

CHAPTER - I V

ELECTROLUMINESCENCE

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4.1 Introduction and Theory of Electroluminescence :

The phenomenon of electroluminescence (EL) is the generation of visible light by the direct action of a.c. or d.c. field on a phosphor. The phosphors exhibiting EL are generally referred to as 'electroluminophors'. To observe EL a suitable electroluminophor dispersed in a proper liquid or solid dielectric medium, is sandwiched between the two electrodes of a condenser system, called 'electroluminescence cell' (EL Cell), and a.c. or d.c. field is applied to the electrodes. In order to observe the emitted light due to electric excitation of phosphor, one of the electrodes has to be transparent i.e. in the form of a wire mesh or conducting glass.

The light emission resulting from the direct action of an electric field was observed as early as 1920 by Gudden and Pohl¹ during their study on photoconductivity of ZnS and by Lossev² in 1924 on SiC. However, electroluminescence was first observed in true sense, by Destriau³ (1936), in copper activated ZnS phosphors, under the action of a.c. field. It is also known as Destriau effect, after the pioneering work of Destriau.

4.1.1 Mechanism of EL Process :

Fig. 4.1 represents various steps involved in the mechanism of EL. They are :

- (a) Excitation of charge carriers,
- (b) Acceleration of charge carriers,
- (c) Transport of energy to radiating site,
- (d) Transfer of energy to radiating centre and,
- (e) Emission of light or radiative de-excitation.

(a) Stage - I Excitation of Charge Carriers :

The charge carriers are excited by three methods :

- i) Field ionisation of valence electrons,
- ii) Field ionisation of impurity ions and
- iii) Injection of minority charge carriers.

The transfer of valence electrons to conduction band may be brought by "quantum mechanical tunnelling" process⁴, producing a free electron and hole⁵ simultaneously. Very high local field (10⁵ to 10⁷ volts/cm) is required for the field ionisation of valence electron.

The field ionisation of impurity centres can be considered on the basis of impact collision mechanism, which does not require a large field as that required in case of ionisation of valence electrons. The

electrons from donor level are injected into conduction band. These electrons attain sufficient kinetic energy to excite or ionize an activator system by means of an in elastic collision. The excited activator radiates a photon or becomes ionized either thermally or with the aid of the local electric field. Alternatively, holes can be injected into valence band from acceptor centres, in the analogous manner, and attain sufficient kinetic energy to excite an activator system by means of in elastic collision.

The injection of minority carriers mechanism⁵ postulated by Lehovc et. al, is proposed to explain the electroluminescence from P-N junction. A strong electric field is not required for the charge carrier injection mechanism.

(b) Stage - II Acceleration of Charge Carriers :

The following conditions must exist to produce EL :

- i) High field region capable of accelerating the charge carriers to large kinetic energies must exist.
- ii) In this high field region, electrons or holes must be injected and

iii) Activator atoms must be located in such a way that absorption of energy is possible by collision.

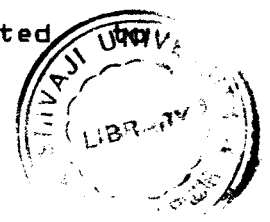
In order to explain the process it has been assumed^{6,7}, that the field applied across phosphor does not exist at the interior of the crystal, but it is concentrated in small local regions giving rise to potential hills called "Mott-Schottky" exhaustion barriers⁸. The electrons are accelerated to large kinetic energies, when injected into such barriers. The electrons collide with impurity centres and loose their kinetic energies to excite impurity centres. The emission results when excited impurity centre returns to ground state.

c) Stage - III Transport of Energy to Radiating site :

The excess energy available with conduction electrons or holes, must be transported to the agent which is eventually taking part in radiative transition leading to EL emission. The transport of the energy is achieved by collision process or by movement of exciton.

d) Stage - IV Transfer of Energy to Radiating Centre :

i) The accelerated charge carriers may transfer their energy by the way of direct collision, as a result of which the electrons from valence bond or impurity level are promoted



conduction band, but it is essential that the energy for such promotion of electrons must be higher than band gap energy (E_g) (At. least 1.5 times E_g).

