

X. OPTICAL AND INFRARED SPECTROSCOPY*

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RESEARCH OBJECTIVES AND SUMMARY OF RESEARCH

The study of solids by means of infrared and Raman techniques continues to be the main field of research. The relation of the optical properties with impurities in various crystal lattices are now being investigated, and mixed-crystal systems continue to be of interest.

An Argon laser is expected to be added to the Raman spectrometer. We plan to add a new double monochromator with photon counting and improved low temperature capabilities as soon as funds are available. A variable temperature cryostat is now operational for the infrared and Raman equipment.

The publications and papers presented at various meetings¹⁻¹² summarize the research accomplished during the past year.

The research in progress and planned for the first half of the coming year includes investigations of phonons in ammonium halides, mixed KCl-KBr crystals and other mixed alkali halides, (Na, K) TaO₃ ferroelectrics, impurity absorption in perovskite fluorides, silver, and thallos halides, rare-earth fluorides, and host crystals containing other rare earths in concentrations varying between 0.1-1.0 mole per cent. Research is also under way on magnetic materials, other ferroelectrics (including SbSI and isostructural materials), and solidified inert gases.

The activities of this group will probably terminate at M.I.T. in the middle of the year 1968.

C. H. Perry

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(X. OPTICAL AND INFRARED SPECTROSCOPY)

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A. OPTICAL PHONONS IN MIXED SODIUM POTASSIUM TANTALATES

1. Introduction

KTaO_3 crystallizes in the cubic perovskite structure (symmetry group O_h). X-ray data by Davis¹ shows that samples with concentrations from zero to approximately 70% NaTaO_3 remain cubic at room temperature, with an almost linear decrease in lattice constant from 3.984 Å-3.944 Å. Further increase in sodium content causes the lattice constants to decrease sharply to show a well-defined A/B ratio. Initially, the structure becomes tetragonal, finally shearing to pseudo-monoclinic as the concentration approaches pure NaTaO_3 .

The dielectric properties of KTaO_3 have been investigated by Wemple² and indicate Curie-Weiss law behavior with an extrapolated Curie Temperature (T_c) of 1-3°K. Davis¹ has obtained dielectric data of the mixed-crystal system NaTaO_3 - KTaO_3 as a function of temperature. T_c rises with Na concentration to a maximum of 65°K for a sample with 48% NaTaO_3 , falls with higher NaTaO_3 concentrations, and becomes negative at approximately 72% NaTaO_3 . The temperature-dependent dielectric constant undergoes a region of anomalous behavior in the mid-range of Na composition as shown in Fig. X-1. This has been interpreted by Davis¹ as a ferroelectric transition at the higher temperature, followed by a phase transition to a tetragonal (C_{4v}) structure at the

(X. OPTICAL AND INFRARED SPECTROSCOPY)

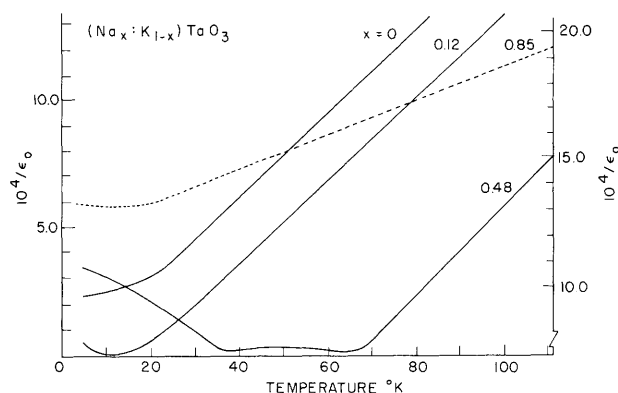


Fig. X-1. Temperature dependence of the dielectric constant for $(\text{Na}_x:\text{K}_{1-x})\text{TaO}_3$, after Davis.¹ Dashed line corresponds to the right-hand scale.

lower. The work presented in this report tends to substantiate this claim.

