

Spectroscopic study of β -Ni(OH)₂ under pressure

CHITRA MURLI, V SUGANDHI*, NANDINI GARG,
SURINDER M SHARMA and S K SIKKA

High Pressure Physics Division; *Spectroscopy Division, Bhabha Atomic Research Centre,
Mumbai 400 085, India

Email: hppd@magnum.barct1.ernet.in

MS received 4 August 1997

Abstract. Infrared absorption and Raman study of β -Ni(OH)₂ has been carried out up to 25 GPa and 33 GPa, respectively. The frequency of A_{2u} internal antisymmetric stretching O–H mode decreases linearly with pressure at a rate of $-0.7\text{ cm}^{-1}/\text{GPa}$. The FWHM of this mode increases continuously with pressure and reaches a value of $\sim 120\text{ cm}^{-1}$ around 25 GPa. There was no discernible change observed in the frequency and width of the symmetric stretching A_{1g} O–H Raman mode up to 33 GPa. The constancy of the Raman mode is taken as a signature of the repulsion produced by H–H contacts in this material under pressure. Lack of any discontinuity in these modes suggests that there is no phase transition in this material in the measured pressure range.

Keywords. β -Ni(OH)₂; phase transition; infrared absorption; Raman study; high pressure.

PACS Nos 78.30; 62.50

1. Introduction

High pressure study of mineral dihydroxides $M(\text{OH})_2$ (where $M = \text{Mg, Ca, Co, Ni, etc.}$) is of importance for understanding the nature of hydrous minerals under compression in the earth's interior. These hydroxides crystallize in trigonal CdI_2 structure with space group $P\bar{3}m1$ [1]. β -Ni(OH)₂ belongs to this family of compounds. It is widely used in nickel batteries because of the unusually high level of activity of hydrogen atoms in this material. It is therefore of interest to understand the high pressure behaviour of hydrogen sublattice in this material. As hydrogen atoms are insensitive to x-ray diffraction techniques, neutron diffraction study of hydroxide compounds is an effective tool for understanding the behaviour of hydrogen sublattice of these compounds under different thermodynamic conditions. However, a simpler technique is the vibrational spectroscopic technique. In this method the reduction in the frequency of O–H mode with pressure is correlated with the enhancement of hydrogen bonding under pressure. This technique also throws light on the pressure induced phase transitions. High pressure studies reported in recent years have revealed pressure induced hydrogen disordering of $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$. In polycrystalline samples of $\text{Ca}(\text{OH})_2$ pressure induced amorphization is reported around 12 GPa [2] whereas the single crystal samples of this compound exhibit a crystal–crystal transition around 6 GPa followed by amorphization

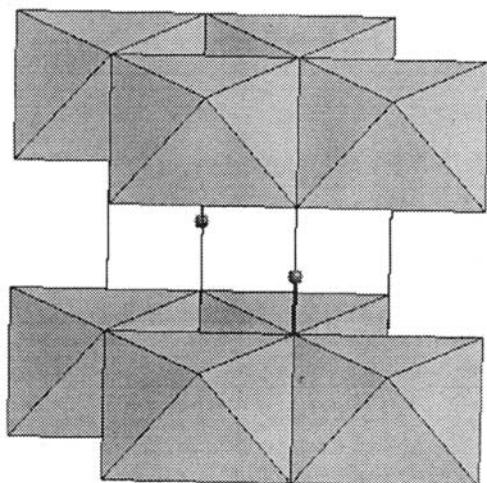


Figure 1. The crystal structure of β -Ni(OH)₂. Hydrogen atoms are shown along with the Ni–O octahedra with the corner positions occupied by oxygen atoms and nickel atoms in the centre. Nickel and oxygen atoms are not shown for the purpose of clarity.

