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Structural phase transition near 825 K in titanite: Evidence from infrared spectroscopic observations

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ABSTRACT

We report the direct experimental observation of a structural anomaly near 825 K in synthetic and natural titanite samples by high-temperature, hard-mode infrared spectroscopy. The anomaly in titanite, $CaTiSiO_5$, is characterized by a break of the temperature dependence of the 562 cm^{-1} Si-O bending mode, the 675 cm^{-1} Ti-O band, and the 900 cm^{-1} Si-O stretching modes, and the rapid decrease of the IR signal at 873 cm^{-1}. The order parameter, as determined from the temperature evolution of the frequencies of the absorption bands in the middle infrared (MIR) region follows a second-order Landau behavior with an order-parameter exponent $\beta = \frac{1}{2}$. At $T > 825$ K, the Ti-O band shows further softening, whereas the Si-O bands at 562 and 900 cm^{-1} show hardening with increasing temperature. In natural samples, the effects of impurities on the high-temperature transition are weak. For pure titanite, the transition temperature, T_c, is about 825 K and increases with increasing impurity concentration.

INTRODUCTION

The room-temperature structure of titanite was first studied in 1930 (Zachariasen 1930) and refined by Speer and Gibbs (1976). Speer and Gibbs (1976) described the room-temperature phase as being antiferroelectric, in which the Ti atoms were displaced from the centers of O octahedra. A high-temperature X-ray study of pure titanite by Taylor and Brown (1976) showed a reversible, displacive phase transition at approximately 500 K. Above that temperature the space group was reported to be A centered (*A*2/*a*), whereas below 500 K the space group is $P2_1/a$. The transition near 500 K was seen as anomalies in the temperature evolution of the optical birefringence and X-ray diffraction intensities (Bismayer et al. 1992), some rather weak changes in the lattice parameters (Ghose et al. 1991; Bismayer et al. 1992), and very strong changes in the frequencies and scattering intensities of Raman-active phonons (Salje et al. 1993) and in the IR-absorbance intensities. The marked softening of infrared-active Ti-O phonons with amplitudes along the crystallographic *a* axis correlates well with the observation of dielectric losses and the measurements of the excess specific heat, C_P, at high temperatures (Zhang et al. 1995).

By fitting the temperature evolution of the order parameter $Q(T)$ ($T < T_c$) to $Q \propto |T - T_c|^\beta$, Bismayer et al. (1992), Salje et al. (1993), and Zhang et al. (1995) noted that the effective exponent, $\beta = \frac{1}{8}$, is compatible with that of a two-dimensional Ising model. The question, however, is whether the phase at $T \geq 500$ K is the correct paraphase of titanite or, alternatively, whether this phase is an intermediate phase and the true high-symmetry phase exists only at much higher temperatures. The previous experimental evidence for this scenario relies on the following observations. First, Bismayer et al. (1992) and Meyer et al. (1996) recorded nonzero excess birefringence, Δn, at temperatures up to 850 K, which is compatible with the assumption that an intermediate phase exists. Second, Salje et al. (1993) observed that the excess intensities of the Raman signals decrease gradually at $T > 500$ K with increasing temperature while additional, very weak lines occur near 400 cm^{-1}. This observation rules out the idea that the phase transition at 500 K occurs between a paraelectric high-symmetry phase and its antiferroelectric low-symmetry phase by a simple shift of the Ti positions in the TiO_6 octahedra. This effect has nothing to do with the additional effect of mobile antiphase boundaries (Van Heurck et al. 1991) simply because only very few antiphase boundaries exist in pure, synthetic titanite crystals (Chrosch et al., in preparation).

The essential question we wish to answer in this paper is whether a second phase transition occurs at high temperatures. Hard-mode spectroscopy was employed in this study because it has been shown that small structural changes correspond to strong changes in the phonon spectra (Zhang et al. 1995). It was expected that IR spectroscopy would provide a sufficiently sensitive tool to detect the additional high-temperature phase transition in titanite. This expectation proved to be correct, and we report the first clear evidence that a second phase transition occurs near 825 K.

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SAMPLES AND EXPERIMENTAL METHODS

The synthetic sample used in our experiments had been extensively studied by optical birefringence and X-ray diffraction techniques (Bismayer et al. 1992), Raman (Salje et al. 1993) and infrared spectroscopy, and dielectric and DSC measurements (Zhang et al. 1995). In addition, the thermal behavior of natural titanite was also investigated. One natural sample is from Rauris, Austria (Fe 1.8%, Al 3.8%). Two other samples were provided by the Smithsonian Institution in Washington, D.C. (B20323 with Fe 2.8% and Al 0.5%, and R4970 with Fe 8.8% and Al 13.9%). The natural samples were recently studied by IR spectroscopy, Raman spectroscopy, optical birefringence, and X-ray diffraction (Meyer et al. 1996).

