CHAPTER-II

PREPARATION OF THE SAMPLES,X-RAY DIFFRACTION AND E.P.R.STUDIES OF SAMPLES

2.1   INTRODUCTION

First of all Canneri (1928) studied the solid-liquid equilibria in the system Li_2O_3-V_2O_5. The compound formation and phase diagram for the K_2O-V_2O_5 system was studied by Holtzberg et al (1956). Kohlmuller et al (1961) and Glazyrin (1965) confirmed the existence of $LiVO_3$. Gornostansky et al (1968) investigated crystal growth method of potassium vanadate. Baughman et al (1970) were reported the crystal growth techniques for KVO_3.Feigelson et al (1972) studied crystal growth and structural properties of $LiVo_3$, $NaVO_3$ and KVO_3. The preparation method and the crystal chemistry of M^+VO_3 (M^+ =Li or Na or K or NH_4 or T_L or Rb or C_s) were given by Hawthorne and Calvo (1977) Ng et al (1978, 1979) synthesized (Na_x-K_{1-x}) VO_3 solid solutions and discussed their structural properties. Patil et al (1986,1987,1988) also studied $(Na_x$-$K_{1-x})VO_3$ solid solutions and discussed their characteristic properties. Recently, Kashid et al (1989) have studied ferroelectric properties of KVO_3 doped with Gd_2O_3 and Patil et al (1989) also reported characteristic properties of ferroelectric KVO_3 doped with Dy_2O_3.

2.2   PREPARATION OF POTASSIUM VANADATE

Potassium vandate is an important member of the perovskite type ceramics.The polycrystalline solid of potassium vanadate is prepared by a method described by Feigelson et al (1972) and Hawthorne and Calvo (1977). In this method a stoichiometric mixture of potassium carbonate (K_2CO_3) and vanadium pentoxide (V_2O_5) is used. The K_2CO_3 was

of purity 99.9% from Glaxo Laboratories, India and V_2O_5 of purity 99.9% from Fluka A.G.Switzerland. Initially, K_2CO_3 is preheated at 300^Oc for 4 hours in order to remove moisture and adsorption of the carbonate. Then stoichiometric mixture (6.910 gm of K_2CO_3 and 9.094 gm of V_2O_5) is slowly heated in a platinum crucible inside a globar furnace and fired at temperature 950^Oc for 5 hours and then cooled to room temperature. During this chemical reaction, decomposition of K_2CO_3 is observed, CO_2 (carbon dioxide) escapes and solid KVO_3 is produced. The chemical reaction is,

$$K_2CO_3 + V_2O_5 \rightarrow 2KVO_3 + CO_2\uparrow \qquad \ldots.2.1$$

2.3 PREPARATION OF KVO_3 DOPED WITH Er_2O_3

For the preparation of solid solutions of KVo_3 doped with different concentration of Er_2O_3 a stoichiometric mixture of KVO_3 and Er_2O_3 is used. Er_2O_3 (purity 99.9%, John Baker Inc; Colorado, USA), is used as an additive having differtent molar concentrations.

2.3(a) Preparation Of KVO_3(0.975 mol %):Er_2O_3(0.025 mol%) Solid Solution

For the preparation of this, 9.660 gm of KVO_3 was thoroughly mixed with 0.0067 gm of Er_2O_3, slowly heated in a platinum crucible inside a globar furnace and fired at 950^Oc for 5 hours. Then it was cooled to room temperature, which gives solid solution of KVO_3 doped with 0.025 mol % Er_2O_3.

2.3(b)   Preparation of KVO_3(0.950 mol %): Er_2O_3(0.050 mol %) Solid

   Solution

In order to prepare this solid solution, KVO_3 (9.658 gm) was thoroughly mixed with Er_2O_3 (0.0134 gm), slowly heated in a platinum crucible inside a globar furnace and fired at 950^0c for 5 hours. Finally it was cooled to room temperature to give homogeneous solid solution of KVO_3 doped with 0.050 mol % of Er_2O_3.

2.3(c)   Preparation of KVO_3(99.9 mol %) : $Er2O_3$(0.1 mol %)   Solid

   Soluion

The solid solution of KVO_3 (99.9 mol %) and Er_2O_3(0.1 mol %) was prepared by mixing 9.653 gm KVO_3 with 0.0268 gm of Er_2O_3. This mixture was then slowly heated in a platinum crucible inside a globar furnace and fired at 950^0c ior 5 hours. After cooling this mixture at room temperature the required solid solution was obtained.

2.3(d) Preparation of KVO_3(99.5 mol %) : Er_2O_3 (0.5 mol %) Solid Solution

The KVO_3 (9.615 gm) and Er_2O_3 (0.134 gm) were thoroughly mixed and slowly heated in a platinum crucible inside a globar furnace, the mixture is then fired at 950^0c for 5 hours. Then it was cooled to room temperature which gives the homogeneous solid solution.

2.3(e)   Preparation of KVO_3(99 mol%) : Er_2O_3 (1 mol %) Solid Solution

In order to prepare this solid solution 9.566 gm of KVO_3 and 0.268 gm of Er_2O_3 were thoroughly mixed. Then this mixture was slowly heated

in a platinum crucible inside a globar furnace and fired at 950^oc for 5 hours. Then it was cooled to room temperature and required solid solution was obtained.

2.3(f) Preparation of KVO_3 (97 mol %) :Er_2O_3(3 mol %) Solid Solution

The solid solution of 97 mol % KVO_3 and 3 mol % Er_2O_3 was prepared by mixing 9.273 gm KVO_3 with 0.803 gm Er_2O_3. Then this mixture was slowly heated in a platinum crucible and fired at 950^oc for 5 hours. Finally this mixture was cooled to room temperature producing the hoogeneous solid solution.

2.4 PELLET PREPARATION

All samples which are in powder form are ground fine so as to pass through a 120 mesh sieve and are subjected to 5 tonne pressure using hydraulic press.Then pellets formed are of same size i.e. each pellet of 1 cm diameter and thickness of about 1 mm. Then all these pellets are sintered on a platinum foil at about 450^0c for 3 hours. The two sides of the sintered pellet are coated with a thin layer of air-drying silver paste to form the full face electrodes for good electrical contact. These pellets are used for experimental investigations.