- ii) An impurity level may capture an electron or hole from the valence band or conduction band.
- iii) The exciton may directly interact with the radiating centre, exciting energy state of radiation centre. This is known as exciton excitation. This exciton excitation does not involve any movement of charge carriers.

e) Stage - V Radiative De-Excitation :

The last stage in the mechanism of EL process is the radiative de-excitation. This stage involves radiative transitions from higher to lower energy levels. The radiative transition can take place in five ways. In case of excited crystal state, the radiative transition takes place by the way of intra band or inter-band or by band-to-impurity state transition. In case of excited impurity state the radiative transition takes place either impurity state to impurity state or impurity state to band transition. Excited crystal state gives rise to the noncharacteristic emission, where as excited impurity state gives rise to the characteristic emission.

4.1.2 Factors Affecting EL Emission :

There are various factors that affect the EL emission. Some of them are applied voltage and frequency, temperature, magnetic field, design of the cell and it's time of operation, dielectric media etc. Some of the relevant factors are discussed below.

a] Voltage Dependence of EL Brightness :

There is no a particular relation between the EL brightness (B) and the applied voltage (V). To find a mathematical expression between these two terms, several attempts have been made. Some of these expressions are based on theoretical ground, but majority of them are empirical.

The first relation between B and V was given by Destriau³ as -

$$B = a \exp. (-b/v) \quad \text{-----} \quad 4.1$$

Which was later modified by himself,

$$B = a V^n \exp. (-b/v) \quad \text{-----} \quad 4.2$$

Where v is applied voltage a and b are constants independent of V, but depend upon temperature, type of phosphor and frequency of applied voltage and 'n' is an integer, the most probable value of which is found to be two.

Waymouth and Bitter⁹ found that for a single phosphor particle, intensity of EL emission varies linearly with applied voltage. They also observed that a minimum threshold voltage is necessary to commence the effect. Similar observations were also made by others.^{10,11,12}

For single crystal of ZnS, Alfrey and Taylor¹² gave the relation as

$$B = a V^n \exp(-b/\sqrt{V}) \quad \text{-----} \quad 4.3$$

This equation was based on exhaustion barrier theory and found to hold good for $n=1$, for ZnS : Mn film.¹³

The equation 4.3 reduces to (when $n=0$)

$$B = a \exp(-b/\sqrt{V}) \quad \text{-----} \quad 4.4$$

This equation was first employed by Alfrey¹², Taylor and Zalm, et.al.¹⁴ It was shown by Thornton¹⁵ and others^{16,17} that the equation 4.4 holds good only at low voltages, but at high voltages the equation

$$B = a \exp(-b/V) \quad \text{-----} \quad 4.5$$

fits more satisfactorily.

Destriau and Ivey¹⁸ proposed an equation.

$$B = a \exp[-b/(V+V_0)] \quad \text{-----} \quad 4.6$$

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Lehmann suggested the equation.

$$B = a.v. \exp [- b/(V+V_0)] \text{ ----- } 4.7$$

Where a, b and V_0 are constant, which vary linearly with frequency.

For microcrystalline ZnS:Mn Luyckx and
20 Stokkink have found,

$$B = a \exp (bv) \text{ ----- } 4.8$$

This equation is valid over two decades of brightness under alternating excitation.

The relation :

$$B = a (V - V_0)^n \text{ ----- } 4.9$$

With $n=3$ was reported by Harman and Raybold for ZnS.

b) Frequency Dependence :

Another factor which strongly influences the EL brightness is frequency (f) of applied a.c. voltage. Various workers have given different relations between brightness and frequency. However, a general trend observed at least in case of inorganic electroluminophors is that EL brightness increases with frequency.

