Raman study of phonon modes in bismuth pyrochlores

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The Raman spectra of the cubic bismuth pyrochlores Bi1.5Zn0.92Nb1.5O6.92, Bi3/2ZnTa2/2O7, Bi3/2MgNb3/2O7, and Bi3/2MgTa3/2O7 have been measured at room temperature. The frequencies of the Raman modes, obtained from first-principles calculations, for Bi1.5TiO3 are presented for comparison. The spectra of the four samples are similar and agree well with the first-principles calculations. Each bismuth pyrochlore shows more than the six modes expected for the ideal pyrochlore structure. The analysis shows that many of the additional modes could be explained as the relaxation of the selection rules due to the displacive disorder. The Raman modes are assigned by reference to spectra of other pyrochlore materials, comparison to infrared data, and the \textit{ab initio} calculations.

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I. INTRODUCTION

Bismuth pyrochlores have been extensively studied for dielectric applications,1 and have earned recent attention for high-frequency filter applications thanks to their low loss, high permittivity, and good temperature stability.2 Their pyrochlore structure is described as consisting of interpenetrating networks of BO6 octahedra and A2O’ chains3 and is assigned to the space group \textit{Fd}3\textit{m}. The nominal composition can be written as \textit{A}_2\textit{B}_2\textit{O}_5 or as \textit{A}_2\textit{B}_2\textit{O}_5\textit{O’} with the latter formula differentiating the oxygen in the \textit{A2O’} chains. The pyrochlore family is fascinating because the \textit{A} and \textit{B} sites can be occupied by a broad range of elements that can give rise to a great variety of physical properties. In the bismuth pyrochlore, Bi1.5Zn0.92Nb1.5O6.92 (BZN), the \textit{A} site is mostly occupied by Bi and the \textit{B} site by Nb; while Nb partially occupies both sites. It is important to note that in the literature, cubic BZN is typically described as having the expected nominal composition of Bi1.5Zn1.0Nb1.5O7. However, phase refinement studies,4 have demonstrated partial substitution of Zn in the \textit{A2O’} chains (with a resulting oxygen deficiency as presented above) to satisfy the crystallochemical balance between ionic bonding, lattice strain, and charge balance.

The BZN structure has been shown to differ from an ideal pyrochlore structure through random displacements of the \textit{A} and \textit{O’} ions.5,6 This disorder has been attributed to the active lone pair of the Bi cation6 and appears in the infrared (IR) spectrum of BZN as additional modes from those predicted by the ideal pyrochlore structure.7,8 The additional IR modes were also observed by Chen \textit{et al.},7 in three other bismuth pyrochlores Bi1.5ZnTa2/2O7 (BZT), Bi3/2MgNb3/2O7 (BMN), and Bi3/2MgTa3/2O7 (BMT). Here, we present complementary Raman measurements and mode assignments for BMN, BMT, BZN, and BZT; the four ceramics materials studied by Chen \textit{et al.}.7 Both Raman and IR spectroscopy are needed for a more complete picture of the vibrational modes. IR spectroscopy detects only vibrations with a net change in dipole moment and Raman detects those with a net change in polarizability. Furthermore, the Raman study of the pyrochlore structure is useful for a system where different substituents can occupy the \textit{A} and \textit{B} sites (such as BZN and the other samples). For the ideal pyrochlore structure, the Raman modes involve movement of oxygen ions only while some IR modes involve motion of the \textit{A} or \textit{B} ions.9 For BZN, the mass difference between Zn and Nb (or Zn and Bi) can lead to splitting of an IR vibrational mode.7 This is also true for the other three compounds studied here. Also, systematic changes in the IR frequencies across different samples could be attributed to both the changes in the cation’s mass and the changes in force constants. In the Raman spectra, however, any systematic differences in frequency are explicitly related to the differences in the force constants for different substituents. The observation of splitting of modes would then suggest appreciable difference in force constant for different substituents in the \textit{A} and \textit{B} sites.