The properties of these ceramic materials depend upon the grain size and actual pellet densities of the samples. The pellet density, X-ray density and % porocity of the samples are determined and are

summarized in Tabler 2.1

TABLE NO.2.1

PELLET DENSITIES OF THE SAMPLES

Sample with Er_2O_3 content (mon %)	Density gm/cm^3	X-ray density gm/km^3	Percentage porosity
0.000	2.50	2.88	13.19
0.025	2.61	3.08	15.26
0.050	2.58	2.89	10.73
0.100	2.51	2.88 ·	12.85
0.500	2.47	2.90	14.83
1.000	2.43	2.93	17.07
3.000	2.40	3.03	20.79

Table 2.1 indicates that the density of the KVO_3 doped with 0.025 mol % Er_2O_3 sample is large and it decreases as Er_2O_3 content in KVO_3 increases. Similarly, change in X-ray density and percentage porocity is observed for different Er_2O_3 content in KVO_3 samples.

2.5   X-RAY DIFFRACTION STUDY

2.5 (a) Introduction

Feigelson et al (1972) studied structural aspects of alkali metavanadates in which they have shown that crystal structure of potassium vanadate is orthorhombic. Then Hawthorne and Calvo (1977) reported that potassium vanadate has a variant of the pyroxene structure belonging to orthorhombic system with the space group Pbcm and its structure is characterized by a $(V^{5+}O_3^{2-})_{\infty}^{-}$ chain extending along the c-axis with adjacent chains linked by the alkali metal cation. All types of chain configuration occur in alkali metal metavanadate structures. Lithium vanadate has an S-rotated chain, sodium vanadate has an O-rotated chain and potassium vanadate has an E-rotated chain. Recently, 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. Bubnova et al (1982) showed that in the $LiVO_3-NaVO_3$ system, the crystalline lattice is deformed maximumm along the b-axis, moderately along a-axis and minimum along the c-axis.

2.5(b)   X-ray Diffraction Study

X-ray diffraction technique is used to confirm and to study solid

structure formation of undoped and Er_2O_3 doped KVO_3 having Er_2O_3 concentrations varying from 0.025 to 3 mol %. X-ray diffration patterns of the samples in the form of a powder are taken from R.S.I.C, laboratory, Nagpur which are shown in Fig. 2.1 to 2.7 respectively. The attempt is made to calculate lattice parameters of polycrystalline undoped and Er_2O_3 doped KVO_3. X-ray diffraction patterns in Fig. 2.1 to 2.7 show observed 'd' values and corresponding (hkl) values for observed 2θ. The lattice parameters are calculated by using indexing method reported by Feigelson et al (1972) for KVO_3 . The formula used for this KVO_3 samples is $\dfrac{1}{d^2} = \dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}$,because KVO_3 belong to orthorhombic crystal system. The lattice parameters are computed by least square method using computer in which MATLAB package is used.

2.5 (c) Least Square Method

This method is investigated by Gauss (1930). It has been further developed by many authors and Rao (1983), has given a list of references for the same. The brief description of the method to calculate estimators of lattice constants (a,b,c) is given below.

The equation for the orthorhombic crystal system (for KVO_3) is given by,

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad\qquad \dots. \; 2.2$$

FIG. 2.1: X.R.D. OF UNDOPED KVO₃

Sample AI 1/492
Recorder full scale 2×10³ cps
2-axis 5mm = 1° 2θ

50

(5.3812)
(5.1683)

(3.9078)
(3.7305)

(3.1191)

(2.8424)
(2.6667)
(2.6219)
(2.5883)

(2.4364)
(2.3918)