4.1.3 Efficiency of Electroluminescence :

The EL efficiency (n_e) is defined as a ratio of the emission intensity 'B' to the electric power absorbed (w) i.e.

$$n_e = B / w \quad \text{-----} \quad 4.10$$

Lehmann²¹ gives an empirical relation to the efficiency as,

$$n_e = (CB)^{1/2} / V^2 \quad \text{-----} \quad 4.11$$

A crude estimation of overall efficiency including ohmic losses may be made on the basis of fundamental consideration. If an elementary charge has to traverse during one half cycle a potential drop across the particle of V volts, in order to give rise to emission of one photon of energy $h\nu$, then the efficiency is $h\nu / eV$.

4.2 Experimental :-

A very fine layer of phosphor ($250 \pm 10 \mu$) was held between the electrodes of electroluminescence (EL) cell and was then subjected to high sinusoidal voltage ranging between 0 to 2kV, at ambient frequencies viz. 500 Hz, 1 kHz, 1.5 kHz and 2 kHz. The EL brightness (B) of phosphor was accurately measured with the help of a very sensitive brightness measuring system. The block diagram of experimental EL set-up is shown in fig. 4.2. It mainly consists of i] EL cell ii] Exciting source and iii] Brightness measuring system.

4.2.1 EL Cell :-

EL characteristics of the phosphor under study, are studied with the help of EL cell. The EL cell required for experimental purpose was designed and fabricated in a departmental workshop. The design of the EL cell depends on the type of phosphor, nature of applied voltage (a.c. or d.c.), the order of applied voltage, frequency and the type of binder. The fig. 4.3 shows schematic diagram of fabricated EL cell. It consists of an aluminium strip ($4 \times 2.5 \times 0.2$ cm) as one electrode and other being a conducting glass ($6 \times 2.5 \times 0.2$ cm). The EL cell is provided with a window (2.2×1.3 cm); so that light emission from phosphor is incident on photomultiplier (PM) tube. The phosphor under study is sandwiched between aluminium and conducting glass

electrodes. Placement of thin mica sheet of uniform thickness between phosphor and conducting glass avoid the electrical breakdown. The phosphor placed between electrodes can be pressed reasonably by using screw and spring action. An iron rod is fixed to the bakelite frame, so as to hold the EL cell in required position.

4.2.2 Exciting Source :-

Phosphors of oxygen dominated lattices, need locally much higher fields for EL than sulphides²². In order to provide high electric field a frequency generator ranging from 0 to 100 kHz is coupled to an amplifier. Output voltage of this amplifier is stepped up using a special type of transformer designed in the laboratory. The output of the transformer provides a.c. voltage of about 2KV at desired frequency, which could be changed with the help of variable knob of frequency generator. Wide voltage range multimeter (MOTWANI TYPE) capable of recording a.c. voltage of high frequency of the order of 2.5 kHz is used to measure the applied a.c. voltage to the electrodes of EL cell.

4.2.3 Brightness Measuring System :-

It mainly consists of a photo-multiplier (PM) tube (IP 21), placed in metallic housing. The electrode connection for the PM tube is shown in fig. 4.4. The PM

tube is operated at highly stabilised d.c. voltage of 700 V. This voltage was kept constant for all further measurements of brightness. The EL brightness was measured with the help of an IP-21 photomultiplier tube coupled with a very sensitive Fet Nano - ammeter (TEM 13, Aplab, India) facilitating measurement of currents from 30 - 0 - 30 nA, full scale to 1 - 0 - 1 mA full scale in 3 - 10 - 30 sequence in ten ranges. The EL cell and photomultiplier unit were placed in a light tight box in order to avoid the stray light entering the PM tube. The EL brightness is measured by varying applied voltage at ambient frequencies.

