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VIBRATIONAL STUDIES OF Na_2SO_4, K_2SO_4, $NaHSO_4$ AND $KHSO_4$ 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 dying, disinfectant manufacture of sodium hydrosulphide, sodium sulphate and soda alumn, liberating CO_2 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 (Na_2SO_4,K_2SO_4) and hydrogen sulphate ($NaHSO_4$, $KHSO_4$) were obtained by using aqueous solution method in crystal growth technique. Sulphuric acid was added to obtain the hydrogen sulphate crystals. For Na_2SO_4 crystals, sodium sulphate solution was prepared for one molar concentration by dissolving 1.432gms of sodium sulphate powder with 10ml of distilled water. For K_2SO_4 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 ($NaHSO_4$ and $KHSO_4$) 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 Na_2SO_4, K_2SO_4, $NaHSO_4$, $KHSO_4$ 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 Na_2SO_4, K_2SO_4, $NaHSO_4$, $KHSO_4$ crystals. Figures 5-8 represent the Laser Raman spectrum of the Na_2SO_4, K_2SO_4, $NaHSO_4$, $KHSO_4$ crystals.

Infrared and Raman frequencies of sulphate (Na_2SO_4, K_2SO_4) and hydrogen sulphate ($NaHSO_4$, $KHSO_4$) 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} (Na_2SO_4), 3414.3 cm^{-1}(K_2SO_4) 3420 cm^{-1} ($NaHSO_4$) and 3410 cm^{-1}($KHSO_4$) are due to OH stretching of the HSO_4 groups. The peak at 1285.7 cm^{-1} (K_2SO_4) 1280cm^{-1} ($KHSO_4$) has been assigned to S-O-H plane bending of HSO_4 group. The bands appeared at 1123 cm^{-1}(Na_2SO_4) 1172.4 cm^{-1}(K_2SO_4) and 1120 cm^{-1} ($NaHSO_4$) 1170 cm^{-1} ($KHSO_4$) are assigned to asymmetric stretching of SO_4 groups. Symmetric stretching of SO_4 groups are appeared at 1100.0cm^{-1}, 1085.9cm^{-1}, 1070 cm^{-1} (K_2SO_4) , 1060 cm^{-1} , 1000 cm^{-1} ($KHSO_4$). The frequency assignment of $KHSO_4$ at 1000 cm^{-1} and 1060 cm^{-1} is qualitatively agree with the values of Goyprian et al./2/ . The IR peaks at 1285.7 cm^{-1} (K_2SO_4) is assigned to S-O-H plane bending of HSO_4 group. The bands appeared below700 cm^{-1} are assigned to the symmetric and asymmetric bending of SO_4 groups. Hence we have assigned the frequency 575 cm^{-1} , 477.8 cm^{-1} (K_2 SO_4) 390 cm^{-1} , 380 cm^{-1} ($NaHSO_4$) 430 cm^{-1}, 400 cm^{-1} ($KHSO_4$) to symmetric bending of the SO_4 groups. The frequency bands observed at 637.7 cm^{-1}, 615.6 cm^{-1} (Na_2SO_4) 612.8 cm^{-1} (K_2SO_4) 610 cm^{-1} ($NaHSO_4$) 605 cm^{-1} ($KHSO_4$) are assigned as asymmetric bending of the SO_4 groups. The peaks observed were assigned to the vibrational modes of the crystals. Raman frequencies of sulphate (Na_2SO_4 and K_2SO_4) and hydrogen sulphate ($NaHSO_4$ and $KHSO_4$) alongwith the assignment are given in tables. The peak observed in the frequency range 3132 cm^{-1} (Na_2SO_4) is assigned to ν_1 ν_3 H_2O stretching of the molecule. The peak at 1521.3 cm^{-1} ($KHSO_4$) is assigned to ν_2 H_2O molecules. The band appeared at 1267.4 cm^{-1} (K_2SO_4) is attributed to S-O-H plane bending of the HSO_4 group. The peaks observed at 1257.4 cm^{-1},1157.9 cm^{-1} ($KHSO_4$), 1147.1 cm^{-1} (Na_2SO_4) 1137.7 cm^{-1},1096.8 cm^{-1} (K_2SO_4) 1099.7 cm^{-1} ($NaHSO_4$) were assigned to asymmetric stretching of SO_4 group. The inorganic sulphate ions absorbs strongly at 1125 – 1080 cm^{-1} due to asymmetric SO_4 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} ($KHSO_4$) 989.3 cm^{-1} ($NaHSO_4$). Symmetric stretching of SO_4 group is assigned in the frequency range 988.4 cm^{-1} (Na_2SO_4) 977.7 cm^{-1} , 930.3 cm^{-1} (K_2 SO_4) 989.3 cm^{-1} ($NaHSO_4$), 1015.5 cm^{-1} ($KHSO_4$). The peak observed at 1015.5 cm^{-1} ($KHSO_4$) of our crystal has in confirmation with the Raman spectrum of $KHSO_4$ by B.Dev et al./3/. in their Infrared and Raman studies of $KHSO_4$ crystals. The frequency observed at 988.4 cm^{-1} (Na_2SO_4) is well agreed with the value obtained by Richard L.Mc Creery /4/. The band appeared at 848.8 cm^{-1} ($KHSO_4$) attributed to S-O-H out of bending of HSO_4 group. The peaks observed in the frequency range 713.8 cm^{-1} , 628.8 cm^{-1} , 459.6 cm^{-1} (Na_2SO_4),707.1 cm^{-1} , 620.4 cm^{-1} , 523.3 cm^{-1} ,447.9 cm^{-1} (K_2SO_4) ,620.7 cm^{-1} , 467.7 cm^{-1} ($NaHSO_4$) 582.0 cm^{-1} ,439.2 cm^{-1} ($KHSO_4$) were assigned to the asymmetric bending of SO_4 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 SO_4 group is observed at the frequency range 314.4 cm^{-1} (Na_2SO_4) , 405.1 cm^{-1} ($KHSO_4$)

