



VIBRATIONAL STUDIES OF Na₂SO₄, K₂SO₄, NaHSO₄ AND KHSO₄ CRYSTALS

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ABSTRACT

Sodium sulphate, Potassium sulphate, Sodium hydrogen sulphate and Potassium hydrogen sulphate crystals were grown by aqueous solution method. FTIR and Laser Raman spectra were measured for the crystals. Sulphate group is identified by the frequency assignments.

Keywords: Sodium sulphate, Potassium Sulphate, Sodium hydrogen sulphate, Potassium hydrogen sulphate, FTIR, Laser Raman Spectra

INTRODUCTION

Sodium sulphate crystals are mainly used for manufacture of craft paper, paper board and glass, filters in synthetic detergents, sodium salts, ceramic glass, processing textiles, fibres, dyes, pharmaceuticals, freezing mix, laboratory reagent, food additive, paper pulp, detergents and soaps, plate and window glass. Potassium sulphate crystals are used in the field of analytical chemistry as reagent, medicine(cathartic), gypsum cements, and fertilizer for alum manufacture, glass manufacture and food additive.

Hydrogen sulphate crystals have received more attention because of their use in fertilizer, perfumes and as lab reagent/1/. Sodium hydrogen sulphate crystals are used as flux or decomposing minerals, substitute for sulphuric acid in dyeing, disinfectant manufacture of sodium hydrosulphide, sodium sulphate and soda alumn, liberating CO₂ in carbonic acid baths in thermophores, carbonizing works, manufacture of manganese cements, paper, soap, perfumes, food, industrial cleaners, metal pickling are mainly used for the conservation of wire bees and tartrate into potassium tartrate, ethyl acetate and lab reagents.

EXPERIMENTAL

Good crystals of sulphate (Na₂SO₄,K₂SO₄) and hydrogen sulphate (NaHSO₄, KHSO₄) were obtained by using aqueous solution method in crystal growth technique. Sulphuric acid was added to obtain the hydrogen sulphate crystals. For Na₂SO₄ crystals, sodium sulphate solution was prepared for one molar concentration by dissolving 1.432gms of sodium sulphate powder with 10ml of distilled water. For K₂SO₄ crystals, potassium sulphate solution was prepared for one molar concentration by dissolving 1.743 gms of potassium sulphate powder with 10 ml of distilled water. For the growth of hydrogen sulphate (NaHSO₄ and KHSO₄) crystals, sulphuric acid prepared for one molar concentration (0.98ml of sulphuric acid with 10ml of distilled water) was mixed well with the sodium sulphate and potassium sulphate solutions respectively. All the four systems were kept in the wooden box in the undisturbed place. After 7-10 days, it was observed that the formation of good crystals were obtained for Na₂SO₄, K₂SO₄, NaHSO₄, KHSO₄ crystals.

The infrared transmission spectra were recorded in the wavelength range 400 cm⁻¹ - 4000 cm⁻¹ using Perkin Elmer 597 spectrometer. The Raman Spectra were recorded using dilor DZ-24 spectrometer in the frequency range of 200cm⁻¹-4000cm⁻¹

