

CHAPTER - III

ELECTRICAL AND STRUCTURAL CHARACTERISATION

CHAPTER-III

ELECTRICAL AND STRUCTURAL CHARACTERISATION :

3.1 Introduction :

The characterisation of phosphors before undertaking any luminescence studies, is indispensable for the proper understanding of the mechanism underlying the luminescence process. Moreover, the luminescence properties of the phosphors depend chiefly on crystal structure, type and amount of impurity doped during the process of preparation. In the present study an attempt has been made to characterise the phosphors on the basis of electrical and structural characterisation.

3.2 Electrical Characterisation :-

The current-voltage (I-V) plots of BaSO_4 :Dy:Tb, BaSO_4 :Dy:Pr, BaSO_4 :Dy:Yb, BaSO_4 :Dy:Cu & BaSO_4 :Dy:Mn phosphors were studied by using EL cell. The construction of EL cell has been fully dealt in the forthcoming Chapter. Fig. 3.1 shows circuit diagram I-V studies. The phosphor under study was packed in EL cell and sinusoidal voltage was applied at different frequencies viz. 500 HZ, 1000 HZ, 1500 HZ and 2000 HZ. The current through phosphor was obtained by measuring P.D. across the resistor of $1\text{ K}\Omega$. Figs. 3.2 to 3.7

depict the I-V curves for typical phosphors, ML1, ML3, ML5, ML7, ML9 and ML21, (BaSO₄:0.075 wt. % Dy:0.001 wt % of Tb, Pr, Yb, Mn, Cu and BaSO₄:0.075 wt% Dy:0.001 wt. % Tb + Na₂SO₄). The curves show ohmic nature upto certain limit and then shoot up departing from linearity. The resistivity of the phosphors was calculated from the slopes of I-V curve using following relation.

$$\rho = \frac{V}{I} \cdot \frac{A}{t} \quad \text{cm.}$$

Where A is electrode area (2.3 x 1.3) cm², and t is thickness of sample (0.025 cm) The resistivity of the phosphors under study is found to be of the order of 10⁸ Ω-cm. The figs. 3.9 to 3.14 shows variation of ρ with respect to frequency for phosphors ML1 and ML21, ML3 and ML23, ML5 and ML25, ML7 and ML27, ML9 and ML29 and ML2 and ML1.

3.3 Results and discussions :-

It is observed that resistivity (ρ) decreases with frequency. (figs 3.9 to 3.14). The mode of decrease of resistivity with frequency seems to be much similar irrespect of activator and co-activator concentration and charge compensator Na₂SO₄.

Fig. 3.8 shows that the resistivity in general decreases with increase of activator concentration. This seems to be quite obvious because

3

higher activator concentration provides larger number of incorporated activator ions, which improves the conductivity of the material. The resistivity versus frequency is plotted in fig.3.9 for BaSO_4 ; 0.075 wt. % Dy : 0.001 wt. % Tb without Na_2SO_4 and with Na_2SO_4 . The resistivity of Na_2SO_4 added phosphor seems to be less than that of phosphor without Na_2SO_4 . Similar observations found in case of Pr, Yb, except Mn and Cu co-doped phosphors. (figs. 3.10 to 3.13). This could be explained on the basis that more number of activator ions being present in the phosphor with Na_2SO_4 than that of phosphor without Na_2SO_4 . The probable mechanism underlying the possibility of more activator ions being incorporated in Na_2SO_4 added phosphor is explained on the basis of charge compensation being dealt in detail in the forthcoming chapter.

Fig. 3.14 shows resistivity versus frequency curves for BaSO_4 ; 0.075 wt. % Dy : 0.0025 wt. % Tb (ML2) and BaSO_4 ; 0.075 wt. % Dy : 0.001 wt. % Tb (ML1) phosphors. It is seen that ML2 exhibits higher resistivity as compared to ML1. In fact, ML2 offers more number co-activator ions to the host lattice than that of ML1. ML2, therefore, should have offered less resistivity as compared to ML1. However, this does not occur. The probable reason underlying this curious behaviour is as follows.

It is well known that the host lattice has

some limit to accept the number of activator ions being pumped by various methods. The upper limit of activator concentration being accepted by the host is known as "Optimum concentration" and phosphors so formed are known as concentration quenched phosphors. It has been 1,2,3 proved by earlier workers, that such optimum concentration especially in case of alkaline earth sulphate phosphor system like CaSO_4 , SrSO_4 , BaSO_4 etc. is around 0.075 to 0.1 wt.% of activator. In such phosphor system only trace of co-activator concentration is being accepted. Any higher concentration of co-activator instead of improving the quality of phosphor, deteriorates it. The probable reason for this behaviour is explained in detail in the forthcoming chapter on the basis of concentration quenching.

3.4 Structural Characterisation :-

In order to investigate structural characteristics of the phosphors, X-ray analysis was performed using X-ray diffraction (XRD) technique. This study revealed structural characteristics of the prepared phosphors. The structural characterisation of the phosphor were made on the basis of X-ray analysis. The X-ray analysis could be performed either with the help of diffraction camera or by recording the intensities of diffracted lines with the help of a

'Geiger Counter'. In the photographic technique certain uncertainties are involved, as far as, the intensity measurements of the diffraction lines are concerned. In the present investigation, therefore, X-ray recording Geiger counter diffractometer with automatic chart recorder was preferred for X-ray diffraction study

BaSO₄ basically belongs to orthorhombic crystal system, with lattice constants

$$a = 8.8625 \text{ A.U.},$$

$$b = 5.4412 \text{ A.U. and}$$

$$c = 7.1401 \text{ A.U.}$$

The number of chemical formula multiples per unit cell is 4. It has optical constants $\alpha = 1.6362$, $\beta = 1.6373$ (Na), $\gamma = 1.6482$ having hardness (Mohl) 3 to 3.5 and density 4.5 gm/cc^{4,5}. BaSO₄ when doped with Dy and Tb, the activator ions enter the lattice substitutionally replacing Ba²⁺ ions. In order to investigate probable sites for these activator ions, XRD studies were carried out. The experimental set up for XRD studies is as follows :-

The basic arrangement of X - ray recording Geiger counter diffractometer (Philips PW 1050/70) is shown in fig. 3.15. The X - ray beam is rendered on specimen through soller and divergence slits. The diffracted X - rays enter the detector system through receiving soller and scatter slits. The other

counterparts of the diffractometer are channel control (PW 1390), Goniometer supply (PW 1373), single pen recorder (PM 8203). The X - ray tube (Nickel filtered, $\text{CUK}\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$) was operated at 35 Kv and 20 mA. The filter could give 52% transmission for $\text{K}\alpha$ and 2% for $\text{K}\beta$. A scanning rate 2.4 degrees per minute was found to be suitable for the purpose. The fig 3.16 depicts functional block diagram of the whole diffractometer system.

The phosphor under study was ground well in agate mortar and sieved through fine mesh screen to assure uniform particle size. The sample holder consists of Aluminium strip (4x2x0.25cm), provided with cavity 1x1 cm. The dry phosphor powder was packed in the cavity and was further smoothed by rubbing glass slide to and fro with reasonable pressure. A care was taken so as to avoid the air cavities in the sample. The surplus powder was gently removed. The sample holder was then placed in appropriate position.

Initially a rapid scan was taken so as to detect prominent peaks and angular region of interest. The scanning rate of 2.4 degrees per minute was then fixed for the angular region of interest (5° to 70°).

3.5 Result and discussion :-

Fig. 3.17 shows XRD patterns of typical

phosphors. (ML3, ML5, ML7, ML23, ML25 and ML27) scanned in the range 5° to 70° . The pattern shows prominent peaks at $2\theta = 20.2^{\circ}$, 20.64° , 23° , 26.2° , 27.2° , 29° , 31.8° , 33° , 42.8° and 49° . It is worth noting that diffraction patterns of all the phosphors have one to one similarity as far as their peak positions are concerned. This indicates that incorporation of activator, co-activator and Na_2SO_4 does not bring about any appreciable change in the crystal structure. Particularly the addition of Na_2SO_4 , during the preparation of phosphor cannot be suspected to give new compound. The role of Na_2SO_4 in the preparation of phosphor, therefore, seems to be purely that of charge compensator. This is more clear when we compare X-ray diffraction patterns a,b,c with d,e,f of fig. 3.17.

It is seen in general that peak intensities of Na_2SO_4 added phosphors are enhanced as compared to the peak intensities of phosphors without Na_2SO_4 , (except BaSO_4 : 0.075 wt, %Dy : 0.001 wt % Mn).

Particularly peaks at $2\theta = 20.2^{\circ}$ and 20.64° get appreciably enhanced in case of Na_2SO_4 added phosphors. The possible mechanism underlying this enhancement effect due to charge compensator Na_2SO_4 has been considered at length in the following chapter. Similar results in case of CaSO_4 phosphor system have been reported earlier.

6.7

It is rather difficult to predict in the complex system like one which is undertaken for the present studies, to indicate which angular sites (2 ⊙) favour incorporation of activator and co-activator ions.