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Table-1:Vibrational assignments of $Na_2 SO_4$ crystals

IR cm^{-1}	Raman cm^{-1}	Assignments
3417.8 (VW)	3132.0	OH stretching of HSO_4 group
2249.8		
2110.9		ν_3 H_2O
1636.8		ν_2 H_2O
	1147.1	ν_{as} SO_4
1123.1		
	988.4	ν_{ss} SO_4
	713.8	
637.7		
	628.8	
615.6		ν_{ab} SO_4
	459.6	ν_{sb} SO_4
	314.4	ν_{sb} SO_4

Table-2:Vibrational assignments of $K_2 SO_4$ crystals

IR cm^{-1}	Raman cm^{-1}	Assignments
3414.3		OH stretching of HSO_4 group
2924.7		
2610.4		
2486.7		
1627.2		
1321.2		
1285.7	1267.4	S-O-H plane bending of
HSO_4 group		
1226.7		
1172.4	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		ν_{ab} SO_4
575.0		
	523.3	
477.8		
	448	ν_{sb} SO_4

Table-3:Vibrational assignments of NaH SO_4 crystals

IR cm^{-1}	Raman cm^{-1}	Assignments
3420		OH stretching of HSO_4 group
2920		
1620		
1120		ν_{as} SO_4
	1099.7	
	989.3	
	620.7	
610		ν_{ab} SO_4
	467.7	
390		
380		ν_{sb} 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		ν_{as} SO_4 (asymmetric stretching)
	1157.9	
1060		
	1015.5	ν_{ss} SO_4
1000		
880		

