CHAPTER 8

STUDY OF LASER RAMAN SPECTRA OF NANOPARTICLES OF
AgI AND HgI₂

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8.1 Introduction

The uniqueness of very small particles lies in the large value for the surface to volume ratio and as the size of the particles decreases the characteristics of the surface atoms and ions become increasingly sharper (1). The break down of the vibrational selection rule $K \neq 0$ forbidden in the case of small particles and the consequent changes observed in the frequency and intensity of Raman lines is known for sometime (2-6). Such studies have been reported in the case of highly dispersed particles of MgO (3,7) and rutile (8). Another factor that influences the Raman spectra of fine particles is the size amorphousness which causes the spectra to be entirely analogous to that of an amorphous film. Electron microscopic and Raman studies on gallium phosphide (1), germanium (9) and silicon particles (10) revealed crystalline nature of the particles with amorphous like Raman spectra. In addition, the presence of a surface causes the existence of vibrational surface modes characterised by specific properties. This problem has been studied for small particles of ionic as well as covalent bonds by infrared absorption (11-13) and Raman scattering (3,14,15). This article is to report the study of laser Raman spectra of nanoparticles of AgI and HgI$_2$. The work was undertaken in view of the scientific and
technological interest on the properties of fine particles in general and the efficiency of laser Raman spectroscopy to probe the structure of these particles in particular. AgI has a number of crystallographic phases and the wurzite AgI called the B-phase is the thermodynamically stable phase and the material closest to the covalent-ionic phase transition.

Raman scattering studies of single crystals of this fast ion conductor have been reported by many workers (16-18). Laser Raman spectra of single crystals of red HgI$_2$ which has a tetragonal crystal structure has also been studied by many researchers (20,21). But Raman spectra of fine particles of these materials have not been reported so far. In this work, the laser Raman spectra of AgI and HgI$_2$ particles of sizes about 23 nm and 30nm respectively have been recorded and the features of the spectra are compared with those of the single crystal spectra of the materials reported in the literature. The shift in frequency and change in intensity of the lines are discussed in the light of the existing theories.

8.2 Experiment and Observation

The nanoparticles of AgI and HgI$_2$ used in the present study were prepared following a procedure similar
to that used for producing nanoparticles of CdS (32) as discussed in section 3 of chapter 4. The sedimented agglomerates of AgI and HgI₂ particles were separated, washed repeatedly with distilled water and dried. The particles were examined using TEM and electron diffraction. The electron diffraction pattern of AgI and HgI₂ particles showed spotty rings indicating a regular arrangement of atoms. Laser Raman spectra of the particles were recorded at room temperature using computer controlled DILOR Z24 Raman spectrometer in the stokes region from 20 to 400 cm⁻¹, using the 647.1 nm line from a Kr⁺ laser at a power of about 50 mw as the exciting radiation (Fig.8.1 & 8.2).

6.3 Discussion

The typical laser Raman spectrum of crystalline B- AgI at room temperature in the 20 to 400 cm⁻¹ region has been reported to contain broad bands centered at 39, 85 and 106 cm⁻¹ (17, 18). The structures at 39 and 85 cm⁻¹ are of second order and the band at 106 cm⁻¹ is a composite of E₂ and TO Phonons of both A₁ and E₁ symmetry. The specifically allowed A₁ (LO) phonon shows up only as an extended tail on the high energy side of the 106 cm⁻¹ line. The Raman spectra of red HgI₂ crystal has been reported to consist in the region above 20 cm⁻¹ of two lines at 28.5 and 11.32 cm⁻¹ corresponding to E₁ and A₁ modes (20). In the present
Fig. 8.1. LRS of nanoparticles of AgI
Fig. 8.2. LRS of nanoparticles of HgI$_2$. 
study, the spectrum of nanoparticles of AgI(Fig 8.1) was found to consist of three bands all of which were frequency shifted with respect to the corresponding bands of the single crystal spectrum. The two bands corresponding to the second order appeared at 33 and 81.4 cm\(^{-1}\) and third band at 103.5 cm\(^{-1}\) compared to the bands at 39, 85 cm\(^{-1}\) and 106 cm\(^{-1}\) respectively of the single crystal B-AgI spectrum. The specifically allowed \(A_1\) (LO) phonon indicated its presence only through the extended tail on the high energy side of the 103.5 cm\(^{-1}\) band as in the case of the single crystal spectrum.