FIGURE CAPTIONS

- Fig. 3.1 Circuit diagram for I-V studies.
- Fig. 3.2 I-V Curves for ML1:BaSO₄ :0.075 wt % Dy:0.001
Wt. % Tb.
- Fig. 3.3 I-V Curves for ML3:BaSO₄ :0.075 wt % Dy:0.001
Wt. % Pr.
- Fig. 3.4 I-V Curves for ML5:BaSO₄ :0.075 wt % Dy:0.001
Wt. % Yb.
- Fig. 3.5 I-v Curves for ML7:BaSO₄ :0.075 wt % Dy:0.001
Wt. % Mn.
- Fig. 3.6 I-V Curves for ML9:BaSO₄ :0.075 wt % Dy:0.001
Wt. % Cu.
- Fig. 3.7 I-V curves for ML21:BaSO₄ :0.075 wt % Dy:0.001
Wt. % Tb + Na SO_{2 4} .
- Fig. 3.8 Resistivity against concentration of Dy
Plot.
- Fig. 3.9 Resistivity against frequency plots for
ML1:BaSO₄ :0.075 Wt. % Dy: .0.001 Wt. % Tb and
ML21:BaSO₄ :0.075 Wt. % Dy: .0.001 Wt. % Tb +
Na SO_{2 4} phosphors.
- Fig. 3.10 Resistivity against frequency plots for
ML3:BaSO₄ :0.075 Wt. % Dy: .0.001 Wt. % Pr and
ML23:BaSO₄ :0.075 Wt. % Dy: .0.001 Wt. % Pr +
Na SO_{2 4} phosphors.
- Fig. 3.11 Resistivity against frequency plots for
ML5:BaSO₄ :0.075 Wt. % Dy: .0.001 Wt. % Yb and

ML25:BaSO₄ :0.075 Wt. % Dy: .0.001 Wt. % Yb +
Na SO_{2 4} phosphors.

Fig. 3.12 Resistivity against frequency plots for

ML7:BaSO₄ :0.075 Wt. % Dy: .0.001 Wt. % Mn and
ML27:BaSO₄ :0.075 Wt. % Dy: .0.001 Wt. % Mn +
Na SO_{2 4} phosphors.

Fig. 3.13 Resistivity against frequency plots for

ML9:BaSO₄ :0.075 Wt. % Dy: .0.001 Wt. % Cu and
ML29:BaSO₄ :0.075 Wt. % Dy: .0.001 Wt. % Cu +
Na SO_{2 4} phosphors.

Fig. 3.14 Resistivity against frequency plots for

ML2:BaSO₄ :0.075 Wt. % Dy: 0.0025 Wt. % Tb and
ML1:BaSO₄ :0.075 Wt. % Dy: 0.001 Wt. % Tb

Fig. 3.15 Geometry of X-ray diffractometer.

Fig. 3.16 Functional block diagram of diffractometer system.

Fig. 3.17 X-ray diffraction patterns of :

ML5:BaSO₄ : .075 Wt. % Dy: .001 Wt % Yb.
ML3:BaSO₄ : .075 Wt. % Dy: .001 Wt % Pr.
ML7:BaSO₄ : .075 Wt. % Dy: .001 Wt % Mn.
ML25:BaSO₄ : .075 Wt. % Dy: .001 Wt % Yb. +
(Na SO_{2 4}).
ML23:BaSO₄ : .075 Wt. % Dy: .001 Wt % Pr. +
(Na SO_{2 4}).
ML27:BaSO₄ : .075 Wt. % Dy: .001 Wt % Mn. +
(Na SO_{2 4}).