The powder samples were obtained by ball milling the crystals in a Spex micromill for 30 min. The even-sized, fine-grained powder was kept in a drying oven at 120 °C to prevent absorption of water. KBr and CsI were used as the matrix materials.

The absorption spectra were recorded under vacuum with the use of a Bruker 113V FT-IR spectrometer. The sample pellets were heated in a cylindrical platinum-wound furnace coupled with a Eurothem type-815 temperature controller with a temperature stability of 1 K. Experiments were performed between 200 and 5000 cm^{-1} at room temperature and in the region of ~500–5000 cm^{-1} on heating and cooling between 300 and 940 K. Each single-beam spectrum was integrated over either 250 or 150 scans with instrumental resolution of 2 cm^{-1} and zero filling factor of 4. The software RAZOR (Spectrum Square Associates) and OPUS/IR (Bruker Analytische Messtechnik GMBH) were used for data analysis.

RESULTS AND DISCUSSION

The room-temperature spectra of Rauris, B20323, R4970, and the synthetic titanite are plotted in Figure 1. The spectra are dominated at high frequencies by the IR band near 900 cm^{-1}, which is attributed mainly to SiO$_4$ stretching modes. Several spectral features are obvious without any analysis. First, the spectra of two natural samples (Rauris and B20323) are similar to that of the synthetic sample. Second, R4970 has much broader bands, which may be mainly due to local structure disorder as well as impurities and defects in the sample. The sample is probably metamict. Third, the varying height of the Ti-O feature near 685 cm^{-1} results from the coupled substitution of Al and Fe for Ti and F for O in the natural samples (Meyer et al. 1996) and is also related to the crystallinity of titanite (Chen et al. 1993). The temperature evolution of MIR spectra of natural and synthetic titanite samples is shown in Figures 2 and 3. The effect of temperature is most clearly seen as an increase in band width, a decrease in band intensity, and a softening of phonon bands. With increasing temperature, the Si-O bending at 563 cm^{-1} and the Si-O stretching band at about 900 cm^{-1} exhibit softening in frequency below 825 K. On further heating they harden again at temperatures above 825 K. Figures 4 and 5 show the break of the temperature dependencies of these phonon modes. Heating to 825 K, the IR band near 875 cm^{-1} broadens and further decreases in intensity. This feature is seen most clearly in sample R4970 (Fig. 3B).

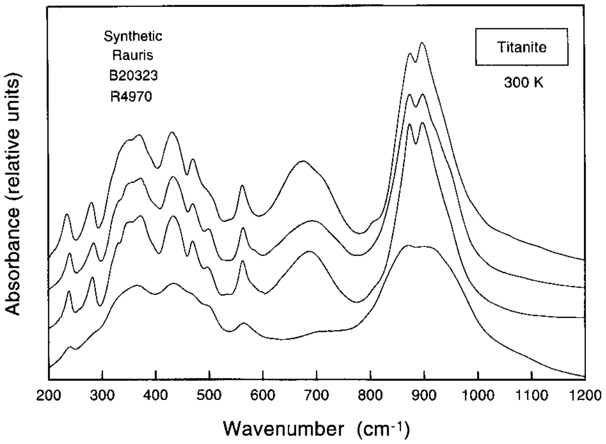


FIGURE 1. Absorption spectra of natural (Rauris, B20323, and R4970) and synthetic titanite samples.

The broad and intense band near 675 cm^{-1} is associated with TiO$_6$ octahedral stretching modes. This signal is polarized strictly along the crystallographic *a* axis (Zhang et al. 1995). Its precise peak position may be influenced by the high dielectric contrast between titanite and the embedding medium and the substitution of Al and Fe for Ti and F for O in the natural samples. The main effect of temperature on this band is the decrease of the band frequency. The integrated intensity also decreases below 825 K and then decreases with much stronger temperature dependencies for well-crystallized samples (Figs. 6 and 7).

The break of the temperature dependence of the phonon frequencies at 563, 685, and 900 cm^{-1} and the rapid decrease in the IR signal at 875 cm^{-1} at about 825 K show that the anomaly is related to structural changes, i.e., the structural state above 825 K is different from that below 825 K, which confirms the existence of the previously suspected intermediate phase between 500 and 850 K (Bismayer et al. 1992; Salje et al. 1993; Zhang et al. 1995).