There are two main purposes to this work. One is to compare the Raman spectra of bismuth pyrochlores to the vibrational frequencies predicted by first-principles calculations for similar pyrochlores. In this work, we present the frequencies of the Raman modes for Bi1.5Ti2O7 from \textit{ab initio} calculations. The spectra of BMN, BMT, BZN, and BZT agree well with the calculations. This is also true when our spectra are compared to \textit{ab initio} work in the literature on the niobate pyrochlore Cd2Nb2O7.11 The second purpose is to compare the behavior of the Raman-active modes among four bismuth pyrochlores with different substituents and to compare them with the reported spectra of other pyrochlores. The results showed that the Raman spectra are on balance quite similar for the bismuth samples. Each sample showed more than six Raman bands whereas six modes is the prediction for the ideal pyrochlore structure. The appearance of the additional Raman bands, which correspond to Raman-inactive modes of the ideal pyrochlore structure, confirms the displacive disorder of the \textit{A} and \textit{O’} sites in the bismuth pyrochlores. The Raman modes were assigned by reference to the Raman spectra of many other pyrochlores,10–29 some of which include lattice-dynamical calculations,12,27,28 and first-principles calculations.11 In the literature, the lattice dynamical and \textit{ab initio} calculations show an interesting difference.
The lattice-dynamical calculations for the Mn and Ti pyrochlores, which use experimental IR and Raman data, are reported to work only when modes observed above 600 cm\(^{-1}\) are assumed to be overtones.\(^{15}\) For Cd\(_2\)Nb\(_2\)O\(_7\), the first-principles calculations by Fischer et al.\(^{11}\) predict a fundamental mode \(F_{2u}\) with a frequency as high as 880 cm\(^{-1}\). Our calculations for Bi\(_2\)Ti\(_2\)O\(_7\) also predict a fundamental mode with frequency above 700 cm\(^{-1}\). All four Bi pyrochlores have a mode at 780 cm\(^{-1}\) with an intensity higher than most fundamentals. As discussed below, the high intensity of this mode, uncharacteristic of a second-order scattering process, presents interesting questions about these systems.

In the assignment of the modes, it was also considered that the displacement disorder in these samples lowers the symmetry of the system and can result in the relaxation of the selection rules. These displacements of the A and O\(^+\) sites could make predicted Raman-inactive modes (including IR \(F_{1u}\) modes) appear in the Raman spectra. Our computational work for Bi\(_2\)Ti\(_2\)O\(_7\), and the work for Cd\(_2\)Nb\(_2\)O\(_7\) by Fischer et al.\(^{11}\) for a disorderless pyrochlore structure, can give the frequencies of the Raman and infrared modes, as well as some optically inactive modes. The comparison between the Raman data, the IR, and the computational work shows that most of the additional modes observed in the studied here pyrochlores can be attributed to relaxation of the selection rules. Finally, the fact that Zn shares the A site with Bi and the B site with Nb in BZN did not have a considerable effect on the spectrum of this pyrochlore. There were no additional bands that were attributed to splitting due to different force constants. This was also true for the other three bismuth pyrochlores.

II. EXPERIMENTAL PROCEDURES

Disk-shaped samples, of 1 cm radius and 5 mm thickness were prepared by conventional solid-state powder processing techniques.\(^{30}\) The samples were polished and appeared light yellow. Room-temperature Raman spectra were measured with a T 64000 Jobin Yvon triple Raman spectrometer equipped with a liquid-nitrogen-cooled back-illuminated charge coupled device detector. We used the 488 and 501.7 nm lines of the Ar\(^+\) ion laser to excite Raman scattering. The measurements were done in the subtractive mode\(^{31}\) with the laser power on the sample not exceeding 6 kW/cm\(^2\) and with an accumulation time of 20 s. The spectra were taken in the back scattering geometry; the scattered light was not polarized while the incident light had vertical polarization.

