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The Raman Spectra of $PbTiO_3$ and Solid Solutions of $NaTaO_3$-$KTaO_3$ and $KTaO_3$ - $KNbO_3$

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The Raman spectra of $PbTiO_3$ and the mixed crystal systems $(Na_x:K_{1-x})TaO_3$ where x = 0, 0.12, 0.40 and 0.85 and $K(Ta_y:Nb_{1-y})O_3$ where y = 0, 0.25, 0.65, 0.89 and 1.0 have been studied over the temperature range 10-800°K.

Complimemtary far infrared reflectance measurements over the same temperature range have been made on $PbTiO_3$ using polarized radiation and on some of the mixed crystal systems. The frequencies of the allowed $\underline{k} \simeq 0$ transverse and longitudinal modes were obtained from a

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Kramers-Kronig analysis of the reflection spectra and provide a starting point for the interpretation of the Raman data.

$PbTiO_3$ remains tetragonal below its Curie temperature at about $760^{\circ}K$. Above $760^{\circ}K$ $PbTiO_3$ exhibits a very weak second order Raman spectrum. Below $750^{\circ}K$ a first order spectrum is superimposed and increases in strength as the temperature is lowered. In the tetragonal phase measurements were made at a number of temperatures between $20-750^{\circ}K$. The bands observed at $760^{\circ}K$ at about $70\ cm^{-1}$, $120\ cm^{-1}$, $180\ cm^{-1}$ and $495\ cm^{-1}$ show considerable temperature dependence. These bands shift approximately $5\ cm^{-1}$, $4.5\ cm^{-1}$ $7\ cm^{-1}$ and $3.5\ cm^{-1}$ for $\triangle T = 100^{\circ}K$ respectively to lower frequency as the temperature is lowered. The lowest frequency mode ($70\ cm^{-1}$) is relatively the softest but the $120\ cm^{-1}$ and the $180\ cm^{-1}$ modes may also approach instability and contribute to the temperature dependence of ϵ_o. However they do not become unstable to the point of allowing a phase transition.

The $(Na_x:K_{1-x})TaO_3$ system exhibits a second order Raman spectrum which for $T > T_c$ and for $x < 0.7$ has the same general features as observed in $KTaO_3$. Below T_c and for $x > 0.7$ (where the structure is no longer cubic) a first order spectrum is superimposed and there is good agreement between the zone center infrared and Raman frequencies. The second order spectra for each composition have been interpreted in terms of phonons at the edge of a psuedo-Brilloin zone.

The $K(Ta_y:Nb_{1-y})O_3$ system displays a considerably more complex Raman spectrum. For the $K(Ta_{0.89}:Nb_{0.11})O_3$ mixed crystal the Raman spectrum is similar to $KTaO_3$. At $\sim 125^{\circ}K$ and $\sim 80^{\circ}K$ phase changes occur and first order bands appear. For y = 0.65, 0.25 and 0 the cubic, tetragonal, orthorhombic and rhombohedral phase transitions have been observed. Marked hysteresis effects in the appearance and disappearance of bands take place at these transitions.

$KNbO_3$ exhibits a spectrum whose temperature dependence is similar to that observed through the same phases in $BaTiO_3$. The first order lines observed in the ferroelectric phases show frequency shifts with composition and temperature and may also be related to the unstable modes above T_c.

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