In hard-mode spectroscopy (Bismayer 1990; Salje 1992, 1994) the order parameter determined by the frequency shifts and profile changes of the infrared absorption is inherently local in character and reveals the microscopic character of the transition rather than its macroscopic nature. The expected frequency changes are correlated with the order parameter. In lowest order theory, this correlation is (Salje 1992)

$$\Delta\omega_i^2(T) = (\omega_i^0 - \omega_i)(\omega_i^0 + \omega_i) = \delta_i Q^2(T) \qquad (1)$$

where Q is the order parameter as "seen" by the phonons. With $(\omega_i^0 + \omega_i)$ approximately constant, the frequency shift becomes

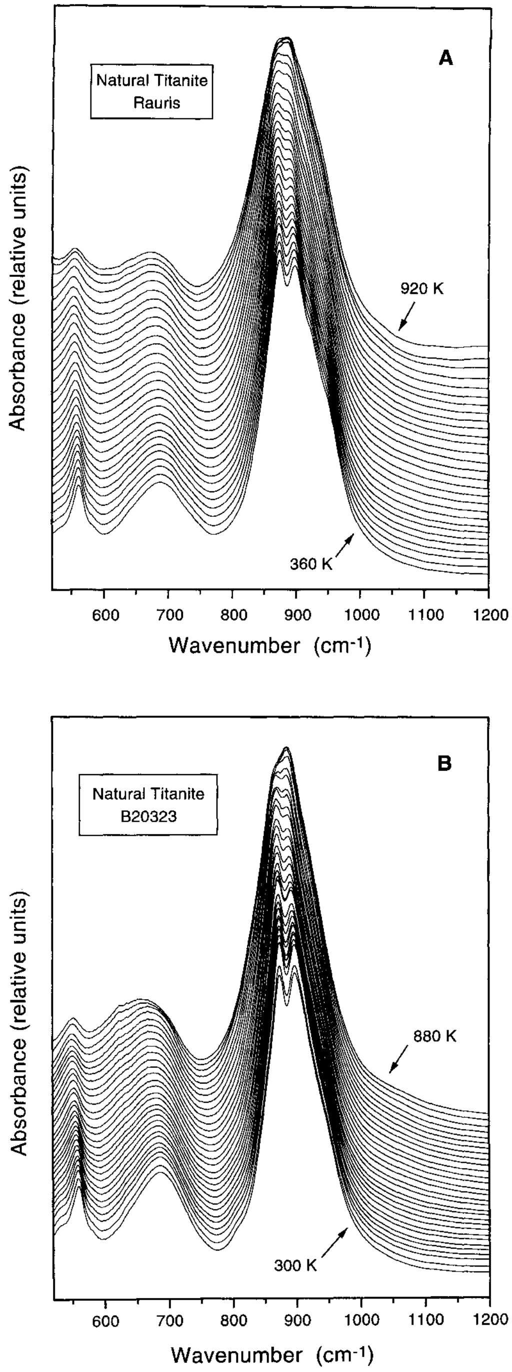


FIGURE 2. Temperature evolution of the IR spectra of titanite samples (**A**) Rauris and (**B**) B20323 between 500 and 1200 cm^{-1}. The temperature interval is 20 K.

$$\Delta\omega_i(T) = (\omega_i^0 - \omega_i) \propto Q^2(T). \qquad (2)$$

As shown in Figures 4–6 for IR bands near 563 and 900 cm^{-1}, there is a strong change in $\partial\omega/\partial T$ at about $T_c = 825 + 20$ K, which is associated with a structural phase transition. Scaling the data at $T > 500$ K to the reduced temperature with a critical exponent, the temperature dependencies of $\Delta\omega(T)$ and $Q^2(T)$ can rewritten as