Phonon calculations at the \(\Gamma\) point of the Brillouin zone were performed for Bi\(_2\)Ti\(_2\)O\(_7\) using a Perdew-Wang approximation\(^{32}\) to the generalized gradient approximation of density-functional theory using the CRYSTAL code.\(^{33}\) The \(Fd\overline{3}m\) cubic cell containing 22 ions was used. In common with previous calculations for the pyrochlore,\(^{34,35}\) we find that the high-symmetry cubic structure is unstable with respect to a lattice distortion. Three modes, of \(F_{1u}\), \(E_u\), and \(F_{2u}\) symmetry, are found to have imaginary frequencies for the cubic structure. However, none of the Raman-active modes have imaginary frequencies. Further details of the lattice distortions and additional IR-active modes which result when an 88 ion unit cell is relaxed without symmetry constraints are reported elsewhere.\(^{36}\)

III. RESULTS AND DISCUSSION

A. Analysis of \(\chi''(\omega)\)

The room-temperature Raman spectra of BMN, BMT, BZN, and BZT are shown in Fig. 1 with scaled and shifted intensities for ease of comparison. The spectra of all four samples were analyzed by solving for the imaginary part of the Raman susceptibility, \(\chi''(\omega)\), which is related to the Raman scattering cross section, \(\delta \sigma / \delta \Omega d\omega\), and the Bose factor, \(n(\omega) + 1\), by the equation

\[
\frac{\delta \sigma}{\delta \Omega d\omega} \propto [n(\omega) + 1] \chi''(\omega),
\]

where \(n(\omega)\) is the Bose-Einstein distribution

\[
n(\omega) = \frac{1}{\text{e}^{\hbar \omega/k_\text{B}T} - 1}.
\]

Equations (1) and (2) show that the scattering cross section increases rapidly at energies lower than \(k_\text{B}T\). For low frequencies, the \(1/\omega\) dependence of the Bose factor affects not only the intensity of each mode but also the location of the peak. Therefore, the analysis in this region is improved by dividing the Raman spectra by the Bose factor, \(n(\omega) + 1\), and obtaining the imaginary part of the Raman susceptibility \(\chi''(\omega)\). To study each mode, the imaginary part of the Raman susceptibility can be modeled using a sum of Lorentzian functions.

![Figure 1](image-url)
where each band has three parameters: a maximum \( A_j \), a center frequency \( \omega_0_j \), and a width, \( \gamma_j \), that is inversely related to the excitation lifetime. This functional form is attributed to samples with homogeneous broadening, where the width of the Raman band is related to the damping coefficient \( \gamma_j \). The other functional form is that of Gaussians

\[
\chi''(\omega) = C + \sum_j I_0_j e^{-(\omega - \omega_0_j)^2/\sigma_j^2},
\]

where \( I_0_j \), \( \omega_0_j \), and \( \sigma_j \) are the height, center frequency, and statistical width of each band, and \( C \) is a constant. The Gaussian functional form is used for inhomogeneous broadening, where the width of a band is due to a statistical distribution of the resonant frequency \( \omega_0_j \). The \( \chi''(\omega) \) of each sample was fitted to the form in Eqs. (3) and (4), by using a least-squares minimization method. For each fit, all parameters for all modes were allowed to vary simultaneously. Figures 2 and 3 show the Lorentzian and Gaussian fits for all four samples and show the individual oscillators from the fit. BZN shows nine features in its spectrum, and therefore nine oscillators were used for the Lorentzian fit. For the other samples, nine oscillators were enough to fit the spectrum, although the fit for BMN showed that eight oscillators were enough and that a ninth oscillator was unnecessary (the introduction of the new oscillator yielded a very weak amplitude for this mode). For the Gaussian fits, the constant \( C \) was necessary to fit the remaining intensity at high frequencies. The Gaussian function has been used to fit the Raman spectrum of BZN previously in the literature. For our fits to the Raman susceptibility, although the Gaussian function seems to produce a good fit, the fit did not always converge to the same parameters. Furthermore, the Lorentzian function produced a better fit in the 300–600 cm\(^{-1}\) region. For the rest of this paper, we will use the parameters extracted from the Lorentzian fittings. The extracted damping coefficient for each mode, \( \gamma_j \), will also be used for comparison to the damping coefficients obtained from the IR of the low-frequency modes. Table I shows the parameters obtained from the Lorentzian function fit to the Raman susceptibility.