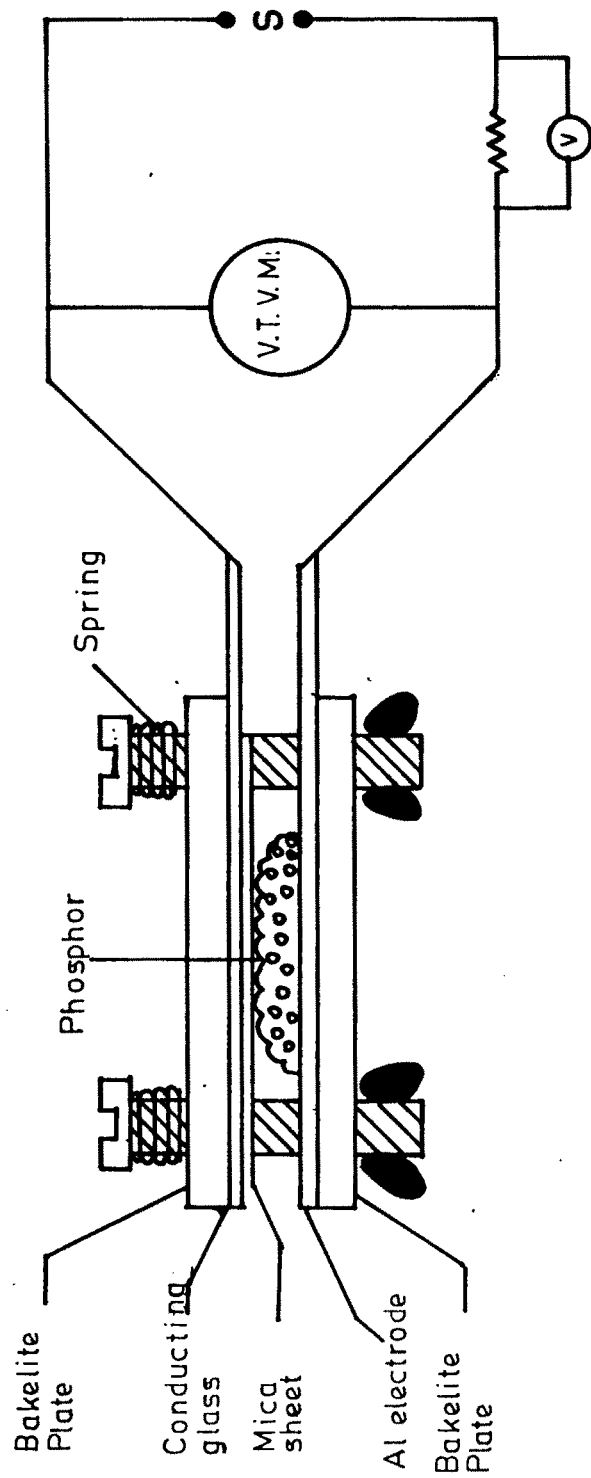


Fig - 3.1

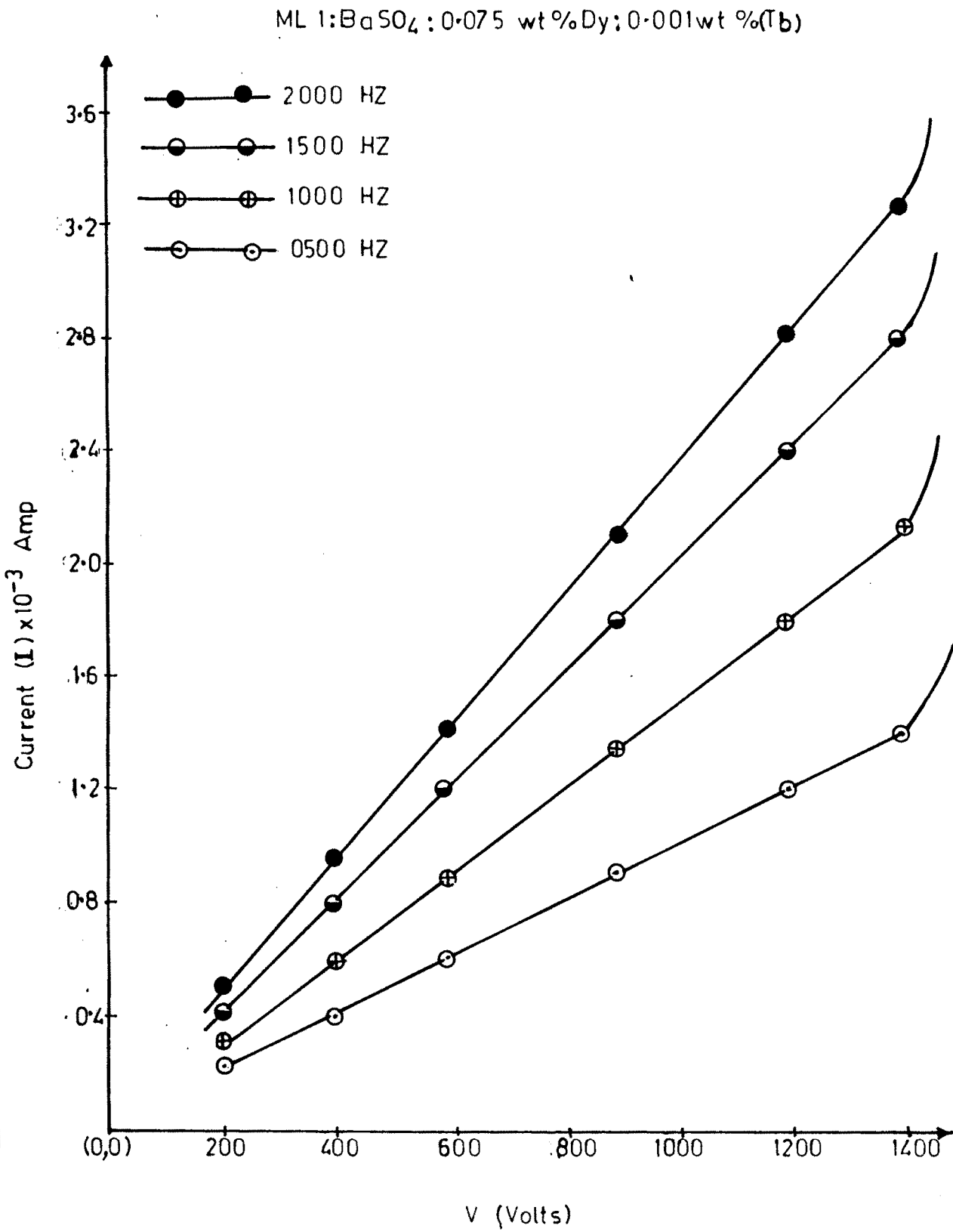


Fig. 3.2

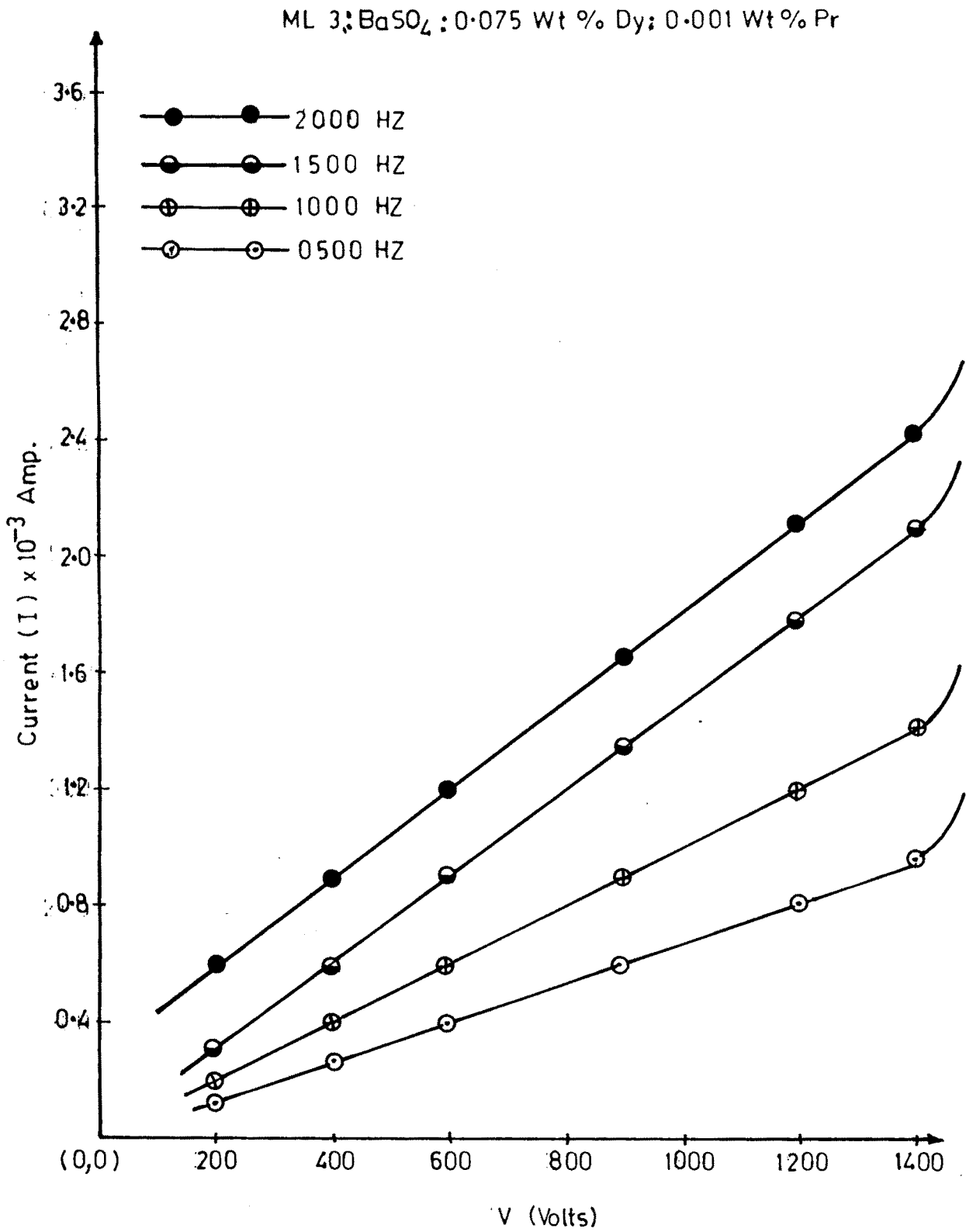


Fig. 3.3

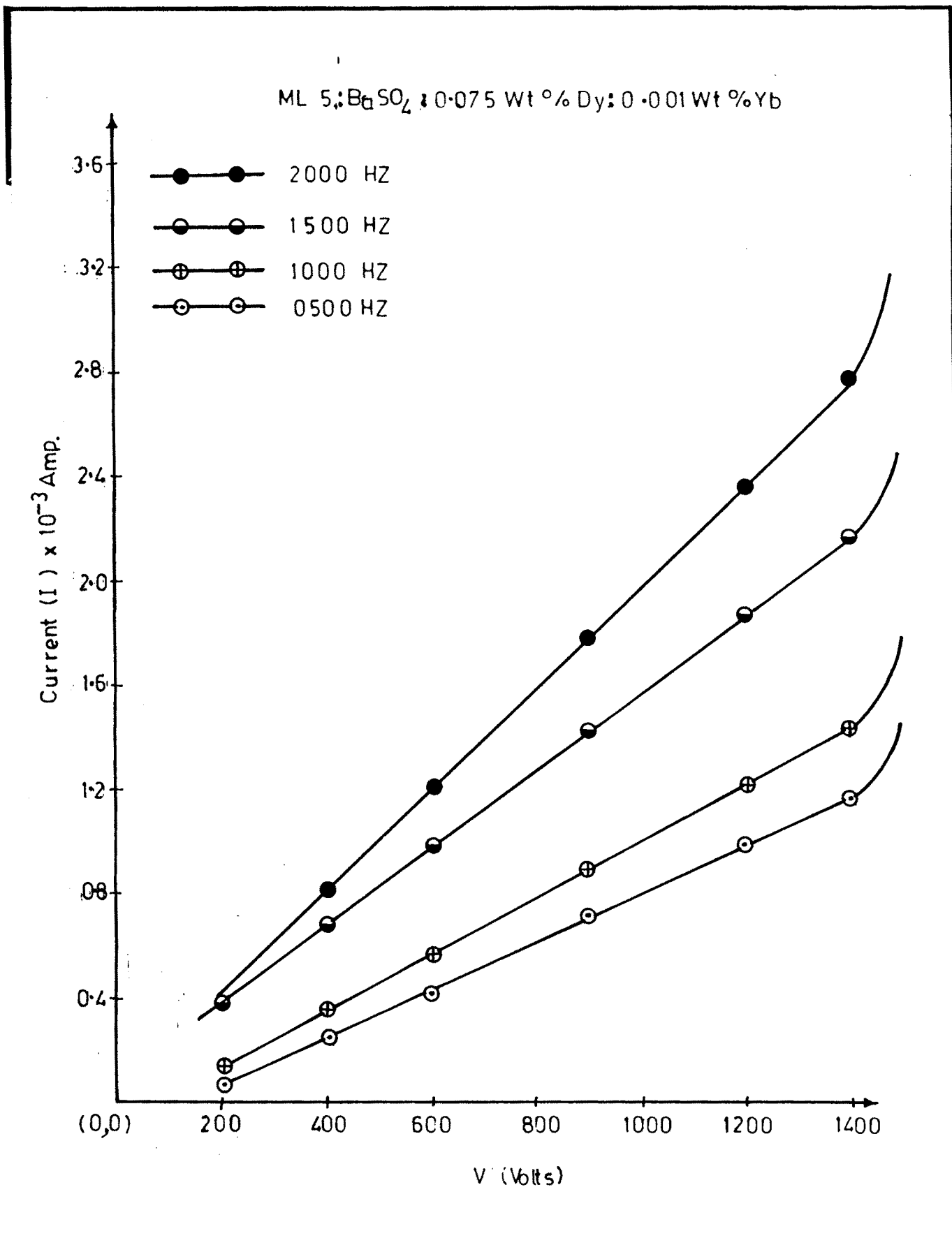


Fig 3.4

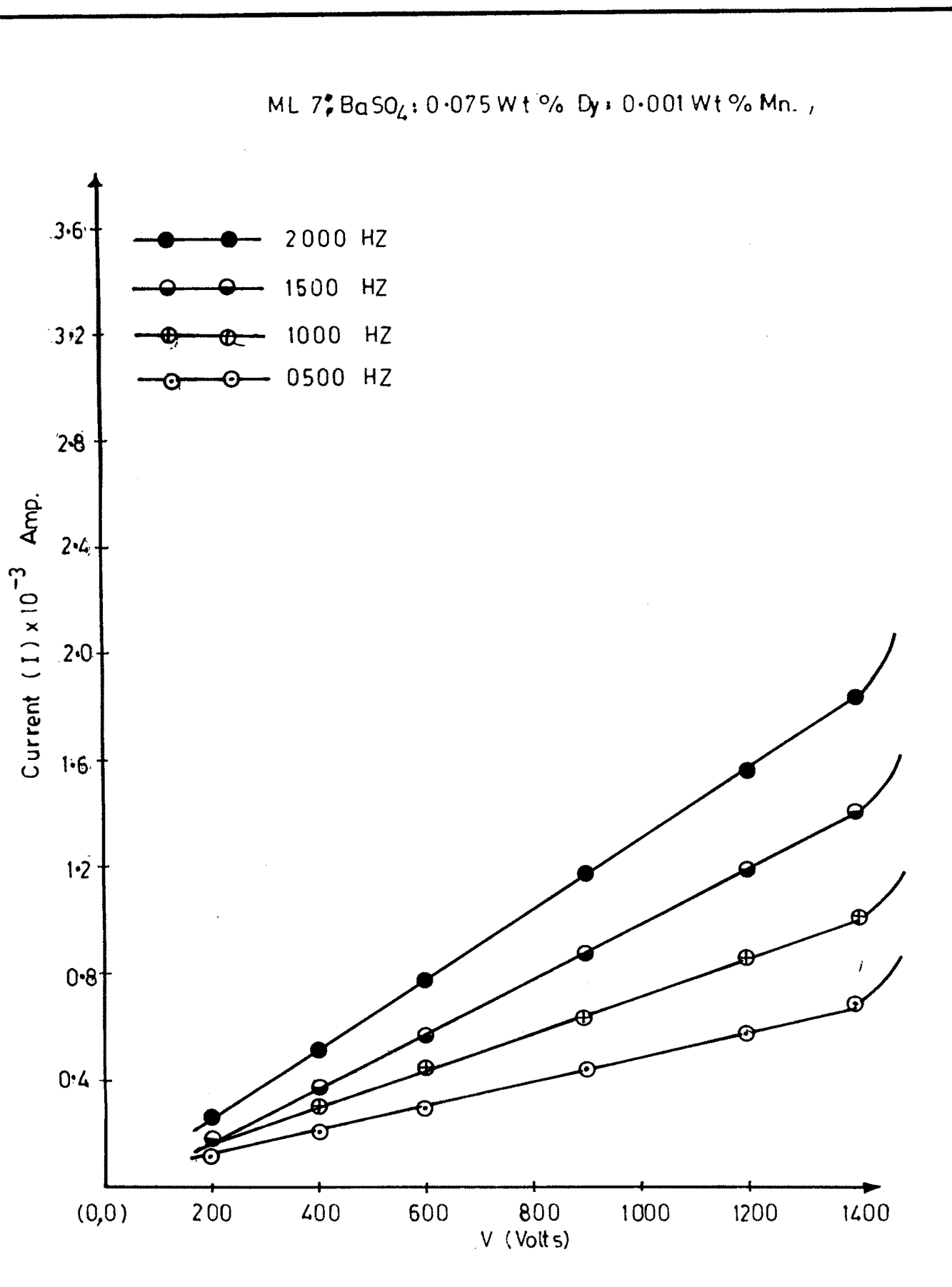


Fig 3.5

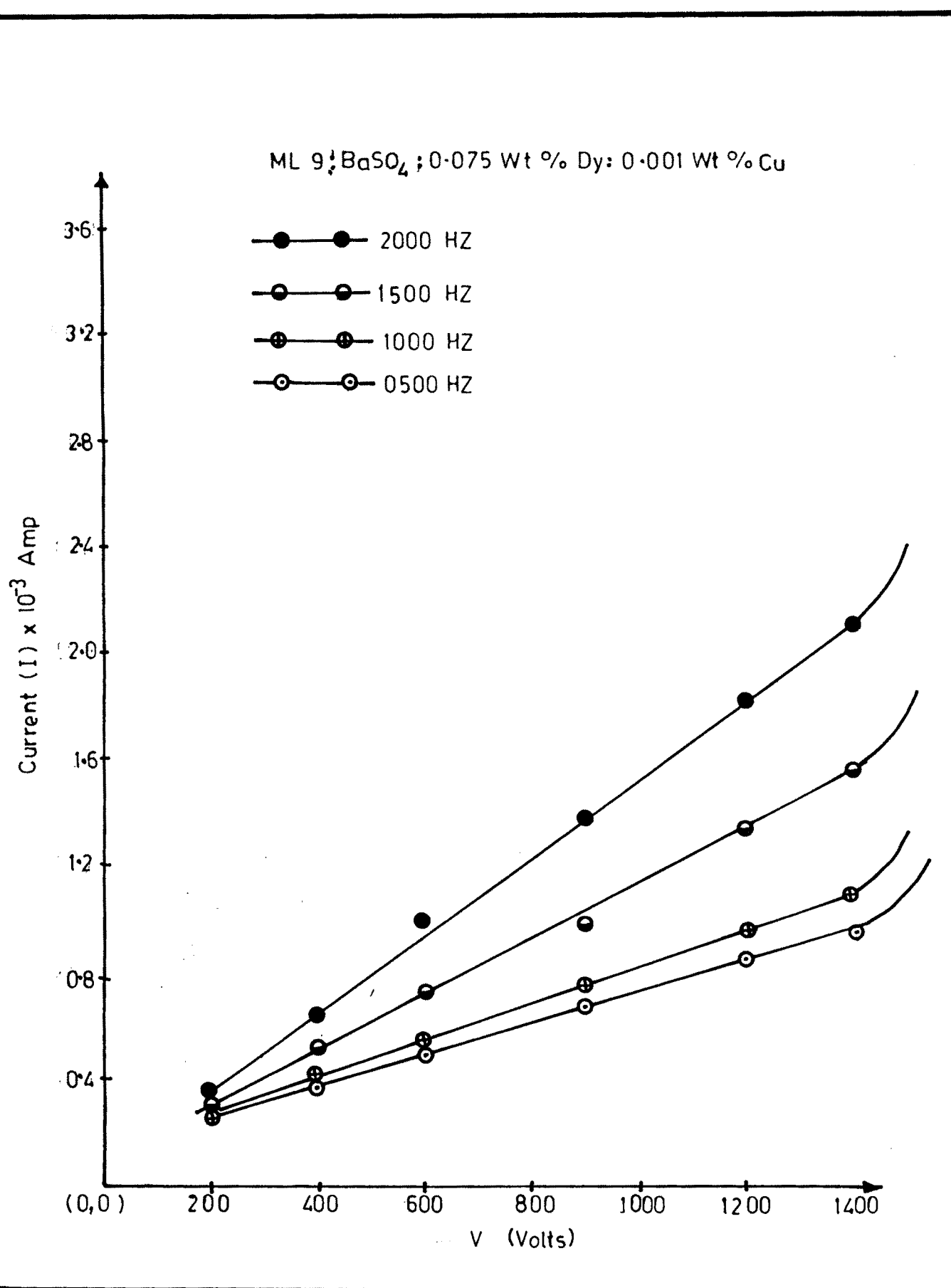