(2.3020)
(2.1017)
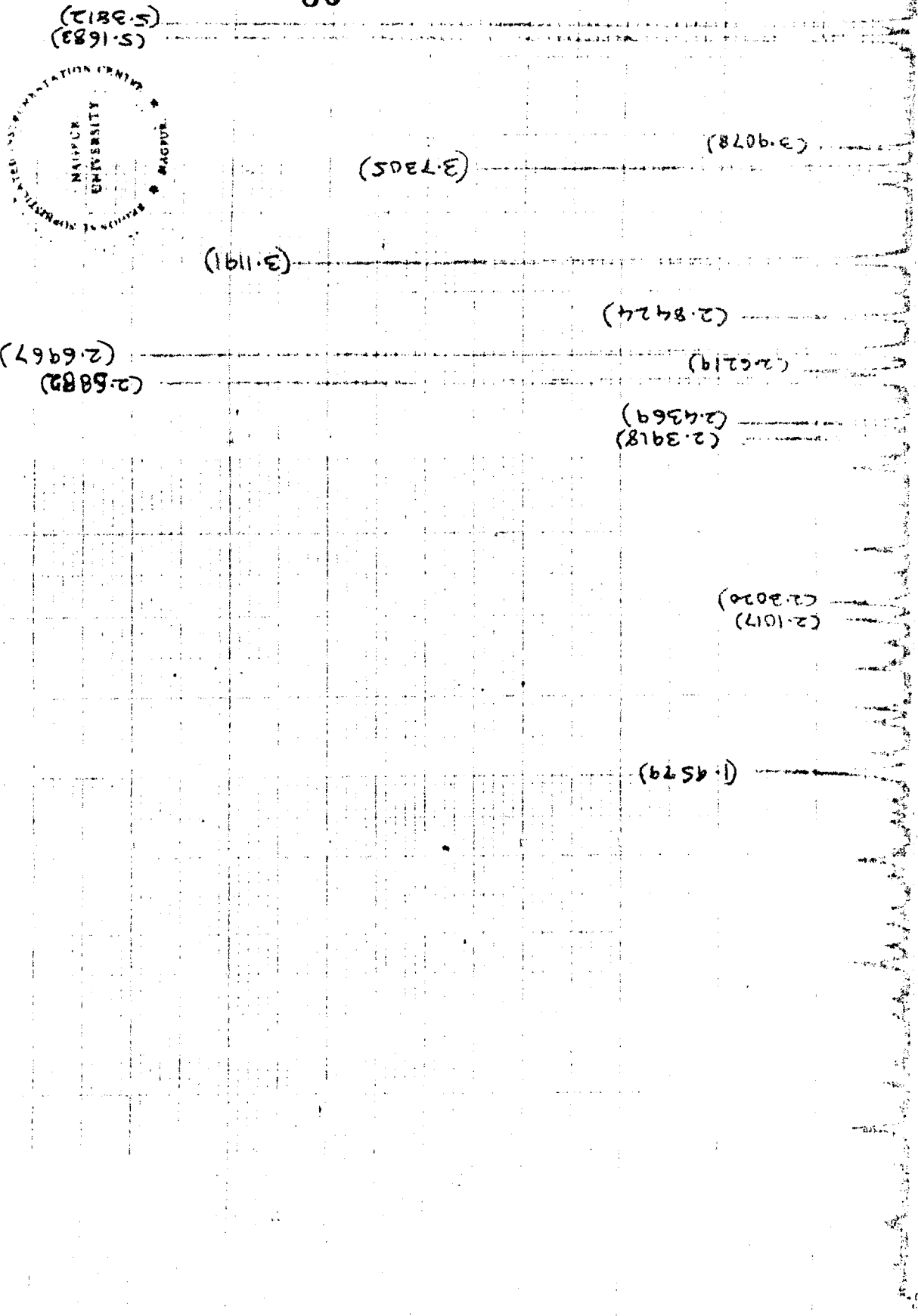
(1.4579)
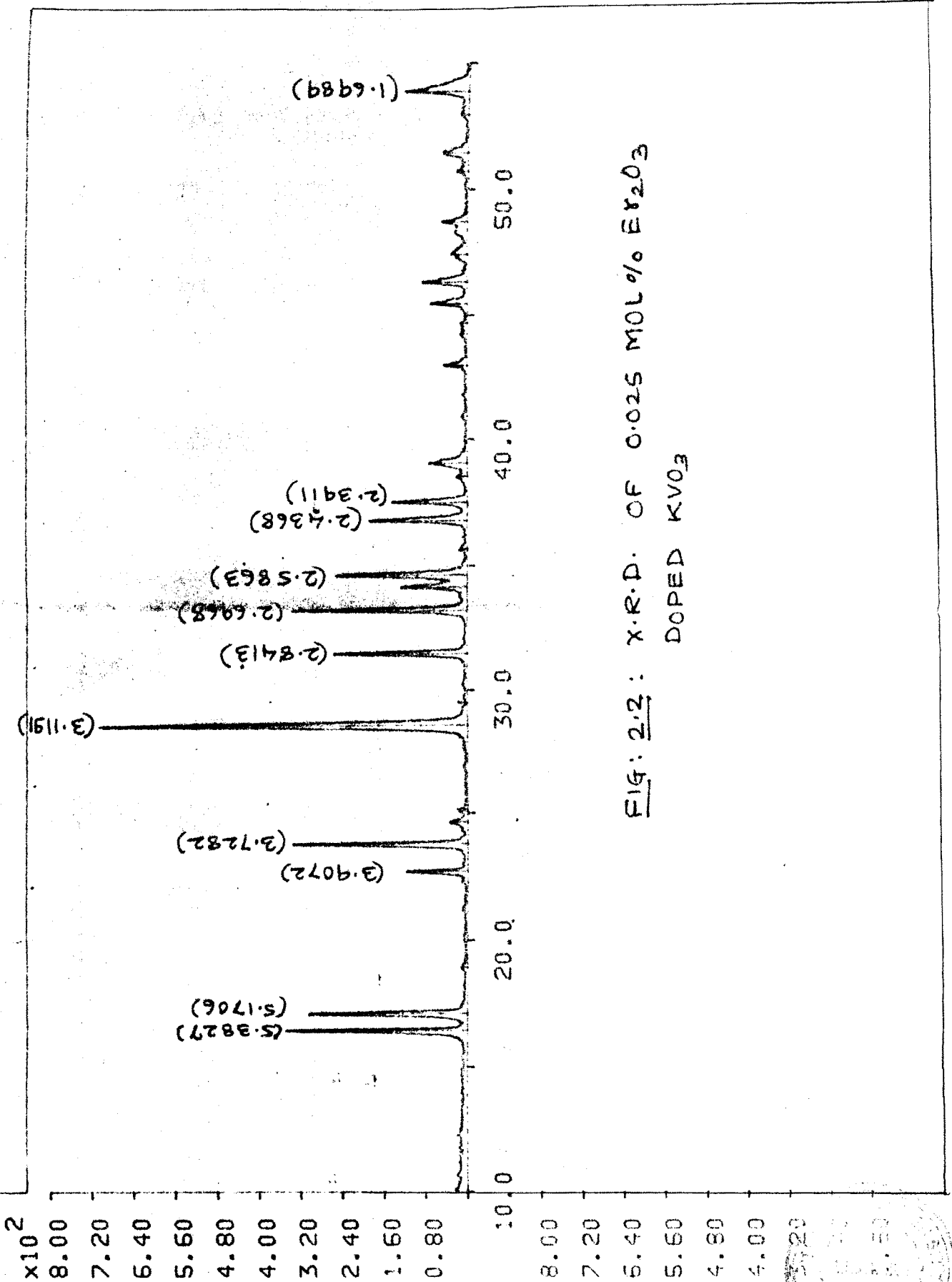
FIG: 2.2 : X.R.D. OF 0.025 MOL% Er₂O₃
DOPED KVO₃
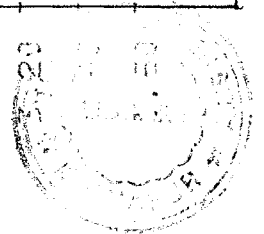
Sample: TS2 File: 739S2.SM

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$\times 10^2$

9.50
8.55
7.60
6.65
5.70
4.75
3.80
2.85
1.90
0.95

10.0   20.0   30.0   40.0   50.0

(5.3867)
(5.1736)

(3.7313)

(3.1196)

(2.8434)
(2.6980)
(2.5883)

(2.4376)
(2.3827)

