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High pressure Raman scattering in $Pb_5Ge_3O_{11}$

R K SONI and K P JAIN
Laser Technology Research Programme, Indian Institute of Technology, New Delhi 110016, India

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Abstract. The pressure dependence of various phonon modes has been investigated through the ferro-paraelectric phase transition. Most mode frequencies harden before levelling off above the phase transition. Mode Grüneisen parameters are estimated from the pressure dependence of phonon frequencies.

Keywords. Raman scattering; high-pressure; ferroelectric; lead germanate.

PACS Nos 78·30; 63·20; 62·5

1. Introduction

Lead germanate ($Pb_5Ge_3O_{11}$) is ferroelectric at room temperature and has the trigonal space group P_3. The unit cell of this material consists of alternating layers of GeO_4-tetrahedra and Ge_2O_7-double tetrahedra. At 450 K it exhibits a structural phase transition to a nonpolar paraelectric phase with hexagonal symmetry P_6. This phase transition has been studied by inelastic light scattering (Burns and Scott 1972; Hosen *et al* 1979; Muller-Lierheim *et al* 1977; Ryan and Hisano 1973).

The vibrational spectrum of $Pb_5Ge_3O_{11}$ can be described by the internal modes of the subunits and the external modes of the crystal. Internal modes are further divided into those which correspond to GeO_4-tetrahedra and those which correspond to Ge_2O_7-double tetrahedra. The external modes, on the other hand, are divided into large number of modes belonging to A-species and degenerate E-modes at Γ-point. The zone-centre optical phonons, both above and below the transition temperature, T_c have been investigated by Raman spectroscopy where considerable interest has been centred on the low-frequency soft mode which shows complicated temperature dependence (Muller-Lierhein *et al* 1977).

Raman measurements of the soft mode have also been made under hydrostatic pressure at temperature below the transition point (Suski *et al* 1979), and it was established that the pressure dependence of the soft mode frequency is similar to the temperature dependence.

In this paper we have investigated the effect of hydrostatic pressure on $Pb_5Ge_3O_{11}$ to ascertain the pressure dependence of the various phonon mode across the ferro-to-para phase transition. The effect of pressure on T_c, reveals that this transition would occur near 23 kbar at room temperature. We have also obtained the mode Grüneisen parameters from our experimental data.

2. Experimental procedure and results

The Raman spectra were recorded using a Jobin-Yvon double monochromator fitted with concave holographic gratings. A cooled photomultiplier tube with a conventional photon counting system was used to detect the Raman signal. Hydrostatic pressure was generated in a diamond anvil cell. Each anvil is a brilliant cut gem quality diamond of flat 0·6 mm^2 area. The anvils are used in gasketed configuration. The extra hard steel gasket allows the sample to be encapsulated in a pressure-transmitting fluid, thus providing truly hydrostatic condition. The sample is confined in a small gasket hole and surrounded by 4:1 mixture of methanol:ethanol. Pressure in the diamond cell was measured by using well-known ruby fluorescence technique. Strong fluorescence line at 6942 Å (R_1-line) of ruby crystal, which was also placed in the cell along with the sample, was recorded and the pressure inside the diamond cell was deduced from its known pressure dependence ($-0{\cdot}75\ cm^{-1}$/k bar) (Piermarini and Block 1975; Barnett *et al* 1973).

Figure 1 shows the Raman spectrum of a sample of $Pb_5Ge_3O_{11}$ at atmospheric pressure. This spectrum has already been reported in the literature and the vibrational modes have been identified, as listed in table 1. Our results are in good agreement with the published results. The vibrational modes below 50 cm^{-1} were not recorded due to strong elastic scattering.