The band at 103.5 cm\(^{-1}\) and the one at 81.4 cm\(^{-1}\) are broad and weaker in intensity compared to the line at 33 cm\(^{-1}\) which shows up as a shoulder on the rising edge of the Rayleigh line. This is in contrast with the single crystal B-AgI spectrum where the bands at 85 and 104 cm\(^{-1}\) are more intense than the band at 37 cm\(^{-1}\). In the case of nanoparticles of HgI\(_2\) (Fig. 8.2), the line corresponding to the \(E_g\) mode was found to be shifted to higher energy side to 30.7 cm\(^{-1}\) while the line having the \(A_{1g}\) symmetry was found to be shifted to the lower energy side to 112.6 cm\(^{-1}\) compared to the lines at 28.5 and 113.2 cm\(^{-1}\) of the single crystal spectrum. The shoulder at 140.5 cm\(^{-1}\) is a new feature of the HgI\(_2\) nanoparticles. A calculation of the Raman
active modes in red HgI₂ showed two allowed modes corresponding to $A_{2u}$ (TO) and $A_{2u}(LO)$ having frequencies 135 and 145 cm⁻¹ respectively (23). The observed shoulder in the spectrum of small particles of HgI₂ happens to be between these two allowed modes.

The study of size induced break down of selection rules for vibrational transitions in the case of MgO (3,7) and rutile (8) have shown that the spectral lines have undergone a frequency shift to lower values as well as a change in intensity. The change in intensity has been accounted for on the basis of contributions to the Raman signal from the surface atoms. The size amorphousness of fine particles has also been relied upon by workers in explaining the shift in frequency and the decrease in intensity of Raman lines. Pioneering work on the effect of size amorphousness on the Raman spectra of highly dispersed germanium particles has shown that a narrow line that is also typical for massive crystals become broader as the particles become smaller and also shifts towards lower vibrational frequencies (20). In addition new wide bands appear and systematically grow in intensity. Similar results have been reported in the case of gallium phosphide and silicon particles (1,10).
The diversity of unusual properties of highly dispersed particles may be linked with the appearance of very high internal pressure in such particles (23). These internal pressures would change the force constants of the bonds linking the vibrational units and may result in a change in frequency of the vibrational lines. High pressure Raman studies in crystals and glasses have shown that the vibrational lines shift towards higher frequencies in both cases (24,25). The shift in vibrational lines accompanying a change in pressure is a direct consequence of the unharmonicity of real vibrations. In the case of fine particles the effective unharmonicity of vibrations increase owing to the contributions from surface atoms (2). In the present study, all the observed lines in AgI particles have been observed to have shifted to lower frequencies and the intensity have been found to be reduced compared to that of the bulk phase. This may be due to the finite size and due to surface amorphousness of the particles. Even though electron diffraction patterns indicate regular arrangement of atoms, the surface may be disordered or amorphous and the contribution of surface amorphousness may be a factor in redistributing Raman intensity. The surface stress seems to have not much effect in shifting the Raman lines, since an increase in pressure should shift the lines to higher values, whereas in this case the lines have been shifted to
lower values. In the case of HgI$_2$ one of the lines has shifted to higher frequency and the other to lower frequency compared to the lines of the bulk spectrum. This indicates that both size effect and surface stress are active in shifting the lines. The decrease in frequency involved in the line at 112.6 cm$^{-1}$ must be due to surface amorphousness while the increase in frequency involved in the line at 30.7 cm$^{-1}$ must be a pressure effect. This is reasonable since surface stress and the resultant internal pressure may modify the selection rules for only one line of the spectrum. The appearance of a shoulder at 140.5 cm$^{-1}$ must be a manifestation of the surface phonon mode.

8.4 Conclusion

The laser Raman Spectra of nanoparticles of AgI and HgI$_2$ have been studied in comparison with the single crystal spectra of corresponding material. The change in frequency and intensity of Raman lines may be due to size effect and surface amorphousness. The high internal stress may be a reason for shifting one of the Raman lines of the HgI$_2$ nanoparticles to high frequency side.
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