A factor group analysis of the ideal pyrochlore structure yields six Raman-active modes (\( R \)), seven IR modes, and one \( F_{1a} \) acoustic mode.
where all six Raman modes involve only motion of oxygen atoms. Each mode was studied and assigned by first referencing the literature on diverse samples with structures close to the ideal pyrochlore structure. Then, the bands were also compared to our ab initio calculations for Bi$_2$Ti$_2$O$_7$ and those in the literature for Cd$_2$Nb$_2$O$_7$. Table II shows the frequencies of the various observed modes for the four samples along with their assignment. We discuss in the following sections each mode and its assignment.

TABLE II. The Raman modes of BMN, BMT, BZN, and BZT are shown along with their tentative assignment. The frequencies calculated for Bi$_2$Ti$_2$O$_7$ from first principles are also reported. The superscript $i$ refers to an unstable mode. The data and assignments for Cd$_2$Nb$_2$O$_7$ are taken from Fischer’s computational work (Ref. 11). The rationale for the assignment of each mode is discussed in the text.

### B. Low-frequency modes (70–180 cm$^{-1}$).

#### Relaxation of the selection rules

All four samples showed bands from 70 to 180 cm$^{-1}$. These modes are lower in frequency than those observed for many pyrochlores. For various A and B substituents, the lowest frequency Raman mode attributed to a symmetry allowed vibration is at 220 cm$^{-1}$. A few examples are (with many other pyrochlores contained in the references): 220 cm$^{-1}$ for Yb$_2$Ti$_2$O$_7$, 230 cm$^{-1}$ for Pb$_2$Sn$_2$O$_7$, 240 cm$^{-1}$ for Cd$_2$Te$_2$O$_7$, 289 cm$^{-1}$ for Ti$_2$Mn$_2$O$_7$, 292 cm$^{-1}$ for In$_2$Mn$_2$O$_7$, 298 cm$^{-1}$ for Tl$_2$Mn$_2$O$_7$, 298 cm$^{-1}$ for Bi$_2$Sb$_2$O$_7$, 301 cm$^{-1}$ for Nd$_2$Ir$_2$O$_7$, 308 cm$^{-1}$ for Sm$_2$S$_2$O$_7$, and 312 cm$^{-1}$ for both Gd$_2$Ir$_2$O$_7$ and Yb$_2$Sn$_2$O$_7$. Since all Raman-active modes only involve motion of oxygen atoms, the high mass of the Bi cation should not be responsible for lower frequencies. Such low-frequency modes would suggest much weaker A–O or O–A–O force constants for Bi than for all the compounds referenced above. For other bismuth pyrochlores, the lowest modes are around 250 cm$^{-1}$ for Bi$_2$Hf$_2$Ti$_2$O$_7$, and 226 cm$^{-1}$ for various Bi$_2$Y$_{(2-x)}$Ti$_2$O$_7$. For BZN, the 180 cm$^{-1}$ band has been reported in the literature but its assignment seems difficult. It has been explained as the splitting of an $F_{2g}$ mode, where one band belongs to a Bi–O stretch at 180 cm$^{-1}$ and the other to a Zn–O stretch at 251 cm$^{-1}$. However, the calculations for the splitting of this mode includes the masses of the Bi and Zn cations. In contrast, other work has assigned it to a $F_{2g}$ mode separate from the 255 cm$^{-1} F_{2g}$ mode.

We propose an alternative assignment. We propose that the band in the 150–180 cm$^{-1}$ region is a normally Raman-inactive, but IR-active $F_{1u}$ mode, that appears in the Raman spectra due to the displacive disorder of the A site in the Bi pyrochlores. We can recall that, based on symmetry, the selection rules result in some vibrational modes being optically inactive. Random displacement disorder can result in the relaxation of the selection rules, and we can expect previously inactive modes to appear in both IR and Raman spectra, and IR only modes in the Raman and vice versa. In the 150–180 cm$^{-1}$ region, the infrared data shows bands with...
very close frequencies to those reported here for the Raman. (Compare Tables II and III.) The attribution of these modes to the relaxation of the selection rules is also consistent with ab initio calculations for Bi$_2$Ti$_2$O$_7$, which predict the lowest $F_{2g}$ mode at 262 cm$^{-1}$. The assignment is also consistent with similar calculations for Cd$_2$Nb$_2$O$_7$ by Fischer et al.[11] which predict the lowest $F_{2g}$ mode at 265 cm$^{-1}$ and an $F_{1u}$ mode at 190 cm$^{-1}$.