RESULTS AND DISCUSSION

Figures 1-4 represent the FTIR spectrum of the Na₂SO₄, K₂SO₄, NaHSO₄, KHSO₄ crystals. Figures 5-8 represent the Laser Raman spectrum of the Na₂SO₄, K₂SO₄, NaHSO₄, KHSO₄ crystals. Infrared and Raman frequencies of sulphate (Na₂SO₄, K₂SO₄) and hydrogen sulphate (NaHSO₄, KHSO₄) alongwith the assignment are given in the Table 1-4. In the table, symbols denotifying as ν_{as} , ν_{ss} , ν_{sb} , ν_{ab} are asymmetric stretching, symmetric stretching, symmetric bending and asymmetric bending respectively. The peaks observed at 3417.8 cm⁻¹ (Na₂SO₄), 3414.3 cm⁻¹ (K₂SO₄), 3420 cm⁻¹ (NaHSO₄) and 3410 cm⁻¹ (KHSO₄) are due to OH stretching of the HSO₄ groups. The peak at 1285.7 cm⁻¹ (K₂SO₄) 1280 cm⁻¹ (KHSO₄) has been assigned to S-O-H plane bending of HSO₄ group. The bands appeared at 1123 cm⁻¹ (Na₂SO₄) 1172.4 cm⁻¹ (K₂SO₄) and 1120 cm⁻¹ (NaHSO₄) 1170 cm⁻¹ (KHSO₄) are assigned to asymmetric stretching of SO₄ groups. Symmetric stretching of SO₄ groups are appeared at 1100.0 cm⁻¹, 1085.9 cm⁻¹, 1070 cm⁻¹ (K₂SO₄), 1060 cm⁻¹, 1000 cm⁻¹ (KHSO₄). The frequency assignment of KHSO₄ at 1000 cm⁻¹ and 1060 cm⁻¹ is qualitatively agree with the values of Goypran et al./2/. The IR peaks at 1285.7 cm⁻¹ (K₂SO₄) is assigned to S-O-H plane bending of HSO₄ group. The bands appeared below 700 cm⁻¹ are assigned to the symmetric and asymmetric bending of SO₄ groups. Hence we have assigned the frequency 575 cm⁻¹, 477.8 cm⁻¹ (K₂SO₄) 390 cm⁻¹, 380 cm⁻¹ (NaHSO₄) 430 cm⁻¹, 400 cm⁻¹ (KHSO₄) to symmetric bending of the SO₄ groups. The frequency bands observed at 637.7 cm⁻¹, 615.6 cm⁻¹ (Na₂SO₄) 612.8 cm⁻¹ (K₂SO₄) 610 cm⁻¹ (NaHSO₄) 605 cm⁻¹ (KHSO₄) are assigned as asymmetric bending of the SO₄ groups. The peaks observed were assigned to the vibrational modes of the crystals. Raman frequencies of sulphate (Na₂SO₄ and K₂SO₄) and hydrogen sulphate (NaHSO₄ and KHSO₄) alongwith the assignment are given in tables. The peak observed in the frequency range 3132 cm⁻¹ (Na₂SO₄) is assigned to $\nu_1 \nu_3$ H₂O stretching of the molecule. The peak at 1521.3 cm⁻¹ (KHSO₄) is assigned to ν_2 H₂O molecules. The band appeared at 1267.4 cm⁻¹ (K₂SO₄) is attributed to S-O-H plane bending of the HSO₄ group. The peaks observed at 1257.4 cm⁻¹, 1157.9 cm⁻¹ (KHSO₄), 1147.1 cm⁻¹ (Na₂SO₄) 1137.7 cm⁻¹, 1096.8 cm⁻¹ (K₂SO₄) 1099.7 cm⁻¹ (NaHSO₄) were assigned to asymmetric stretching of SO₄ group. The inorganic sulphate ions absorbs strongly at 1125 – 1080 cm⁻¹ due to asymmetric SO₄ stretching. The symmetric stretch is normally forbidden symmetry but may occasionally be seen as a very weak shrap band at 1000 cm⁻¹. This statement agrees with the value of 1015.5 cm⁻¹ (KHSO₄) 989.3 cm⁻¹ (NaHSO₄). Symmetric stretching of SO₄ group is assigned in the frequency range 988.4 cm⁻¹ (Na₂SO₄) 977.7 cm⁻¹, 930.3 cm⁻¹ (K₂SO₄) 989.3 cm⁻¹ (NaHSO₄), 1015.5 cm⁻¹ (KHSO₄). The peak observed at 1015.5 cm⁻¹ (KHSO₄) of our crystal has in confirmation with the Raman spectrum of KHSO₄ by B.Dev et al./3/. in their Infrared and Raman studies of KHSO₄ crystals. The frequency observed at 988.4 cm⁻¹ (Na₂SO₄) is well agreed with the value obtained by Richard L.Mc Creery /4/. The band appeared at 848.8 cm⁻¹ (KHSO₄) attributed to S-O-H out of bending of HSO₄ group. The peaks observed in the frequency range 713.8 cm⁻¹, 628.8 cm⁻¹, 459.6 cm⁻¹ (Na₂SO₄), 707.1 cm⁻¹, 620.4 cm⁻¹, 523.3 cm⁻¹, 447.9 cm⁻¹ (K₂SO₄), 620.7 cm⁻¹, 467.7 cm⁻¹ (NaHSO₄) 582.0 cm⁻¹, 439.2 cm⁻¹ (KHSO₄) were assigned to the asymmetric bending of SO₄ group. This is in confirmity with the peaks observed for S.Gunasekaran et al. of "characterisation of Triglycine Sulphate (TGS) and Triglycine sulphate phosphate (TGSP) by FTIR and microwave analysis for 615 and 459 for asymmetric bending. Symmetric bending of SO₄ group is observed at the frequency range 314.4 cm⁻¹ (Na₂SO₄), 405.1 cm⁻¹ (KHSO₄)