(1.6995)
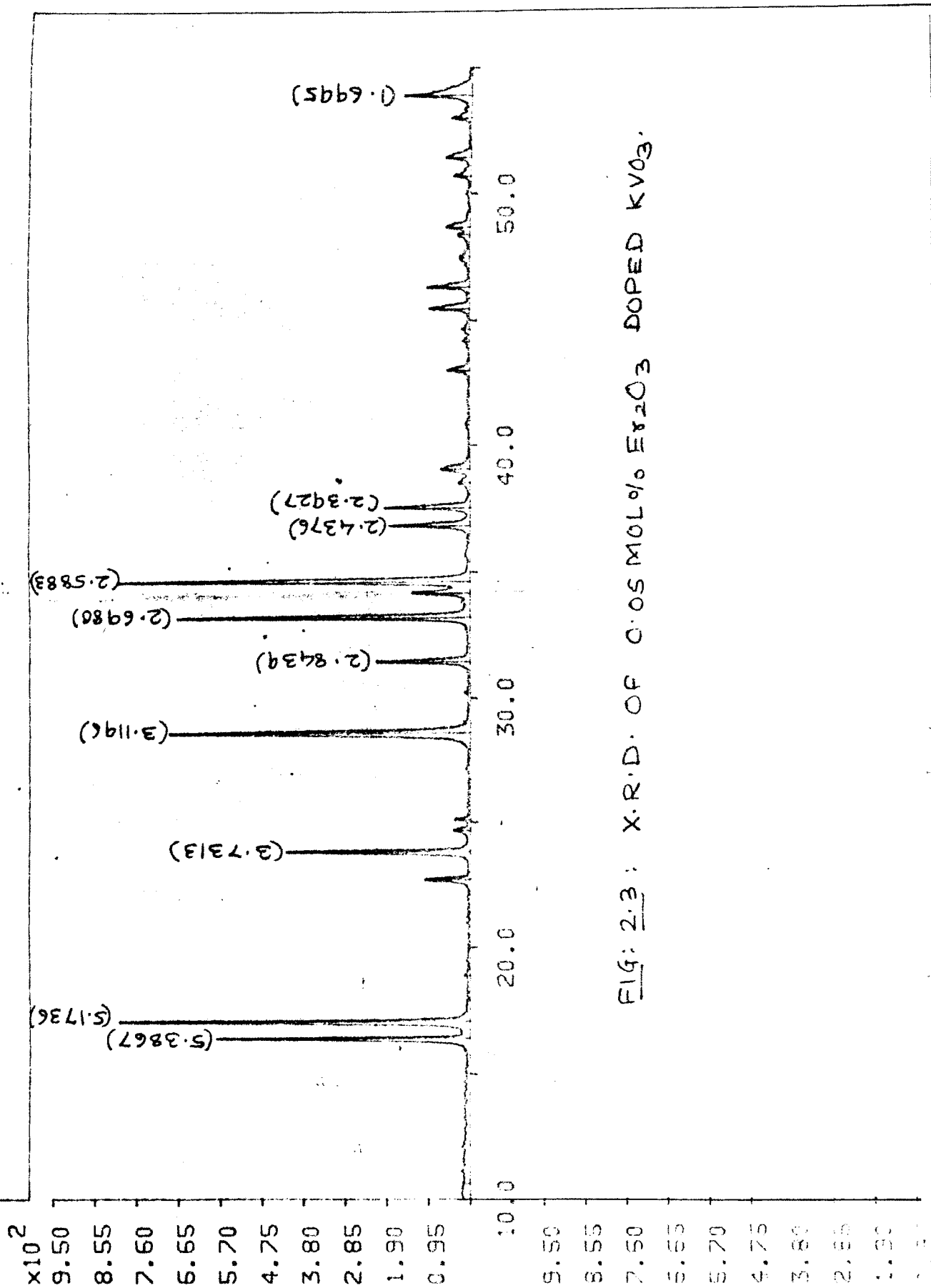
FIG: 2.3 : X.R.D. OF 0.05 MOL% Er₂O₃ DOPED KVO₃.
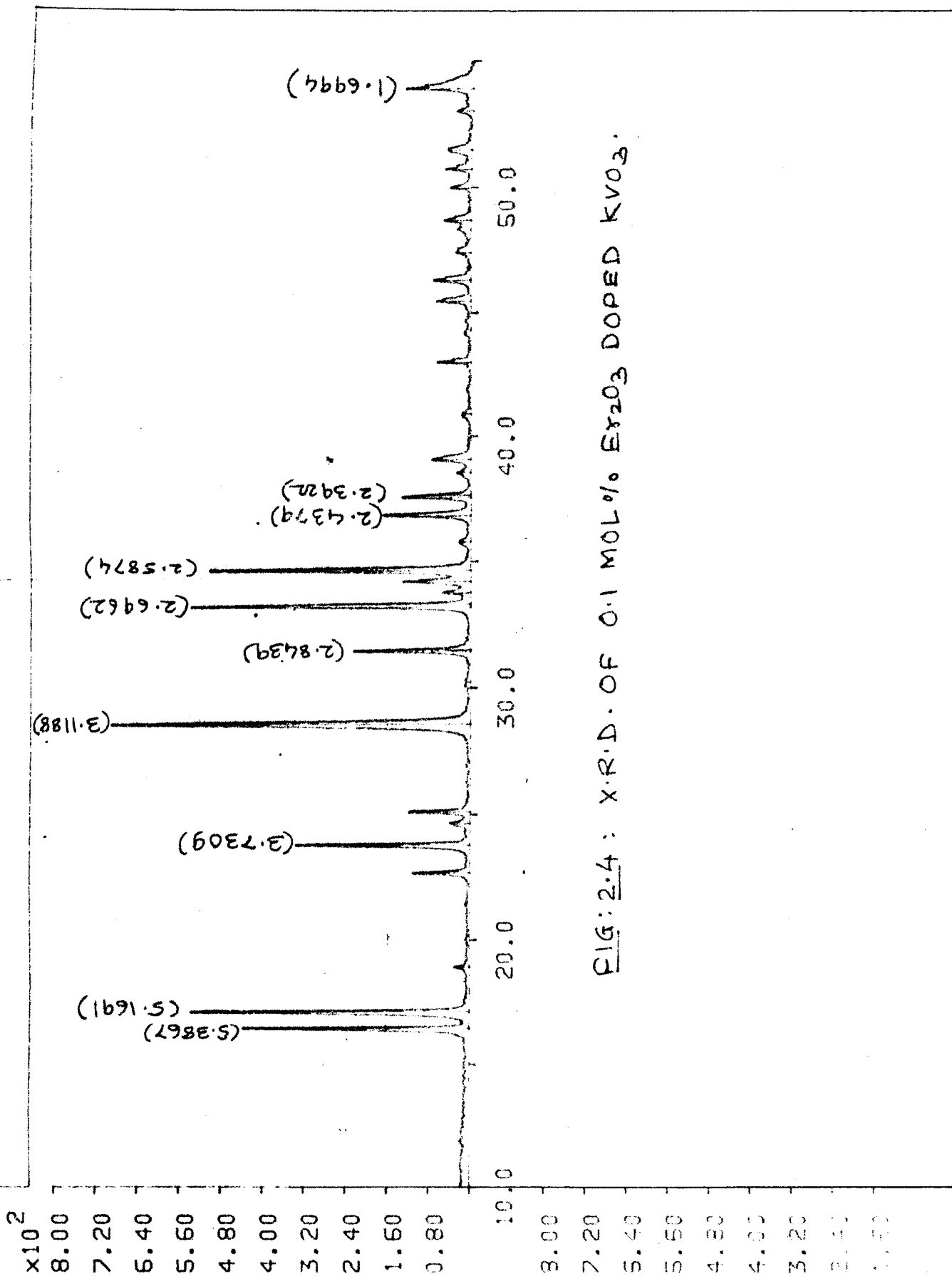
FIG: 2.4 : X.R.D. OF 0.1 MOL% Er₂O₃ DOPED KVO₃.