The cubic perovskites, with 5 atoms per unit cell, necessarily possess $15N$ degrees of freedom. Recourse to simple group theory³⁻⁵ predicts that at the center of the Brillouin zone these will consist of three triply degenerate infrared active (optic, symmetry F_{1u}) modes, one triply degenerate infrared and Raman inactive (optic, symmetry F_{2u}) mode, and one triply degenerate translational (acoustic, symmetry F_{1u}) mode. A further consideration, however, is the existence of long-range electrostatic forces between the component ions.^{6,7} These cause the boundary conditions for the longitudinal and transverse modes to differ,⁶ thereby lifting the degeneracy of optic modes of F_{1u} symmetry.⁸ Thus the final description of the $K \approx 0$ phonon system of such crystals gives three doubly degenerate transverse optic modes and three nondegenerate longitudinal modes, one doubly degenerate transverse optic mode, which in turn is degenerate with a single longitudinal mode, and three acoustic modes (with $\omega = 0$).⁹

Miller and Spitzer¹⁰ have studied the infrared active modes of pure KTaO_3 at room temperatures by the reflectance technique, Perry and McNelly¹¹ have studied the lower frequency modes as a function of temperature, and recently Nilsen and Skinner¹² and Perry, Fertel, and McNelly¹³ have studied its temperature-dependent Raman activity. McNelly¹⁴ made limited initial studies of both the temperature-dependent infrared and Raman spectra of the $(\text{Na}/\text{KTaO}_3)$ system, and the present investigation has provided more reliable and extensive data over a wider range of frequency and temperature.

The principle objective of this research is the delineation of the phonon contributions to the various Raman bands. Although no first-order Raman transitions are allowed in the cubic phase, all two-phonon combinations and overtones are, at both general and symmetry points in the Brillouin zone^{7,15} Thus with the aid of neutron data on the phonon dispersion curves¹⁶ and such theoretical work as Cowley's,⁹ zone-edge phonon

(X. OPTICAL AND INFRARED SPECTROSCOPY)

frequencies may be estimated. This task is complicated by the large number of such phonon combinations. Although they are possible throughout the Brillouin zone, their density of states tends to be highest at the symmetry points described by Boukaert and his co-workers,¹⁵ whose notation is used here. Thus if N is the number of irreducible representations which the symmetry group at a point in the Brillouin zone comprises, $N(N-1)/2$ is the number of both the summation and difference bands, and N is the number of overtones. For perovskites, the symmetry points, with corresponding N 's, are Γ ($k \approx 0$), 6; Δ , 10; X , 10; Σ , 15; M , 11; Λ , 10; R , 6.⁹ Since current neutron data are available only for Δ and X , estimates must be restricted to those. The possible contributions to a given Raman band may be further restricted by noting the behavior of intensity and frequency under temperature variation, and frequency with mass variation. Also, the reduction in symmetry, ensuing with increasing Na concentration and the ferroelectric phase change, allows a first-order Raman spectrum and thus a further restriction of possible phonon combination on the basis of frequency dependencies thus discerned. Also of interest is the nature of the phase change itself and the behavior of the "soft" ferroelectric mode. This behavior seems to correspond quite well with the calculations of Anderson,¹⁷ Cochran,¹⁸ and Nakamura,¹⁹ and thus is important in the verification of the theory of displacive ferroelectrics.

2. Experiment

The $(\text{Na}_x/\text{K}_{1-x})\text{TaO}_3$ crystals used had $x = 0, .12, .40, \text{ and } .85$ and were grown by the method used by Wemple,²⁰ modified as described by Davis.¹ They were cut and polished to square plates approximately $1 \times 6 \times 6$ mm with the (100) planes in the surfaces.

The infrared reflectance measurements below 250 cm^{-1} were done with the Michelson Interferometer²¹ used by Perry and McNelly.¹¹ At higher frequencies, a Perkin-Elmer model 521 grating instrument was used. Temperature control was achieved through the use of an ordinary cold-tail dewar. The interferometer path-length difference was extended to that necessary for 2 cm^{-1} resolution (.5 cm), the time taken being about 1/2 hour. The time constant used was .3 or 1 second in all cases. The grating data were taken with 5-cm^{-1} slit width (approximately), and 10-sec time constant.

The Raman studies were made on a Cary model 81 with He/Ne laser excitation and right-angle scattering with X(ZZ)Y symmetry, X, Y, and Z laying in the (100) directions in the sample. Symmetry changes to X(YZ)Y and X(YX)Y did not make important qualitative changes and merely reduced line intensity uniformly. Temperature control at reduced temperatures in this case was obtained with a continuous gas transfer dewar with quartz windows. The cold gas was obtained either by passing N_2 through a coil immersed in a solid CO_2 /acetone bath or liquid nitrogen in a dewar, or by transferring He boiled off by power dissipated in a helium dewar. By suitable gas flow and