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Table-1: Vibrational assignments of Na₂ SO₄ crystals

IR cm ⁻¹	Raman cm ⁻¹	Assignments
3417.8 (VW) 2249.8	3132.0	OH stretching of HSO ₄ group
2110.9 1636.8		ν ₃ H ₂ O ν ₂ H ₂ O
	1147.1	ν _{as} SO ₄
1123.1	988.4 713.8	ν _{ss} SO ₄
637.7	628.8	
615.6		ν _{ab} SO ₄
	459.6 314.4	ν _{sb} SO ₄ ν _{sb} SO ₄

Table-2: Vibrational assignments of K₂ SO₄ crystals

IR cm ⁻¹	Raman cm ⁻¹	Assignments
3414.3 2924.7 2610.4 2486.7 1627.2 1321.2 1285.7		OH stretching of HSO ₄ group
HSO ₄ group 1226.7 1172.4	1267.4	S-O-H plane bending of
	1137.7	ν _{as} SO ₄
1100.9	1096.8	
1085.9 1070.8		ν _{as} SO ₄
1014.5 1003.8		
	977.7	
946.3 931.6		
	930.3	

887.0		
850.2		
820.6		
735.7		
721.2		
	707.1	
706.8		
664.4		
651.6	620.4	
612.8		$\nu_{ab} \text{SO}_4$
575.0		
	523.3	
477.8		
	448	$\nu_{sb} \text{SO}_4$

Table-3: Vibrational assignments of NaHSO_4 crystals

IR cm^{-1}	Raman cm^{-1}	Assignments
3420		OH stretching of HSO_4 group
2920		
1620		
1120		$\nu_{as} \text{SO}_4$
	1099.7	
	989.3	
	620.7	
610		$\nu_{ab} \text{SO}_4$
	467.7	
390		
380		$\nu_{sb} \text{SO}_4$

Table-4: Vibrational assignments of KHSO_4 crystals

IR cm^{-1}	Raman cm^{-1}	Assignments
3410		OH stretching of HSO_4 group
1630		
	1521.3	
1280		S-O-H plane bending
1170		$\nu_{as} \text{SO}_4$ (asymmetric stretching)
	1157.9	
1060		
	1015.5	$\nu_{ss} \text{SO}_4$
1000		
880		

