CHAPTER - II

PREPARATION OF THE SAMPLES AND X-RAY DIFFRACTION STUDY

C H A P T E R - II

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Part - I : Preparation of the samples.

2.1 Introduction :

The method of preparation and optical properties were confirmed by Sorum (1943) for sodium vanadate ($NaVO_3$). Similarly, Glayzyrin et al (1964) reported the method of preparation and optical properties of sodium pyrovanadate ($Na_4V_2O_7$), sodium orthovanadate (Na_3VO_4) besides sodium vanadate and also classified sodium vanadate under the monoclinic system. Feigelson et al (1972) has given crystal growth and structural properties of Lithium Vanadate, Sodium Vanadate and Potassium Vanadate. Preparation method and the crystal chemistry of the M^+VO_3(M^+ = Li, Na, K, NH_4, Ti, Rb and Cs) were reported by Hawthorne et al (1977). Structural aspects and growth of $NaVO_3$ was given by Ramani et al (1975); Shaikh et al (1978) and Seetharaman et al (1983).

The addition of Gd_2O_3 to KVO_3 and $LiVO_3$ showed no change in the curie temperature, was reported by Lapiuye et al (1960), Yamaji et al (1977) and Issa et al (1984). Kuroda and Kubota (1980) studied the diffuse phase transition of $(Ba_X - Sr_{1-X})Nb_2O_6$ doped with praseodymium (Pr^{3+}) and Neodymium (Nd^{3+}) by measuring the spontaneous polarization and

dielectric constant. The temperature dependence of dielectric constant and loss tangent values for $BaTiO_3$ ceramic with varying concentrations of Nd and Mn was reported by Murugaraj and Kutty (1985).

2.2 Preparation of Sodium Vanadate :

We have prepared polycrystalline solid of sodium vanadate ($NaVO_3$) from a stoichiometric mixtiure of sodium carbonate (Na_2CO_3) and vanadium pentoxide (V_2O_5) by the method similar to that described by Hawthorne et al (1977). The carbonate used was of purity 99.9% from Glaxo Laboratories, India and Vanadium pentoxide of purity greater than 99% from Fluka AG, Switzerland. Sodium carbonate was preheated at 300°C for 4 hr before weighing to remove moisture.

For the preparation of sodium vanadate, the stoichiometric mixture of preheated sodium carbonate (5.298 gm) and vanadium pentoxide (9.094 gm) was heated slowly in a platinum crucible inside a globar furnace and fired at temperature about 750°C for 4 hr. The cooled melt was of sodium vanadate, obtained by the following chemical reaction.

$$Na_2CO_3 + V_2O_5 \longrightarrow 2\ NaVO_3 + CO_2\uparrow$$

From this, carbon dioxide escaped to the surrounding and sodium vanadate was obtained by the above chemical reaction.

2.3 Preparation of Ferroelectric Sodium Vanadate Doped with Neodymium Oxide :

The mixture of sodium vanadate and Neodymium Oxide was prepared by firing in the platinum crucible, inside a globar furnace, at temperature 950°C for 5 hr and then cooled to room temperature.

2.3 (a) Preparation of $(NaVO_3)_{99.975} - (Nd_2O_3)_{0.025}$:

For this preparation, 8.132 gm of sodium vanadate was thoroughly mixed with 0.006 gm of Neodymium Oxide, slowly heated in a platinum crucible inside a globar furnace and fired at 950°C for 5 hr. The mixture was finally cooled to room temperature which gives homogeneous doping mixture of sodium vanadate with Neodymium Oxide.

2.3 (b) Preparation of $(NaVO_3)_{99.950} - (Nd_2O_3)_{0.05}$:

In order to prepare this mixture, 8.129 gm of sodium vanadate and 0.011 gm of Neodymium Oxide was slowly heated in a platinum crucible and fired at 950°C for 5 hr.

