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Far-infrared reflectivity and Raman spectra of $Ba_5Nb_4O_{15}$

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We report low-temperature, far-infrared reflectivity, and Raman-scattering measurements for layered $Ba_5Nb_4O_{15}$. We find that this material is characterized by a strong anharmonic lattice where the symmetric stretching vibration of the empty octahedra, a singular feature of this layer compound, splits into two narrow Raman-active bands. We assign them to the same phonon in a slightly different environment, and suggest a small local departure of the reported centrosymmetric D_{3d}^3-$P3m1$ space group. We think that the infrared and mainly the Raman band profiles indicate that the lattice of $Ba_5Nb_4O_{15}$ is close to collapsing into a lower symmetry structure.

The ternary oxide of Nb, $Ba_5Nb_4O_{15}$ is the simplest representative of a five-layer compound derived from the classical perovskite structure. The latter represents the backbone of most of the current research for new materials with low-dimensional transport properties. $Ba_5Nb_4O_{15}$ has a sequence of five close-packed layers, each containing one barium and three oxygens accounting for the five barium and 15 oxygens in the unit cell.[1] The Nb ions are located in octahedral holes between layers. However, since there are four Nb ions on each five-layer sequence, there is an empty octahedra which avoids direct face sharing on the NbO_6 sublattice. This configuration implies strong anharmonicity thus making this compound very attractive for optical studies. It shares a lattice environment that in related systems, such as in oxide conductors, may be obscured by carrier activity. Here we present low-temperature far-infrared reflectivity and Raman spectra of $Ba_5Nb_4O_{15}$.

Our 4 cm^{-1} resolution reflectivity and transmission measurements were performed with a Bruker 113v Fourier interferometer from 40 to 5000 cm^{-1}. The sample was mounted on the cold finger of an Oxford DN 1764 cryostat and a gold mirror was used as 100% reference.

Near 90° Raman spectra were measured in increments of 0.5 cm^{-1} with a 1401 double grating Spex-Ramalog spectrophotometer with conventional photon counting system. The spectra were excited with the 4880 and 5145 Å lines of an Ar^+ ion laser. The sample was mounted on the cold finger of a Displex He closed-cycle refrigerating system.

Our samples were pellets prepared by heating in air the stoichiometric mixture of $BaCO_3$ and Nb_2O_3 at temperatures ranging from 1100 to 1500 °C. The sinterization time was 24 h.

The space group of isomorphous $Ba_5Ta_4O_{15}$ was determined by Schannon and Katz[2] as D_{3d}^3-$P3m1$. Recent Rietveld analysis of neutron-diffraction measurements confirmed the structure of $Ba_5Nb_4O_{15}$ with one formula unit per unit cell.[3] The factor group analysis for that centrosymmetric space group predicts the irreducible representations

$$\Gamma_{\rm opt}=8A_{1g}+2A_{2g}+10E_g+3A_{1u}+10A_{2u}+13E_u$$

for Brillouin-zone center phonons. The acoustical modes, which transform like $A_{2u}+E_u$, have been already subtracted.

Figure 1 shows the reflectivity spectrum of $Ba_5Nb_4O_{15}$ at 80 K. It has the phonon structure of a compound with a distorted perovskite structure, where the internal stretching and bending modes, are around 700 and 300 cm^{-1}, respectively. The most intense band, having a sharp reststrahlen reflectivity at $\approx$128 cm^{-1}, is assigned to the metal-oxygen stretching mode of the oxygen-sharing empty octahedra. Our assignments and frequency positions seem to be in overall agreement with an earlier frequency listing by Kemmler-Sack, Treiber, and Fabini.[4]

We have performed a more quantitative analysis of the reflectivity spectrum representing the infrared-active phonons by damped Lorentzian oscillators in a classical formulation for the dielectric function.[5] Thus, keeping in mind that our formulation is the result of averaging the dielectric