4.3 Results and discussion :-

The phosphor in powder form is generally sandwiched between the electrodes of EL cell. A suitable binder such as castor oil, nitrobenzene, polystyrene, polymethyl, silicon grease is employed, which forms a paste with the powder sample, under test. The role of these binders is generally passive, in a sense, that they do not take any part in the EL process. They neither help to enhance EL output of phosphor nor they deteriorate the same. The use of binders is reported in case of sulphide phosphors, which need locally much low electric field. However, it has been previously reported that EL of certain phosphor tend to deteriorate in the presence of the said binders. These observations have

been reported particularly in the phosphors of oxygen dominated lattice ²²⁻²⁴. The phosphor powders of oxygen dominated lattices require locally much higher fields ²² for EL than the EL of sulphides. This high electric field is achieved by pressing dry phosphor powder of uniform thickness between the electrodes. The high field is believed to be attained due to concentration of a field at a grain. The presence of dielectric medium disperses such high field concentration. Taking into account the above effect of dielectric medium, the EL of BaSO₄ : Dy : Tb, Pr, Yb, Cu and Mn phosphors was studied without using any binder. The results are discussed below.

4.3.1 EL of BaSO₄ : Dy : Tb/ Yb/ Pr/ Mn and Cu Phosphors and Their Voltage Dependence :-

The voltage dependence of EL brightness at ambient frequencies (500 Hz, 1kHz, 1.5 kHz and 2 kHz) has been studied for the BaSO₄ : 0.075 wt % of Dy : 0.001 wt % Tb, Pr, Yb, Mn and Cu phosphors (ML1, ML3, ML5, ML7, and ML9). The growths of EL brightness (B) with respect to applied voltage (V) have been plotted for the said phosphors. (figs 4.5 to 4.9)

It is observed from these curves that light out put is an increasing function of applied voltage. The EL brightness is found to grow rapidly at higher

frequencies. The nature of the curves is further investigated by plotting following graphs :

- i] The logarithm of (B/V) as a inverse function of V.
- ii] The logarithm of (B/V) as a inverse function of \sqrt{V} .
- iii] The logarithm of B as a inverse function of V.
- iv] The logarithm of B as a function of V and
- v] The logarithm of B as a inverse function of \sqrt{V} .

These curves (not shown here) were found to deviate from linearity. However, logarithm of brightness when plotted as a function of logarithm of applied voltage, a linearity has been observed (fig. 4.10-14). The linearity observed in case of log-log plots between brightness and applied voltage indicates that the brightness obeys power law relation with applied voltage, in the form,

$$B = a V^n .$$

Here 'a' is a constant and 'n' corresponds to slope of log-log plots. The existence of power law relationship between the brightness and voltage indicates the possibility of a bimolecular recombination process with luminescence centres. Similar conclusion has been drawn (25-27) by others.

The curves for all the phosphors under study have similar nature and they obey the same power law

relation viz $B = aV^n$. This indicates that the basic mechanism of EL process (whatever may it be) doesnot change with the nature of co-dopant under study. However the intensity of EL brightness varies from one co-dopant to other.

The EL brightness is originated from the excited luminescence centres and for this various steps have been proposed in fig. 4.1. Basically, excitation of luminescence centres requires the generation of free charge carriers, which depends on the applied voltage. Thus the variation of brightness is a function of applied voltage. The voltage dependence of EL brightness could also be explained on the basis of visual observations made, that, initially the number of particles in which EL takes place is small, but on increasing the voltage, more and more active regions are exposed to voltage gradient above the threshold level.

Table 4.1 gives the values of n (slopes of log-log plots) for Tb, Pr, Yb, Mn and Cu co-doped phosphors, at ambient frequencies. It is seen that value of ' n ' for a given phosphor doesnot change remarkably with frequencies, in general. However, n may change from one phosphor to other e.g. values of ' n ' for rare-earth co-doped phosphors (i.e. Tb, Pr, Yb, Co-doped phosphors) is much higher as compared to values of ' n ' for non rare- earth co-doped phosphors (i.e. Cu and Mn

co-doped phosphors) This indicates that EL performance of rare-earth co-doped phosphors is much better as compared to non-rare earth co-doped phosphors.