848	S-O-H out of bending	
840		
605		
515	582	ν_{ab} SO ₄ (asymmetric bending)
450		
430	439.2	
400	405.1	ν_{ab}

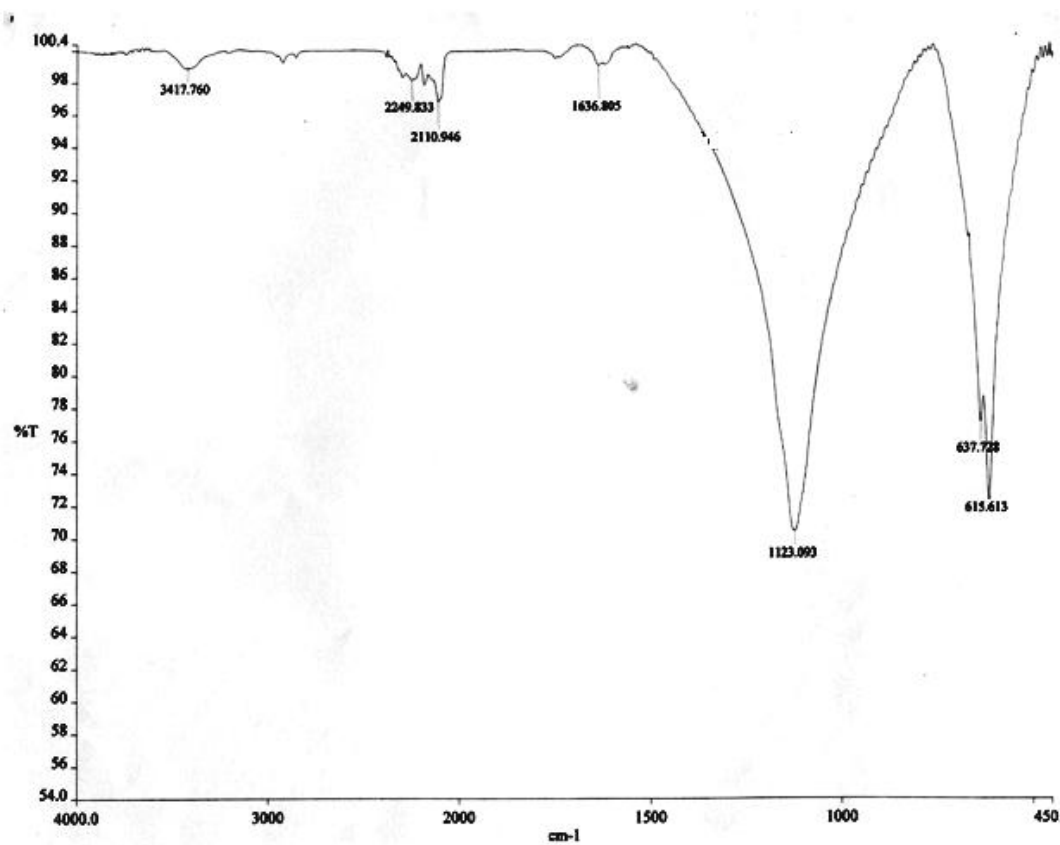


Fig.-1: FTIR spectrum of Na₂SO₄ crystals

