octahedral breathing mode typically appears as a broad band at low concentrations on the B-site and increases in intensity until $x=0.5$. The increase in intensity with x may be simplistically interpreted as an increase in the volume fraction of the octahedra experiencing an asymmetric rather than a symmetric breathing mode. The origin of the mode, however, is irrefutably chemical in nature and does not relate to structural distortions of the lattice away from simple cubic symmetry. Hence, a signature of any such mode in a ferroelectric perovskite solid solution such as BaTiO₃ is that its width and intensity are largely temperature independent in the vicinity of the cubic to tetragonal phase transition.

The site occupancy and defect chemistry of dopants in BaTiO₃ is a very controversial subject with particularly great debate as to the compensation mechanism for aliovalent species.^{7,8} Commercially, how dopants enter the BaTiO₃ lattice is of great importance since all temperature stable multilayer capacitors use different combinations of Ba and Ti substituents to control temperature stability within the Electrical Industry Alliance criteria, e.g., X8R capacitors will often have Ca and RE₂O₃, in addition to

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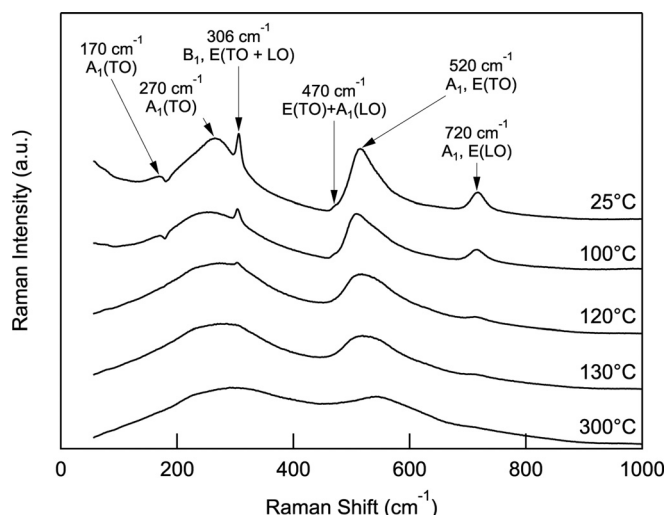


FIG. 1. Temperature evolution of the Raman spectra for undoped BaTiO₃ between room temperature and 300 °C.

more minor dopants, to achieve a stability of $\pm 15\%$ of the room temperature capacitance within the regime $+150$ to -55 °C.⁹ Direct measurements of the coordination of ions in the perovskite structure are very difficult to achieve and are restricted to techniques such as x-ray photoelectron spectroscopy, electron paramagnetic resonance, and extended x-ray absorption fine structure (EXAFS) measurements. No single technique offers a simple, comprehensive method of determining site occupancy and coordination, and techniques such as EXAFS generally require central national facilities. As a result, site occupancies are usually inferred from a combination of x-ray diffraction data, i.e., Vegard's Law, which predicts that lattice parameters will change monotonically with increasing x until the solid solution reaches either its solubility limit or a structural phase transition occurs,¹⁰ and, in the case of BaTiO₃, the manner in which T_C varies as a function of temperature (differential scanning calorimetry or capacitance versus temperature measurements). Often, such techniques are sufficient but in some controversial cases, further proof may be required and a simple in-house technique which gives further information concerning site occupancies/compensation mechanisms would be extremely useful.

In this article we propose that in some cases Raman spectroscopy is a useful tool for distinguishing between certain site occupancies and compensation mechanisms. In particular, the appearance and relative intensity of the A_{1g} octahedral breathing mode can provide additional information about the type of species present on the B-site. Proof of this concept will be demonstrated in well-known cases where site occupancy and compensation mechanisms are relatively well-established, e.g., Sr-, Zr-, and La-doped BaTiO₃, and by the determination of site occupancy and compensation for more controversial systems such as Ca-doped BaTiO₃.