The damping coefficients for the Raman modes around 180 cm$^{-1}$ obtained from the fit in Eq. (3) were compared to those from the IR data of Chen et al.[7] The IR analysis used a Lorentzian oscillator model for the susceptibility, which also uses a damping coefficient $\gamma_j$:

$$\chi(\omega) \approx \sum_j \frac{\alpha_{o_j}^2}{(\omega_{o_j}^2 - \omega^2) - i\omega\gamma_j}. \quad (6)$$

The imaginary part of each term in Eq. (6) approaches a Lorentzian function in Eq. (3) when $\omega \approx \omega_{o_j}$ and $\gamma_j \ll \omega_{o_j}$. We compared the damping coefficients of the 150–180 cm$^{-1}$ modes, extracted from the Lorentzian fit and listed in Table I, to the damping coefficients from the IR. (Tables I–IV of Ref. 7). The comparison suggests that the 150–180 cm$^{-1}$ IR and Raman bands arise from the same vibration. It should be mentioned that Rayleigh scattering could add an unknown to this region of the Raman spectrum and affect the fit. Nonetheless, the parameters from the Raman fits yielded values close to the IR and the comparison is worth mentioning. Specifically, for BZN, the 180 cm$^{-1}$ mode had damping coefficients of 88 cm$^{-1}$ for the Raman and 84 cm$^{-1}$ for the IR. For BZT, the widths of the mode near 150 cm$^{-1}$ were also close (32 and 34 cm$^{-1}$). BMT has center frequencies for the Raman and IR that are nearly identical (148 and 149 cm$^{-1}$) and the widths are close (35 and 38 cm$^{-1}$). As for BMN, the weak mode at 164 cm$^{-1}$ is closest to the 178 cm$^{-1}$ in the IR, and their widths are 72 cm$^{-1}$ for the Raman and 84 cm$^{-1}$ for the IR.

All four bismuth pyrochlores show a feature in the Raman spectra around 80 cm$^{-1}$ (Fig. 1). This mode has also been observed in BZN by Wang et al.[41] The ab initio calculations for Bi$_2$Ti$_2$O$_7$ predict an $F_{1u}$ mode around 86 cm$^{-1}$ that is consistent with the IR data. And, the calculations for Cd$_2$Nb$_2$O$_7$ by Fischer et al.[11] predict an IR $F_{1u}$ mode around 71 cm$^{-1}$, and an optically inactive $E_u$ mode at 69 cm$^{-1}$. Therefore, we have assigned this mode to a normally Raman-inactive mode. After correcting for the Bose factor and fitting the data, the mode in our four samples had a center frequency about 70 cm$^{-1}$. This is relatively close to IR modes near 80 cm$^{-1}$. However, the fitting was not as reliable for the Raman since the data was available only above 50 cm$^{-1}$. Furthermore, Rayleigh scattering in this region can also affect the fit. In summary, the similarity of the low-frequency Raman bands to IR modes, and the agreement with ab initio calculations on the pyrochlores Bi$_2$Ti$_2$O$_7$ and Cd$_2$Nb$_2$O$_7$, suggest that these low-frequency modes arise from the relaxation of selection rules.