Figure 2 displays the pressure variation of low-frequency portion (50–200 cm^{-1}) of the Raman spectrum of $Pb_5Ge_3O_{11}$. All four Raman modes (labelled M, N, N′ and O) show increase in their frequency with increasing pressure and have almost identical

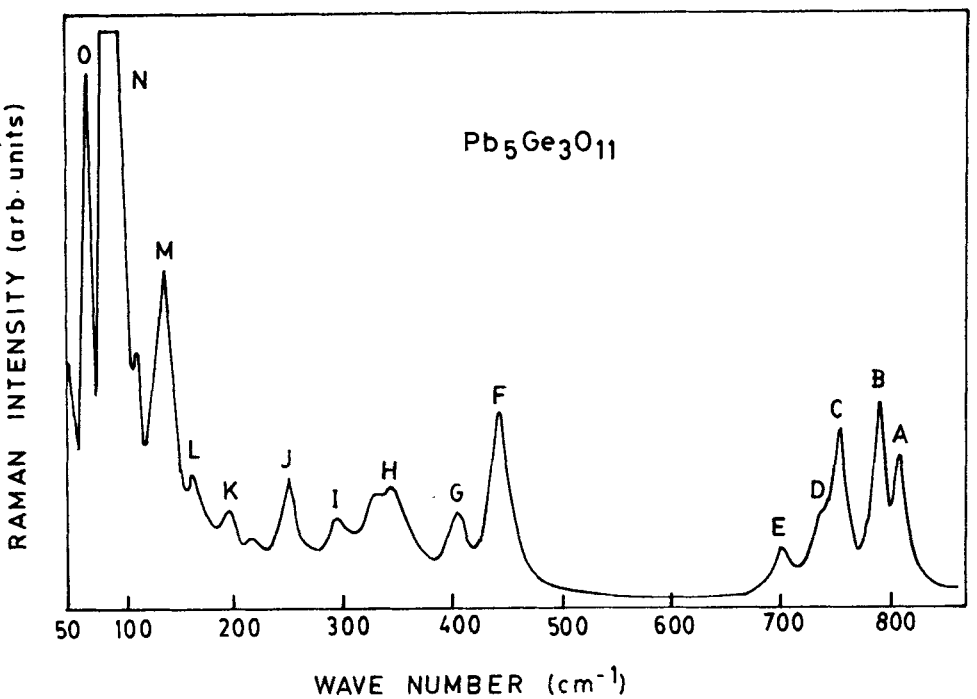

Figure 1. Unanalyzed Raman spectrum of $Pb_5Ge_3O_{11}$ taken with 4880 Å laser line at ambient pressure and temperature.

Table 1. Frequency and Grüneisen parameter of Raman mode in $Pb_5Ge_3O_{11}$.

Raman Mode	Frequency (in cm^{-1}) Pressure (in kbar) 1	13	20	30	42	46	Grüneisen* parameter
A	806	—	—	—	—	—	—
B	790	798	800	804	810	810	0·251
C	750	760	770	770	774	775	0·526
D	732	—	—	760	766	—	—
E	700	710	724	730	740	742	0·674
F	440	450	454	458	460	460	0·626
G	409	410	412	418	420	—	0·142
H	350	—	—	—	—	—	—
I	300	—	308	308	310	—	0·52
J	252	258	264	—	—	—	0·93
K	200	—	—	—	—	—	—
L	164	—	—	—	—	—	—
M	140	144	150	150	150	152	1·37
N	92	96	100	98	100	100	1·26
N′	82	87	90	91	93	93	1·86
O	70	74	76	74	76	76	1·65

* Mode Grüneisen parameters are calculated for low-pressure phase upto 20 k bar (below transition pressure $P_c = 23$ k bar).

behaviour. Their frequency increases upto 20 kbar, decreases slightly at 30 kbar and then increases again above it. This break-in pressure dependence is probably due to ferro-to-paraelectric phase transition around 23 kbar. It should be mentioned that low frequency 32 cm^{-1} phonon becomes soft near ferro-to-para phase transition. This phase transition occurs at temperature $T_c = 450$ K at atmospheric pressure and is a pressure dependent quantity,

$$dT_c/dp = -6{\cdot}7\ K/\text{kbar},$$

where K is the compressibility ($-2{\cdot}5 \times 10^{-3}$ kbar^{-1}). Therefore at room temperature, the pressure-induced phase transition should be around 23 kbar.

