

studies of KH_2PO_4 to 9.3 kbar a soft mode in the crystal became underdamped with the application of pressure [155]. Studies with RbH_2PO_4 were made at 21 kbar using Raman spectra as the optical probe [156]. These results indicated a large decrease in transition temperature with pressure and a disappearance of the ferroelectric state at all temperatures for $p \geq 15.2$ kbar, and a decrease with pressure of the Curie constant and dielectric constant in the paraelectric phase.

(6) Molybdates, tungstates, sulfates

The Raman spectra of CaMoO_4 and CaWO_4 have been obtained at pressures to 40 kbar [157]. A new pressure phase for each compound was found. The pressure dependencies of the internal modes for these compounds were determined and found to range from 0.0 to $1.0 \text{ cm}^{-1} \text{ kbar}^{-1}$.

Some sulfates were superficially examined at high pressures [64]. ν_4 of SO_4^{2-} anion showed shifts of 3 cm^{-1} at 35 kbar, while a lattice mode at 183 cm^{-1} showed a blue shift of 52 cm^{-1} .

(7) Bihalide salts

The bihalide salts of NaHF_2 , KHF_2 , NH_4HF_2 , $(\text{CH}_3)_4\text{NHCl}_2$ and $(\text{C}_2\text{H}_5)_4\text{NHCl}_2$ were investigated by IR techniques at pressures up to 40 kbar [158]. In these strong hydrogen bonded systems the ν_3 vibration in the HX_2^- anion shifts to higher frequencies while the ν_2 vibration shifts to lower energies with an increase in pressure. The ν_1 frequency was deduced from the behavior of combination bands and found to shift toward higher frequencies. These results are typical expectations for a simple model of strong hydrogen bonding. A new phase of NaHF_2 was found at 40 kbar.

(8) Ionic conductors

The pressure dependent Raman spectra of the fast ion conductors $\beta\text{-Ag}_2\text{HgI}_4$ and $\beta\text{-Cu}_2\text{HgI}_4$ were measured [159]. The Raman spectra of $\beta\text{-Cu}_2\text{HgI}_4$ ($I42m$ (D_{2d}^{11}), $z = 2$) was followed at 25°C to 24 kbar, and no phase transition was observed. The breathing motion of the iodide lattice against the Cu^{2+} ions at 85 cm^{-1} undergoes a more rapid blue shift than the Hg—I stretch at 127 cm^{-1} , indicative of greater anharmonicity in the CuI_4 stretching mode as compared to the HgI_4 stretch. The 36 cm^{-1} mode shows a negative pressure dependence.

$\beta\text{-Ag}_2\text{HgI}_4$ (I_4^- (S_4^2), $z = 2$) shows several phase changes in the 0–10 kbar region. Table 13 shows band positions in Ag_2HgI_4 at various pressures and at 60°C . At 6.1 kbar and 25°C , the HgI stretching vibration lowers from 124 to 116 cm^{-1} and may indicate a change from 4-coordinate to a 6-coordinate environment. Figure 9 shows the Raman spectra of $\beta\text{-Ag}_2\text{HgI}_4$ as a function of pressure. A second phase is observed between 7.5–44 kbar and another phase at pressures greater than 44 kbar.

The Raman spectra of these materials have been found useful in screening potential ionic conductors [160,161]. Broad Raman bands are indicative of

crystalline Ag_2HgI_4 at various pressures^a [159]

Position (cm^{-1})				
	24.2 (s)	29.5 (w)	34.9 (s)	80 (w, br)
	23.8	—	35.1	—
19.1 (s)			32.8 (w)	
19.3			34.2	
17 (s, br)			123 (s, br)	~142 (m, sh)
	29 (m)	114 (vs)		

anvil cell with paraffin oil as a pressure transmitting liquid was used.