2.3 (c) Preparation of $(NaVO_3)_{99.9} - (Nd_2O_3)_{0.1}$:

For the preparation of this mixture, 8.125 gm of sodium vanadate and 0.022 gm of Neodymium Oxide was heated in a

platinum crucible and fired at 950°C for 5 hr inside a globar furnace.

2.3 (d) Preparation of $(NaVO_3)_{99.5} - (Nd_2O_3)_{0.5}$:

For this preparation, a mixture of 8.012 gm of $NaVO_3$ and 0.111 gm of Neodymium Oxide was heated in a platinum crucible and fired at temperature 950°C for 5 hr and then cooled.

2.3 (e) Preparation of $(NaVO_3)_{99.0} - (Nd_2O_3)_{1.0}$:

In order to prepare this mixture, 7.971 gm of sodium vanadate and 0.222 gm of Neodymium Oxide was slowly heated in a platinum crucible and fired at 950°C for 5 hr.

2.4 Fabrication of the pellet of the samples :

All samples, under consideration, are ground to pass a 120 mesh sieve and are pressed by applying five tonnes pressure, using hydraulic press, to form pellets of diameter 1 cm and thickness about 1 mm without using binder. The pellets of sodium vanadate, were sintered on a platinum foil at about 450°C for 3 hr while that of doping mixtures were sintered at about 500°C for 3 hr. The two sides of these sintered pellets were coated with a thin layer of air-drying silver paste to form the full face electrodes for good electrical contact. These pellets were then used for experimental investigations.

The properties of the ceramic materials depend upon the

grain size and actual pellet densities of the samples. The pellet densities of the samples were determined and are summarized in Table (2.1).

Table 2.1 : Pellet densities of the samples.

Sample	Density gm/cm^3
$NaVO_3$	2.78
$(NaVO_3{}_{99.975} - Nd_2O_3{}_{0.025})$	2.61
$(NaVO_3{}_{99.950} - Nd_2O_3{}_{0.05})$	2.65
$(NaVO_3{}_{99.900} - Nd_2O_3{}_{0.1})$	2.69
$(NaVO_3{}_{99.500} - Nd_2O_3{}_{0.5})$	2.75
$(NaVO_3{}_{99.000} - Nd_2O_3{}_{1.0})$	2.68

Part II : X-Ray diffraction study.

2.5 Structural Characteristics :

Feigelson et al (1972) reported the structural characteristics of alkali metal metavanadates, in which they have shown that sodium vanadate belongs to the monoclinic system and its space group could be C_C as well as C_2/c. Chain configuration occurs in alkali metal metavanadate structures. Sodium vanadate has an O - rotated chain. For pyroxene structure, O - rotated chain configuration is shown in fig 2.1. Recently, the structure of sodium vanadate has been confirmed by Marumo et al (1974). Ramani et al (1975) reported that $NaVO_3$ belongs to monoclinic system with space

group C_c in the room temperature ferroelectric phase while the space group in the high temperature paraelectric phase is C_{2}/c. Sodium vanadate belongs to the pyroxene family and has infinite linear VO_3^- chains formed by VO_4 tetrahedra sharing two corners with the others, these chains are held together by sodium ions. A typical form of such a chain along the C-axis is shown in fig. 2.2. The crystal structure may be viewed as consisting of alternate channels of sodium polyhedra and linear chains of VO_3^- ions in fig.2.3. Each sodium ion is surrounded by six oxygens forming an octahedral co-ordination. The co-ordination polyhedron around the sodium atom is nearly a regular octahedron. Raman spectroscopic studies on sodium vanadate by Seetharaman et al (1983) confirmed the C_c ferroelectric space group in the room temperature phase.

Ng et al (1978,1979) reported that $(Na_X - K_{1-X})VO_3$ and $(Na_X - Li_{1-X})VO_3$ are having the same structure as that of Lithium vanadate and sodium vanadate.