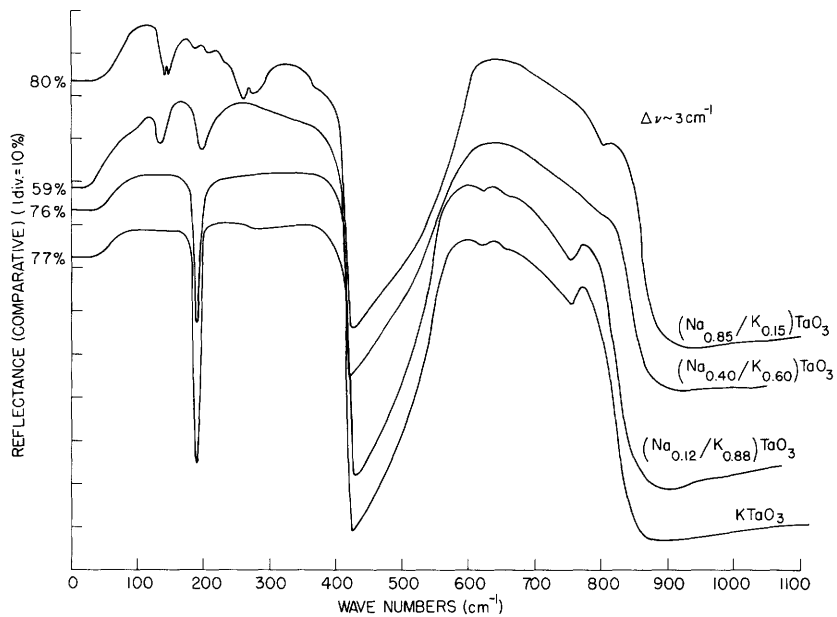


Fig. X-2. Room-temperature reflectance spectra for the four samples investigated.

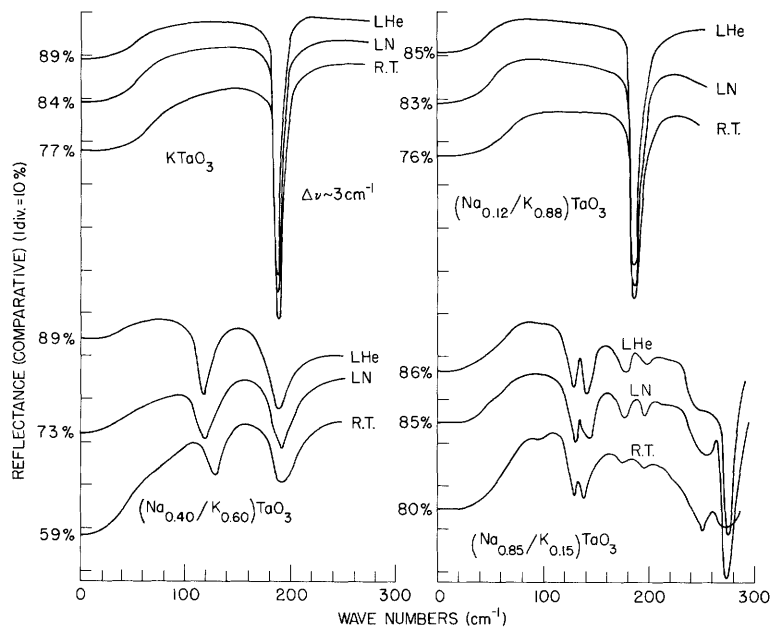


Fig. X-3. Low-frequency reflectance spectra as a function of sample and temperature.

(X. OPTICAL AND INFRARED SPECTROSCOPY)

heat-shielding modifications, this procedure allows temperature control to less than a degree within the regions 8° - 50° , 77° - 120° , 210° - 300° K. Temperature was monitored by a precisely calibrated doped germanium 4-wire resistance thermometer, and by a copper-constantin thermocouple, both of which were mounted on the small bracket that holds the sample. Elevated temperatures were obtained with a Variac-controlled 40-W heating element on which the sample was mounted with a copper bracket, inside an enclosure to restrict convection but not conduction or radiation. These temperatures were monitored with the copper-constantin thermocouple. Temperature control with this arrangement was $\pm 5^{\circ}$ K. All of the spectra were run with a slit width of approximately 10 cm^{-1} , at a rate of 0.25 to $1 \text{ cm}^{-1}/\text{sec}$ with time constants of 2 - 20 sec, but always less than the time taken to scan one spectral slit-width. The single exception to this is the very lowest frequency portion of the 30° K runs of the 40% NaTaO_3 sample, for which the slit width was 2 cm^{-1} , the rate was $0.01 \text{ cm}^{-1}/\text{sec}$, and the time constant was 70 sec.