4.3.2 Frequency Dependence of EL Brightness

Table 4.2 shows effect of activator and co-activator on EL brightness at different frequencies and at fixed applied voltage. The general trends is that as the frequency increases EL brightness increases. This can be understood as follows :

In the present studies the nature of applied electric field is sinusoidal obeying the relation

$$e = e_0 \sin f t$$

Where, e_0 is the field at $t = 0$ and f is the frequency of applied field. The phosphor is exposed twice to the peak value of e in a cycle, emitting two quanta by the luminescence centres per cycle. As the frequency f increases the number of emitting quanta also increases. Thus this explains why the EL brightness is increasing function of applied frequency. It is quite interesting to investigate the nature of relation existing between applied frequency and EL brightness, so as to see whether EL brightness is linear or non linear function of frequency. However, these studies are not extended to this effect over here. The reason is that the main

intention of the present dissertation is not to study the details of EL mechanism underlying the process, but, EL is utilized here as a tool to study the performance of the phosphor system under study.

4.3.3 Effect of Various Co-activators on EL Brightness of BaSO₄ : Dy Phosphors:

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There are various means and ways to prepare efficient luminophors. To choose appropriate host material and activator is the first step. One can further improvise the luminescence output of the phosphor by optimising the activator concentration. Further improvisation is possible by using co-activator, sensitizer and charge compensator.

Various workers have considered effect of co-activator in the enhancement of luminescence output in different phosphor system²⁸⁻³⁰. Desai and Mulla have reported enhancement effect of luminescence of BaSO₄ phosphor system activated by Dy³⁺ and co-activated by a trace amount of Tb^{3+,31}. Awasthi and Thakar²⁹ have considered the enhancement effect of luminescence in CaS : Dy: Tb. In the present investigation BaSO₄ : Dy has been co-doped by Tb, Yb, Pr, Cu and Mn. These co-activators could be categorised in two groups viz. rare-earth co-activator Tb³⁺, Yb³⁺, Pr³⁺ and non-rare earth co-activator Cu²⁺, Mn²⁺. It is interesting to make

comparative study of rare-earth co-doped phosphors and non-rare earth co-doped phosphors.

Fig 4.15 represents B-V curves at fixed frequency $f = 1.5$ KHz for BaSO_4 : 0.075 wt % Dy: 0.001 wt% Tb, Pr, Yb, Mn, Cu phosphors. It is seen that B-V curve for Tb co-doped phosphors lies in the uppermost region indicating that EL response of Tb co-doped phosphor is the highest. Yb, Pr, Cu, and Mn co-doped phosphors show successively lower EL responses. Categories-wise it could be said that rare earth co-doped phosphors show better EL brightness than those of non rare-earth co-doped phosphors. Among the various co-dopants Tb shows maximum brightness and Mn shows minimum brightness. The EL brightness of Yb doped phosphor lies in the second place, that of pr in the third place, Cu in the fourth place and so on. In brief it could be said in general that rare earth co-activators viz . Tb³⁺, Yb³⁺, Pr³⁺, suit in the host lattice of BaSO_4 more than Cu²⁺ and Mn²⁺. The probable reason for better performance of rare -earth Co-doped phosphors over non rare earth co-doped phosphors may be considered in terms of ionic radii. The substitutional incorporation of co-activator ions in the host lattice of BaSO_4 depends on how close the ionic radii of co-activator ions are with ionic radius of Ba²⁺. It could be easily seen from periodic table that ionic radii of rare-earth co-activators are close to ionic radius of

Ba^{2+} . There is a vast difference between ionic radii of non-rare earth co-activators such as Mn and Cu and ionic radius of Ba^{2+} . This could be probable reason why the chances of rare-earth co-activator ions being incorporated in the host lattice being more than those of non-rare earth co-activator ions. This gives the probable explanation why rare earth co-doped phosphors show better performance as compared to non-rare earth co-doped phosphors.