2.6 X-ray diffraction studies :

X-ray diffraction is tool to study solid structure and therefore, we have used the same, to confirm the formation of the samples. In the present study an attempt has been made to determine the lattice parameters of undoped sodium vanadate and doped with different concentrations of Neodymium Oxide

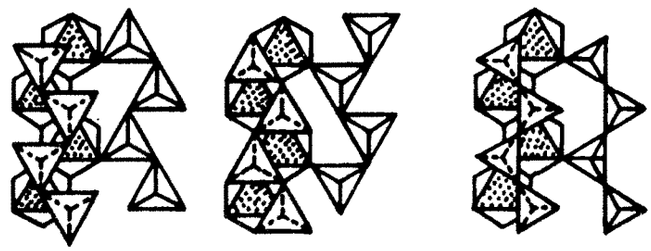


Fig. 2·1 Some geometrical stacking possibilities for pyroxenes structures, illustrating the three different chain configurations: (a) O-rotated chain; (b) S-rotated chain; (c) E (extended) chain.

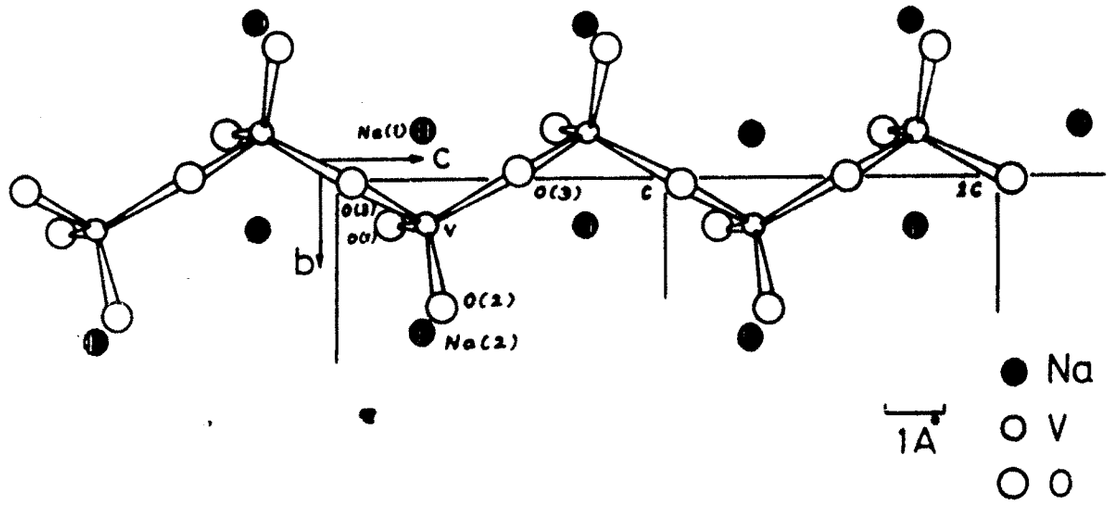


Fig. 2·2 A view of the infinite linear chain of VO_4 tetrahedra along the c-axis. Only one such chain is shown for clarity.