II. EXPERIMENTAL PROCEDURES

The BT-based ceramics were synthesized by the conventional mixed oxide route. The starting reagents ($>99.9\%$ pure) were weighed in appropriate ratios and ball-milled in propanol overnight using ZrO₂ media. The slurry was dried

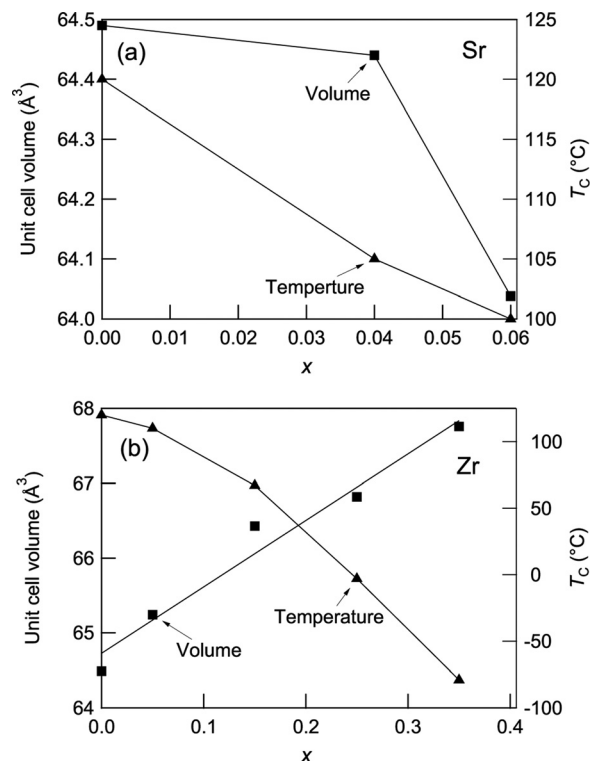


FIG. 2. Unit cell volume and T_C as a function of composition for (a) Sr- and (b) Zr-doped BaTiO₃ as a function of composition.

and then calcined for 6 h between 1100 and 1200 °C, depending on composition. The calcined powders were remilled and then pressed into pellets which were sintered for 4 h at the required temperatures and atmospheres. All samples were $>95\%$ theoretical density.

X-ray diffraction was performed at room temperature on a STOE diffractometer, using Cu $K\alpha$ radiation. Data were collected over the 2θ range of 20 – 70° , with a step width of 0.1° and a count time of 60 s. Si was used as an internal standard to determine accurate lattice parameters.

Fixed frequency capacitance measurements were obtained using a Hewlett–Packard 4284a LCR (Palo Alto, USA) meter connected via HP 16048 D test leads to a compression-type sample jig. Gold-electrode paste was painted onto the major faces of the pellets, and fired at 800 °C for 2 h. Temperature control was achieved by inserting the jig into a Lenton tube furnace (Hope, UK). The data were collected using LABVIEW software (National Instruments, USA).

A Renishaw inVia micro-Raman spectrometer was used for the spectroscopic measurements. Raman spectra were excited with the 514.5 nm line of an Ar-laser and recorded in the back-scattering geometry. Laser power of ~ 10 mW was focused on a ~ 2 μm spot. To obtain data above room temperature, a Linkam THMS600 cell was used. The obtained spectra were corrected for the Bose–Einstein thermal factor.