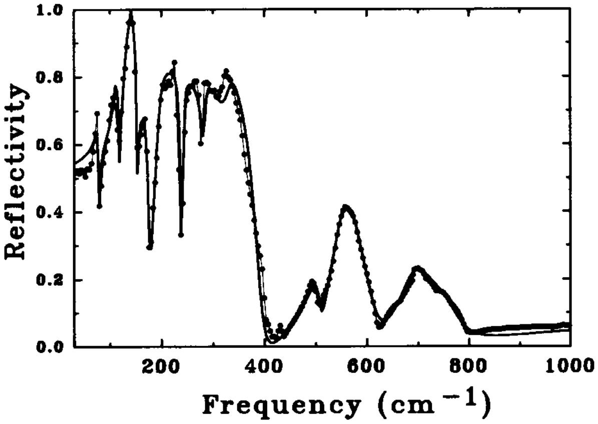

FIG. 1. Far-infrared reflectivity of $Ba_5Nb_4O_{15}$ at 80 K (dotted line) compared with results of a multioscillator fit (full line).

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TABLE I. Multioscillator fit dispersion parameters and transmission frequencies at 80 K and Raman frequencies at 25 K. (str) strong; (strsh) strong shoulder; (vw) very weak; (vstr) very strong; (w) weak; (vwsh) very weak shoulder.

Ω_{TO} cm^{-1}	γ_{TO} cm^{-1}	Ω_{LO} cm^{-1}	γ_{LO} cm^{-1}	S_j	Ω_{TO} [a] cm^{-1}	Raman cm^{-1}
					40 (?)(str)	
75.4	7.95	77.35	0.65	3.05	77 (str)	74 (vw)
						84 (vw)
111.05	6.75	115.7	2.11	9.02	110 (str)	118 (str)
128.8	7.47	149.29	2.48	17.50	145 (strsh)	
152.16	17.56	176.2	7.16	1.71	168 (str)	160 (w)
						172 (w)
195.4	12.27	236.86	4.06	4.76		
242.0	5.88	280.99	11.18	0.69	228 (strsh)	242 (vw)
283.0	9.5	328.0	39.69	0.12	270 (strsh)	286 (w)
328.1	31.69	390.58	23.14	0.00378	307 (vstr)	310 (vstr)
						322 (str)
					390 (sh)	387 (vw)
					415 (vw)	
					430 (w)[b]	426 (w)
503.11	23.91	508.99	14.33	0.13678	499 (str)	498 (vw)
546.9	30.17	611.25	59.26	0.6274	563 (vstr)	546.5 (str)
					627 (strsh)	624 (vw)
						649 (w)
682.88	57.78	730.28	130.86	0.238	706 (vstr)	685 (w)
755	77.02	770.51	75.0	0.028		773 (vstr)
					802 (vw)	848 (str)
					854 (w)	
$\epsilon_\infty=3.5163$					876 (vwsh)	

[a] From transmission measurements at 80 K.

[b] Also a very weak reflectivity band.

function $\epsilon_{\mathrm{av}}(\omega)$ due to the uncertain weighted contribution of the **c** and **a**=**b** hexagonal axis in our polycrystalline sample, we have

$$\boldsymbol{\epsilon}_{\mathrm{av}}(\boldsymbol{\omega})=\boldsymbol{\epsilon}_\infty\prod_j^N \frac{\boldsymbol{\Omega}_{j\mathrm{LO}}^2-\boldsymbol{\omega}^2+i\,\boldsymbol{\gamma}_{j\mathrm{LO}}\boldsymbol{\omega}}{\boldsymbol{\Omega}_{j\mathrm{TO}}^2-\boldsymbol{\omega}^2+i\,\boldsymbol{\gamma}_{j\mathrm{TO}}\boldsymbol{\omega}}\ . \tag{1}$$

Optimizing the calculated normal incident reflectivity against the experimental points we obtained, as shown in Table I, the high-frequency dielectric constant $\boldsymbol{\epsilon}_\infty$; the transverse and longitudinal jth optical-phonon frequencies, $\Omega_{j\mathrm{TO}}$ and $\Omega_{j\mathrm{LO}}$; and, their transverse and longitudinal damping constants, $\gamma_{j\mathrm{TO}}$ and $\gamma_{j\mathrm{LO}}$; respectively. Figure 2 shows some of the optical functions calculated from this fitting.