beyond 20 GPa [3]. Mg(OH)₂ is reported to be stable up to 80 GPa with no signature of amorphization [4]. However, disordering of hydrogen sites involving shift of H positions away from the three fold axis in the $P\bar{3}m1$ structure around 1 GPa has been detected by spectroscopic studies of this compound [5]. This is confirmed by a neutron diffraction study which gives evidence of a hydrogen disordering around 5–10 GPa [6]. In Co(OH)₂ infrared and Raman spectroscopy under pressure document that the hydrogen sublattice loses long range order between 7 to 11 GPa [7]. However, x-ray diffraction shows that Co–O sublattice is ordered up to 30 GPa. In the $P\bar{3}m1$ structure, there are two allowed internal hydroxyl stretching modes, the Raman active A_{1g} symmetric stretching mode where hydroxyl ions vibrate in phase and the A_{2u} antisymmetric stretching infrared mode where the hydroxyl ions vibrate out of phase. The A_{2u} antisymmetric stretching internal OH mode in β -Ni(OH)₂ is observed at 3645 cm^{-1} which is higher than the value of $3570 \pm 10\text{ cm}^{-1}$ for an unperturbed OH⁻ ion [8]. The larger value is indicative of the repulsive effect of the lattice due to short H–H contact of 1.92 \AA [12] at 0.1 MPa between layers of Ni–O octahedra (figure 1) and of weak hydrogen bonding in the system. To understand the high pressure behaviour of this compound we have carried out infrared absorption and Raman spectroscopic studies.

2. Experimental

High quality pure polycrystalline sample of β -Ni(OH)₂ was obtained from Aldrich. The cell constants determined at 0.1 MPa are $3.11 \pm 0.02\text{ \AA}$ and $c = 4.59 \pm 0.02\text{ \AA}$ [9] which are in good agreement with the values ($a = 3.12\text{ \AA}$ and $c = 4.60\text{ \AA}$) reported earlier [10]. High pressure experiments were carried out using Syassen Holzapfel type of diamond anvil cell with diamonds of culet size $500\text{ }\mu$. The sample was filled in a $150\text{ }\mu \sim 200\text{ }\mu$

Spectroscopic study of β -Ni(OH)₂ under pressure

hole of a steel gasket preindented to a thickness of 80 μ . Ruby fluorescence technique was used for pressure calibration. CsI was used as a pressure transmitting medium. IR absorption study was carried out using BOMEM DA3.003 FTIR spectrometer with a globar source and InSb detector. The resolution setting was 2 cm^{-1} in the spectral region 3400–3800 cm^{-1} of our study. The IR absorption data were analysed using a

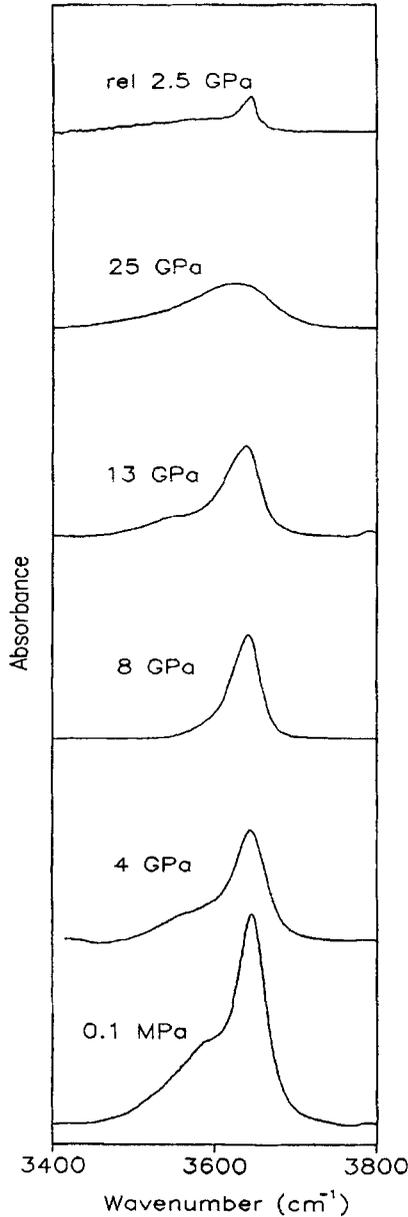


Figure 2. A_{2u} internal antisymmetric stretching infrared hydroxyl mode of β -Ni(OH)₂ at different pressures.