Fig. 3-6

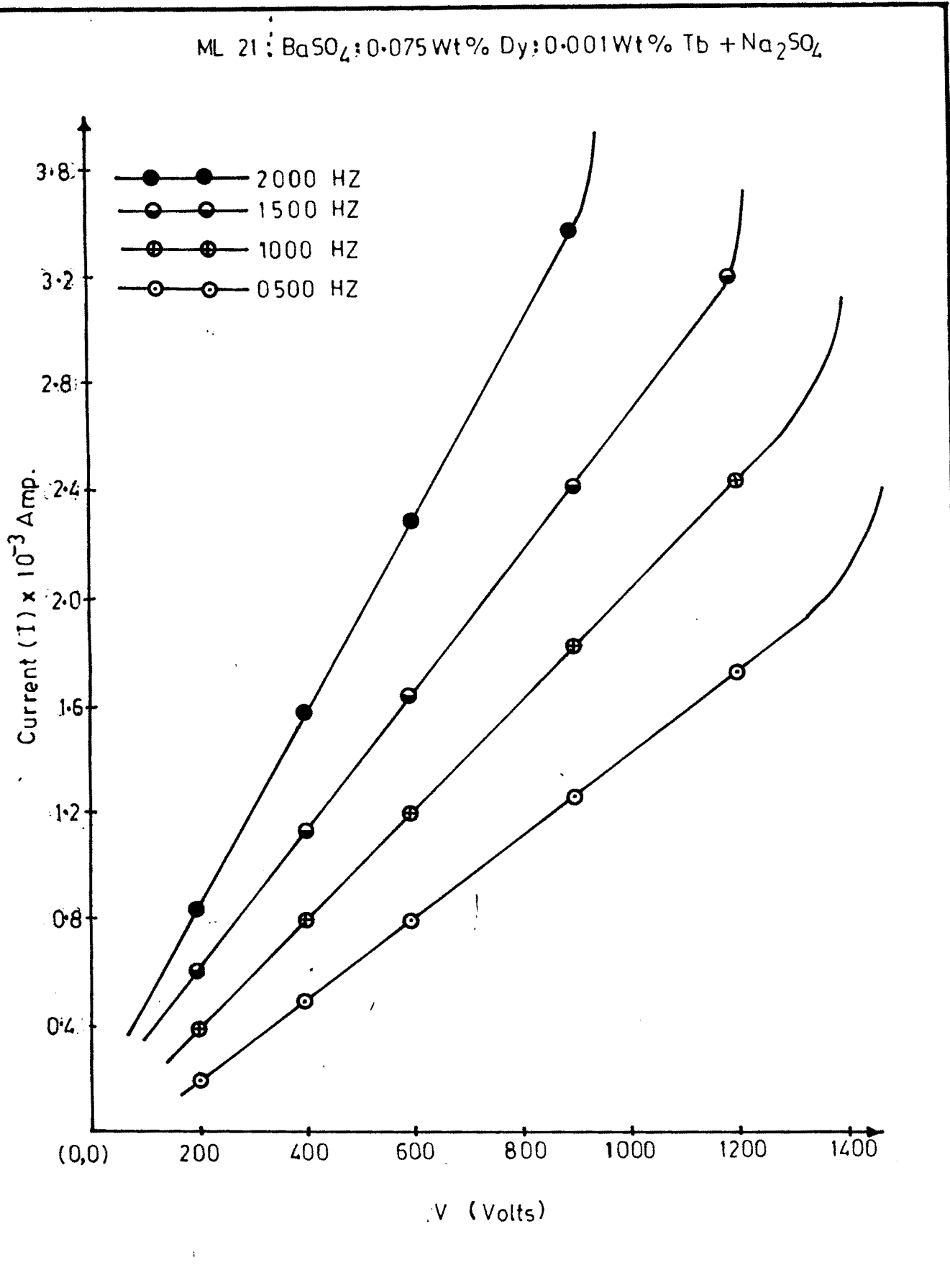


Fig. 3.7

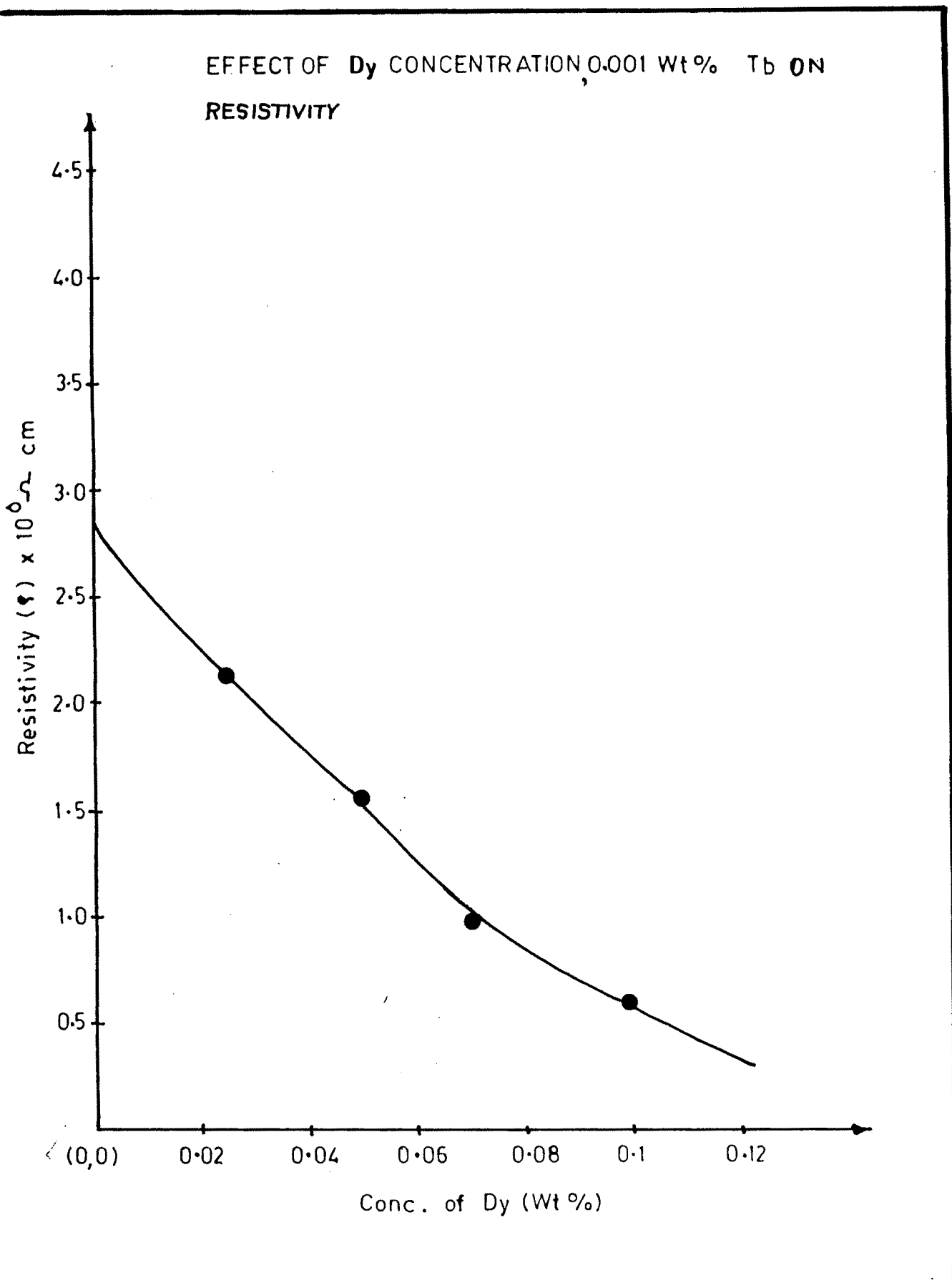


Fig. 3-8

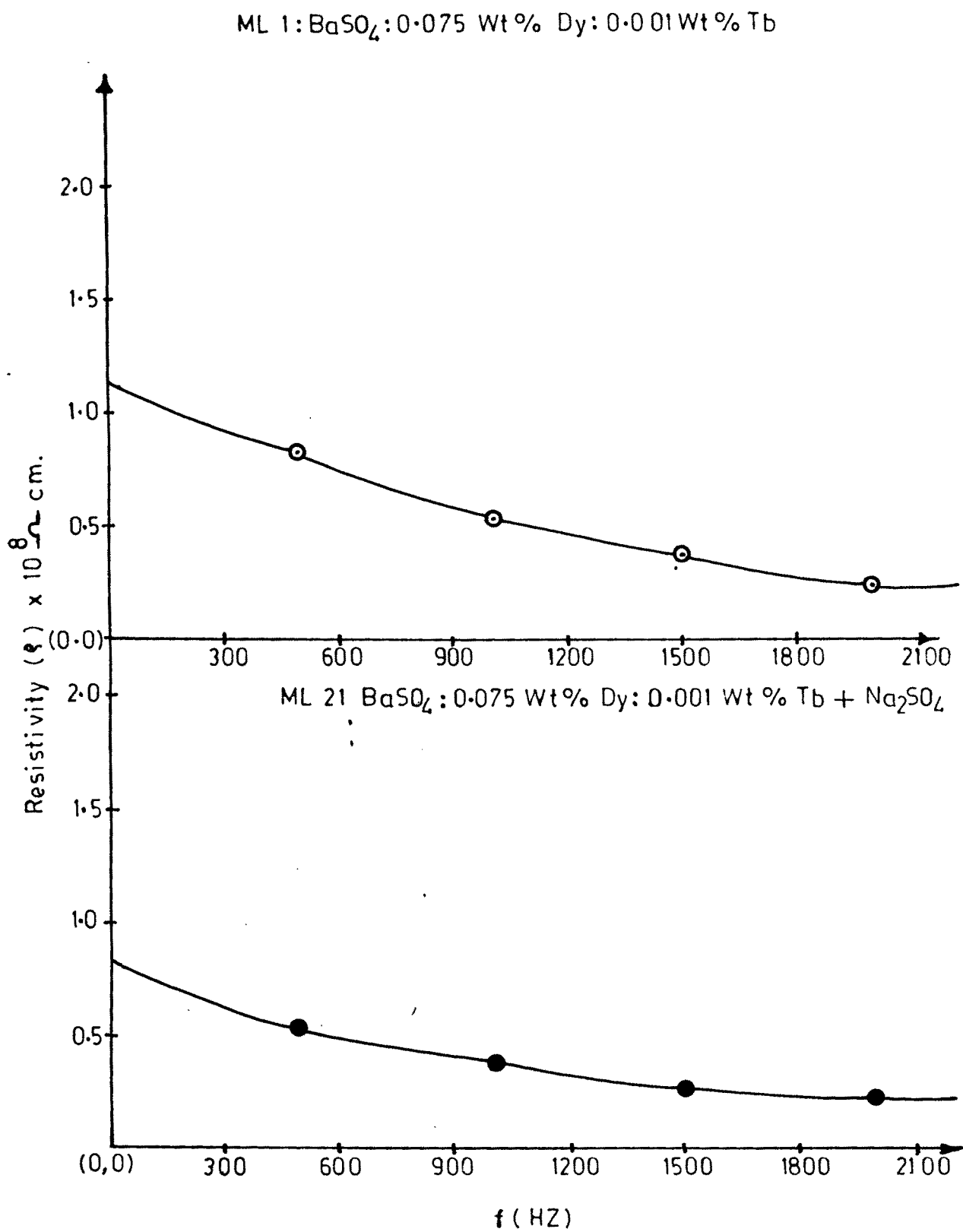


Fig.3.9

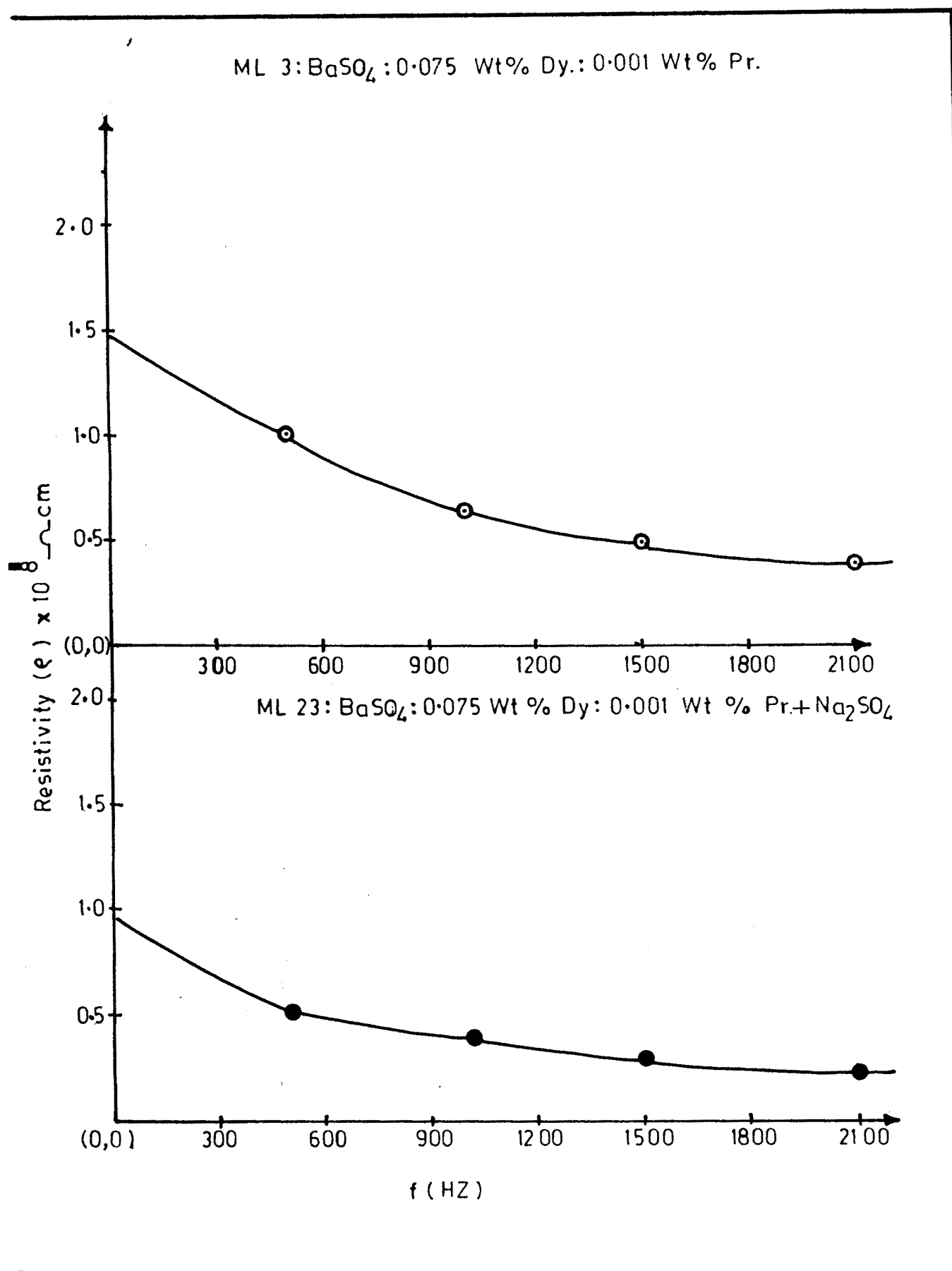


Fig 3.10

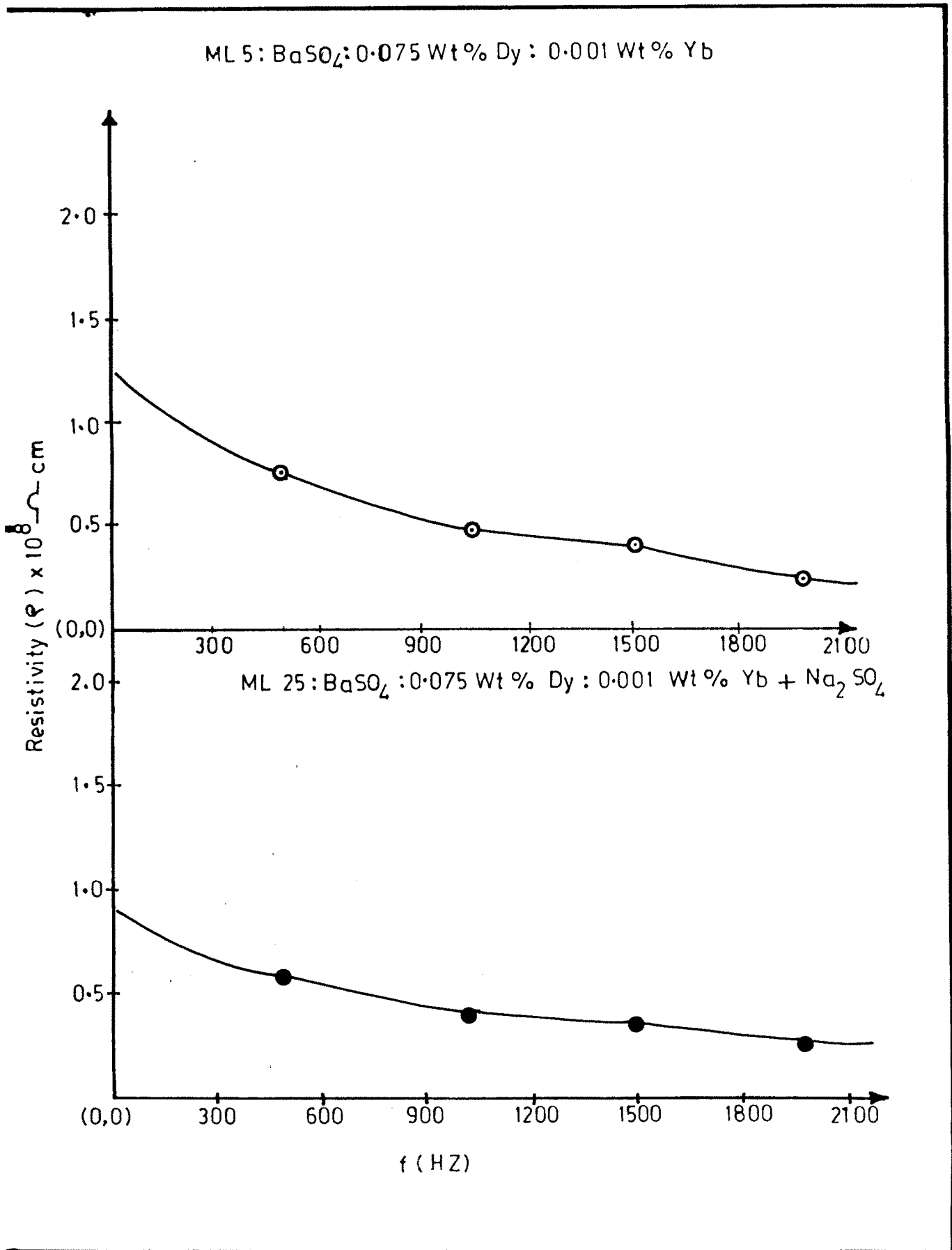


Fig. 3.11

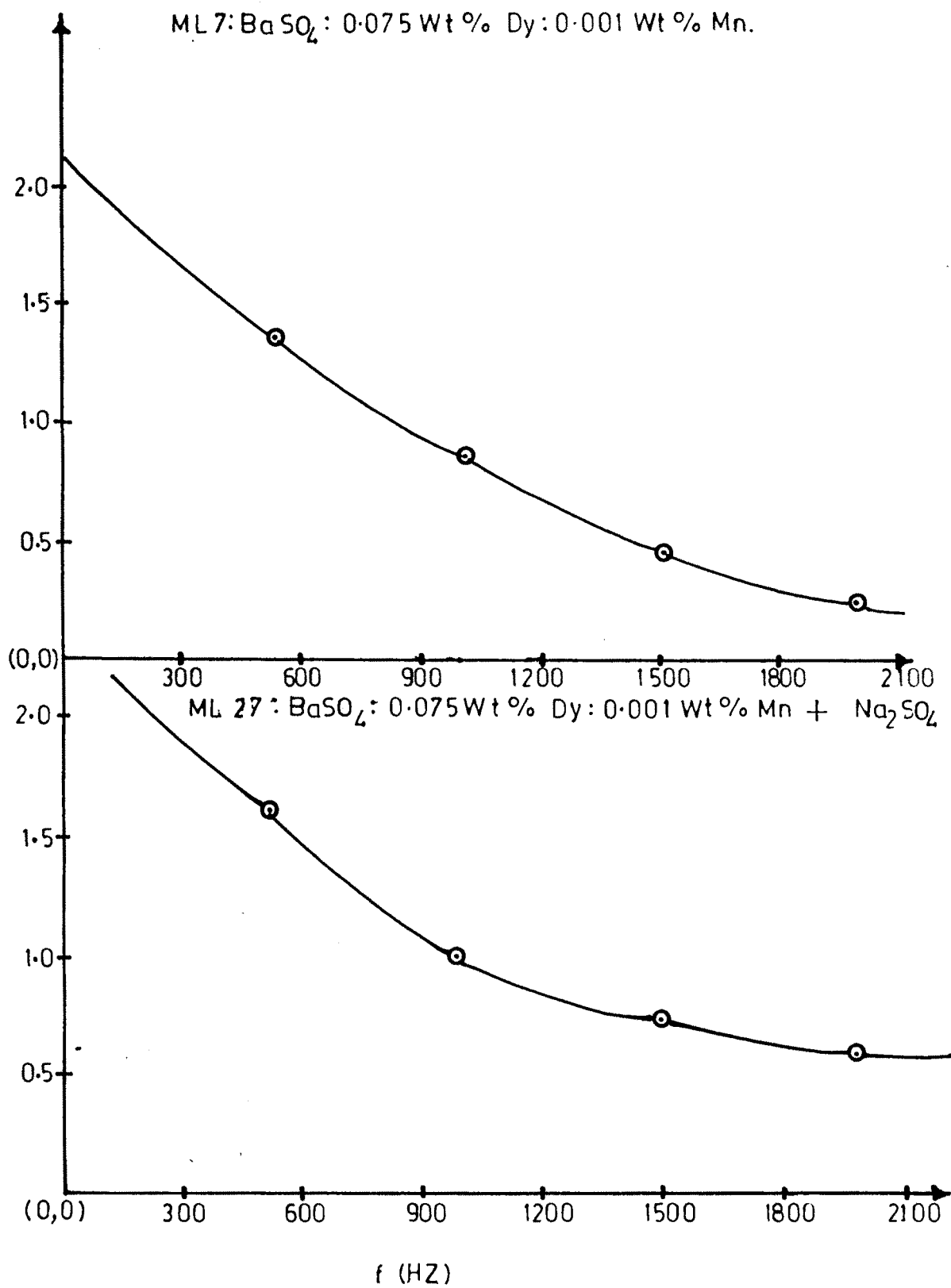