From the absorption spectra at 80 K of pellets made of CsI or polyethylene and powder of $\mathrm{Ba_5Nb_4O_{15}}$, Fig. 3(a), we obtain another estimate of $\Omega_{j\mathrm{TO}}$. Table I also displays the strengths S_j for the jth oscillator given by

$$S_j=\Omega_{j\mathrm{TO}}^{-2}\,\frac{\left(\prod_k \boldsymbol{\Omega}_{k\mathrm{LO}}^2-\boldsymbol{\Omega}_{j\mathrm{TO}}^2\right)}{\left(\prod_{k\neq j} \boldsymbol{\Omega}_{k\mathrm{TO}}^2-\boldsymbol{\Omega}_{j\mathrm{TO}}^2\right)}\ . \tag{2}$$

In the Raman spectra of $\mathrm{Ba_5Nb_4O_{15}}$ at 300 K and 25 K shown in Figs. 3(b) and 3(c), respectively, we notice three

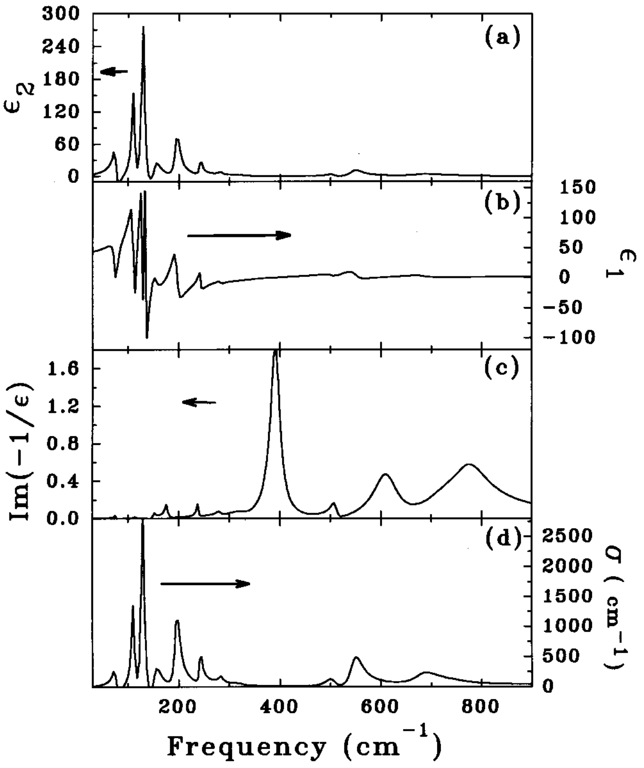

FIG. 2. (a) Imaginary part of the dielectric function of $\mathrm{Ba_5Nb_4O_{15}}$; (b) real part; (c) imaginary part of the reciprocal of the dielectric function; (d) optical conductivity.