4.3.4. Enhancement Effect of EL With Respect to Activator Concentration :

Figs. 4.16 and 4.17 show B-V curves plotted at fixed frequency $f = 1.5$ kHz for the phosphors in which co-activator concentration of Tb are kept constant and activator concentration is varied. It is seen that $BaSO_4$: 0.075 wt.%, Dy: 0.001 wt.%, Tb shows better EL brightness (fig.4.16)(ML1) as compared to the phosphor $BaSO_4$: 0.1 wt.%, Dy; 0.001 wt.%, Tb (ML 11). Similar observations are obtained from the B-V curves (not shown here) plotted for Yb, Pr, Mn, Cu co-doped phosphors. Fig.4.17 shows B-V curves plotted at fixed frequency $f = 1.5$ kHz for the phosphor having constant Tb concentration (0.0025 wt.%) and variable activator concentration of Dy viz. 0.075 wt.% and 0.1 wt.% respectively . In this case also a phosphor of 0.075 wt.% Dy shows better EL brightness than that of a

phosphor having activator concentration 0.1 wt.%. Dy. Or in other words activator concentration more than 0.075 wt.%. Dy tends to deteriorate EL brightness. This is also clearly indicated in the fig. 4.18 which shows the effect of activator concentration on EL brightness. 0.075 wt.% Dy concentration of activator seems to be optimum concentration above which concentration quenching begins.

The explanation for concentration quenching has been considered in different ways, depending upon the phosphor system under study. Viersanu³² has considered the concentration quenching in case of highly concentrated solutions of fluorescence substances, on the basis of fit and unfit molecules. The concentration quenching has also been contemplated in terms of increased radiationless transition with excess of activator ions in lattices³³. Nambi³⁴ has considered the concentration quenching in terms of resonant transfer of energy from one activator atom to other, bringing in the possible migration of energy from one activator atom to other, which has more probability of getting dissipated without luminescence, at quenching site. The latter explanation seems to suit the concentration quenching in the present phosphor system.

4.3.5. Enhancement Effect of E L With Respect to Co-activator Concentration :

Co- activator play very important role in the enhancement of luminescence of number of phosphor system. Guo Change- xin, Zhang Wei - ping and Shi Chao-
³⁰ Shu have reported enhancement effects of cathodluminescence (CL) and photoluminescence (PL) of Eu^{3+} , Sm^{3+} and Dy^{3+} in Y_2O_3 by a trace of Tb^{3+} . It has been observed that a trace of Tb^{3+} in a oxygen lominated lattice phosphorr system like Y_2O_3 plays an important role in the enhancement of luminescence of the said phosphor system. The phosphor system undertaken for the present studies is rich in oxygen (like Y_2O_3) and hence the outhor of present dissertation was tempted to make similar effort of trace co-activation in case of BaSO_4 : Dy phosphor system. The results so obtained are discussed below.

Fig. 4.19 depicts B - V curves plotted for BaSO_4 : 0.075 wt.% Dy: 0.001 wt.%. Tb^{3+} (ML1) and BaSO_4 : 0.075 wt% Dy : 0.0025 wt% Tb^{3+} (ML2) at fixed frequency 1.5 kHz. It is observed that B - V curves for ML2 lies below the B - V curves of ML1. B-V plots shown in fig 4.20 for the phosphor BaSO_4 : 0.1 wt% Dy: 0.001 wt.%. Tb^{3+} (ML11) and BaSO_4 : 0.1wt. %. Dy: 0.0025 wt. % Tb^{3+} (ML12) also give the similar results. It indicates that a trace amount of Tb^{3+} has enhancement effect of luminescence in

BaSO₄ : Dy phosphor system. Similar observations are also obtained from the B - V curves plotted (not shown here), for BaSO₄ : Dy: Pr, Yb, Cu, Mn phosphor system. The reason for the enhancement of this kind, on account of an addition of a trace amount of co-activator, has been explained with appropriate model in the chapter V.