Sample: TS4   File: 739S4.SM

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$x10^3$

1.40	
1.26	
1.12	
0.98	
0.84	
0.70	
0.56	
0.42	
0.28	
0.14	

(5.3875)
(5.1751)
(3.7328)
(3.1212)
(2.4976)
(2.5879)
(2.3924)
(1.6995)

10.0   20.0   30.0   40.0   50.0
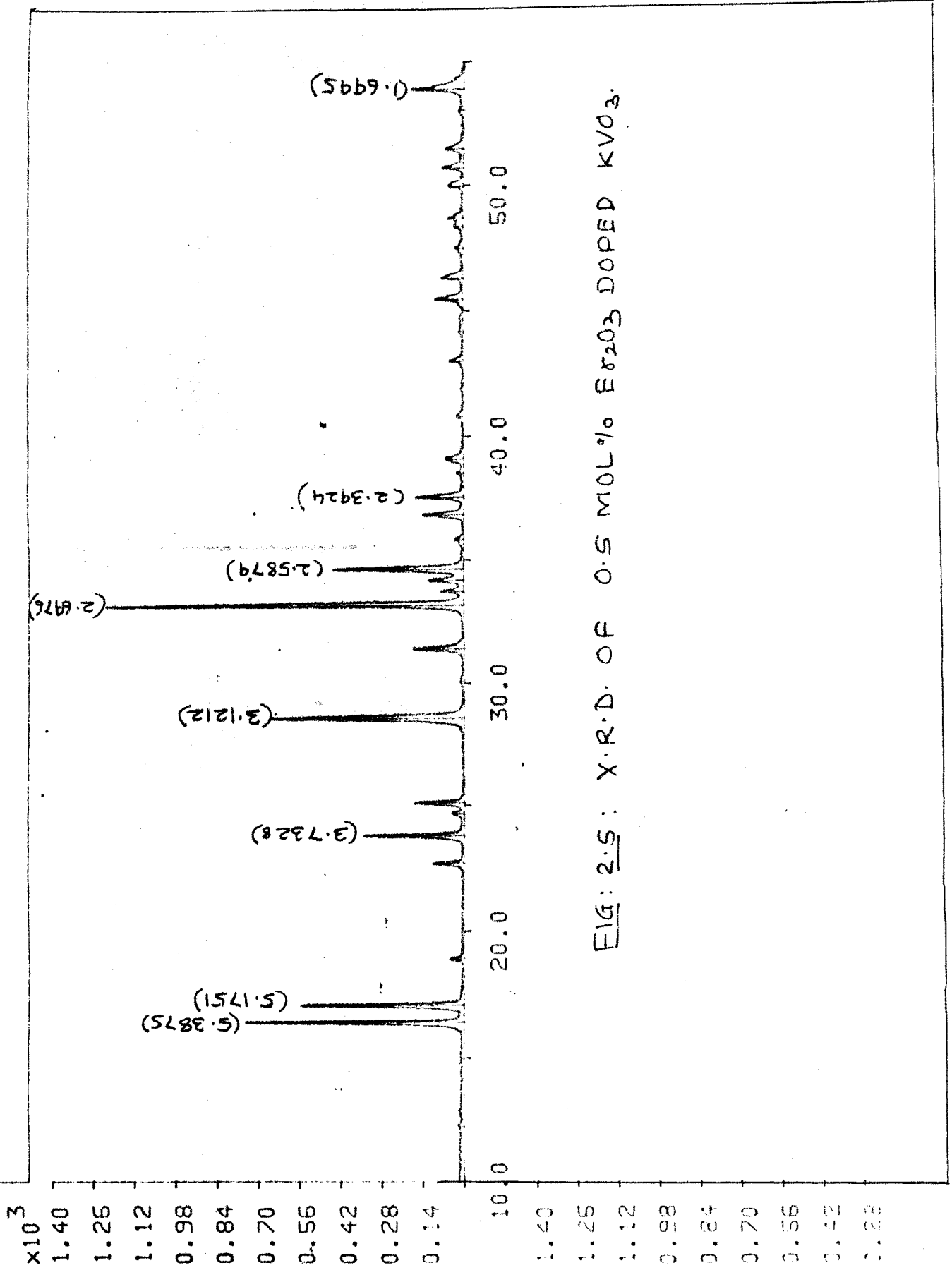
FIG: 2.5 : X.R.D. OF 0.5 MOL% Er_2O_3 DOPED KVO_3.
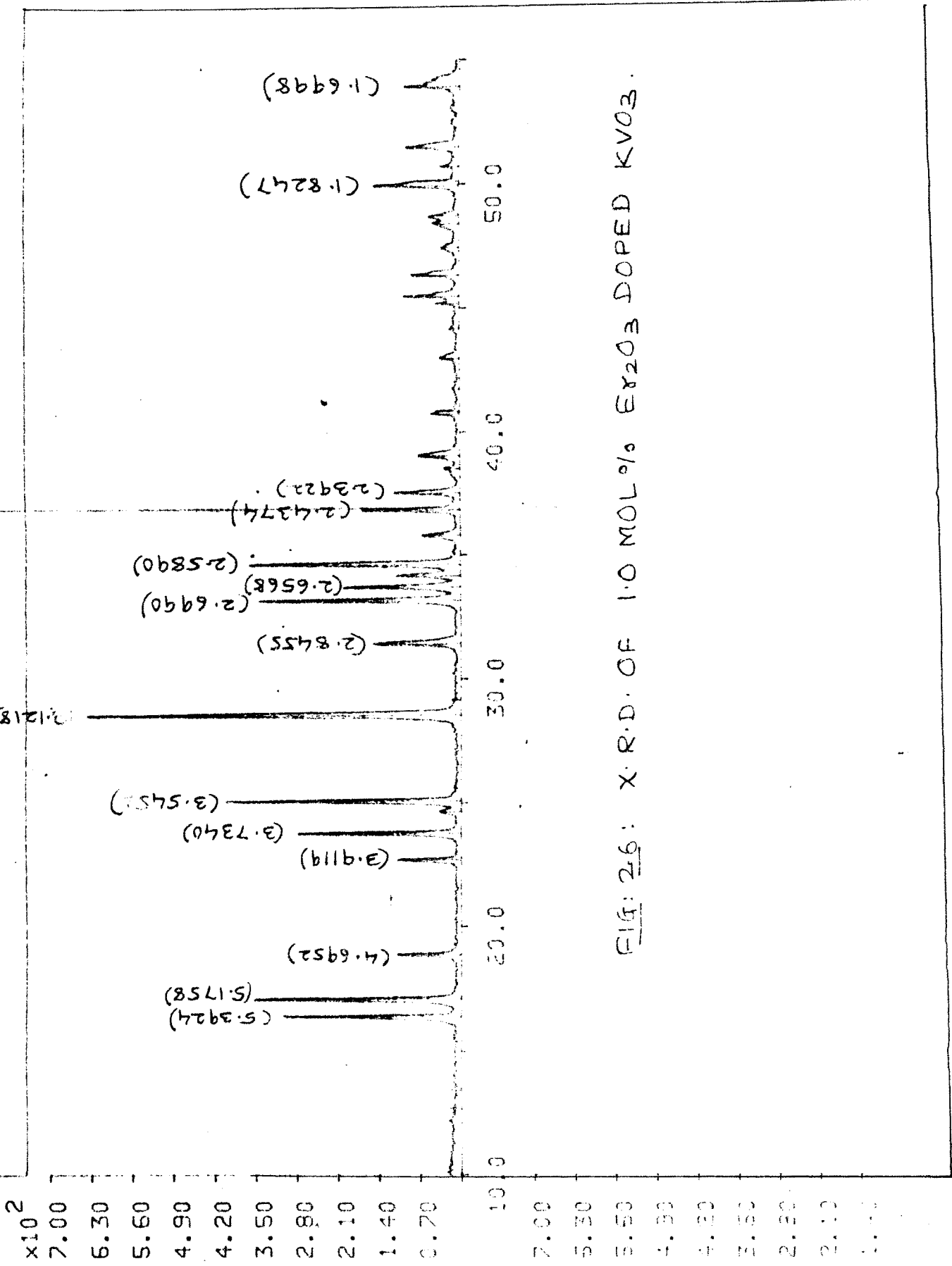
FIG: 26: X.R.D. OF 1.0 MOL% Er₂O₃ DOPED KVO₃.