	848	S-O-H out of bending
840		
605		
	582	ν_{ab} SO_4 (asymmetric bending)
515		
450		
	439.2	
430		
	405.1	
400		ν_{ab}

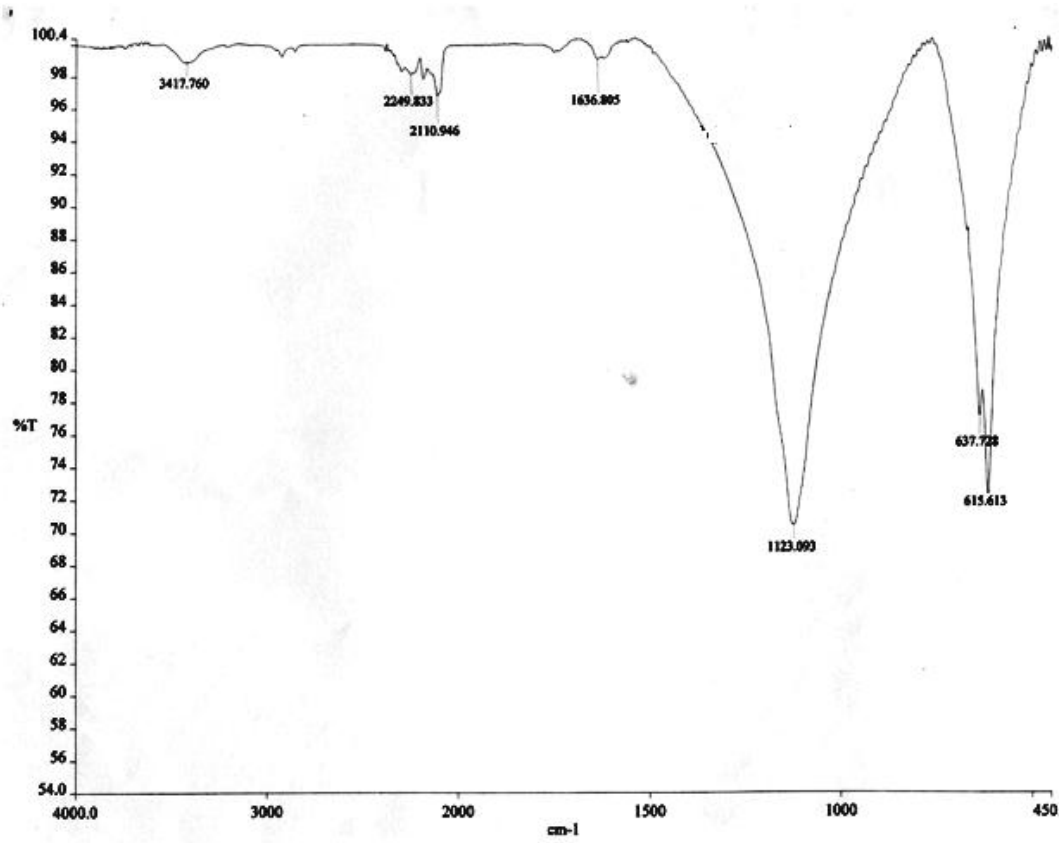

Fig.-1: FTIR spectrum of Na_2SO_4 crystals