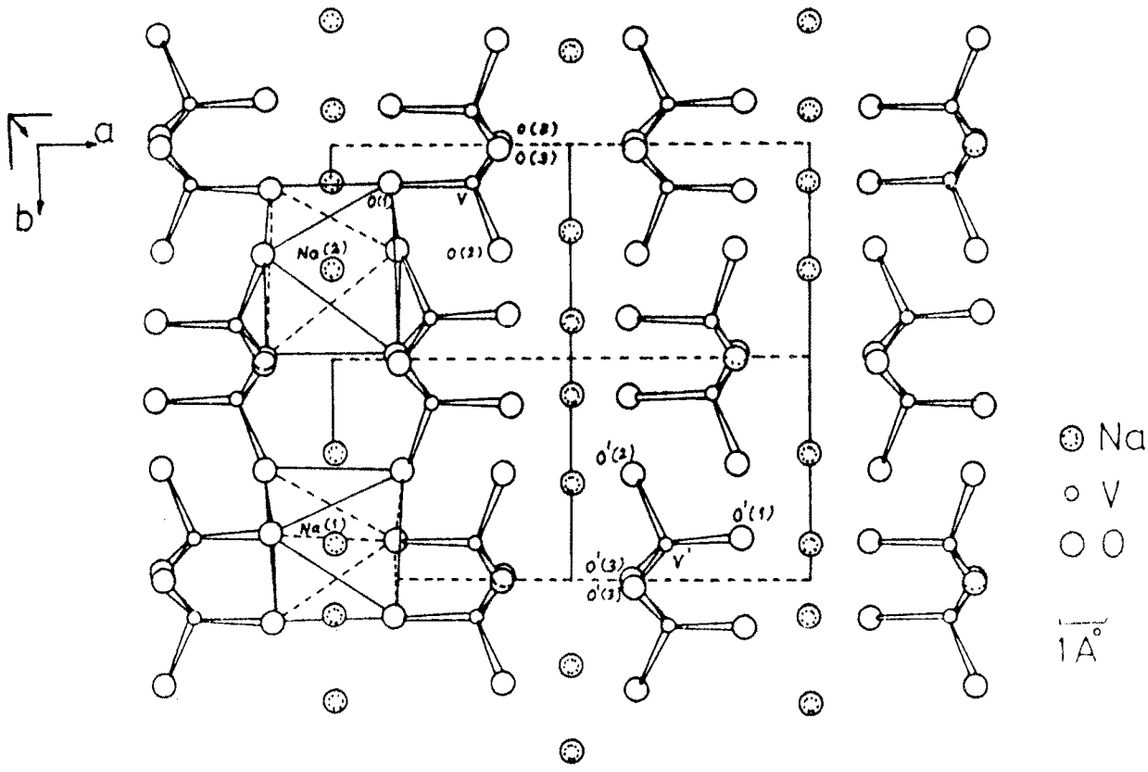


Fig. 2·3 A view of the structure looking down the (001) direction. The octahedral co-ordination around sodium ions Na(1) and Na(2) is shown. All the octahedra are not shown for clarity.

(0.025 to 1 mol%). Powder diffraction patterns of these samples are shown in figs.2.4 to 2.9 respectively. In these

Table 2.2 : Lattice Parameters of Different Samples :

Sample	Present Work	Earlier Results		
	Present work	Ramani et al (1975)	Sorum (1943)	Feigelson et al (1972)
$NaVO_3$	a(A^o)=10.431 b(A^o)= 9.461 c(A^o)= 5.865	10.494 9.434 5.863	10.14 9.45 5.86	10.530 9.465 5.864
$[NaVO_3{}_{99.975}$-$Nd_2O_3{}_{0.025}]$	a(A^o)=10.319 b(A^o)= 9.461 c(A^o)= 5.881			
$[NaVO_3{}_{99.950}$-$Nd_2O_3{}_{0.05}]$	a(A^o)=10.615 b(A^o)= 9.458 c(A^o)= 6.023			
$[NaVO_3{}_{99.9}$---$Nd_2O_3{}_{0.1}]$	a(A^o)=10.301 b(A^o)= 9.463 c(A^o)= 5.864			
$[NaVO_3{}_{99.5}$---$Nd_2O_3{}_{0.5}]$	a(A^o)=10.316 b(A^o)= 9.468 c(A^o)= 5.871			
$[NaVO_3{}_{99}$-----$Nd_2O_3{}_{1}]$	a(A^o)=10.287 b(A^o)= 9.461 c(A^o)= 5.785			

patterns, 'd' values of prominent lines for different samples are shown. The results obtained from the analysis of these patterns are summarized in table 2.2 along with the data

Fig 2.4 - X-ray diffraction pattern of $NaVO_3$.