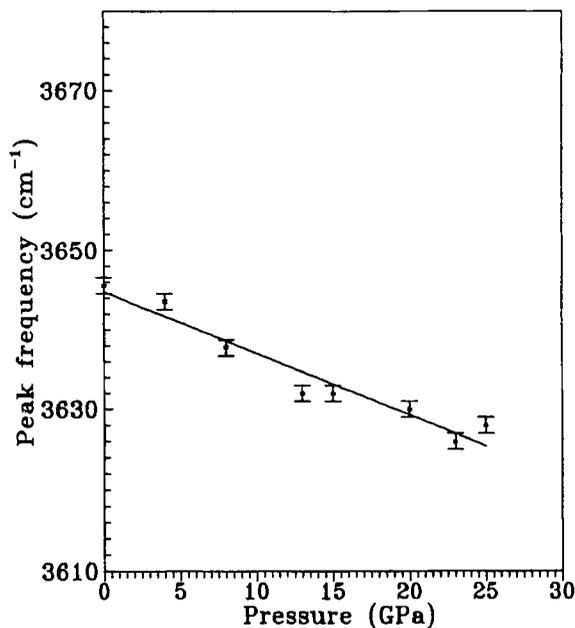


Figure 3. The change in frequency of A_{2u} mode of β-Ni(OH)₂ with pressure.

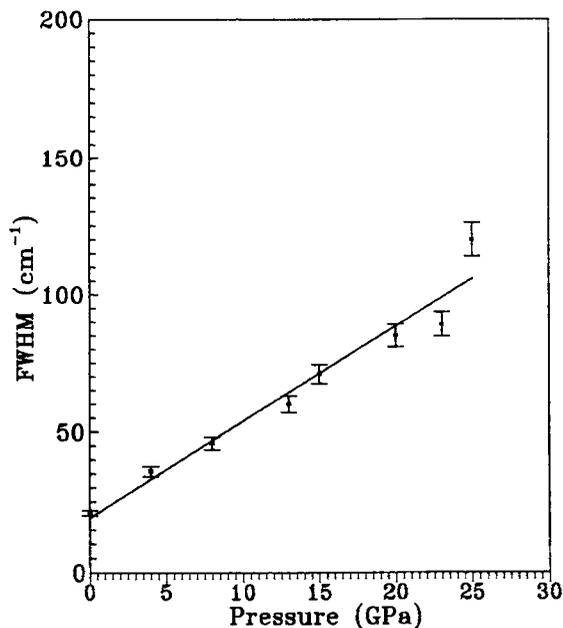


Figure 4. Variation of FWHM of A_{2u} mode of β-Ni(OH)₂ with pressure.

spectracalc software package. Raman study was carried out using a single stage double pass 500 mm Chromex scanning monochromator with a holographic supernotch filter for an Ar-ion excitation line 514.5 nm. The data was recorded using a photomultiplier

Spectroscopic study of β -Ni(OH)₂ under pressure

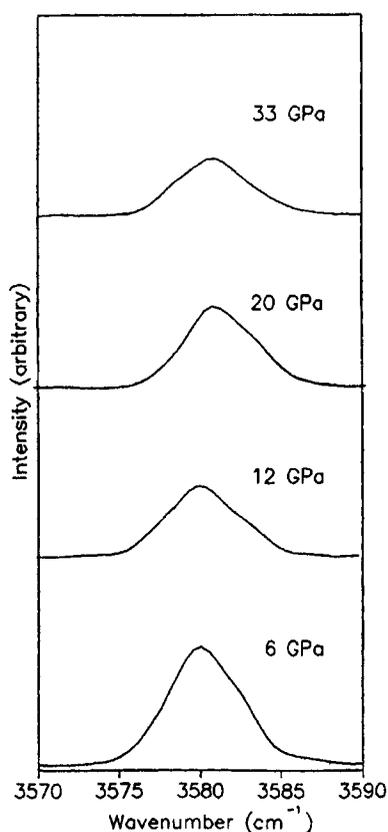


Figure 5. A_{1g} symmetric stretching internal Raman hydroxyl mode of β -Ni(OH)₂ at different pressures.

tube and a computer controlled data acquisition system. The A_{1g} Raman mode under ambient conditions was found to be 3580 cm^{-1} which is consistent with the value reported earlier [11].