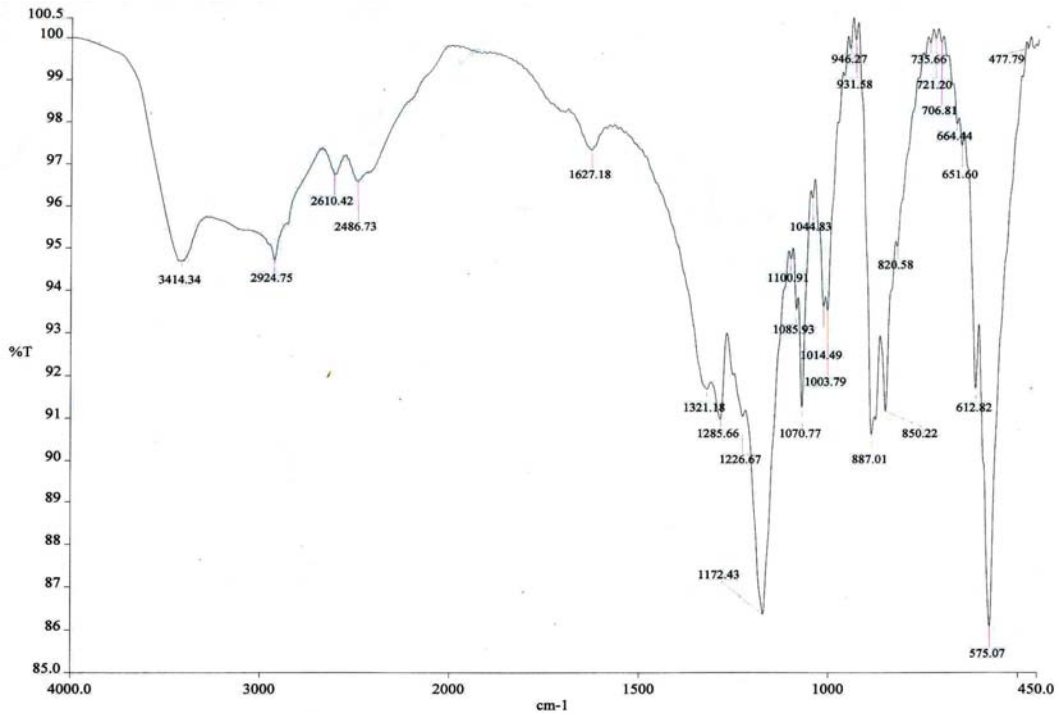

Fig.-2: FTIR spectrum of K_2SO_4 crystals

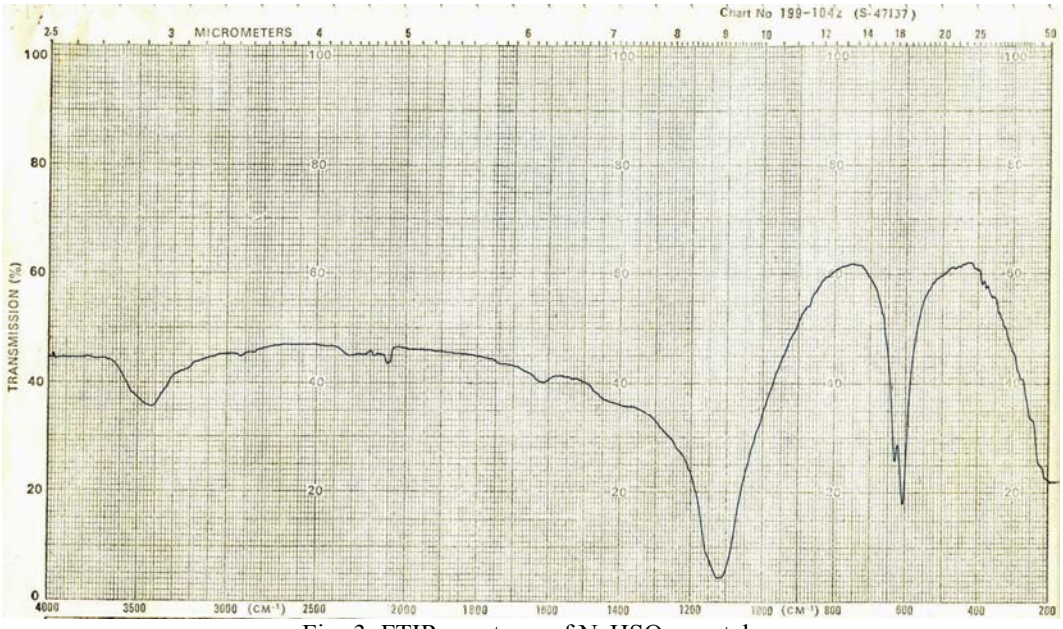

Fig.-3: FTIR spectrum of $NaHSO_4$ crystals

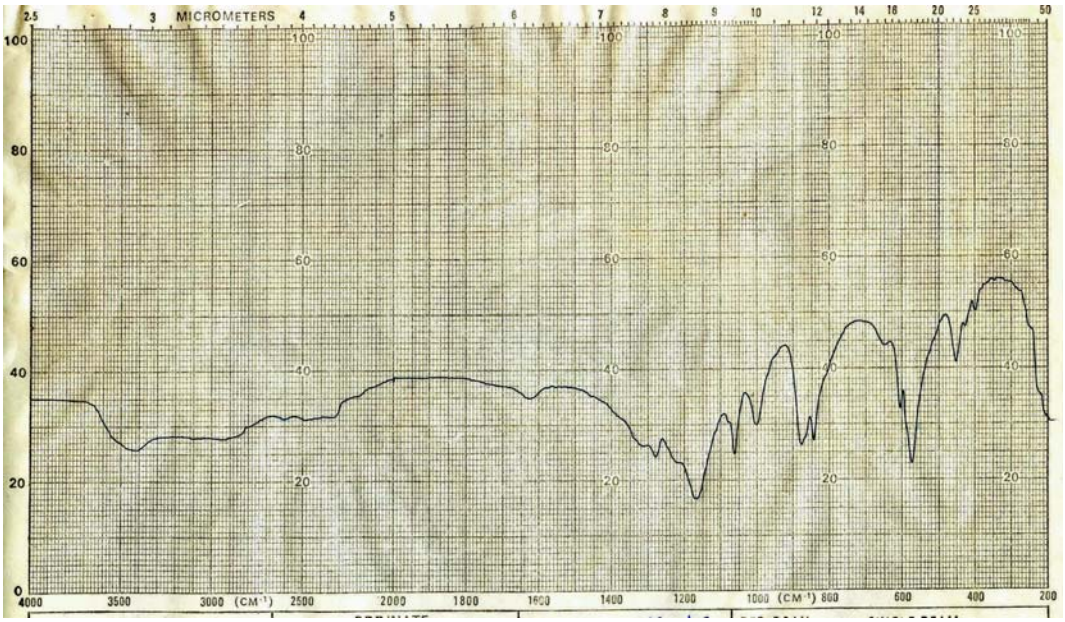

Fig.-4: FTIR spectrum of $KHSO_4$ crystals