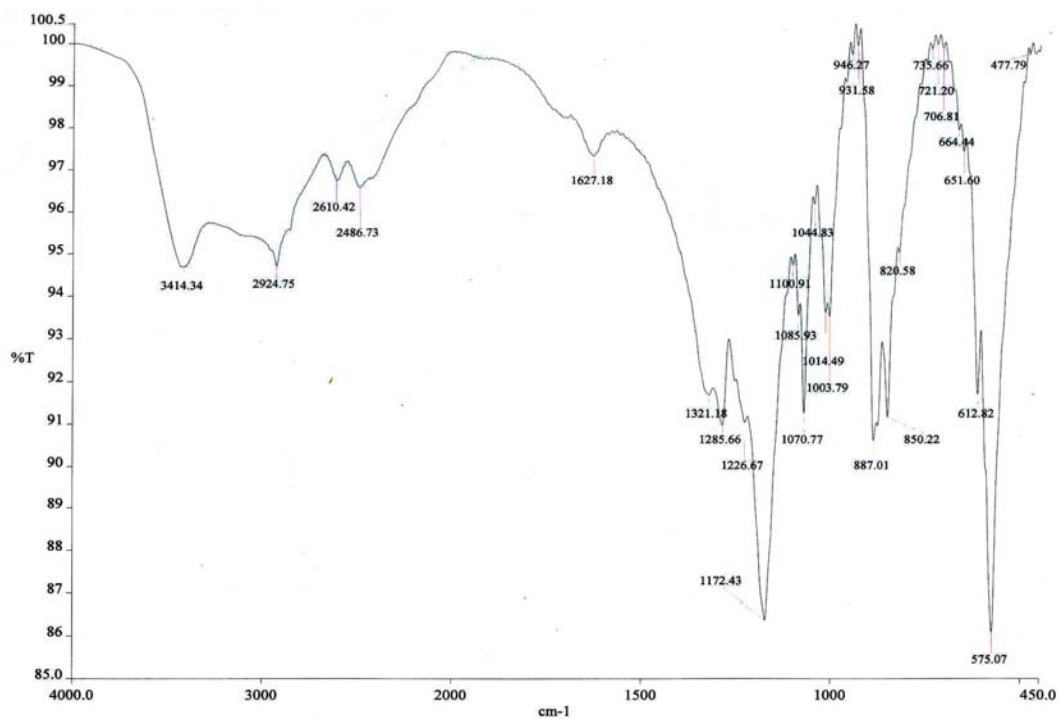


Fig.-2: FTIR spectrum of K₂SO₄ crystals

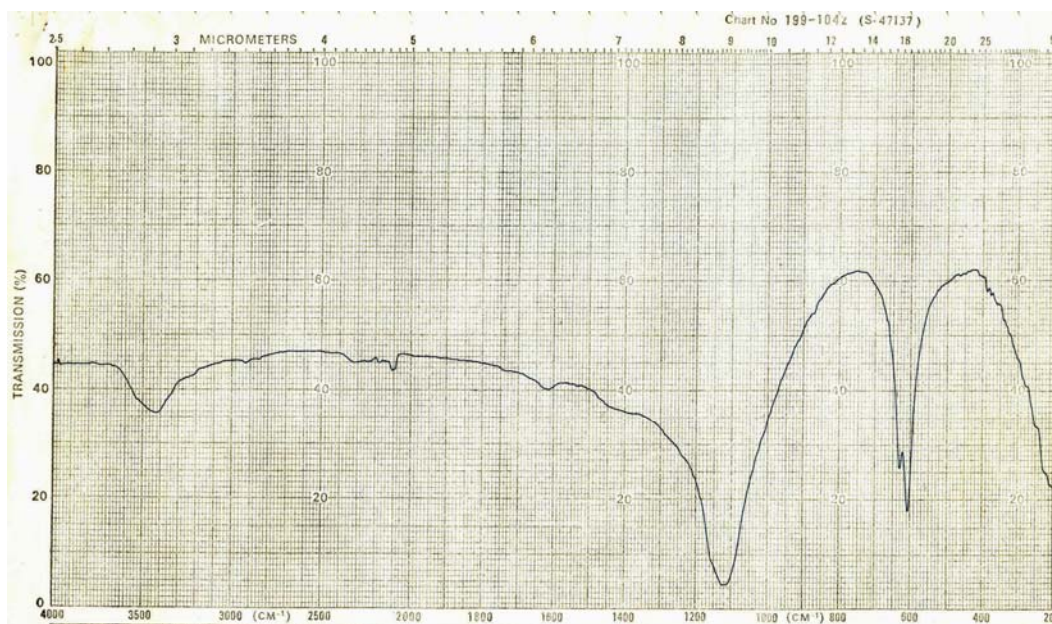


Fig.-3: FTIR spectrum of NaHSO₄ crystals

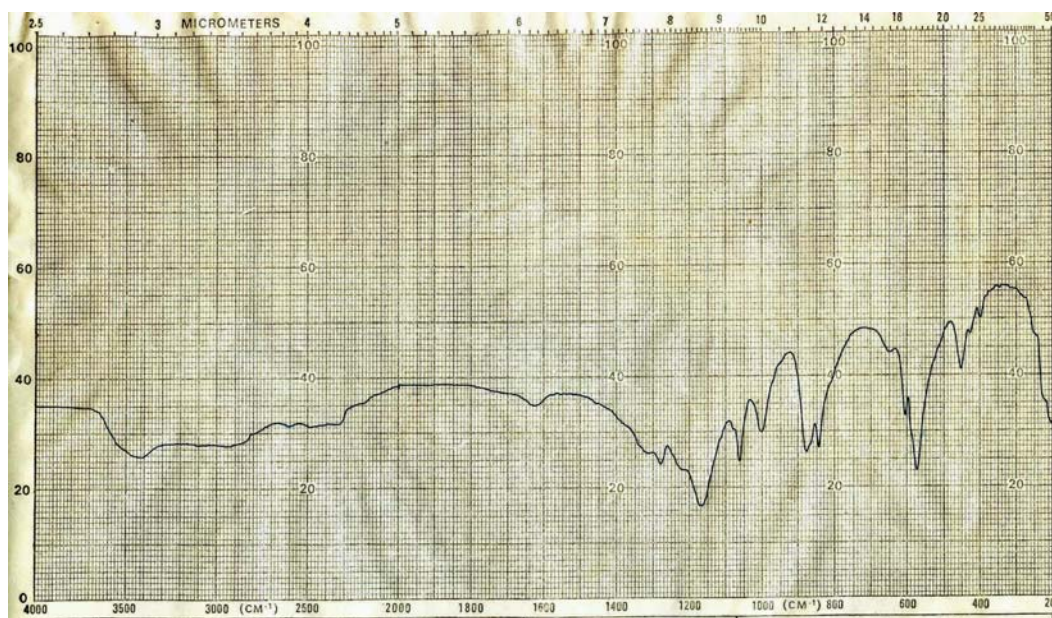


Fig.-4: FTIR spectrum of KHSO₄ crystals