III. RESULTS AND DISCUSSION

A. Sr- and Zr-doped BaTiO₃ (isovalent)

Figures 2(a) and 2(b) show the change in unit cell volume and T_C for Ba_{1-x}Sr_xTiO₃ (BST100x) and BaZr_xTi_{1-x}O₃

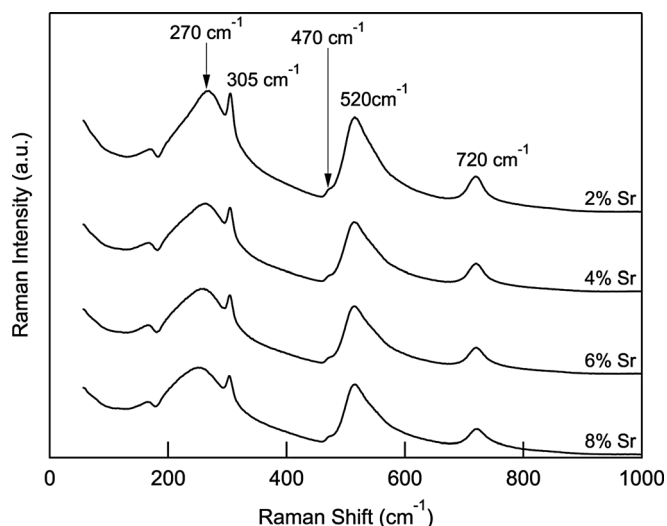


FIG. 3. Room temperature Raman spectra of Sr-doped BaTiO₃ as a function of composition.

(BTZ100x), respectively, as a function of x . In each case, T_C decreases, but for BST100x the unit cell volume also decreases whereas for BTZ100x it increases. This is consistent with the premise that the A–O bond length shrinks in BST100x since the ionic radius of Sr ($r_{\text{Sr}} = 0.149$ nm) is less than that of Ba ($r_{\text{Ba}} = 0.16$ nm) and the B–O bond length increases in BTZ100x since $r_{\text{Zr}} (0.074 \text{ nm}) > r_{\text{Ti}} (0.0605 \text{ nm})$.¹¹

Figure 3 shows the room temperature Raman spectra for BST100x. No further modes are observed; specifically, it is evident that with Sr substitution for Ba, the A_{1g} mode at $\sim 800 \text{ cm}^{-1}$ remains Raman inactive. Figure 4 shows the room temperature Raman spectra for BTZ100x.¹² An extra broad mode which is independent of temperature appears at $\sim 800 \text{ cm}^{-1}$. In undoped and A-site doped BT the A_{1g} octahedral breathing mode is symmetrical and therefore, Raman inactive, however, with two different cation species occupying the B-site (Zr and Ti), the mode becomes asymmetric and Raman active. It increases in relative intensity as x increases, i.e., the volume fraction of the B-site exhibiting an

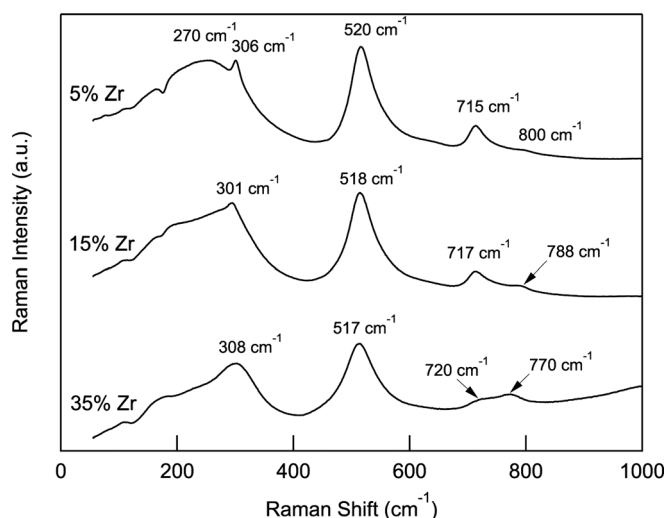


FIG. 4. Room temperature Raman spectra for Zr doped on the B-site of BaTiO₃ as a function of composition.

asymmetric breathing mode increases with x . The preceding data confirm that the A_{1g} breathing mode at $\sim 800 \text{ cm}^{-1}$ is sensitive only to modifications of the B-site occupancy and that direct substitutions onto the A-site do not result in a Raman active band unless further ionic compensation methods occur.