4.3.6. Enhancement Effect of EL With Respect to Charge-Compensator :

The charge compensator Na₂SO₄ has pronounced effect on EL brightness of BaSO₄ : Dy: Tb, Yb, Pr, Mn, Cu phosphors. The enhancement effect has clearly been observed in case of 0.001 wt.%. Tb, Yb, Pr co-doped in BaSO₄ : 0.075 wt% Dy: phosphor (figs. 4.21, 4.22, 4.23) Basically BaSO₄ : Dy phosphor gets enhanced in its luminescence output on account of a trace amount of co-activator like Tb, Yb, Pr etc. A further enhancement effect is achieved due to the addition of charge compensator Na₂SO₄. The enhancement effect due to a trace amount of co-activator is dealt in length with appropriate model in chapter V. The enhancement effect due to charge compensator Na₂SO₄ could be explained on the basis of charge compensation theory as follows.

The charge neutrality in the preparation of BaSO₄ :RE³⁺ phosphors demands the removal of three Ba²⁺ ions to incorporate two RE³⁺ ions. This mounts Ba²⁺ ion

vacancies in the host lattice. The host lattice defects produced during the preparation of phosphors due to such Ba^{2+} ion vacancies restrict the entry of RE^{3+} activator ions in the lattice structure. However, the addition of Na_2SO_4 to $\text{BaSO}_4 : \text{RE}^{3+}$ phosphor wipes out the host lattice defects created by Ba^{2+} ion vacancies and brings about an appropriate charge compensation.



This is in accordance with the charge compensation theory of Kroger and Hellingman.³⁵ Such charge compensation enables more RE^{3+} ions to introduce in the host lattice, increasing the number of active luminescence centres. Greater the population of luminescence centres, greater is the probability of these luminescence centres to get collided with accelerated charge carriers. This accounts for the enhancement of EL brightness of Na_2SO_4 added phosphors.^{2 4}

It is however, worth while to note that such enhancement of EL brightness due to addition of Na_2SO_4 in case of Mn and Cu co-doped phosphors is not observed. It is seen that EL brightness tends to drop due to addition of charge compensator Na_2SO_4 in case of Mn and Cu co-doped phosphors (figs. 4.24 and 4.25). The cause of deterioration of EL output seems to be obvious particularly in case of Mn and Cu doped phosphors. Mn²⁺

or Cu^{2+} with addition of charge compensator ion Na^+ produces charge imbalance. Hence, chances of introducing co-activator ions (Mn/Cu) in the host lattice of BaSO_4 become less probable. This may be probable cause for deterioration of EL brightness of Mn/Cu co-doped phosphors.

Out of number of phosphors prepared for the present studies BaSO_4 : 0.075 wt%. Dy: 0.001 wt%. Tb with charge compensator Na_2SO_4 seems to be most efficient phosphor. Addition of Na_2SO_4 in the phosphors having activator and co-activator concentration greater than their optimum values (0.075 wt% of activator and 0.001 wt% of co-activator) has adverse effect on EL brightness of these phosphors. This result is indicated in figs. 4.26, 4.27, 4.28, 4.29, 4.30, 4.31.