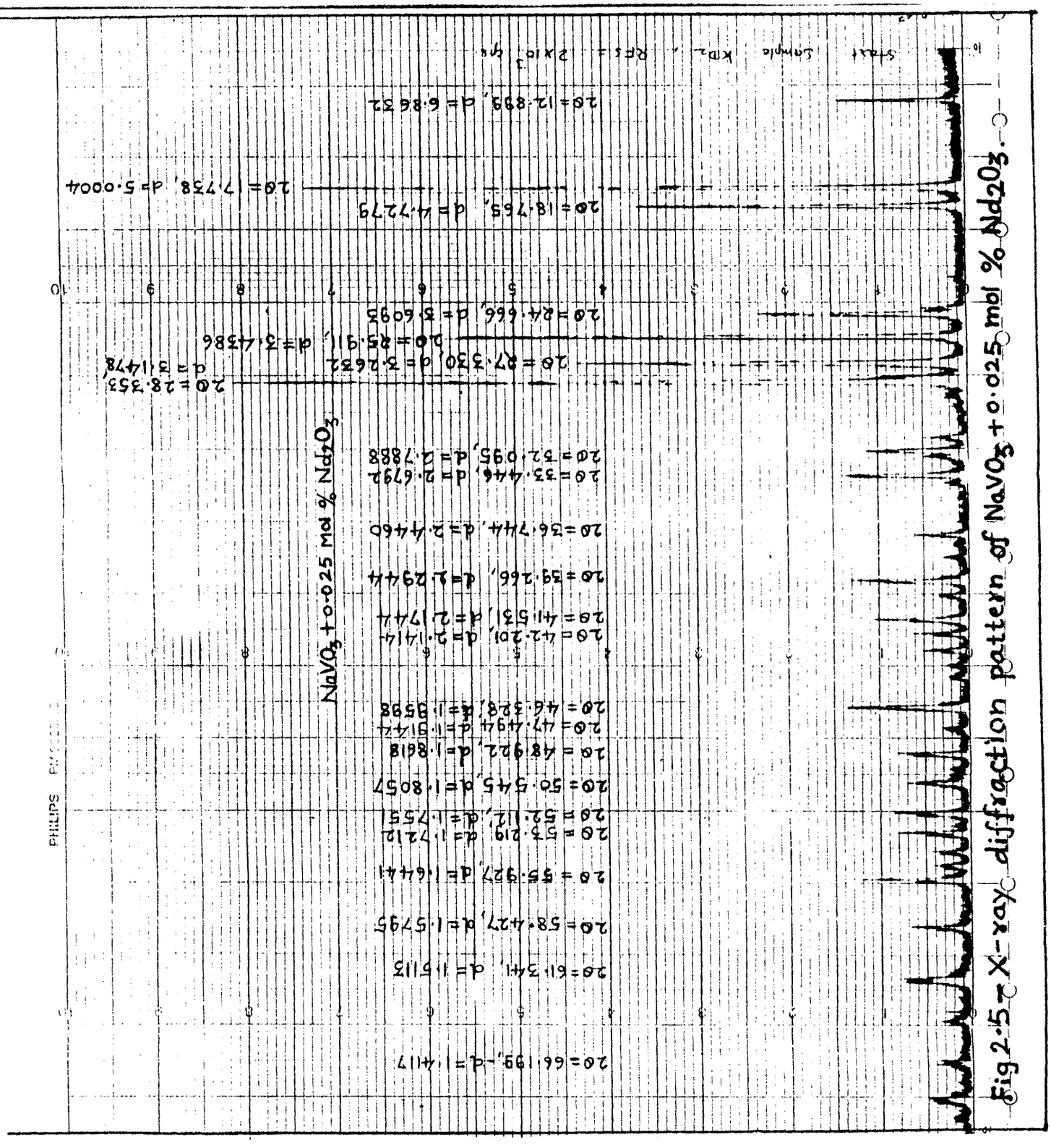