3. Results

The computed reflectance obtained from the interferometer was matched to the data of the grating instrument by renormalizing the reflectance given by the former

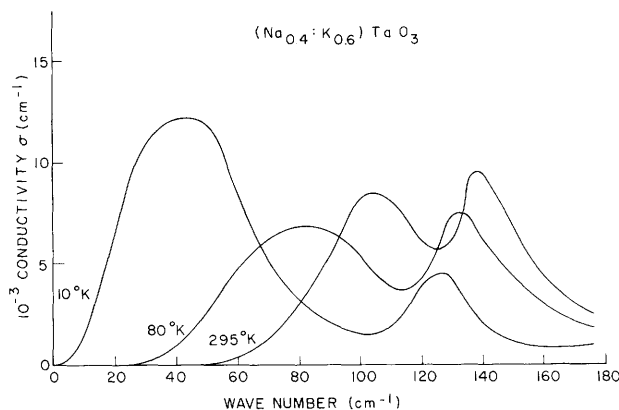


Fig. X-4. Low-frequency conductivity derived from Kramers-Krönig analysis of the reflectance spectra.

to agree with that of the latter over the spectral region in which they both gave dependable data. This procedure could be done unambiguously in all cases, and generally resulted in quite reasonable values for the maximum in the low-level reflectivity and the value of the DC dielectric constant. Examples of the reflectance spectra thus obtained are presented in Fig. X-2, while the low-frequency

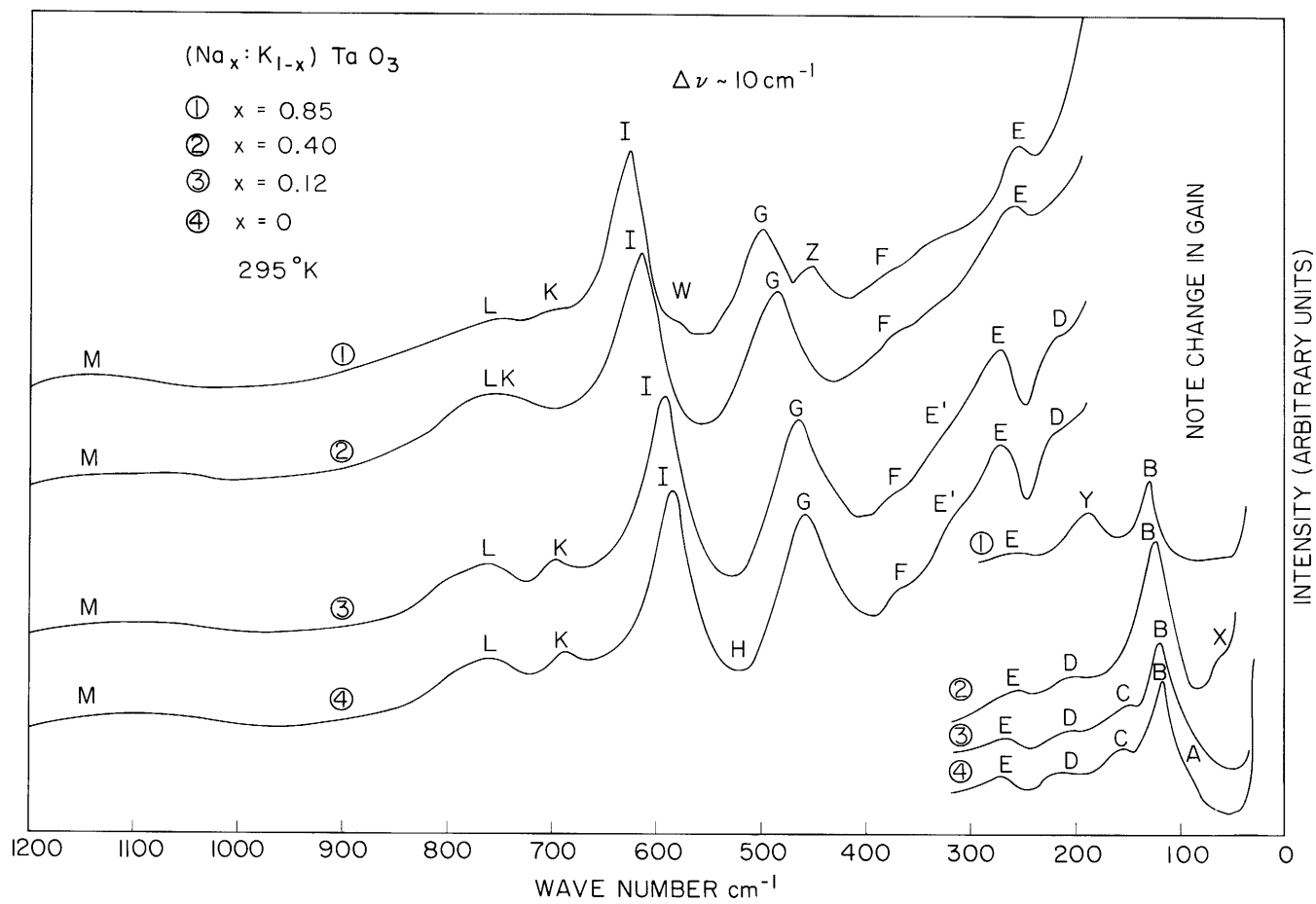


Fig. X-5. Room-temperature Raman spectra four samples.