The pressure dependence of the high-frequency part of the spectrum (200–850 cm^{-1}) is shown in figure 3. Here again, modes labelled A to J harden with increasing pressure. Their frequencies show smooth increase upto 20 kbar and beyond that there is no great pressure dependence, except for the far-high-frequency modes (labelled A to E) where pressure variation of the frequency is still large. This is as expected, since the high-frequency vibration involve the GeO_4 tetrahedra, which are unaffected by the phase transition.

In table 1, mode Grüneisen parameters for all the modes are listed, this parameter is defined as

$$\gamma = \frac{1}{K}\frac{d\ln\omega_i}{dp},$$

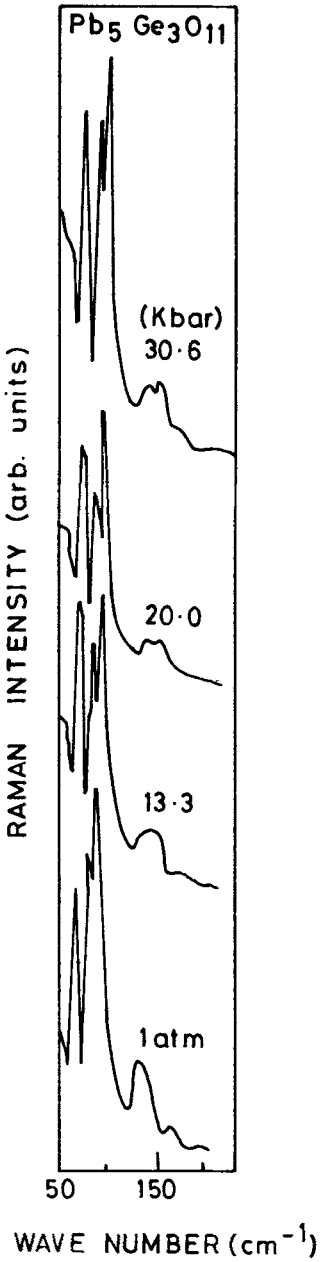

Figure 2. Pressure dependence of low-frequency part of the Raman spectrum of $Pb_5Ge_3O_{11}$ up to 30 kbar. Above this, no pressure dependence was observed and therefore not included in the figure.

where compressibility $K(-2{\cdot}5 \times 10^{-3}\,\text{kbar}^{-1})$ was obtained from elastic constant data given in the literature (Barsch *et al* 1975; Yamada *et al* 1972).

Figure 4 summarizes pressure variation of mode-frequency of all the observed modes in $Pb_5Ge_3O_{11}$.