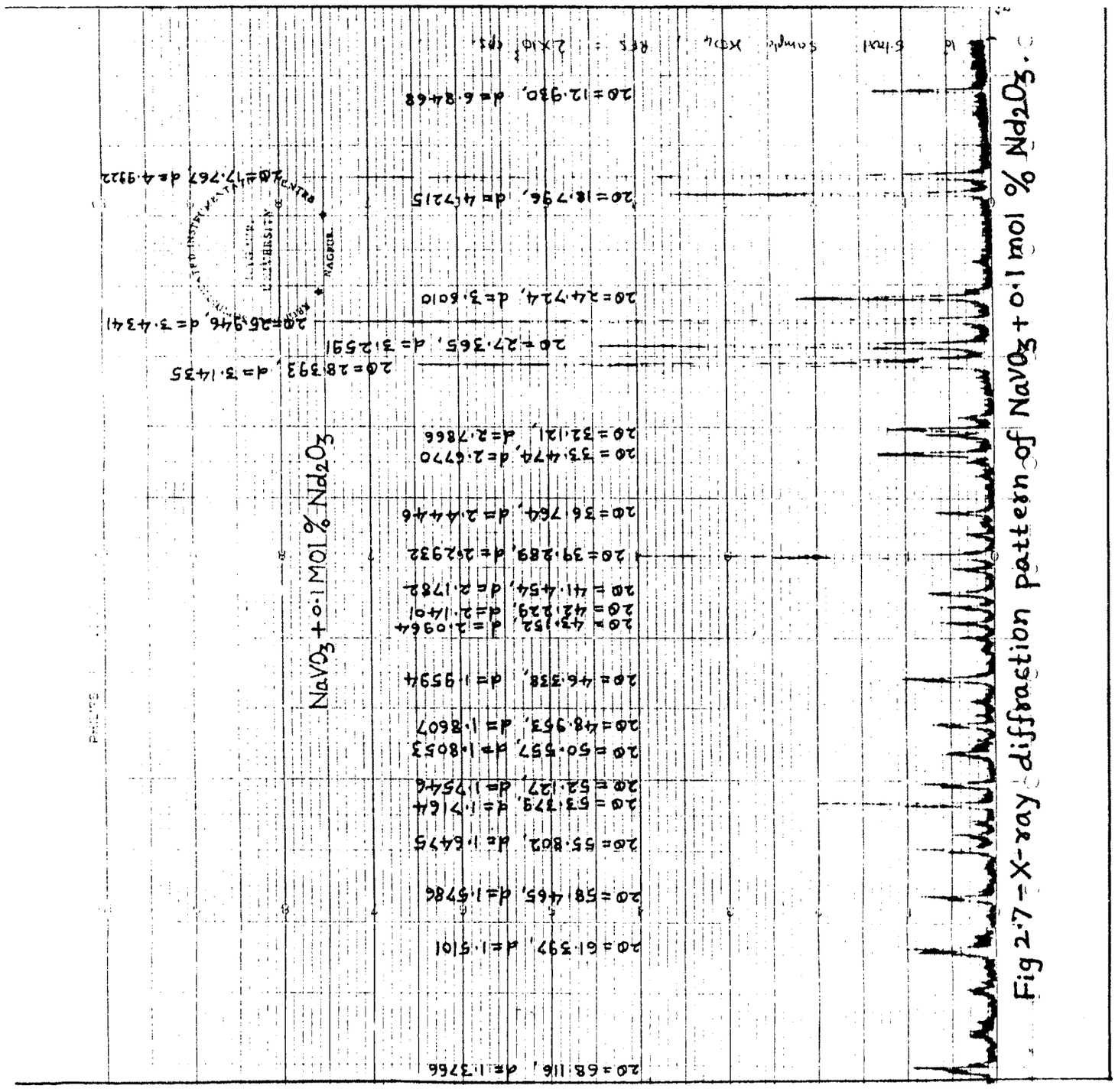