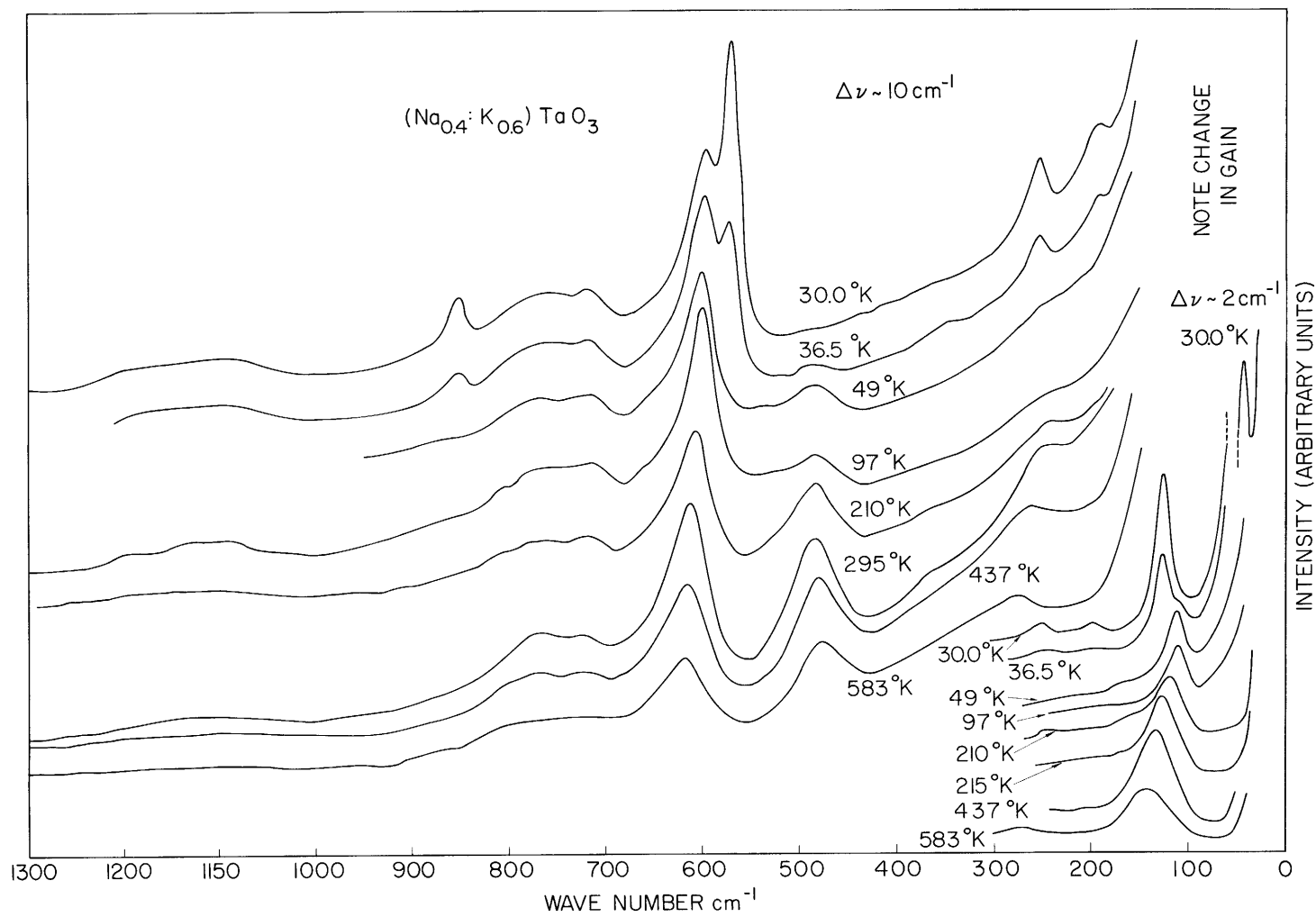


Fig. X-6. Temperature-dependent Raman Spectrum of $(\text{Na}_{.40}:\text{K}_{.60})\text{TaO}_3$.