B. Ca-doped BaTiO₃ (iso- and alio-valent)

Ca-doped BaTiO₃ has recently received significant attention since when Ca substitutes onto the A-site it is considered to enhance the cubic–tetragonal T_C by up to 10 °C for doping levels of $\sim 8 \text{ mol. \%}$.⁷ This has practical applications in the development of X8R capacitors. However, there is considerable controversy as to the principle substitution mechanism for Ca-doped BT and Ca is known to have solubility on the A- and B-sites with upper limits of ~ 25 and 4 mol. %, respectively.^{7,13} If the case of Sr- and Zr-doped BaTiO₃ is used as a guide, Raman spectroscopy should be able to distinguish between these two possibilities based on whether the A_{1g} octahedral breathing mode is Raman active (B-site) or inactive (A-site).

Figures 5(a) and 5(b) shows the plots of T_C and unit cell volume versus x for ceramics batched according to the formulae, Ba_{1-x}Ca_xTiO₃ (BC100xT) and BaCa_xTi_{1-x}O_{3-x} (BTC100x), respectively. For A-site doped compositions, T_C initially increases while the unit cell volume decreases. For compositions batched for B-site occupancy, T_C decreases sharply with x but the unit cell volume increases. The decrease in unit cell volume is attributed to a decrease in A–O bond length since $r_{\text{Ca}} (0.135 \text{ nm}) < r_{\text{Ba}}$.¹¹ In contrast, the

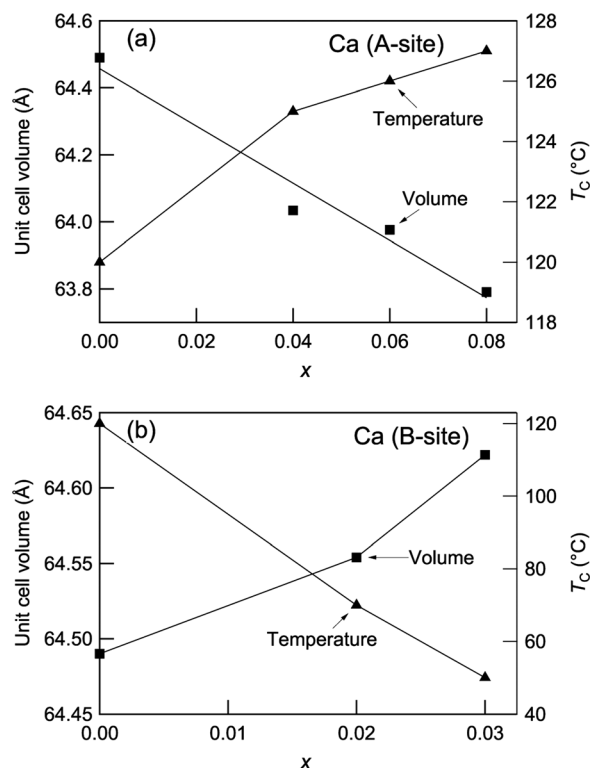


FIG. 5. Unit cell volume and T_C as a function of composition for Ca-doped BaTiO₃ on the (a) A-site and (b) B-site.

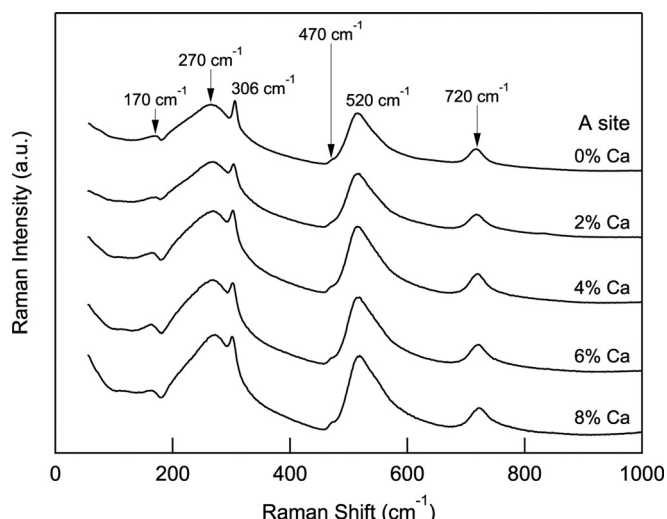


FIG. 6. Room temperature Raman spectra for Ca doped on the A-site of BaTiO_3 as a function of composition.