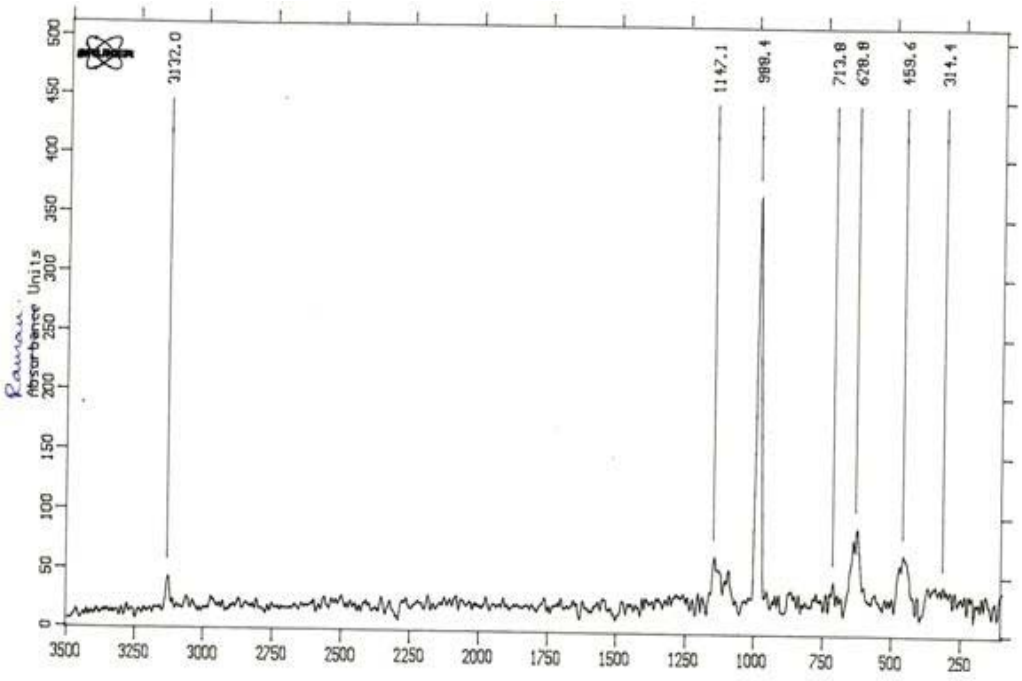

Fig.-5: Laser Raman spectrum of Na_2SO_4 crystals

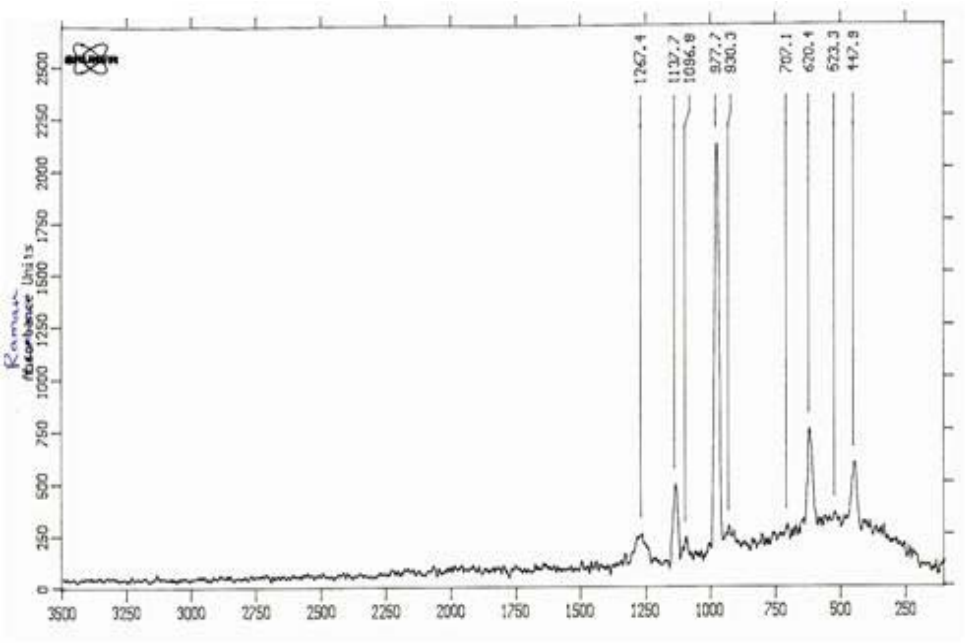

Fig.-6: Laser Raman spectrum of K_2SO_4 crystals