(X. OPTICAL AND INFRARED SPECTROSCOPY)

details of all samples and temperatures appear in Fig. X-3. Each of the details in Fig. X-3 is the result of the average of at least two interferometer runs, and of as many as six. The reflectance spectra thus obtained were subjected to a Kramers-Krönig (K-K) analysis,^{22,23,10} to obtain the real and imaginary parts of the dielectric constant (ϵ' and ϵ''), the conductivity ($\sigma = \epsilon''\nu/2$), the index of refraction, the extinction coefficient, and the absorption coefficient. A representative series of low-frequency conductivities is presented in Fig. X-4.

The Raman spectra are the average of several retracings of the regions of interest. Room temperature results for all samples are presented in Fig. X-5, while Fig. X-6 shows the results for the entire temperature range for the sample nearest midrange of composition. Regrettably, a helium shortage on this run, together with the sample's current use in other work, has prevented an examination of the very low-frequency region and a series of polarization studies.

The Cary 81 is capable of running with either the conventional single slit or with a double slit for greater signal. The last is usable only above $\sim 200 \text{ cm}^{-1}$. This accounts for the appearance of the Raman spectra presentation, the lower intensity plots below 300 cm^{-1} being single-slit results, and the remainder double-slit results. No effort has been made to renormalize one or the other of these for purposes of presentation, since the current form is considered more indicative of the quality of the results obtained.

4. Discussion

The principle objective of the infrared studies has been to provide the frequencies of the independent first-order lattice modes, to provide a starting point for the Raman studies. In Fig. X-2 the large dip, which occurs between 450 cm^{-1} and 550 cm^{-1} , corresponds to the highest frequency transverse optic mode (TO_4), the shoulder at the left to the lowest mode (TO_1 , the "soft" mode), and for the two with the lowest per cent of Na composition the dip between 190 cm^{-1} and 200 cm^{-1} corresponds to the next highest mode (TO_2). Proceeding to the reflectance spectra for the two samples with the highest per cent of sodium, however, one can see that the reduction in lattice symmetry becomes visible through the splitting of previously obtained lines, and the introduction of new ones. On the $(\text{Na}_{.40}:\text{K}_{.60})\text{TaO}_3$, for example, the TO_2 mode has moved slightly higher, while the $\text{TO}_1:\text{LO}_1$ system has become split into a soft mode and a higher mode. Further evidence of this may be seen in the spectrum for $(\text{Na}_{.85}:\text{K}_{.15})\text{TaO}_3$. The soft mode is still visible, of course, while the dip above it is clearly split. The TO_2 is now also clearly split, while the previously degenerate and infrared-silent $\text{LO}_2:\text{TO}_3$ modes (formally of F_{2u} symmetry) are now visible in the region $210\text{-}280 \text{ cm}^{-1}$. These low-frequency details and their temperature dependence may be seen more clearly in Fig. X-3. The frequencies of the active TO modes may be obtained from the maximum of the conductivity²³ obtained from the K-K analysis and are presented in Table X-1.

Table X-1. Comparison of infrared and Raman frequencies for $k \approx 0$ modes.

Na (%)	12						40						85					
	295	295	80	110	10	30	295	295	80	97	10	30	295	295	80	109	10	24
Temperature (°K)																		
Type	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R
Mode																		
TO ₁	75		50		48		102		81		39 42		75		60 70		57 65	
	132		132		132		132		129 128		144		132 130		132 130		132 130	
	144		147		147		147		147		147		147		147		147 150	
LO ₁ TO ₂	198		198		198		204		201		198 200				196 200		196 205	
LO ₂ TO ₃											255		246		246		246	
	255		255		255		255		255		255		258		261		261	
	270		270		270		270		270		270		270		270		270	
LO ₃													430 450		430 450		430 450	
TO ₄	540		540		540		576		573		570 572		584		584		584 580	
LO ₄	816		816		816		860		855		850 850		870		870		870	