Fig 3.12

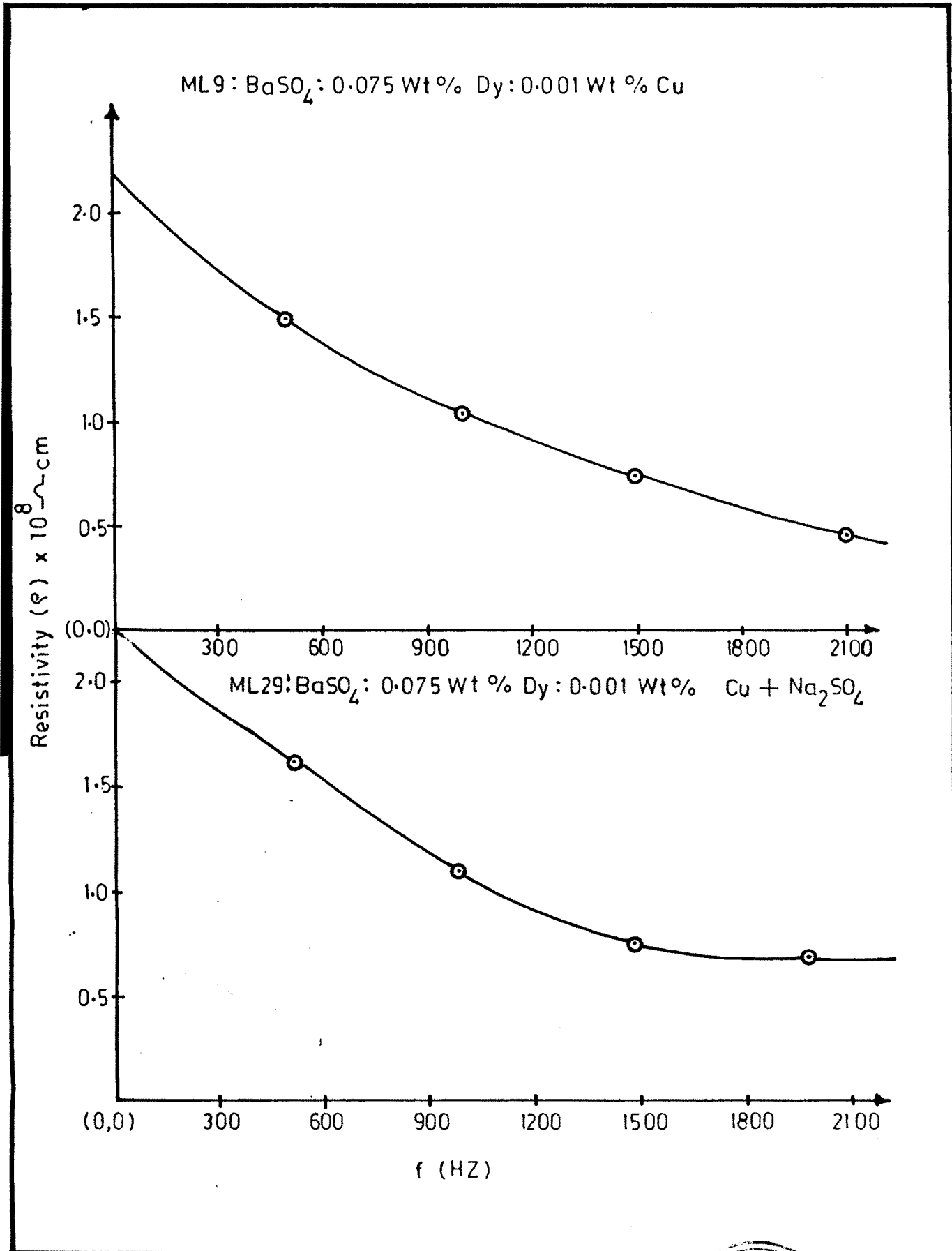


Fig. 3.13



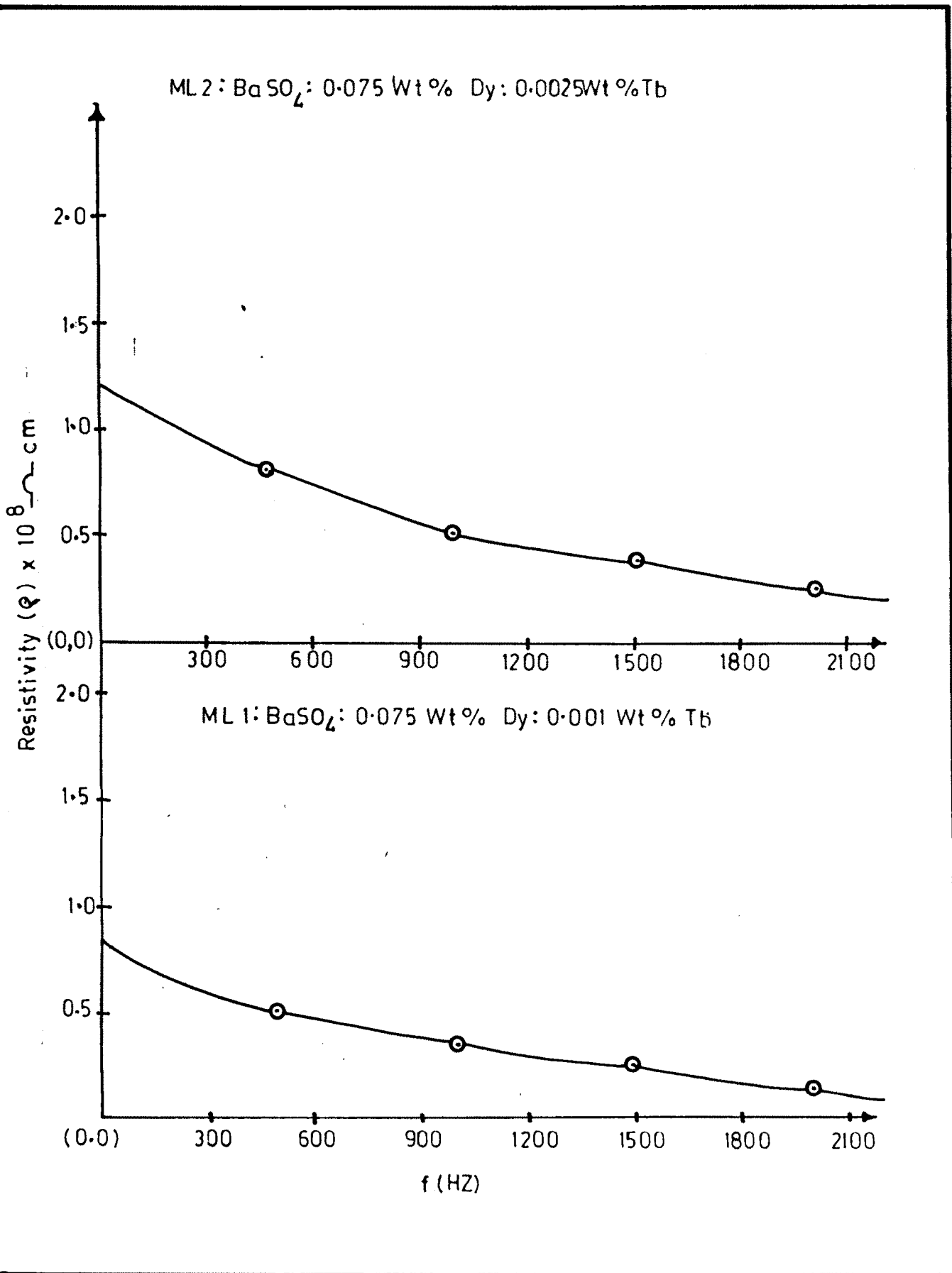


Fig. 3-14

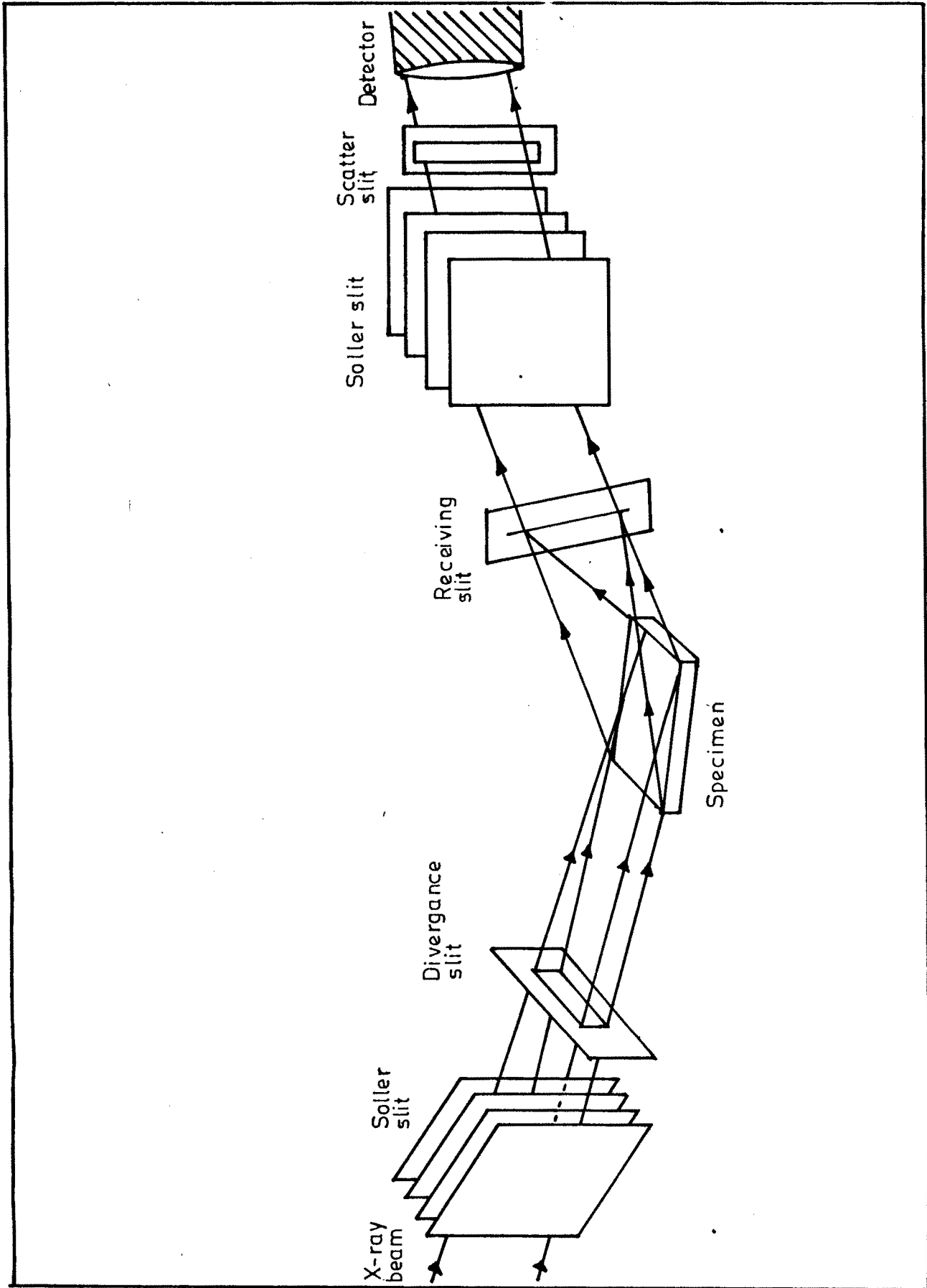


Fig - 3.15

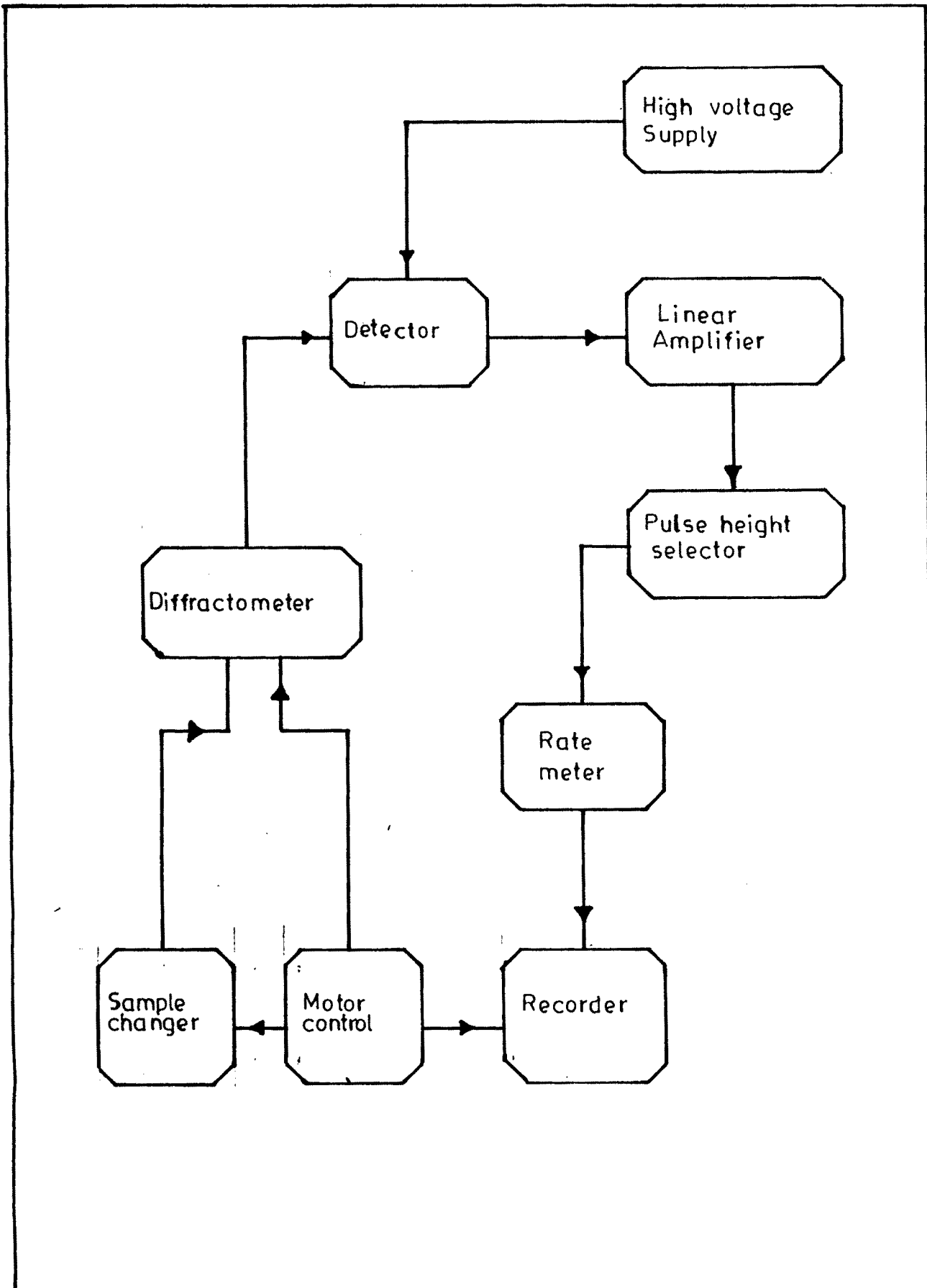


Fig - 3-16

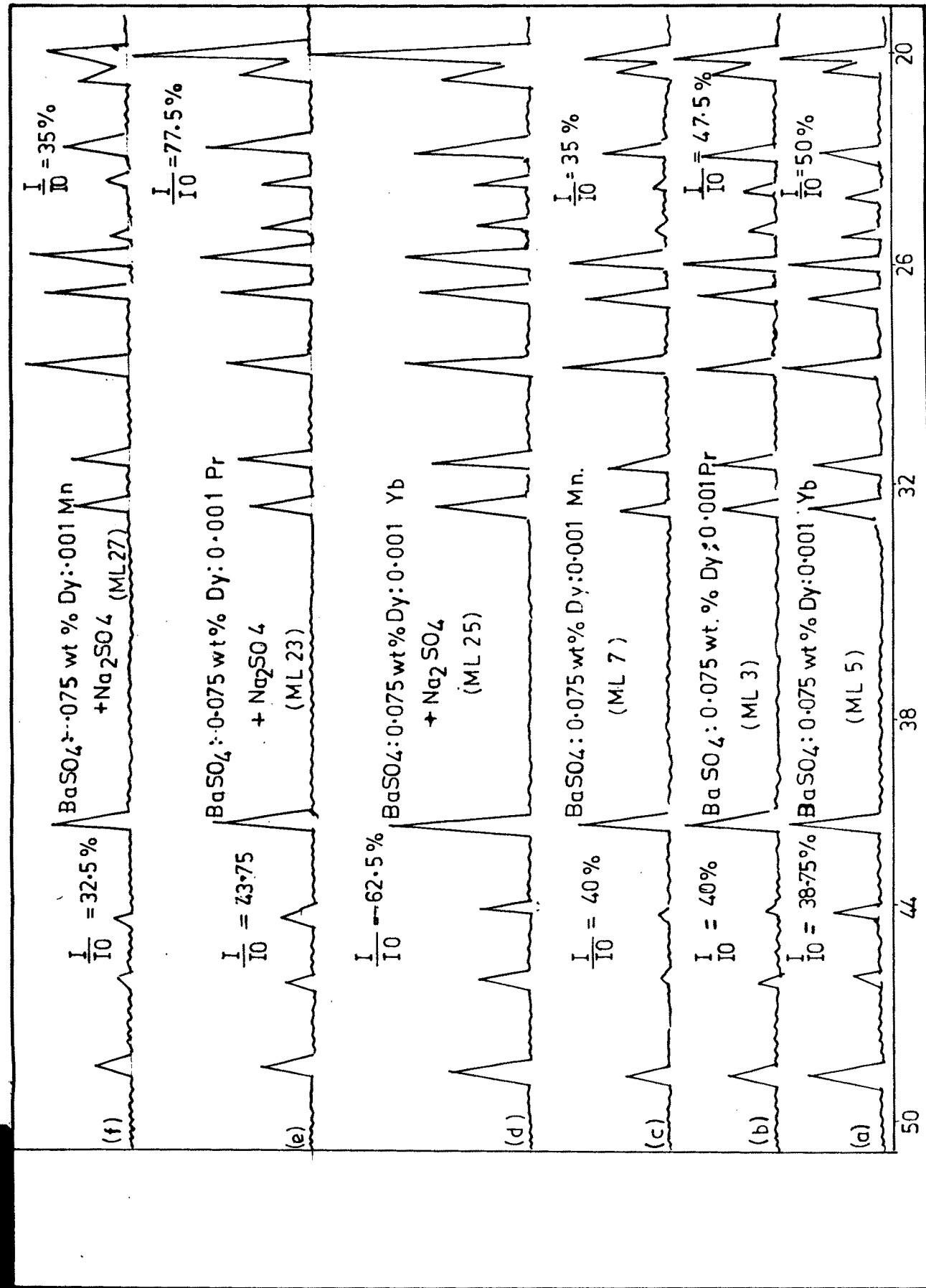