The frequency of the band attributed to the lowest frequency $F_{2g}$ mode varies significantly for pyrochlores. This mode is assigned to a band around 200–240 cm$^{-1}$ for various titanates,[10,22] 250 cm$^{-1}$ for Cd$_2$Re$_2$O$_7$,[19] and 300–310 cm$^{-1}$ for some manganates[12,13] and stannates.[28] For other niobates and tantalates, this mode is at 245 cm$^{-1}$ for Cd$_2$Ta$_2$O$_7$,[29] and 279 cm$^{-1}$ in Cd$_2$Nb$_2$O$_7$.[11] Table II shows the frequencies of this mode for our bismuth samples. The proximity of the frequency of this band to that of other pyrochlores makes the $F_{2g}$ assignment the most reasonable. In the literature, the band assigned to $E_g$ also has significantly varying frequencies: 294 cm$^{-1}$, 297 cm$^{-1}$, 300 cm$^{-1}$, 310 cm$^{-1}$, 327 cm$^{-1}$, 330 cm$^{-1}$, 331 cm$^{-1}$, 340 cm$^{-1}$, 346 cm$^{-1}$, 350 cm$^{-1}$, 379 cm$^{-1}$, and 405 cm$^{-1}$, for Nd$_2$Nb$_2$O$_7$,[26] Bi$_2$Ti$_2$O$_7$,[14] Cd$_2$Re$_2$O$_7$,[19] Y$_2$Ti$_2$O$_7$,[14] Ti$_2$Mn$_2$O$_7$,[13] Tb$_2$Ti$_2$O$_7$,[21] Eu$_2$Ti$_2$O$_7$,[22] La$_2$Sn$_2$O$_7$,[16] In$_2$Mn$_2$O$_7$,[13] Pb$_2$Sb$_2$O$_7$,[24] Lu$_2$Sn$_2$O$_7$,[16] and La$_2$Zr$_2$O$_7$,[27] respectively. This is a variance of 10% for the samples mentioned. Our calculations for Bi$_2$Ti$_2$O$_7$ predict the $E_g$ mode around 281 cm$^{-1}$. Fischer’s calculations for Cd$_2$Nb$_2$O$_7$ offer further insight into this band.[11] They estimate 300 cm$^{-1}$ for the $E_g$ mode, but they also predict an additional $F_{2g}$ at 332 cm$^{-1}$. The large width of the Raman band, as seen in Fig. 2 would suggest that the $E_g$ and $F_{2g}$ modes were not resolved in our spectra. It should be noted that this is the only major difference between our calculations for Bi$_2$Ti$_2$O$_7$ and those of Fischer for Cd$_2$Nb$_2$O$_7$. Our calculations for Bi$_2$Ti$_2$O$_7$ do not show a mode near $E_g$ but instead near the $A_{1g}$ mode. Interestingly, our calculations for Bi$_2$Ti$_2$O$_7$ also yield an $F_{1u}$ mode at 262 cm$^{-1}$,[36] which is also observed in the IR.[7] Due to the relaxation of the selection rules, we must consider that the IR and Raman spectra may show the same vibration. This analysis would explain the trend, also present in the IR, of higher frequencies observed for the lighter B cation in BZN and BMN, than for BMT and BZT. However, based on Fischer’s calculations, and the proximity of an $F_{2g}$ mode to the $E_g$ mode in other pyrochlores,[10,12–14,19–22,25,26,28,29] we have assigned the ~300 cm$^{-1}$ feature in the Raman spectrum to the $E_g$ mode and one of the $F_{2g}$ modes.
The $A_{1g}$, and one of the $F_{2g}$ modes of the ideal structure are assigned to bands at 530 cm$^{-1}$ and 420 cm$^{-1}$, respectively. These modes are mostly due to vibrations of the BO$_6$ octahedra, as found by lattice dynamic calculations on other pyrochlores. Unlike the $E_g$ mode, the frequency of the $A_{1g}$ mode does not vary greatly for different pyrochlores: 488 cm$^{-1}$, 489 cm$^{-1}$, 495 cm$^{-1}$, 498 cm$^{-1}$, 500 cm$^{-1}$, 510 cm$^{-1}$, 510 cm$^{-1}$, 512 cm$^{-1}$, 513 cm$^{-1}$, 520 cm$^{-1}$, 523 cm$^{-1}$, and 525 cm$^{-1}$, for Nd$_2$Mn$_2$O$_7$, Tb$_2$Mn$_2$O$_7$, La$_2$Sn$_2$O$_7$, La$_2$Zr$_2$O$_7$, Cd$_2$Re$_2$O$_7$, In$_2$Sn$_2$O$_7$, Lu$_2$Sn$_2$O$_7$, Tb$_2$Ti$_2$O$_7$, Pb$_2$Sb$_2$O$_7$, BiYT$_2$O$_7$, Y$_2$Ti$_2$O$_7$, and Eu$_2$Ti$_2$O$_7$, respectively. This is a variance of less than 3%. The frequency of the $A_{1g}$ mode is remarkably constant despite all the different substituents mentioned above. For our samples, the frequencies of this mode agree with other pyrochlores and also agree well with our calculations for Bi$_2$Ti$_2$O$_7$.

