CHAPTER-10
LASER RAMAN SPECTROSCOPIC STUDY OF SPHERULES AND IMPACT MELTS
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10.1 Introduction

Vibrational spectroscopy dominantly Laser Raman serves as an important tool for investigating the structural reorganization of crystalline and amorphous materials such as silicate glasses (Brawer 1975; Mysen et al 1980; Richet and Bottinga 1986 and references therein). Raman spectroscopy has been proposed as suitable analytical technique for Martian, Lunar (Wang et al 1995; Wang 2009) and more recently Venus exploratory missions for in-situ investigation of minerals in rocks, soils, breccias and impact melt glass (Clagg et al 2009). Since, this technique is sensitive for changing crystal lattice after amorphisation derived to shock metamorphism can be successfully applied for determining structural changes in the impactites. Therefore, it can be successfully employed for finding the irreversible structural and mineralogical changes occur in target rock due to intense shock pressure and temperature during impact event (French and Short 1968; Gratz et al 1992; Huffman et al 1993). Raman spectra of analog basaltic glass matrix with low concentration of minerals relatively applicable for spectral studies of Venusian surface (Sharma et al 2011). Furthermore, chemical composition and degree of polymerization of volcanic glasses has also been inferred by Raman spectra (Genova et al 2015). In Raman spectra, the frequencies in the range of 1200-800 cm\(^{-1}\) are known as anti-symmetric stretching frequencies while 700-450 cm\(^{-1}\) is corresponds to symmetric stretching frequencies (Sidorov 2007). Vibration studies of silicate glasses and melts suggested bands in the 1200-800 cm\(^{-1}\) region has been commonly attributed to Si-O stretching vibrations of SiO\(_4\) silicate units (McMillan 1984). While structural studies of natural glasses including desert glass, tektites and obsidians of various compositions, and some lunar glasses suggested that the wave number of the 400–600 cm\(^{-1}\) band varies with the degree of polymerization of the network and with Si-O-Si bridging bond angles (White and Minser 1984). In addition, Raman spectra impact glasses show two broad bands at 491 and 821 cm\(^{-1}\) which indicate a high degree of amorphization (Gucsik et al 2004). The presence of characteristic silica vitreous glassy matrix with small inclusions of \(\alpha\)-cristobalite (high pressure polymorph of quartz) in Libyan desert glass (LDG) and Darwin impact glass was confirmed by Raman spectroscopy showing peaks at
114, 231, and 418 cm\(^{-1}\) (McHone et al. 2000; Gomez-Nubla et al. 2015). Raman vibrational spectra revealed the structural differences from crystalline to amorphous phase with varying variable shock pressures (Heymann and Hörz 1990; Jaret et al. 2014; McMillan et al. 1992; Champagnon et al. 1996; Okuno et al. 1999 and references therein). Spectral similarities have been observed between impact glasses quenched from high temperature molten liquid and its melts (Markin and Sobolev 1960; Sweet and White 1969; Sharma et al. 1978a; Piriou and Arashi 1980; Kashio et al. 1980; Seifert et al. 1981). This technique has become so well developed that spectroscopic measurements of melts at high temperatures are routine (Cormier et al. 2001; Mysen et al. 2003; Behrens and Yamashita 2008). Raman spectroscopy has been one of the tools of choice with which to probe the structure of glass (and more specifically the connectivity of the glass network) and its immediate precursor, melt. This technique is useful to study the short-range order present in impact glasses and melts and preferred over other existing spectroscopic techniques as it is more sensitive to characterize the glassy state and also enable us to understand the lattice dynamics of shocked minerals (McMillan and Hofmeister 1985; Ostroumov et al. 2002). In addition, it gives sharp non-overlapping bands that are better suited for the identification specific silicate and other minerals (Wang et al. 1995). The benefit of using Raman as a tool for chemical identification of minerals is its non-destructive nature, and the sample size under investigation can be as small as a few micrometers.

Impact melt and spherules of the present study can be used as an ideal material for spectroscopic analyses to determine the changes and associated vibrational assignments of crystalline target basalt and its subsequent impact melt based on spectral characteristics. This approach of the experimental spectra thus, helps us to compare glassy impactites of with those of other worldwide impact structures and also compare with the spectral data of impactites from the planetary bodies.