Sample; TS-6   File; 739AS6.SM

01-JUL-89

x10²
8.00
7.20
6.40
5.60
4.80
4.00
3.20
2.40
1.60
0.30

20.0   30.0   40.0   50.0

(5.3900)
(5.1721)
(4.6890)
(3.9144)
(3.7313)
(3.5432)
(3.1204)
(2.8448)
(2.6568)
(2.5874)
(2.5078)
(2.4362)
(2.2118)
(1.8243)
(1.8238)

FIG: 2.7 : X.R.D. OF 3 MOL% Er₂O₃ DOPED KVO₃.

where d is observed value, (h,k,l) are corresponding known values and (a,b,c) are to be determined.

Rewritting equation 2.2 as,

$$D^* = AH^* + BK^* + CL^* \qquad \ldots\ldots 2.3$$
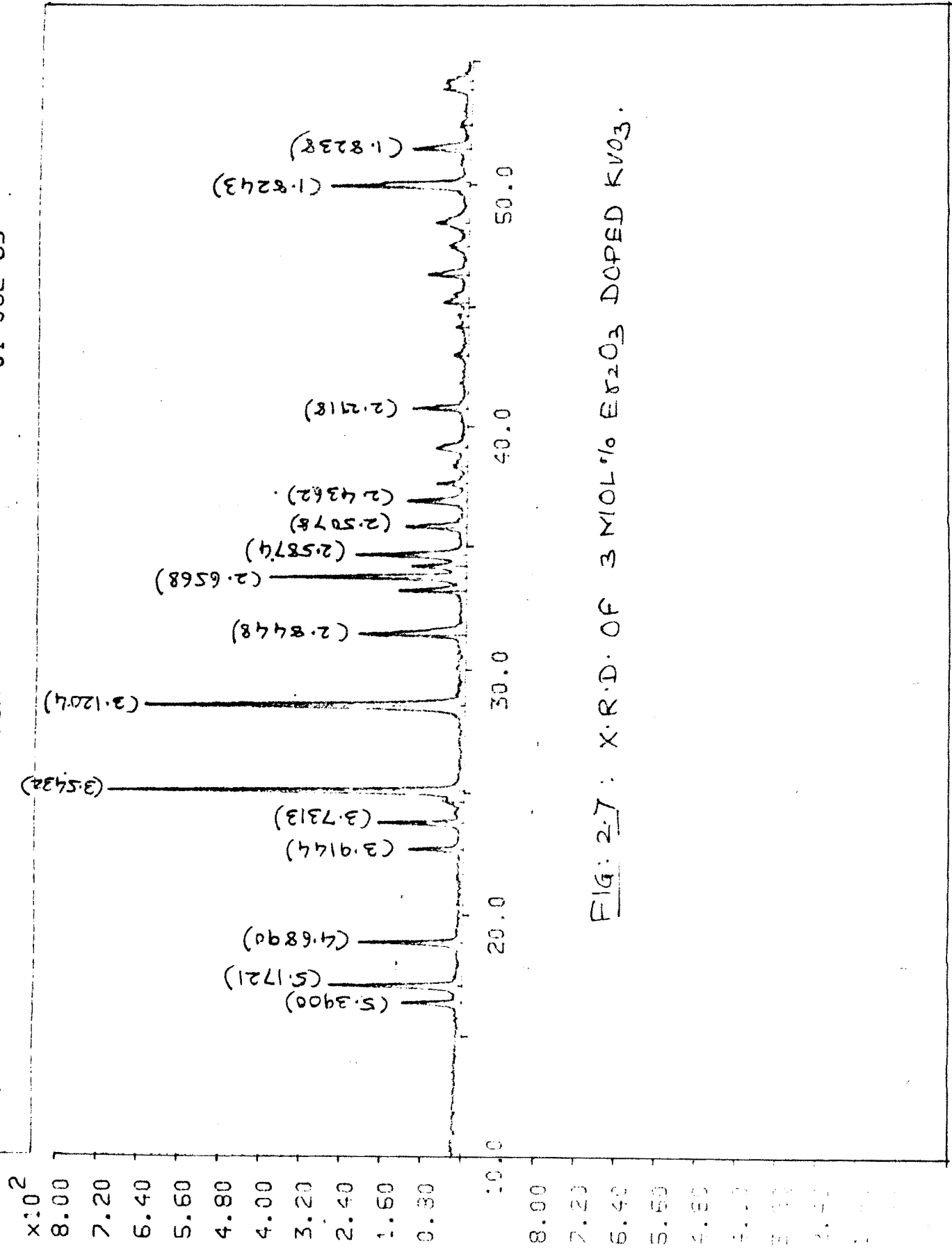
where $D^* = 1/d^2$, $A = 1/a^2$, $B = 1/b^2$, $C = 1/c^2$, $H^* = h^2$, $K^* = k^2$ and $L^* = l^2$

Here we observed D^* for different sets of $(H^* K^* L^*)$ according to equation 2.3.