The $A_{1g}$ mode can give insight into the force constants of the pyrochlore structure. According to the lattice-dynamical calculations by Vanderborre and Brown, the $A_{1g}$ mode is mainly due to the vibration of the BO$_6$ octahedra. The main contribution to the frequency of this mode comes from force constants related to O-B-O bending ($\sim$80% of the potential-energy distribution). Based on the strong agreement in the $A_{1g}$ frequency of so many different pyrochlores, and the characterization of this vibration by Vanderborre and Brown, we expect the force constants responsible to be similar for pyrochlores. This is the case for many titanates and manganates, where the bending force constants for the two O-B-O bends are reported around 0.4 and 0.3 N cm$^{-1}$. Therefore, it is reasonable to expect our samples to have similar O-B-O force constants. Comparing the Nb samples to the Ta samples, there was a 3% systematic increase in frequency for the $A_{1g}$ mode for BMT over BMN and BZT over BZN. This result corroborates the suggestion that oxygen binds more tightly to Ta than to Nb in the octahedron. The Raman band around 430 cm$^{-1}$ also has similar frequencies to other pyrochlores. This mode is assigned mostly to the B-O stretch force constant. The fact that the Ta samples shows higher frequencies for this mode also suggests stronger force constants in the octahedra for BZT and BMT than for BZN and BMN.

### E. High-frequency modes (600–900 cm$^{-1}$)

The Raman spectra of all four samples show bands around 620 and 780 cm$^{-1}$. We will begin our discussion with the 620 cm$^{-1}$ band. The highest frequency band assigned to an $F_{2g}$ mode for various pyrochlores is around 620 cm$^{-1}$, a few examples are: 590 cm$^{-1}$ (Yb$_2$Ti$_2$O$_7$), 590 cm$^{-1}$ (La$_2$Zr$_2$O$_7$), 598 cm$^{-1}$ (Er$_2$Mn$_2$O$_7$), 618 cm$^{-1}$ (Nd$_2$Ir$_2$O$_7$), and 620 cm$^{-1}$ (Lu$_2$Sn$_2$O$_7$). These frequencies are in good agreement for such different substituents. However, this 600 cm$^{-1}$ mode is not observed in single crystals of the pyrochlores Cd$_2$Re$_2$O$_7$ and Nd$_2$Mn$_2$O$_7$. The ab initio calculations by Fischer predict a mode at 617 cm$^{-1}$ but with an $F_{1g}$ symmetry (optically inactive) instead of an $F_{2g}$ symmetry. For some titanates, there is a mode near 550 cm$^{-1}$ assigned to $F_{2g}$ while the mode around 610 cm$^{-1}$ is associated with an impurity phase due to rutile TiO$_2$. Our calculations for Bi$_2$Ti$_2$O$_7$ predict an $F_{2g}$ mode around 535 cm$^{-1}$. For the samples studied here, the assignment of the modes becomes further problematic in that the IR also shows modes with frequencies very close to those in the Raman. (See Tables II and III) Perhaps, the strongest evidence to assign this mode to any type of symmetry are the studies on single crystal Dy$_2$Ti$_2$O$_7$ by Mcazeka et al. These polarization-dependent studies on a single crystal show that the 580 cm$^{-1}$ mode has an $F_{2g}$ symmetry.

The mode around 620 cm$^{-1}$ was also observed with higher frequencies for the Ta samples compared to the Nb samples. The higher frequency $F_{2g}$ mode is mostly attributed to the B-O force constant in the octahedron by Vanderborre for different stannates and titanates, and attributed to O-B-O bending force constants for manganates by Brown et al. This mode also corroborates that the force constants of the BO$_6$ octahedron are comparable for the Bi pyrochlores to other pyrochlores and that they are slightly larger for the Ta samples. If we consider the possibility that this mode is a normally Raman-silent $F_{1g}$ mode, the conclusion for the force constants remains the same.