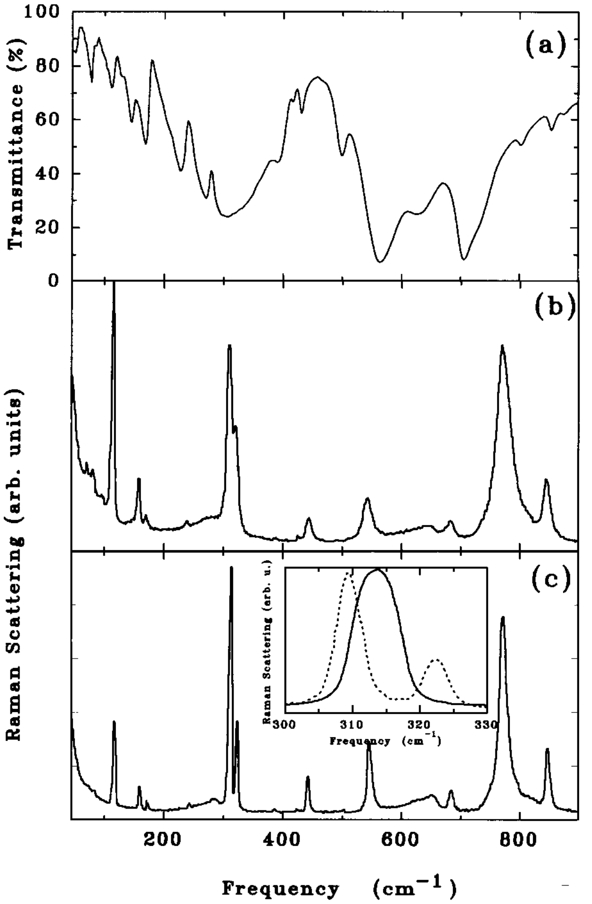

FIG. 3. (a) Phonon frequencies of $Ba_5Nb_4O_{15}$ measured in the transmission spectrum at 80 K; (b) Phonon frequencies of $Ba_5Nb_4O_{15}$ measured from Raman shifts at 300 K; (c) Phonon frequencies of $Ba_5Nb_4O_{15}$ measured from Raman shifts at 25 K. The inset shows the symmetric stretching mode of the empty octahedral cage for $Ba_5Nb_4O_{15}$ (dashed line) and $Ba_5Ta_4O_{15}$ (full line).

main points. First, that the phonon activity may be grouped in a set of very strong modes at 800 and 310 cm^{-1}. They are assigned to the symmetric stretching octahedra internal modes.[4] Second, that the mode at $\approx$310 cm^{-1} has a very narrow splitting at 25 K. It changes its intensity in a fashion that seems to be related to the change of the band assigned to the metal-oxygen vibration at 117 cm^{-1}. This feature is shown in Figs. 3(b) and 3(c). This band undergoes a striking reduction in its cross section as the temperature is lowered, while the one at $\approx$310 cm^{-1} has a strong enhancement. This narrow doublet is assigned to the empty octahedra symmetric stretching phonon and is understood to be a consequence of a small local departure from the D_{3d}^3-$P3m1$ space group determined from x-ray and neutron-diffraction studies. Those two narrow bands arise from the same vibration in a slightly different environment and probably involve octahedra reorientation, pointing to the strong anharmonicity of this compound. To verify this assertion we also measured the corresponding spectrum of $Ba_5Ta_4O_{15}$. Its Raman spectrum at 25 K has well-defined near Lorentzian band shapes, either weak or strong, with a one-to-one correspondence with most of the features found in the spectrum for $Ba_5Nb_4O_{15}$. As expected, it shows the phonon activity of a stable lattice. The replacement of Nb by Ta induces a hardening of most phonons producing an upwards frequency shift in spite of the heavier Ta ion. In particular, the split band shown in the inset of Figs. 3(c) exhibits a classical phonon band profile for a vibrational mode in a shallow potential. Our infrared and Raman spectra of $Ba_5Ta_4O_{15}$ are in Ref. 6.

A third point to note in our Raman spectra of $Ba_5Nb_4O_{15}$ is the relatively broad weak asymmetric bands like that at 649 cm^{-1} with very weak features on its lower frequency shoulder at 624 cm^{-1}. Such bands are characteristic of Raman-active extra phonons in this compound. They may change from sample to sample bringing into question how accurately the centrosymmetry applies. When the ungerade and gerade peak positions in Table I are compared, we note that some of them obey the exclusion rule within few wave numbers. Other infrared modes have a direct counterpart in very weak Raman-active bands. This supports our conclusion inferred from the mode at 310 cm^{-1}, that in $Ba_5Nb_4O_{15}$ we have a strong anharmonic lattice at the border of collapsing from the space group D_{3d}^3-$P3m1$ into a lower symmetry structure. However, before closing we mention that because Nb and Ta compounds are known to have d-state luminescence we cannot rule out vibronic coupling activity that would also help to explain forbidden absorption lines.[7]

Summarizing, we have presented low-temperature transmission and reflectivity far-infrared and Raman-scattering measurements of $Ba_5Nb_4O_{15}$. Although the number of detected active modes is close to those predicted from factor group analysis, the behavior of the bands assigned to modes of the empty octahedron shows that its centrosymmetry is locally lost. We believe that this fact is due to intrinsic defects enhanced by a strong anharmonicity and that the lattice is close to collapsing into a lower symmetry structure. We also mention that vibronic activity may help to understand extra weak absorptions that are forbidden according to factor group analysis.

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