3. Results and discussion

The IR absorption spectrum of β -Ni(OH)₂ could be followed up in a diamond anvil cell up to 25 GPa in the region 3400 to 3800 cm^{-1} . The IR absorption spectrum under ambient conditions was recorded and the frequency of the A_{2u} mode was determined to be 3645 cm^{-1} which is in good agreement with the values reported earlier [12]. Figure 2 shows this mode at different pressures. The asymmetry on the lower frequency side is due to particle size effect [12]. The frequency of this mode decreases linearly with pressure (figure 3) at a rate of $-0.7\text{ cm}^{-1}/\text{GPa}$. This is unlike Co(OH)_2 which shows a discontinuity around 11 GPa. The FWHM of this mode increases continuously with pressure and reaches a value of 120 cm^{-1} around 25 GPa (figure 4). This behaviour is similar to that of Mg(OH)_2 . On release this mode retrieves its initial frequency indicating the reversibility of the high pressure behaviour.

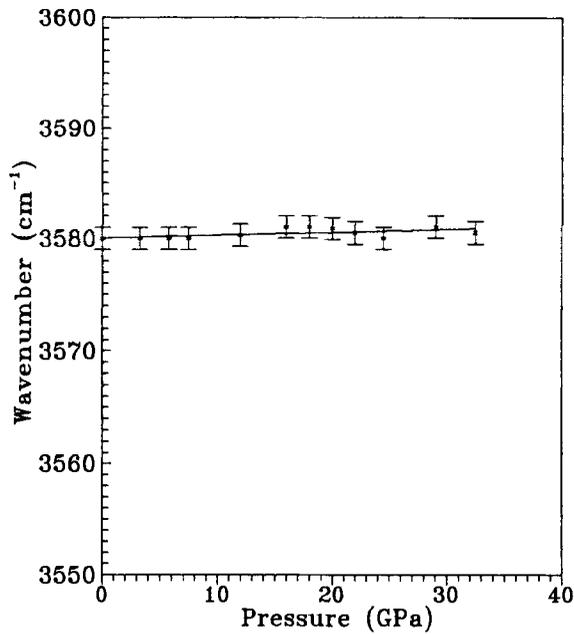


Figure 6. Frequency of A_{1g} Raman mode versus pressure for β -Ni(OH)₂.

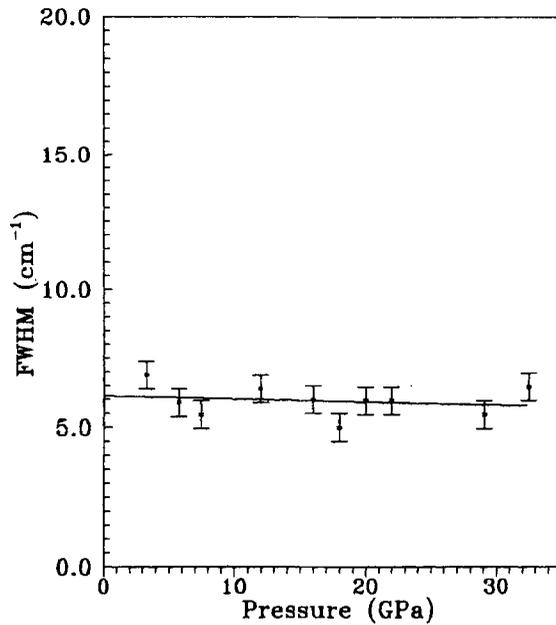


Figure 7. FWHM of A_{1g} mode of β -Ni(OH)₂ versus pressure.