10.2 Methodology

The Laser Raman spectroscopic study has been performed on polished stubs of spherules and melts fragments using Laser Raman (Renishaw, Germany) System 1000B Spectrometer with 785nm Ar-ion laser and a thermo-electrically cooled CCD detector at Indian Institute of Technology, Kharagpur, India. The Laser Raman instrument has an edge filter to cut off light at
200 cm\(^{-1}\) and the grating is 1800 l/mm. The lateral resolution of the focused laser probe was measured at 1 \(\mu\)m using 50x objectives that focus the size of the laser beam to about 1 \(\mu\)m at the surface of the sample. The power of the laser beam on the sample is less than 5 mW. Calibration is performed during measurements in a silicon semiconductor mode at 520.7 cm\(^{-1}\). The spectra were obtained in the spectral range of 200-1800 cm\(^{-1}\) with approximately 30 sec total exposure time. Raman spectra were taken from 2-3 spot on the sample surface.

### 10.3 Results and Inferences

In the present study, Raman spectra of nearly all the impact melt samples exhibiting low wave number spectral region (15-1500 cm\(^{-1}\)), corresponding to vibrations of the silicate network contrarily hydrous silicate glasses also show high wave number region (3100-3750 cm\(^{-1}\)), which relates to OH stretching vibrations of H\(_2\)O molecules and OH groups (Gucsik et al 2004). Raman spectra of impact melt shows two broad spectral regions the low wavelength region (LW) ranges from (250-700 cm\(^{-1}\)) originate from stretching and some of the bending vibrations in silicon-oxygen linkage (Si-O) and the region of higher wavelength (800-1200 cm\(^{-1}\)) associated with stretching vibrations of inter silicon-oxygen (Si-O) linkages within tetrahedral silicate units (SiO\(_4\) tetrahedron) (McMillan 1984; Baert 2012). Raman spectral patterns of nearly all the investigated impact melt samples are characterized by four well-resolved peaks at 642, 665,744 and 824 cm\(^{-1}\) usually attributed due to the Si-O bending modes and stretching vibrations of tetrahedral silicate units respectively shown in the Fig. 10.1 (i-vi). Among them most prominent and sharp peak of highest intensity observed at 824 cm\(^{-1}\) attributed due to Si-O stretching vibrations signify plagioclase crystals that becomes optically isotropic due to high shock pressure with broader emissions centered near 491 and 525 cm\(^{-1}\)corresponds to maskelynite (Fig. 10.1, iii). While Raman peaks of relatively low intensities such as doublet with narrow peaks at 640 and 672 cm\(^{-1}\), 738 and 762 cm\(^{-1}\) and minor peak at 394 cm\(^{-1}\)signifies the presence crystalline pyroxene dominantly augite results from coupled symmetric and asymmetric bending vibrations of Si-O\(_b\)-Si (O: bridging atom of oxygen) that links the silica tetrahedra in the pyroxene chain and narrow peaks at 395 cm\(^{-1}\) may result from the bending and stretching modes Mg-O octahedron metal-oxygen (Huang et al 2000). In general, the bands in the region of 700-400 cm\(^{-1}\) have been related with the Si-O-Si linkages of the structure. Beyond 800 cm\(^{-1}\)the development of
a high peak in the $825\text{cm}^{-1}$ region suggests increased polymerization due to the formation of new Si-O bonds. In addition, minor peak to broad shoulder observed at $915\text{cm}^{-1}$ (Fig. 10.1, i-iii) indicates structural disorder occurred in the crystalline structure of pyroxene probably due to shock melting. In addition, weaker peaks observed at $1114$ and $1188\text{cm}^{-1}$ related to the vibrational stretching modes $\text{Si-O}_{nb}$ ($\text{O}$: nonbridging atom of oxygen) in $\text{SiO}_4$ tetrahedra has been attributed by abundant of plagioclase microlites or embryonic crystals within the glassy matrix. Earlier, it has been reported that most of the weak peaks are generally attributed to the $\text{SiO}_4$ tetrahedron vibrations, which shows strong polymeric character with the molten silicates and has relatively high vibrational and structural entity (Colomban et al 2006). However, at places peak broadening and shifting of band occur towards lower frequency with peak broadening that perhaps indicates a disturbed state of crystalline structure due to the structural disorder (phase conversion) has been seen (Fig. 10.1, iv) (Velde et al 1989). In addition, nearly all the studied melt samples shows an intense band with the appearance of broader humps in $\sim400-600\text{cm}^{-1}$ region centered at $421, 525$ and $575\text{cm}^{-1}$ respectively in Fig. 10.1, i) shows conversion of crystalline plagioclase to amorphous state that is maskelynite produced due to a stretch-bend mixed vibration across $\text{Si-O-Si}$ bridging bonds suggesting that the impact glasses are quenched from the impact melt. However, the intensity of $400-600\text{cm}^{-1}$ band varies with degree of polymerization of the network and with Si-O-Si bridging bond angle as seen in case of synthetic and natural glass. It is evident from the (Fig. 10.1, iv) that rather than sharp peak, broadening and shifting of band occur towards lower frequency at $764\text{cm}^{-1}$ due to the structural disorder (phase conversion). The structural deformation of the crystalline phase has been revealed by the broader band-widths at $764\text{cm}^{-1}$ showing similarity with the Raman spectra of shocked anorthite obtained from the core of a plagioclase grain the lunar meteorite. Earlier studies have reported the progressive flattening and subsequent “disappearance” of peaks with increasing pressure due to an increased luminescent background in experimentally shocked (diaplectic glass) single plagioclase grains (Heymann and Horz 1990). However, the Raman spectra impact melt sample LM-12 (Fig. 10.1, vi) is slightly differ from rest of the samples display multiple narrow peaks of very low intensities at $395$ and $575,750$ and $820\text{cm}^{-1}$ intermixed with broader hump contributed by the embryonic crystal or primary quenched crystals/minute microlites dominantly of plagioclase and
pyroxenes formed due to rapid cooling/ quenching of impact melts as revealed in the petrographic studies of impact melt.