Furthermore, since

$$\epsilon' = \epsilon_{\infty} + \frac{(\epsilon_0 - \epsilon_{\infty}) \left[1 - (\omega/\omega_0)^2 \right]}{\left[1 - (\omega/\omega_0)^2 \right]^2 + (\omega/\omega_0)^2 (\gamma/\omega_0)^2},$$

where ϵ_0 is the DC dielectric constant, ϵ_{∞} is the high-frequency dielectric constant, ω_0 is the frequency of the transverse mode, ω is the photon frequency, and γ is the damping constant, we see that if the damping is small ($\gamma \approx 0$), $\epsilon' = 0$ not only at $\omega = \omega_0$ but also at $\omega = \left(\frac{\epsilon_0}{\epsilon_{\infty}} \right)^{1/2} \omega_0$, which, by the Lyddane, Sachs, Teller relation,²⁵ is a means of obtaining the LO mode of a single oscillator and is known as Drude's rule. Although not strictly applicable to multiple-oscillator systems, its use for finding the approximate LO₄ frequency is justified on the grounds that this oscillator is strong, not too strongly damped, and its frequency is well separated from the others, thereby reducing their effect on ϵ' . The approximate LO₄ frequencies also appear in Table X-1. While it may be checked that the TO₁ (soft mode) frequencies for the sample with 85% NaTaO₃ lie within experimental error ($\pm 5 \text{ cm}^{-1}$) of those given by $\omega_0^2 \propto (T - T_c)$, which is the expected behavior,¹¹ those for 40% NaTaO₃ cannot be expected to do so, for this data, since its T_c is approximately 55°K, and those for 12% NaTaO₃ would be expected to deviate considerably, because of the non-Curie-Weiss behavior found by Davis.¹ Furthermore, exact data for this region is necessary for a meaningful comparison. For pure KTaO₃ this study has already been made.¹¹

Figures X-5 and X-6 are representative of the Raman spectra obtained, and correspond to the diagonal elements of the Raman tensor resulting from the scattering symmetry employed. The most important feature to be noticed in Fig. X-5 is the close correspondence between the Raman spectra as the NaTaO₃ concentration is varied. The frequency change is quite gradual, relative intensities remain the same, and for the most part no new frequencies occur. We take this to mean that while the unit cell cannot be strictly the same in each case, nevertheless there must exist a pseudo Brillouin zone whose nature varies very little as the composition is varied. One then expects the most important effects to arise from the average mass change and the average change in lattice constant. The frequencies obtained in this study, however, do not compare well with those expected from variations in the reduced mass. The nature of the anharmonicity of the lattice vibrations would have to be known to deal with the relation between frequency and lattice constant. All that we can conclude, then, is that the assignments of the phonon contribution to the various bands will be consistent from one composition to the next. The final points of interest in Fig. X-5 are the bands marked W, Z, Y on the spectrum for 85% NaTaO₃. These are interpreted as the TO₄, LO₃, and

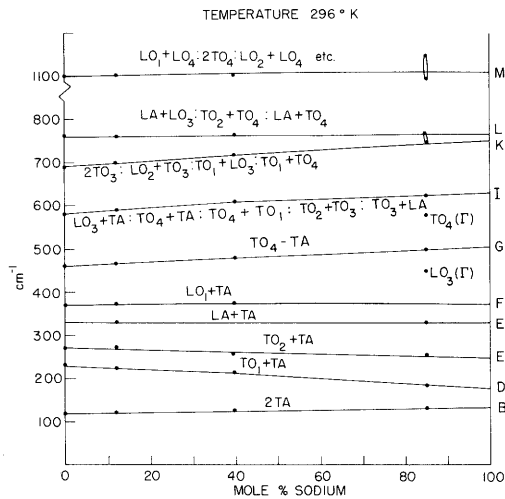


Fig. X-7.

Phonon combination assignment and their frequency dependence on composition. Letters at right correspond to peak labels in Fig. X-5.