Fig 2·5 – X-ray diffraction pattern of $NaVO_3$ + 0·025 mol % Nd_2O_3.

2θ = 68·114, d = 1·3756
2θ = 61·381, d = 1·5104
2θ = 58·470, d = 1·5785
2θ = 55·791, d = 1·6477
2θ = 53·254, d = 1·7201
2θ = 52·141, d = 1·7542
2θ = 50·532, d = 1·8062
2θ = 48·944, d = 1·8610
2θ = 46·362, d = 1·9585
2θ = 42·245, d = 2·1387
2θ = 41·416, d = 2·1802
2θ = 39·311, d = 2·2919
2θ = 36·757, d = 2·4451
2θ = 35·514, d = 2·5729
2θ = 32·114, d = 2·7874
2θ = 28·399, d = 3·1428
2θ = 27·397, d = 3·2578
2θ = 25·949, d = 3·4356
2θ = 24·705, d = 3·6044
2θ = 24·337, d = 3·6573
2θ = 18·781, d = 4·7224
2θ = 17·726, d = 4·9523
2θ = 12·932, d = 6·8489
NaVO3 + 0·05 Mol % Nd2O3
Fig 2·6 X-ray diffraction pattern of NaVO3 + 0·05 mol % Nd2O3.


2θ = 68.116, d = 1.3766
2θ = 61.397, d = 1.5101
2θ = 58.446 5, d = 1.5786
2θ = 55.802, d = 1.6475
2θ = 53.379, d = 1.7164
2θ = 52.127, d = 1.7546
2θ = 50.557, d = 1.8053
2θ = 48.953, d = 1.8607
2θ = 46.338, d = 1.9594
2θ = 43.152, d = 2.0964
2θ = 42.229, d = 2.1401
2θ = 41.454, d = 2.1782
2θ = 39.289, d = 2.2932
2θ = 36.764, d = 2.4446
2θ = 33.474, d = 2.6770
2θ = 32.121, d = 2.7866
2θ = 28.393, d = 3.1435
2θ = 27.365, d = 3.2591
2θ = 25.946, d = 3.4341
2θ = 24.724, d = 3.6010
2θ = 18.796, d = 4.7215
2θ = 17.767, d = 4.9922
2θ = 12.930, d = 6.8468
NaVO3 + 0·1 MOL% Nd2O3
Fig 2·7 - X-ray diffraction pattern of NaVO3 + 0·1 mol % Nd2O3.