Perhaps the most interesting mode in our data is at 780 cm$^{-1}$. Modes with such high frequency are usually assigned as combination bands or overtones. For example, Tb$_2$Ti$_2$O$_7$ shows a weak band at around 670 cm$^{-1}$ but the mode is assigned as an overtone by stating that the highest frequency $F_{2g}$ mode should not exceed 600 cm$^{-1}$, in reference to lattice-dynamical calculations by Gupta et al. for other titanates. In contrast, ab initio calculations by Fischer predict a $F_{2g}$ mode with a frequency as high as 880 cm$^{-1}$. And, our calculations for Bi$_2$Ti$_2$O$_7$ predict an $F_{2g}$ mode at 711 cm$^{-1}$. In BZN, this mode has been previously attributed to an overtone and also to a stretching of the Nb-O bond. For BZN, no physical process has been suggested to be responsible for the high amplitude of this mode. Normally, a two phonon-scattering process is expected to have a much lower probability than a first-order process. Physical processes such as resonant raman scattering, where the incident laser frequency is close to a resonance in the material, can greatly increase the amplitude of an overtone or combination band. Strong anharmonic coupling can also lead to the appearance of combination and overtone bands. There is no strong resonance in this region for our Bi pyrochlore samples and the high amplitude observed for this mode for different laser frequencies suggests it is not a resonant scattering process. Strong anharmonicity could explain the high amplitude of an overtone but our current set of data cannot offer insight into this suggestion.

The mode near 780 cm$^{-1}$ shows interesting trend for our samples. The mode in the Nb samples has a higher frequency than the Ta samples. If this mode is a fundamental Ramam-active mode and the BO$_6$ force constants are higher for Ta samples than for Nb samples, then we expect the opposite. We can explore the possibility of an optically inactive mode where the B cation moves as well as the oxygen. To estimate, let us consider a vibrational mode with a reduced mass of...
\[ \mu = \frac{m_B \times 6m_O}{m_B + 6m_O}, \]  
(7)
to predict the frequency ratio
\[ \frac{\omega_{\text{new}}^2}{\omega_{\text{old}}^2} = \frac{k_{\text{new}} \mu_{\text{Ta}}}{k_{\text{old}} \mu_{\text{Nb}}}, \]  
(8)

A force-constant ratio \( k_{\text{Nb}} / k_{\text{Ta}} \) of 0.91, as reported by Wang et al.,\(^{\text{39}}\) yields a ratio \( \theta_{\text{new}} / \theta_{\text{old}} \) of 1.03. This is indeed in good agreement with our results, (see Table II), and consistent with a suggestion that this band is a normally Raman-inactive mode that involves the motion of \( B \) cations (or the overtone of such a mode). In summary, the high amplitude and high frequency of this mode, as well as the difference in predictions from lattice dynamical and \textit{ab initio} calculations, make the assignment of this mode difficult. Future work on the synthesis of single crystals would make the assignment of this mode more clear. This was the case for \( \text{Dy}_2\text{Ti}_2\text{O}_7 \) single crystals, where it was showed that all the modes above 590 cm\(^{-1} \) have \( A_{1g} \) symmetry and the modes are attributed to overtones.\(^{\text{23}}\) Also, more \textit{ab initio} calculations for other pyrochlores would greatly benefit the study of this region of the spectrum. If the mode is indeed an overtone, it would be interesting to explore why the \textit{ab initio} calculations for both \( \text{Cd}_2\text{Nb}_2\text{O}_7 \) and \( \text{Bi}_2\text{Ti}_2\text{O}_7 \) seem to agree well with experiment on most of the Raman modes, but overestimate the highest frequency mode.

Lastly, very weak bands around 800 cm\(^{-1} \) were observed for all samples. These high-frequency modes have been attributed to unequall lengths for the \( A-O' \) bond in the \( A_2\text{O}' \) substructure.\(^{\text{44}}\) However, the \textit{ab initio} calculations by Fischer et al. suggest the higher frequency \( F_{2g} \) mode may be in this spectral region.

\begin{thebibliography}{99}
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