Fig. 3.17 : X-RAY DIFFRACTION PATTERNS FOR TYPICAL SAMPLES

REFERENCES

- 1] Sommerdijk, J.L.A. Bril. (Philips Res. Lab. Eindhoven Netherlands), J.Electrochem. Soc. (U.S.A.) Vol^m. 122 No.7, P. 952-4 (Jully 1975)
- 2] Hopx-Strix (Philips Res. Lab Eindhoven. Netherlands) Philips Res. Rep. Netherland, Vol^m 32, No.3, P. 149-59 (1977).
- 3] Mulla, M.R. and Pawar, S. H. Journal of Luminescence 40 and 41, 179-80 (1988) North-Holland Amsterdam.
- 4] Philips, F.C. " An Introduction to Crystallography" Longman Green and Co. 3rd Edition (1963).
- 5] Roberts, I.R., Weber J. and Rapp., J.R. Encyclopaedia of Minerals 50, 51 Van Nostrand and Reinhold. Co. New Yark (1974) .pa
- 6] Mulla, M. R. and Pawar, S.H. On study of Point defects in CaSO :Dy:Br, By XRD technique. Proc. Nuclear Physics and Solid State Phys. Symposium, New Delhi 276 Vol³. 23(C) (1980).
- 7] Mulla, M.R. Ph.D. Thesis, Shivaji University Kolhapur (1980).