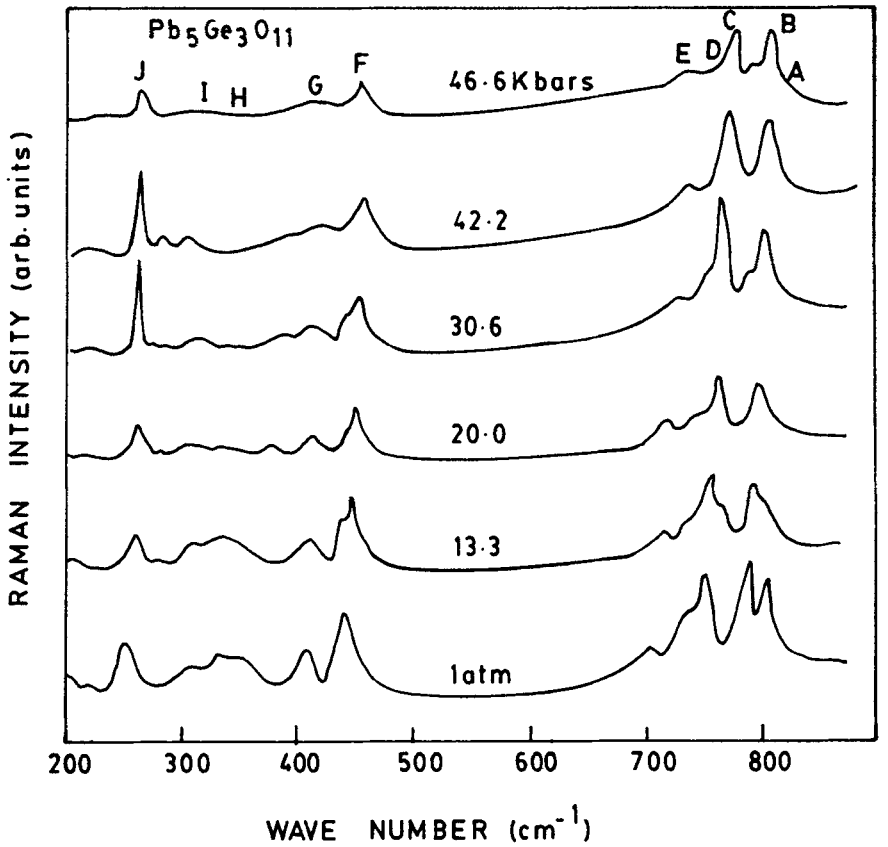

Figure 3. Pressure dependence of the high-frequency part of the Raman spectrum of $Pb_5Ge_3O_{11}$.

3. Concluding remarks

We have investigated the pressure coefficients of various phonon modes in $Pb_5Ge_3O_{11}$ and find evidence for the ferro-to-para electric phase transition near 23 kbar at room temperature. The Grüneisen parameters for various modes were also determined from the pressure dependence of the modes. Unfortunately we could not study the softening of the 32 cm^{-1} phonon upto the ferro-to-para transition due to strong elastic light scattering, and this will be reported in a future publication.

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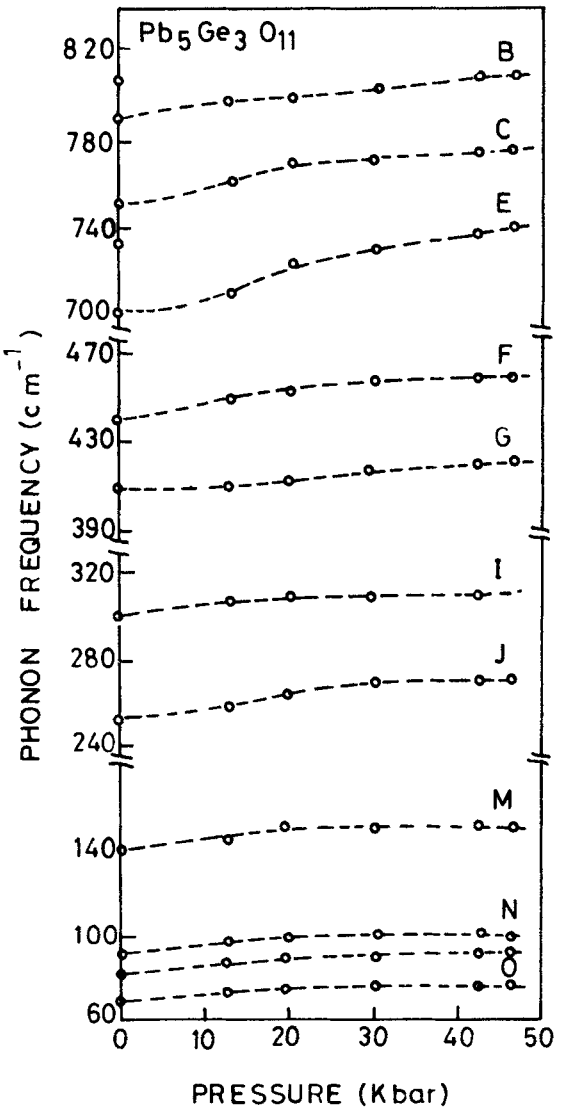

Figure 4. Variation of phonon frequency with pressure for all Raman-active phonons observed in the frequency range (50–850 cm^{-1}).

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