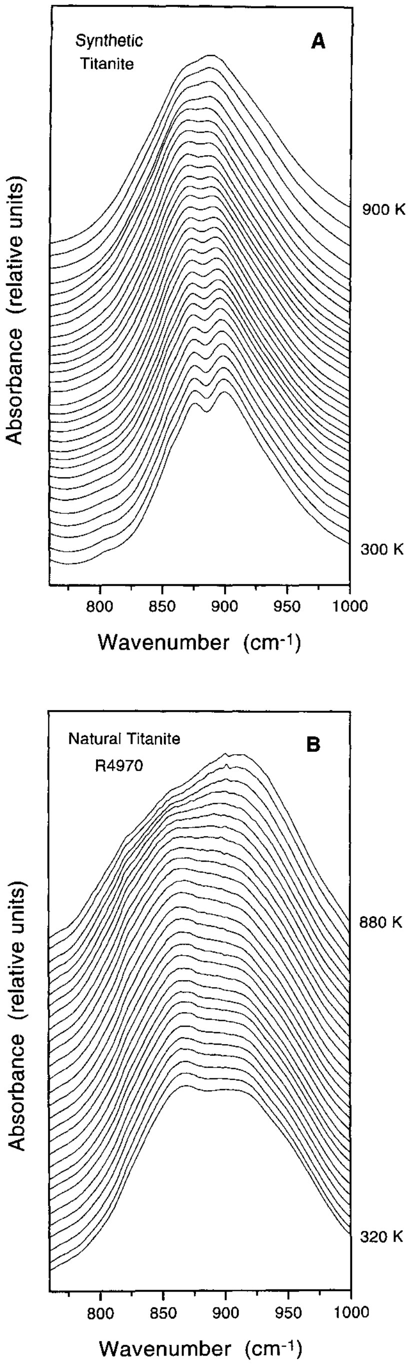


FIGURE 3. Stack plot of the IR spectra of (**A**) synthetic titanite and (**B**) sample R4970 between 720 and 1000 cm^{-1}, showing details of the spectral changes during the structural phase transition. The temperature interval is 20 K.

$$\Delta\omega_i(T) \propto Q^2(T) \propto (T_c - T)^{2\beta} \quad T < T_c \qquad (3)$$