increase in unit cell volume for $\text{BTC100}x$ is attributed to an increase in the B–O bond length since $r_{\text{Ca}} > r_{\text{Ti}}$. These indirect methods imply that Ca can substitute on both the A- and B-sites depending on the batched stoichiometry. Figure 6 shows room temperature Raman spectra for $\text{BTC100}x\text{T}$. No extra modes appear in the 800 cm^{-1} region of the spectra, thereby confirming that Ca resides on the A-site. In contrast, the spectra for $\text{BTC100}x$, shown in Fig. 7, exhibit a broad A_{1g} breathing mode at $\sim 800\text{ cm}^{-1}$, thereby confirming B-site occupancy.

C. La-doped BaTiO_3 (aliovalent)

Figure 8 shows a plot of the unit cell volume and T_C versus x for ceramics batched in accordance with the formula, $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-1/4x}\text{O}_3$ ($\text{BLT100}x$), and processed in a flowing oxygen atmosphere ($p\text{O}_2 = 1\text{ atm}$). The unit cell volume monotonically decreases with increasing La concentration which is accompanied by a decrease in T_C . The only possible

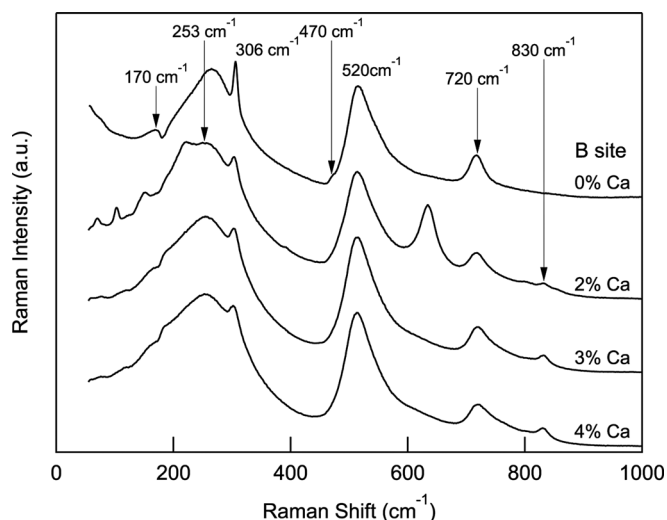


FIG. 7. Room temperature Raman spectra for Ca-doped on the B-site of BaTiO_3 as a function of composition.

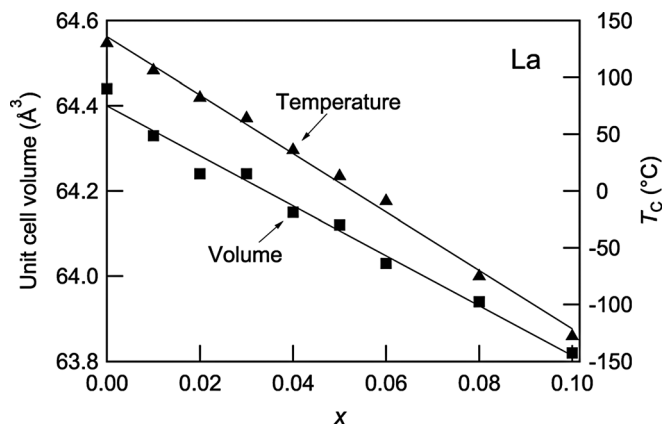


FIG. 8. Unit cell volume and T_C vs x for ceramics batched in accordance with the formula $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-1/4x}\text{O}_3$ ($\text{BLT100}x$).

