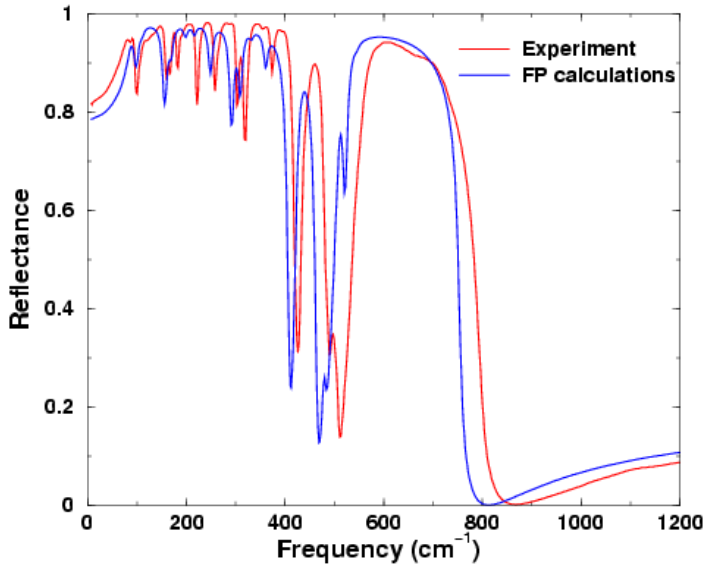
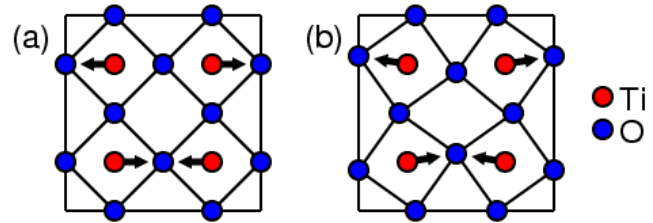


IR reflectance of  $\text{CaTiO}_3$ 


**Figure 2: Comparison of the experimental infrared reflectance spectrum of  $\text{CaTiO}_3$  with that computed from first principles. (Experimental results courtesy of V. Zelezny)**

Except for a systematic shift of the FP results toward slightly lower frequencies, the agreement between the two spectra is excellent. The results clearly demonstrate that FP calculations are able to compute IR reflectance spectra for perovskite-type oxides such as CT.

Given the accuracy of the FP calculations, it becomes possible to interpret the IR spectrum in terms of crystal structure and chemistry in unprecedented detail. In fact, a number of unexpected results were found. Many of these concern the importance of the tilting of the oxygen octahedra. If the oxygen octahedra were not tilted, only 3 phonon triplets would contribute to the dielectric function of CT, instead of the 25 modes for CT with octahedral tilting. Previous interpretations of the IR reflectance spectrum of CT were based on fitting the results to a 3 phonon model. However, the FP results show that it is impossible to correctly fit the experimental results with only 3 phonons, because the oscillator strengths of some of the modes that arise due to octahedral tilting are *larger* than those associated with the ideal perovskite structure. The three sets of phonons associated with the ideal perovskite structure have frequencies of approximately  $80\text{ cm}^{-1}$ ,  $220\text{ cm}^{-1}$ , and  $550\text{ cm}^{-1}$ , respectively. However, the modes near  $160\text{ cm}^{-1}$  that arise due to octahedral tilting have higher oscillator strength than those near  $220\text{ cm}^{-1}$  and are more dominant in the spectrum.



**Figure 3: A phonon mode which is (a) nonpolar in the perovskite structure with untilted octahedra becomes (b) polar upon octahedral tilting.**

One of the most significant features in the spectrum is the deep dip in reflectivity near  $400\text{ cm}^{-1}$ . This feature arises due to the octahedral tilting as shown in Fig. 3. In one of the normal modes of vibration of a perovskite, the atoms that are in the centers of oxygen octahedra (Ti for CT) vibrate out of phase with each other (Fig. 3(a)). When the octahedra are tilted (Fig. 3(b)), the same normal mode now has a net in-phase motion of Ti ions along one direction. In-phase motion of charged ions leads to a nonzero mode effective charge  $Z^*$ , and thus a contribution to the dielectric constant and IR reflectance spectrum.

An issue particularly relevant to industry is the temperature dependence of dielectric constants. Here, too, FP calculations have led to insight into the connection between the structure of CT and its rapidly decreasing dielectric constant as a function of temperature. FP calculations show that the large dielectric constant of CT is dominated by the contributions of the low-frequency phonons, which have both high  $Z^*$  and low  $\gamma$ . The large  $Z^*$  of these modes is due to the nature of the vibration. The Ti vibrate against the oxygen octahedra, while the Ca vibrate in-phase with the Ti. Experimentally, one finds that  $\epsilon'$  decreases as temperature increases because the frequencies of the lowest-frequency phonons increase. The structure of CT also changes as the temperature increases. In particular, the oxygen octahedra tilting angles decrease. FP calculations on the phonon frequencies as a function of octahedral tilting show that the frequencies increase as octahedral tilting decreases, in agreement with experiment. The increase in phonon frequency can be explained by the shortening of Ti-O bonds as tilting decreases and the sensitivity of Ti-O force constants to bond length.

### For More Information On This Topic

V. Zelezny, E. Cockayne, J. Petzelt, M. F. Limanov, D. Usvyat, V. V. Lemanov, and A. A. Volkov, "Temperature Dependence of Infrared-Active Phonons in  $\text{CaTiO}_3$ : A Combined Spectroscopic and First Principles Study", submitted to Physical Review B

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