The A_{1g} Raman mode observed at 3580 cm^{-1} under ambient conditions was recorded up to a pressure of 33 GPa (figure 5). The frequency as well as FWHM of this mode was found to remain nearly constant in this pressure range (figures 6 and 7) in contrast to

Spectroscopic study of β -Ni(OH)₂ under pressure

Table 1. Comparison of A_{2u} (IR) and A_{1g} (Raman) internal ν_{OH} modes and their pressure derivatives for various compounds. The data are compiled from references [2] and [5] for Mg(OH)₂ and Ca(OH)₂, ref. [7] for Co(OH)₂ and this work for β -Ni(OH)₂.

Material	$\nu_{OH}(\text{cm}^{-1})$		$d\nu_{OH}/dp$ ($\text{cm}^{-1}/\text{GPa}$)	
	IR	Raman	IR	Raman
Mg(OH) ₂	3688	3652	-0.6	-7.68
Ca(OH) ₂	3633	3620	-3.5	-3.68
Co(OH) ₂	3631	3570	~ -2.3	~ -4.00
β -Ni(OH) ₂	3645	3580	-0.7	0.00

the reported disappearance of this mode below 10 GPa in Co(OH)₂ and Ca(OH)₂. Thus the persistence of this mode suggests lack of any signature of a structural change. The negligible change in the frequency of this mode is in contrast to the observations for other hydroxides (table 1). This can be interpreted as a signature of repulsion produced by decreasing H–H contacts under pressure [13, 14]. This observation is also supported by x-ray diffraction studies carried out in our laboratory [9]. The c/a value was found to be almost pressure independent. The material was found to be very less compressible up to a pressure of 33 GPa. The bulk moduli K_0 , K_{0c} and K_{0a} of the sample were determined to be ~221 GPa, 379 GPa and 1391 GPa respectively using Birch–Murnaghan equation of state [9]. These values are the largest compared to the other reported dihydroxide compounds [9] and indicate that this compound is very stiff in this family of compounds.

4. Conclusion

Lack of any discontinuity observed in the frequency and FWHM of IR and Raman hydroxyl modes in β -Ni(OH)₂ suggests that there is no phase transition in this compound up to 33 GPa. The increase in the FWHM of the A_{2u} IR mode is indicative of a slow hydrogen disordering of this compound with pressure. The negligible change in the values of A_{1g} Raman mode is a signature of the repulsion produced by decreasing H–H contacts in this compound under pressure.

References

- [1] H E Petch and H D Megaw, *J. Opt. Soc. Am.* **44**, 733 (1954)
- [2] C Meade and R Jeanloz, *Geophys. Res. Lett.* **17**, 1157 (1990)
- [3] S K Ekbundit, K Leinenweber, J L Yarger, J S Robinson, M Verhelst-Voorhees and G H Wolf, *J. Solid State Chem.* **126**, 300 (1996)
- [4] Y Fei and H K Mao, *J. Geophys. Res.* **98 B7**, 11875 (1993)
- [5] T S Duffy, C Meade, Y Fei, H K Mao and R J Hemley, *Am. Mineral* **80**, 222 (1995)
- [6] M Catti, G Ferraris, S Hull and A Pavese, *Phys. Chem. Miner.* **22**, 200 (1995)
- [7] J H Nguyen, M B Kruger, R Jeanloz, *Phys. Rev. Lett.* **78**, 1936 (1997)
- [8] H D Lutz, W Eckers and H Haeusler, *J. Mol. Struct.* **80**, 221 (1982)
- [9] Nandini Garg, Chitra Murli, Surinder M Sharma and S K Sikka (sent for publication)
- [10] A Szytula, A Murasik and M Balanda, *Phys. Status Solidi* **43**, 125 (1971)

- [11] C Johnston and P R Graves, *App. Spectroscopy* **44**, 105 (1990)
- [12] C Greaves and M A Thomas, *Acta. Cryst.* **B43**, 51 (1986)
- [13] S K Sikka and S M Sharma, *Curr. Sci.* **63**, 317 (1992)
- [14] G N Ramachandran and V Sasisekharan, *Adv. Protein Chem.* **23**, 283 (1968)