We can write any ith observation as

$$\frac{1}{d_i^2} = \frac{h_i^2}{a^2} + \frac{k_i^2}{b^2} + \frac{l_i^2}{c^2} + \varepsilon_i$$

i.e $\quad D_i^* = H_i^* A + K_i^* B + L_i^* C + \varepsilon_i \qquad \ldots 2.4$

where ε_i is unobservable error component and $i = 1,2,\ldots n$.

This system of equations can be written in the matrix form as follows.

$$\underline{D}^* = H\underline{A}^* + \underline{\varepsilon} \qquad \ldots 2.5$$

where

$$H = \begin{pmatrix} h_1^2 & k_1^2 & l_1^2 \\ h_2^2 & k_2^2 & l_2^2 \\ \vdots \\ h_n^2 & k_n^2 l_n^2 \end{pmatrix}$$

and

$$\underline{D}^* = (D_1^* \ldots D_n^*)', \quad \underline{A}^* = (A,B,C)'$$

and

$$\underline{\varepsilon} = (\varepsilon_1, \varepsilon_2, \ldots \varepsilon_n)'$$

we want to solve this system of equations. The solution of above equations is given as,

$$\hat{\underline{A}}^* = (H'H)^- (H'\underline{D}^*) \qquad \qquad \dots 2.6$$

where $(H'H)^-$ is usual inverse if $(H' H)$ is nonsingular, otherwise it is g-inverse. Such inverse is directly obtained on computer by using MATLAB pakage.

From equation 2.6, we get,

$$\hat{A}^* = (\hat{A}, \hat{B}, \hat{C}) = (\frac{1}{\hat{a}^2}, \quad \frac{1}{\hat{b}^2} \quad \frac{1}{\hat{c}^2})$$

$$\hat{a} = 1/\sqrt{\hat{A}} \qquad \hat{b} = 1/\sqrt{\hat{B}} \qquad \text{and} \quad \hat{c} = 1/\sqrt{\hat{C}}.$$

The calculated values of lattice parameters of the samples along with the data reported by earlier workers are summarised in Table 2.2.

TABLE 2.2

LATTICE PARAMETERS AND UNIT CELL VOLUME OF THE SAMPLES

Sample		.Present work (L.S.M.)	Earlier results Hawthorne Calvo	Feigelson
Undoped KVO_3	$a(A^o)$	5.6980	5.176	5.70
	$b(A^o)$	10.7833	10.794	10.82
	$c(A^o)$	5.1778	5.680	5.22
	$V(A^{o3})$	318.14	317.3	321.9
KVO_3	$a(A^o)$	5.5048	-	-
doped	$b(A^o)$	10.2062	-	-
with	$c(A^o)$	5.3000	-	-
0.025 mol%	$V(A^{o3})$	297.77	-	-
Er_2O_3				
KVO_3	$a(A^o)$	5.6980	-	-
doped	$b(A^o)$	10.7833	-	-
with	$c(A^o)$	5.1778	-	-
0.05 to 3	$V(A^{o3})$	318.14	-	-
mol % Er_2O_3				

Table 2.2, reveals us that, the values of lattice parameters(a,b,c) of the undoped KVO_3 are found to agree favourably with the results of the earlier workers. Similarly, for the samples containing KVO_3 doped with 0.05 to 3 mol % Er_2O_3 , the lattice parameters remain unchanged. But for KVO_3 doped with 0.025 mol % Er_2O_3, the considerable changes in lattice parameters are observed. We have observed deformation of the unit cell maxiimum along the b-axis, moderately along a-axis and minimum along the c-axis. The similar deformation was observed by Bubnova et al (1982) for $LiVo_3$-$NaVO_3$ system. Due to this decrease in volume of unit cell of KVO_3 doped with 0.025 mol % Er_2O_3, the density of pellet increases which is a favourably agree with density shown in Table 2.1.

2.6 E.P.R. STUDIES

2.6 (a) INTRODUCTION

The electron paramagnetic resonance (EPR) is also called the electron spin resonance (ESR). This phenomenon is shown by atoms having an odd number of electrons, ions having partly filled inner electron shells and other molecules that carry angular momentum of electronic origin. The main interest of ESR lies in the study of free radicals having unpaired electrons. Substances with unpaired electrons are mainly paramagnetic in nature e.g. molecules like NO, O_2 and No_2, and the ions of transition metals and rare earth elements. In ESR, the energy levels are produced by the interaction of the magnetic moment of an unpaired electron in an ion with an applied magnetic field. The ESR spectrum results in due to the transitions between these energy levels by absorbing

radiations of microwave frequency. Thus, the ESR spectrum of a free electron would consist of a single peak corresponding to a transition between these levels. When the absorption occurs, the following relation holds good, i.e.,

$$2 \mu_e H = h\nu \qquad \qquad \text{.... 2.7}$$

where, ν is the frequency of the radiation, μ_e is the magnetic moment of the spinning electron, h is planck's and H is the applied field. As the relation 2.7 holds good for a free electron, the energy (ΔE) of transition is more accurately given by the relation,

$$\Delta E = h\nu = g \beta H \qquad \qquad \text{... 2.8}$$

where, β is Bohr's magneton and g is the proportionality factor which is a function of the electron's environment. It is also called the spectroscopic splitting factor or Lande's splitting factor. The value of g is not constant, but it is a tensor quantity. For a free electron its value is 2.0023, but this value is slightly modified for electrons in molecules. Virtually all free redicals and some ionic crystals have almost same value of g as for free electrons, but this value is modified by 0.003. The reason for this is essentially that in free radicals, the electron behaves in very much the same way as an electron in free space. The peak height of the absorption curve does not provide much information. However, the total area covered by absorption curve is proportional to the number of unpaired electrons in the sample. This number can be calculated by comparing this area with the area that of standard sample.

The width of an ESR depends on the relaxation time of the spin state under study. For most of the samples, 10^{-7} second is a relaxation time and if we substitute this value in Heisenberg's uncertainty relation, we can calculate a frequency uncertainty (line width) which comes out to be ≈ 1 gauss. A shorter relaxation time will increase this width. The broadening of spectral lines in ESR may also occur if the concentration of the paramagnetic species is very high. In complex substnaces, the ESR spectrum will not contain all the lines expected because the g-factor and conpling values are such that two lines may overlap and, thus, the line are not resolved.

Burns et al (1966) were studied EPR properly of Cr^{3+} and rare earth doped $LiNbO_3$. Effect of doping of Cr^{3+} and Cr^{5+} in sodium vanadate was discussed by Dmitrieva et al (1973). EPR of Fe^{3+} in $KNbO_3$ at $300^{O}K$ was studied by Siegel and Urban (1975).Grunin et al were observed ESR spectrum of Cr^{5+} ions in alkali metavanadates. Similarly effect of Mn^{2+} in $CdTiO_3$ lattice by EPR method was discussed by Geifman et al (1983).