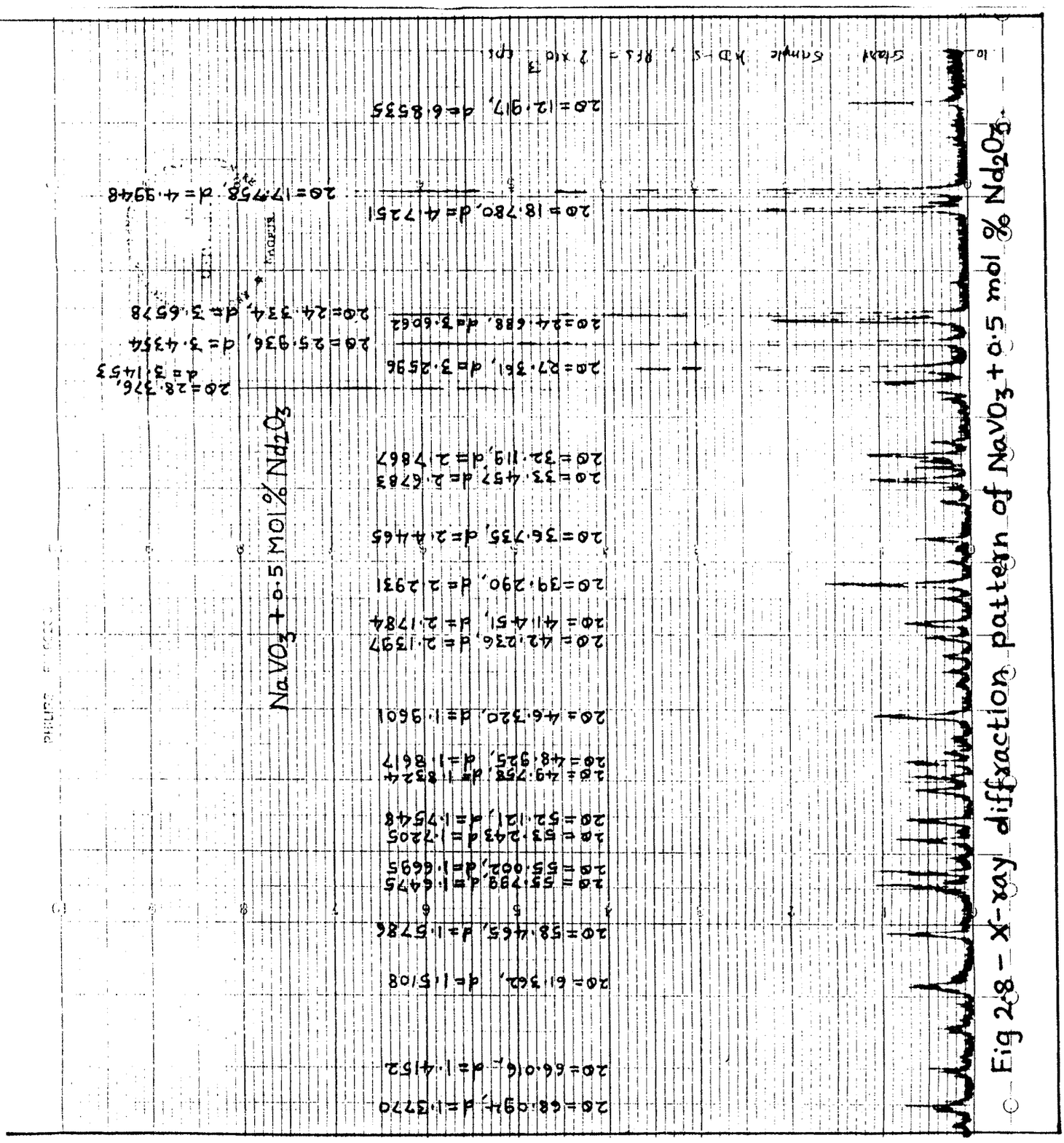


Fig 2.8 – X-ray diffraction pattern of $NaVO_3$ + 0.5 mol % Nd_2O_3

2θ = 68.112, d = 1.3766
2θ = 66.023, d = 1.4150
2θ = 61.376, d = 1.5105
2θ = 58.434, d = 1.5794
2θ = 55.787, d = 1.6479
2θ = 53.232, d = 1.7206
2θ = 52.170, d = 1.7561
2θ = 50.460, d = 1.8086
2θ = 48.388, d = 1.8811
2θ = 46.347, d = 1.9591
2θ = 41.437, d = 2.1791
2θ = 39.296, d = 2.2928
2θ = 36.743, d = 2.4460
2θ = 34.841, d = 2.5894
2θ = 33.456, d = 2.6784
2θ = 32.132, d = 2.7606
2θ = 28.380, d = 3.1448
2θ = 27.751, d = 3.2602
2θ = 25.934, d = 3.4357
2θ = 24.324, d = 3.6583
2θ = 18.794, d = 4.7215
2θ = 17.756, d = 4.9952
2θ = 12.927, d = 6.8482
NaVO3 + 1 Mol % Nd2O3
Fig 2.9 X-ray diffraction pattern of NaVO3 + 1 mol % Nd2O3.

reported by earlier workers.

The lattice parameters were calculated by using indexing reported by Feigelson et al (1972) for sodium and potassium vanadate as shown in table 2.2. The table 2.2 shows the values of the lattice parameters of undoped $NaVO_3$ are found to agree with the results of the earlier workers. Also, the values of the lattice parameters of $NaVO_3$ doped with different percentage of Nd_2O_3 (0.025 to 1 mol%) are nearly similar to the results of the undoped $NaVO_3$.

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