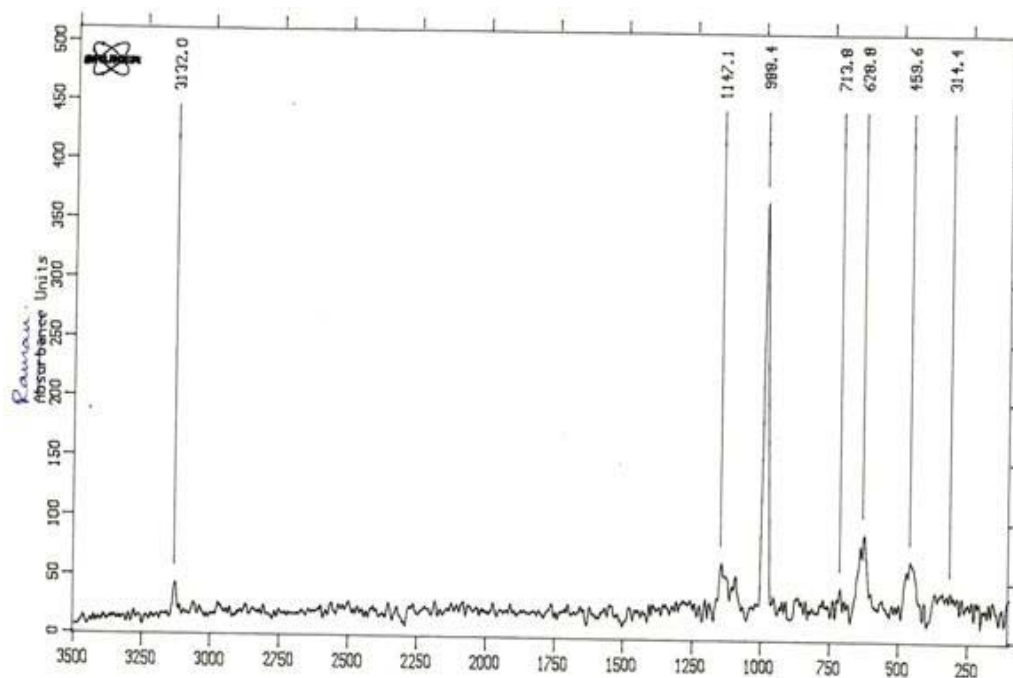


Fig.-5: Laser Raman spectrum of Na₂SO₄ crystals

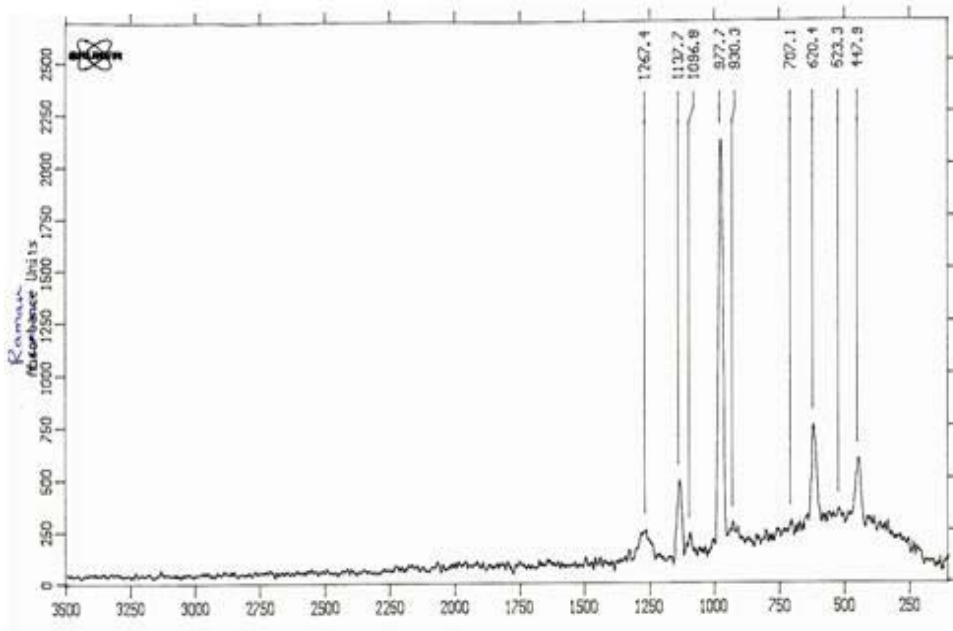


Fig.-6: Laser Raman spectrum of K₂SO₄ crystals