explanation for a decrease in unit cell volume and T_C is if La substitutes on the A-site since $r_{\text{La}} (0.135\text{ nm}) < r_{\text{Ba}} (0.16\text{ nm})$. A B-site substitution would result in an increase in the unit cell volume since $r_{\text{La}} > r_{\text{Ti}} (0.0605\text{ nm})$.¹¹ The only remaining question is what is/are the major compensation mechanism(s). The three possible compensation mechanisms are,¹⁴

Ti vacancies: $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-1/4x}\text{O}_3$, $\text{La}_{\text{Ba}}^{\bullet} \equiv 1/4V_{\text{Ti}}^{\prime\prime\prime}$,

Ba vacancies: $\text{Ba}_{1-x/2}\text{La}_x\text{TiO}_3$, $\text{La}_{\text{Ba}}^{\bullet} \equiv 1/2V_{\text{Ba}}^{\prime\prime}$,

Electronic compensation: $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$, $\text{La}_{\text{Ba}}^{\bullet} \equiv e^{\prime}$.

Figure 9 shows the room temperature spectra for $\text{BLT100}x$. As x increases, the A_{1g} mode at 840 cm^{-1} increases in intensity, i.e., the volume fraction of octahedra exhibiting an asymmetric breathing mode increases with x . The only compensation mechanism which induces mixed species on the B-site is via $V_{\text{Ti}}^{\prime\prime\prime}$. Compensation via the other two mechanisms ($V_{\text{Ba}}^{\prime\prime}$ and e^{\prime}) is not completely excluded but they do not dominate the defect chemistry of La-doped BaTiO_3 prepared in $p\text{O}_2 = 1\text{ atm}$. The model of compensation primarily by $V_{\text{Ti}}^{\prime\prime\prime}$ for such La-doped BaTiO_3 samples is well-accepted and is confirmed here by the Raman spectroscopy data.

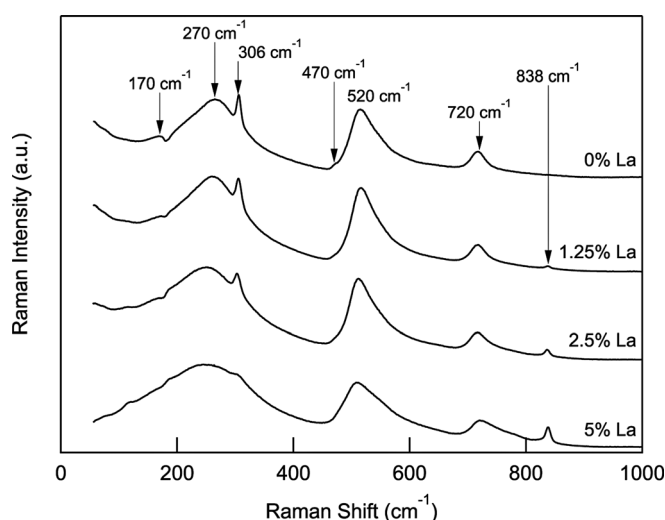


FIG. 9. Room temperature Raman spectra for La-doped BaTiO_3 as a function of composition.

IV. CONCLUSIONS

- (i) In conjunction with indirect methods such as XRD (Vegard's Law) and fixed frequency capacitance measurements as a function of temperature, Raman spectroscopy can indicate the primary site occupancy of key dopants/substituents in BaTiO₃.
- (ii) For direct B-site substitution the A_{1g} octahedral breathing mode becomes Raman active and its relative intensity increases with x .
- (iii) For donor A-site substitutions, the A_{1g} octahedral breathing mode also becomes Raman active, confirming that V_{Ti}^{'''} is the primary ionic compensation mechanism for samples prepared in flowing oxygen.

ACKNOWLEDGMENTS

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