where, $\beta = \frac{1}{2}$. This corresponds to classical second-order

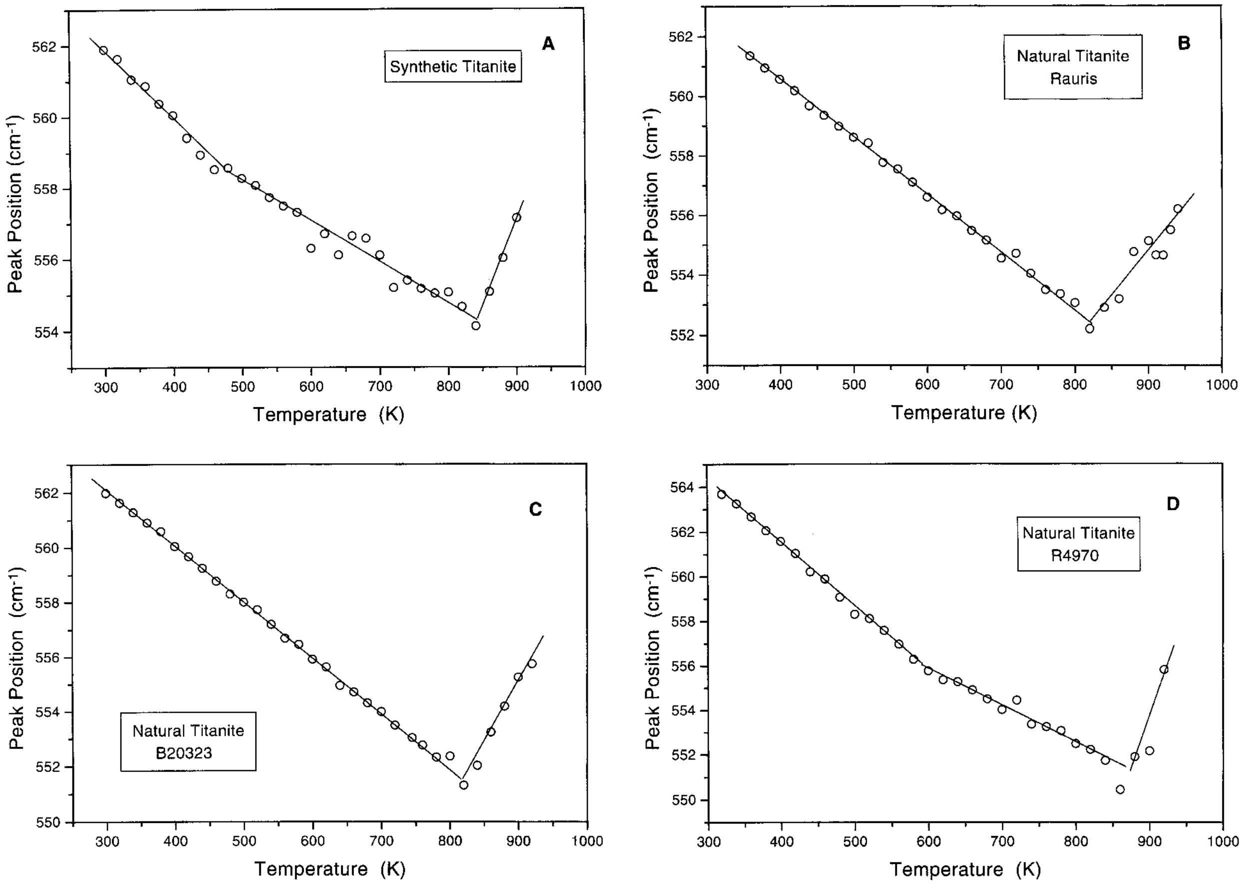


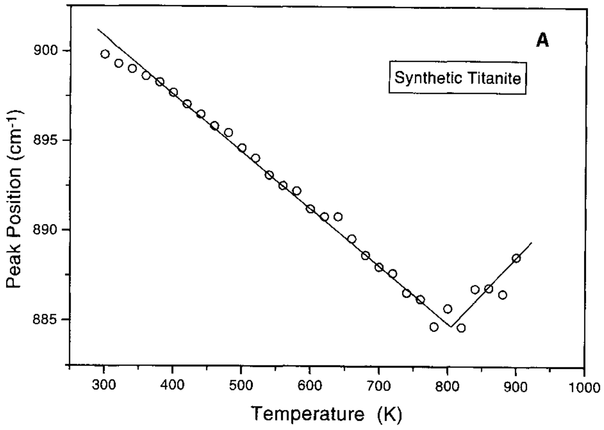
Figure 4. The temperature dependence of the IR band at 563 cm^{-1}. The slope change near 825 K indicates a second-order phase transition in the synthetic sample (**A**), the sample from Rauris (**B**), B20323 (**C**), and R4970 (**D**). The average errors for the peak positions are 0.25 cm^{-1} near room temperature and 1.0 cm^{-1} for high temperatures. The lines are visual guides.

behavior, which has been predicted (Salje et al. 1993; Salje 1993).

Comparison of the temperature dependence of the Ti-O phonon frequency at 675 cm^{-1} with that of other Si-O bands reveals a systematic difference. Although the Ti-O band softens at $T > 825$ K, the Si-O modes at 563 and 900 cm^{-1} harden. This observation has physical significance: It shows that the SiO_4 and TiO_6 polyhedra react differently to the structural phase transition. Although the SiO_4 tetrahedra behave as a rigid body both above and below T_c they become softer near T_c. Surprisingly, this is the case not only for the O-Si-O bending motion but also for the Si-O stretching modes. This softening may reflect a general weakening of the Si-O band because of the polarization effects of Ca, i.e., one expects the Ca position to be directly involved in the transition mechanism.

The behavior of the TiO_6 octahedron is very different from that of the SiO_4 tetrahedra. The stretching mode of the octahedron shifts to lower frequencies on heating at temperatures below T_c and almost collapses in the high-temperature phase. It is difficult to imagine that the near collapse stems simply from a deformation of the O octahedron. It appears more likely that the Ti position inside the octahedron changes during the transition. A probable scenario is that the Ti atoms are distributed over split positions at $T < T_c$ (i.e., the structure remains locally antiferroelectric on a long time scale in comparison with that of phonons), whereas at $T > T_c$ the Ti atoms move in one global, shallow potential well. In summary, we may envisage the phase transition to be related to changes in the Ca positions, a weak distortion of the SiO_4 tetrahedra, and a change in the local potential of the Ti positions (but with little effect on the volume-averaged Ti position).

We now focus on the effects of the impurities in natural titanite on the phase transitions. With substitution of Al and Fe for Ti, the low-temperature phase transition at about 500 K is smeared in natural samples (Figs. 4 and 7), so the transition point could not be determined. We suspect that the weak break in the temperature dependence of the phonon at 563 cm^{-1} in the sample R4970 at about 580 K corresponds to the phase transition at 500 K in pure titanite. The impurities in the natural titanite exhibit much less effect on the second phase transition near 825 K, however. The three natural samples show a thermal behavior that is similar, within our experimental res-