In contrast to Lonar impact melt, the Raman spectra of impact spherules are featureless without characteristic discernible peaks showing a broad hump between ~400 and 800 \text{cm}^{-1} wave numbers (Fig. 10.2, i - iv). Most of the spherules of present study are characterized with smooth and symmetric bell shaped hump centered at 786\text{cm}^{-1} (Fig. 10.2, i) indicating that all the preexisting crystalline phases of the target basalt undergone complete amorphization and converted into glass formed under extremely high temperature and pressure while narrow hump seen at 538\text{cm}^{-1} (Fig. 10.2, i) corresponds to the spectra of shock melted plagioclase that has been completely amorphised to glass. In addition, some of the spherules generally exhibit two broad bands in the region (450-650\text{cm}^{-1}) centered at 550 and 558\text{cm}^{-1} respectively (Fig. 10.2, iii - iv) attribute due to the completely amorphised plagioclase grains into glass and region 650-850\text{cm}^{-1} centered at 737 and 748\text{cm}^{-1} respectively indicates amorphization of pyroxene, with characteristic peaks in the 600 and 800\text{cm}^{-1} region corresponding to bending and stretching vibrations of the silicate network. It has been observed that with increasing glassy state the impact melt glass Raman spectral signature displays develops a broader band in the 500-800 \text{cm}^{-1} region with a sharp drop in intensity.
Fig. 10.1 (i-vi) Raman spectra of impact melt of the present study showing well resolved peaks at 642, 665, 744 and 824 cm$^{-1}$ usually attributed due to the Si-O bending modes and stretching vibrations of tetrahedral silicate units respectively. In addition intense band with the appearance of broader humps in ~400-600 cm$^{-1}$ region centred at 421, 525 and 575 cm$^{-1}$ shows conversion of crystalline plagioclase to maskelynite amorphous state. As glassy state increases the impact melt glass develops a broader band in the 500-800 cm$^{-1}$ regions with a sharp drop in intensity. Beyond 800 cm$^{-1}$ the development of a high peak in the 825 cm$^{-1}$ region suggests increased polymerization due to the formation of new Si-O bonds.
Fig. 10.2 (i-iv) Raman spectra of spherules of the present study displaying symmetric bell shaped smooth bell shaped glassy hump in between 450-850 cm\(^{-1}\) suggesting typical glassy nature. Note the Raman spectra (iii) and (iv) showing two broad attribute due to the amorphised state of different mineral inclusions (plagioclase and pyroxene).