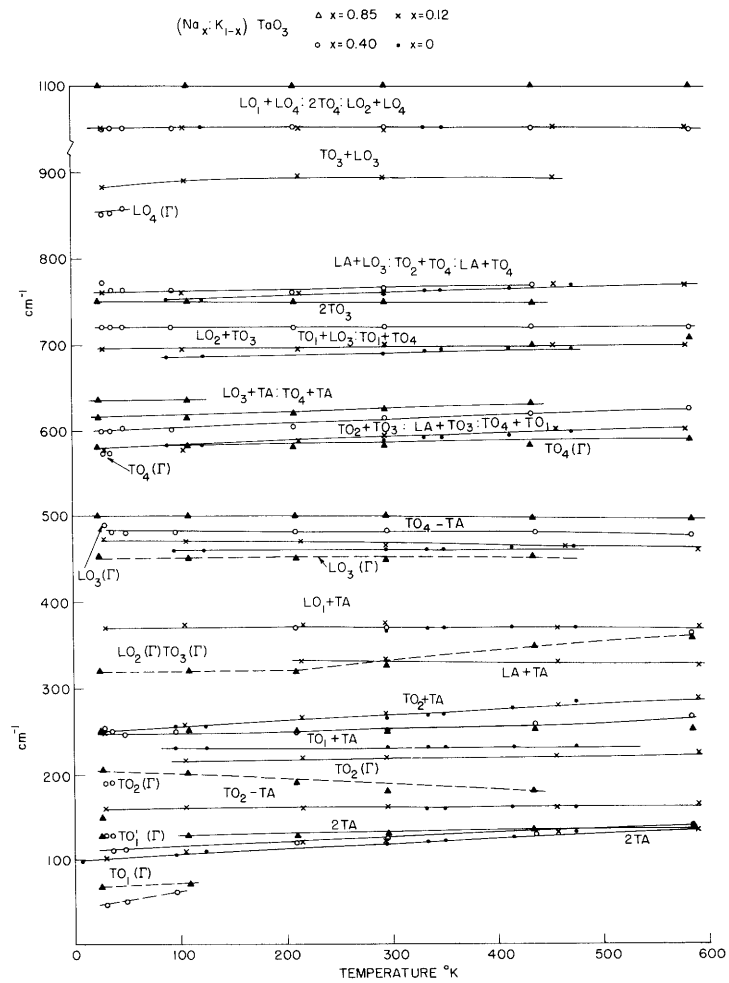


Fig. X-8. Complete tabulation for all compositions of frequency vs temperature. Γ refers to phonons with $k \approx 0$.

Table X-2. Zone edge assignments based on Figs. X-7 and X-8.

Na (%)	0							12							40							85																				
Temperature (°K)	4	90	123	295	348	413	473	30	110	214	295	458	591	30	36.5	49	97	210	296	437	583	33	109	210	296	433	586															
Mode																																										
TA	50	52	53	58	60	63	65	50	55	58	60	65	67	55	55	56	57	60	62	66	70	64	65	66	66	67	69															
LA																																										
TO ₁	178 177 172 170 167 165							160 159 159 157																																		
LO ₁	312 310 307 305							320 315 312 310 305 303							315 315 314 313 310 308 304 300																											
TO ₂	200	203	204	210	212	213	215	200	200	204	208	213	220	200	197	191	191	190	192	192	195	183	183	184	185	186	185															
TO ₄	512	513	518	520	523	525	522	525	527	528	531	531	539	539	540	540	541	542	545	548	564	565	566	565	564	565																

(X. OPTICAL AND INFRARED SPECTROSCOPY)

LO_1 or TO_2 at zone center that become Raman active, because of the reduction in symmetry with increasing $NaTaO_3$ percentage mentioned above.

The only departures from uniform temperature dependence occurred (see Fig. X-6) in $(Na_{.40}K_{.60})TaO_3$. Here, the sharp peaks that arise at lowest temperatures at $\sim 42\text{ cm}^{-1}$, 128 cm^{-1} , 200 cm^{-1} , 255 cm^{-1} , 572 cm^{-1} , and 850 cm^{-1} are the TO_1 (soft mode), TO'_1 , TO_2 , TO_3 and LO_2 , TO_4 , and LO_4 , respectively, and from Table X-1 these frequencies can be seen to agree vary well with the bands seen in the infrared. This, then, is certainly the advent of a first-order spectrum caused by a symmetry change, and can be seen to occur at approximately the same temperature as the lower temperature minimum of the plot for 48% $NaTaO_3$ in Fig. X-1, and it corresponds to Davis' conjecture.¹ The T_c for this sample is 55°K , but there are no new lines at 49°K , thereby invalidating a departure from cubic symmetry at T_c .

In Fig. X-7 frequencies of the Raman bands are plotted as a function of composition. The phonon combination assignments are restricted not only by the symmetry and frequency considerations discussed above, but also by self-consistency under the implied variation of frequencies with composition and temperature. The letters at the right of the plot correspond to the letters identifying peaks in the spectra of Fig. X-5. The corresponding plot of frequencies for all compositions as a function of temperature occurs in Fig. X-8. For the bands at higher frequencies the large number of possible assignments and the breadth of the bands themselves lead to ambiguity in assignment. The assignments have been based on the work of Perry, Fertel, and McNelly,¹³ and of Nilsen and Skinner¹²; both these in turn depended on the neutron work of Shirane, Nathans, and Minkiewicz¹⁶ for the assignment of the low-frequency modes.

Table X-2 lists those zone-edge frequencies that may be determined unambiguously on the basis of these assignments.

We would like to acknowledge the cooperation of Mr. T. G. Davis in providing the samples and participating in certain aspects of this work.

N. E. Tornberg, C. H. Perry

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(X. OPTICAL AND INFRARED SPECTROSCOPY)

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