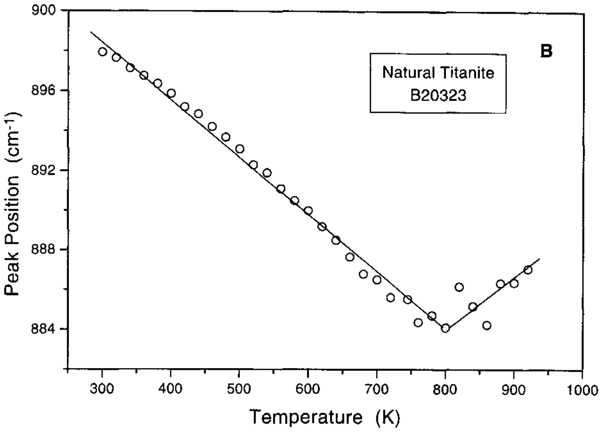


Figure 5. The temperature evolution of the Si-O stretching band near 899 cm^{-1}. (**A**) Synthetic sample; (**B**) B20323.

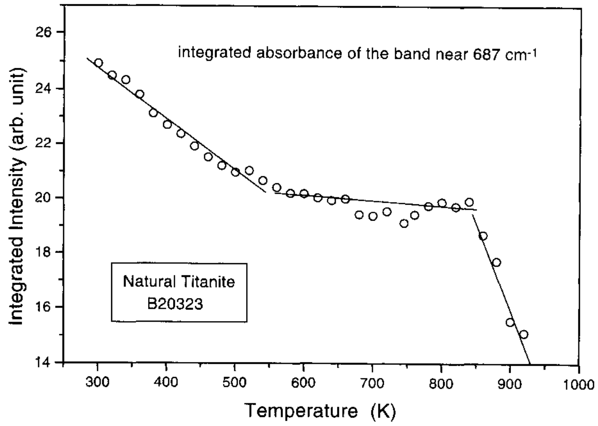


Figure 7. The integrated intensity of the 687 cm^{-1} band in sample B20323 shown as a function of temperature. For integration, a linear baseline between the spectral minima on either side of the peaks was used. The change in temperature dependence between 500 and 600 K corresponds to the phase transition at 500 K for the synthetic titanite sample (Bismayer et al. 1992; Salje et al. 1993; Zhang et al. 1995). The lines are visual guides.

olution, to that of the pure synthetic sample (Fig. 4). The Rauris and B20323 samples, which have lower concentrations of Al and Fe, show nearly the same transition temperature as pure titanite. The transition point for the sample, R4970, with the most impurities is modified by the effect of the impurities and shifts to higher temperature. The different dependencies of the two transition mechanisms on doping of the Ti positions allow us to characterize the driving forces of the phase transitions even further. The phase transition near 500 K is antiferroelectric on a macroscopic scale. The transition shows a strong dependence on the chemical occupancy of the position that is filled by Ti in the pure material. This result is correlated with the observation that the antiferroelectric displacement of Ti in the TiO_6 octahedron is the essential driving mechanism of the low-temperature phase transition.

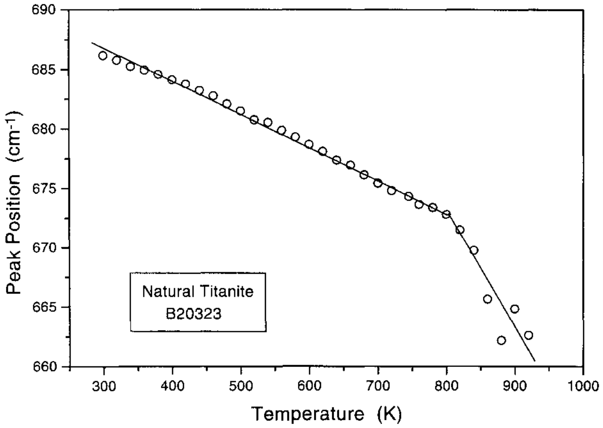


Figure 6. The IR band near 685 cm^{-1} of sample B20323 shows strong phonon softening at temperatures above 825 K.

The high-temperature phase transition shows a completely different behavior. It does not depend much on any dopant replacing Ti, nor does the Ti-O stretching mode show hardening in the high-temperature phase as discussed before. These observations indicate that the TiO_6 octahedron plays only a minor role in the mechanism of the high-temperature phase transition. If we assume, furthermore, that the weak changes in the phonons related to the SiO_4 tetrahedra can be explained by depolarization effects by Ca (and some small geometric changes in the tetrahedra), we expect that the Ca polyhedra play an essential part in the structural phase transition near 825 K.

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