2.6 (b) EPR Studies Of Undoped And Er_2O_3 Doped KVO_3

EPR technique is used to study the effect of doping of Er_2O_3 (0.025 mol %) in KVO_3. EPR spectra of undoped and 0.025 mol % Er_2O_3 doped KVO_3 in the form of a powder are taken at 300° K from R.S.I.C.(I.I.T), Bombay which are shown in Figure **2.8**. The attempt is made to calculate Lande's g-factor, the line width and total intensity of the pure KVO_3 and Er_2O_3 (0.025 mol %) doped KVO_3, by using EPR spectrum; and are summarized in Table 2.3.
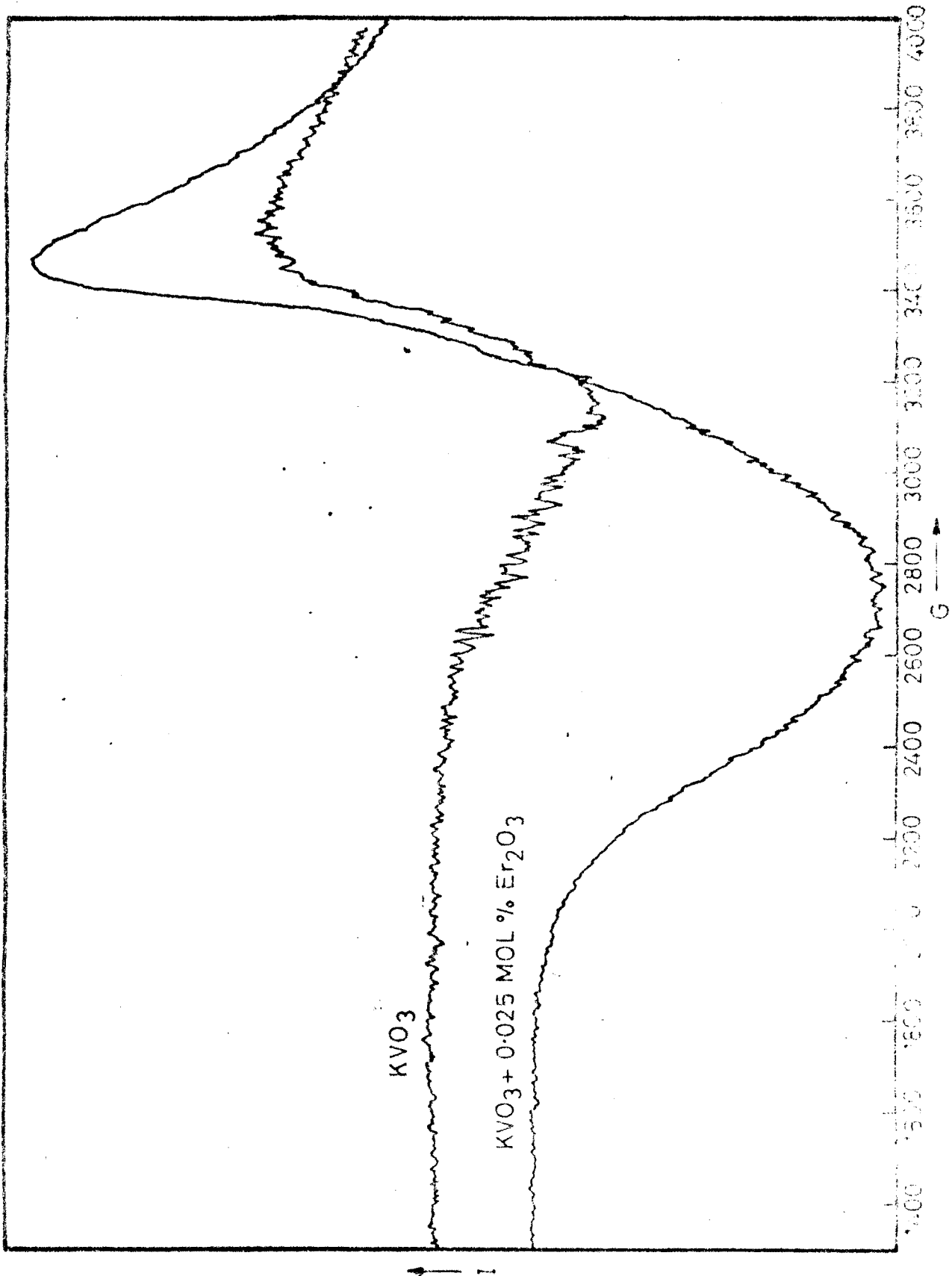
Fig.2·3 EPR SPECTRA OF UNDOPED AND 0·025 MOL % Er_2O_3 DOPED KVO_3 .

KVO₃

$KVO_3 + 0·025$ MOL% Er_2O_3

$G \longrightarrow$

TABLE 2.3

EPR PARAMETERS FOR UNDOPED AND 0.025 %Er_2O_3 DOPED KVO_3

EPR parameters	Undoped KVO_3	Er_2O_3(0.025 mol % doped KVO_3
g-factor	1.979	2.027
Line-width	410.000	720.000
Total Intensity	663995.000	4950720.000

Table 2.3 reveals us that there is appreciable change in Lande g-factor due to Er_2O_3 content in KVO_3 which produces free radicals of doped sample. Similarly, due to doping line width of the spectrum increases decreasing the relaxation time. The total intensity also increases showing the increase in number of unpaired electrons due to Er_2O_3 content in KVO_3. This investigation suports the following conclusions.

1. The addition of 0.025 mol % Er_2O_3 in KVO_3 shows change in Lande g-factor, indicating ionic substitution of Er^{3+} in place of K^{+1}.

2. EPR spectrum of undoped and Er_2O_3 doped KVO_3 shows single peak showing no resolution or hyperfine splitting.

3. Due to doping of Er_2O_3 in KVO_3, total intensity of the peak increases, indicating the increase of unpaired electrons.

4. EPR peak is broadened due to addition of paramagnetic species i.e. rare earth ions(Er^{3+}) in the lattice of KVO_3, showing

solubility limit of Er_2O_3 in KVO_3 lattice.

5. The EPR spectrum and X.R.D. analysis for 0.025 mol % Er_2O_3 content in KVO_3 are quite in agreement with each other. EPR spectrum results for studied ceramic are quite in agreement with results obtained by E.Siegel and W.Urban (1975) in the E.P.R. of Fe^{3+} in $KNbO_3$ at 300^0K.

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