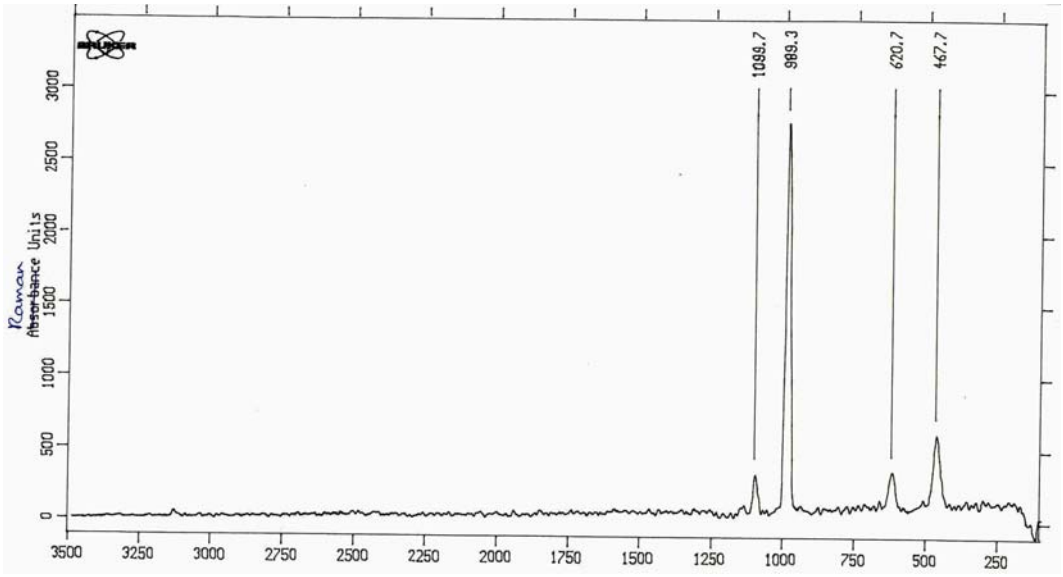

Fig.-7: Laser Raman spectrum of $NaHSO_4$ crystals

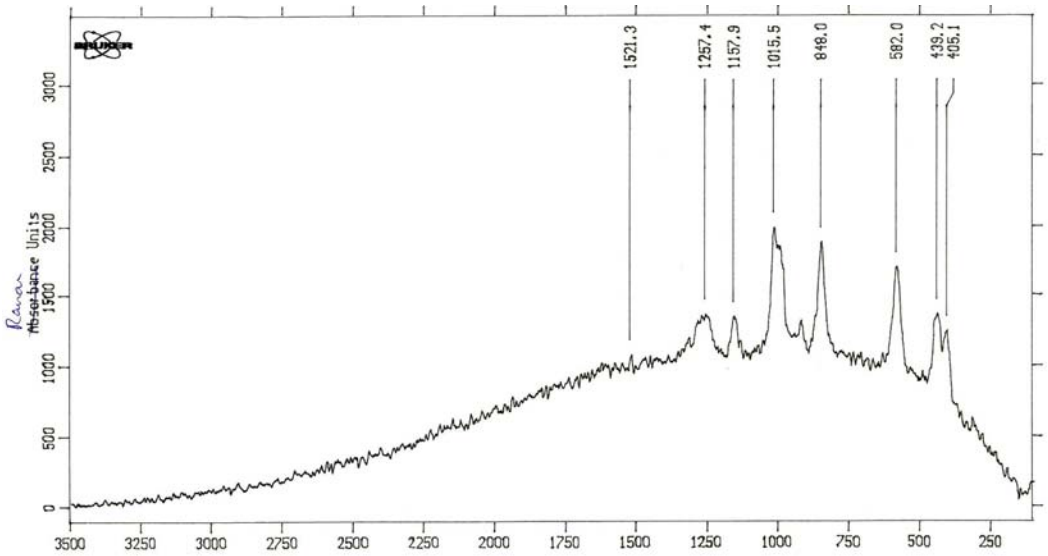

Fig.-8: Laser Raman spectrum of $KHSO_4$ crystals

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