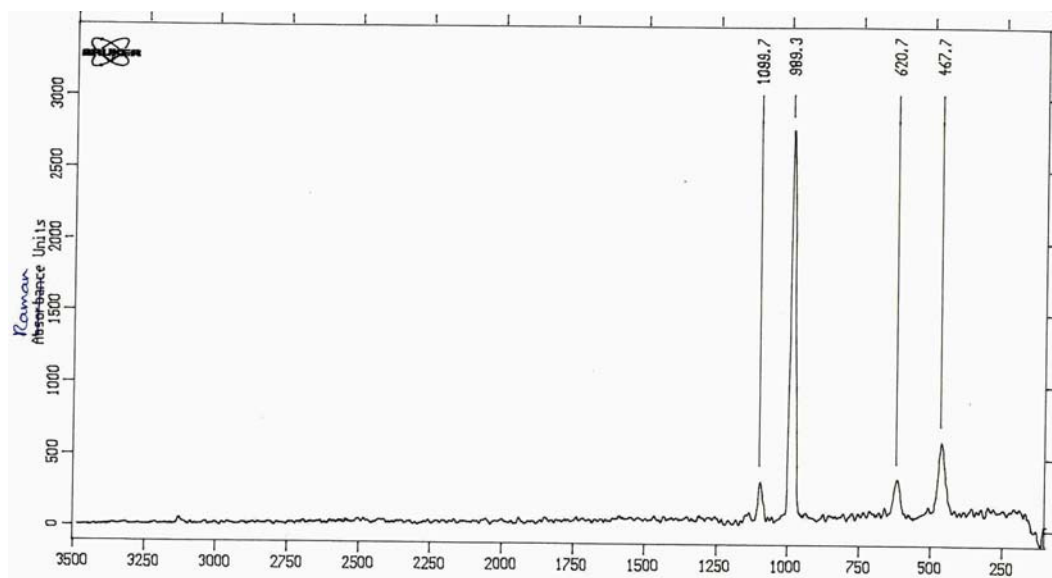


Fig.-7: Laser Raman spectrum of NaHSO₄ crystals

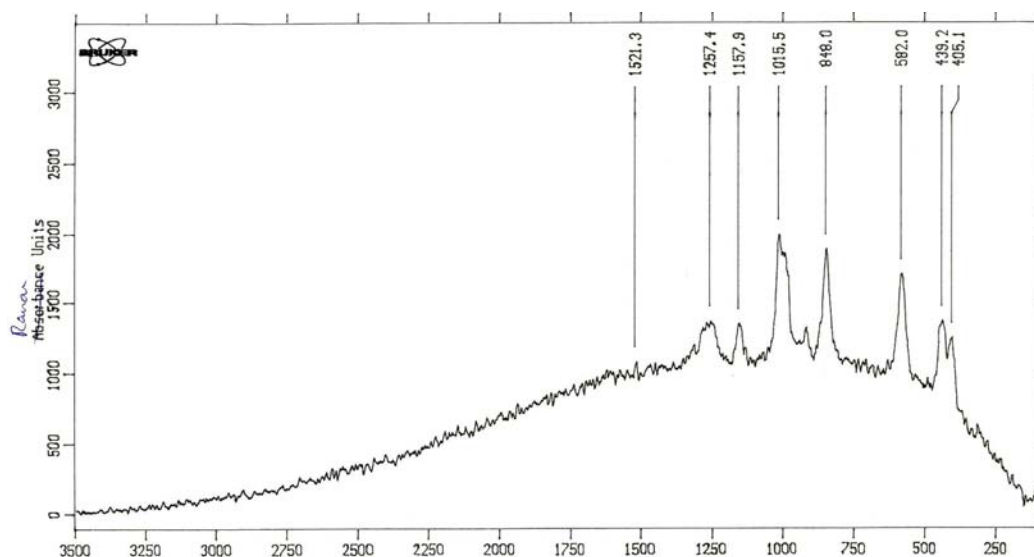


Fig.-8: Laser Raman spectrum of KHSO_4 crystals

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