TABLE 4.1

Values of 'n' (slopes) obtained from logB, Vs, logV. plots

Sample No.	Phosphor BaSD ₄	Slope 'n' of logB - log V Plots			
ML1	0.075 Wt% Dy : 0.001 Wt% Tb	4.44	3.43	3.84	4.00
ML3	0.075 Wt% Dy : 0.001 Wt% Pr	3.71	3.60	2.48	2.50
ML5	0.075 Wt% Dy : 0.001 Wt% Yb	3.13	3.20	3.00	2.67
ML7	0.075 Wt% Dy : 0.001 Wt% Mn	2.16	2.26	2.72	3.33
ML9	0.075 Wt% Dy : 0.001 Wt% Cu	3.33	2.65	2.60	2.40

TABLE 4-2

Phosphor		Applied voltage 1500 V					Applied voltage						
		EL brightness (Arb units) at					EL brightness (Arb units) at						
		500Hz	1kHz	1.5kHz	2kHz	2kHz	500Hz	1kHz	1.5 kHz	2kHz			
Sample No	BaSO ₄												
ML1	0.075 Wt% Dy : 0.001 Wt% Tb	100	165	250	340	200	300	500	640				
ML3	0.075 Wt% Dy : 0.001 Wt% Pr :	55	130	225	300	115	235	385	525				
ML5	0.075 Wt% Dy : 0.001 Wt% Yb	75	140	235	320	150	275	450	575				
ML7	0.075 Wt% Dy : 0.001 Wt% Mn	30	75	150	205	75	175	330	390				
ML9	0.075 Wt% Dy : 0.001 Wt% Cu	40	90	160	225	100	225	340	450				
ML21	0.075 Wt% Dy : 0.001 Wt% Tb+ Na ₂ SO ₄	125	273	350	401	221	313	600	653				

FIGURE CAPTIONS

- Fig. 4.1 A chart showing the process involved in electroluminescences.
- Fig. 4.2 Experimental set up for electroluminescence studies.
- Fig. 4.3 Schematic diagram of EL cell
 a) Front view
 b) Three dimensional view
- Fig. 4.4 Electrode connection for a Ip - 21 photomultiplier tube
- Fig. 4.5 B - V plots at different frequencies for typical phosphor (ML 1)
- Fig. 4.6 B - V plots at different frequencies for typical phosphor (ML 3)
- Fig. 4.7 B - V plots at different frequencies for typical phosphor (ML 5)
- Fig. 4.8 B - V Plots at different frequencies for typical phosphor (ML 7)
- Fig. 4.9 B - V plots at different frequencies for typical phosphor (ML 9)
- Fig. 4.10 A plot of $\log \frac{B}{10} - \log \frac{V}{10}$ for (ML1), at different frequencies.
- Fig. 4.11 A plot of $\log \frac{B}{10} - \log \frac{V}{10}$ for (ML3), at different frequencies.

- Fig. 4.12 A plot of $\log_{10} B - \log_{10} V$ for (ML5) at different frequencies.
- Fig. 4.13 A plot of $\log_{10} B - \log_{10} V$ for (ML 7), at different frequencies.
- Fig. 4.14 A plot of $\log_{10} B - \log_{10} V$ for (ML 9), at different frequencies.
- Fig. 4.15 A B - V plot showing comparative EL brightness for different co-activators.
- Fig. 4.16 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 1) and (ML 11).
- Fig. 4.17 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML2) and (ML12)
- Fig. 4.18 EL brightness (B) against concentration of Dy at given applied voltage & frequency.
- Fig. 4.19 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 1) and (ML2).
- Fig. 4.20 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 11) and (ML 12).
- Fig. 4.21 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 21) (ML 1).
- Fig. 4.22 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 23)

- and (ML 3)
- Fig. 4.23 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 25) and (ML 5)
- Fig. 4.24 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 7) and (ML 27)
- Fig. 4.25 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 9) and (ML 29)
- Fig. 4.26 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 2) and (ML 22)
- Fig. 4.27 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 12) and (ML 32)
- Fig. 4.28 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 21) and (ML 31)
- Fig. 4.29 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 22) and (ML 32)
- Fig. 4.30 Comparative B - V plots at 1.5 kHz frequency for typical phosphors (ML 21) and (ML 22)

Fig. 4.31 Comparative B - V plots at 1.5 kHz
frequency for typical phosphors (ML 31)
and (ML 32).

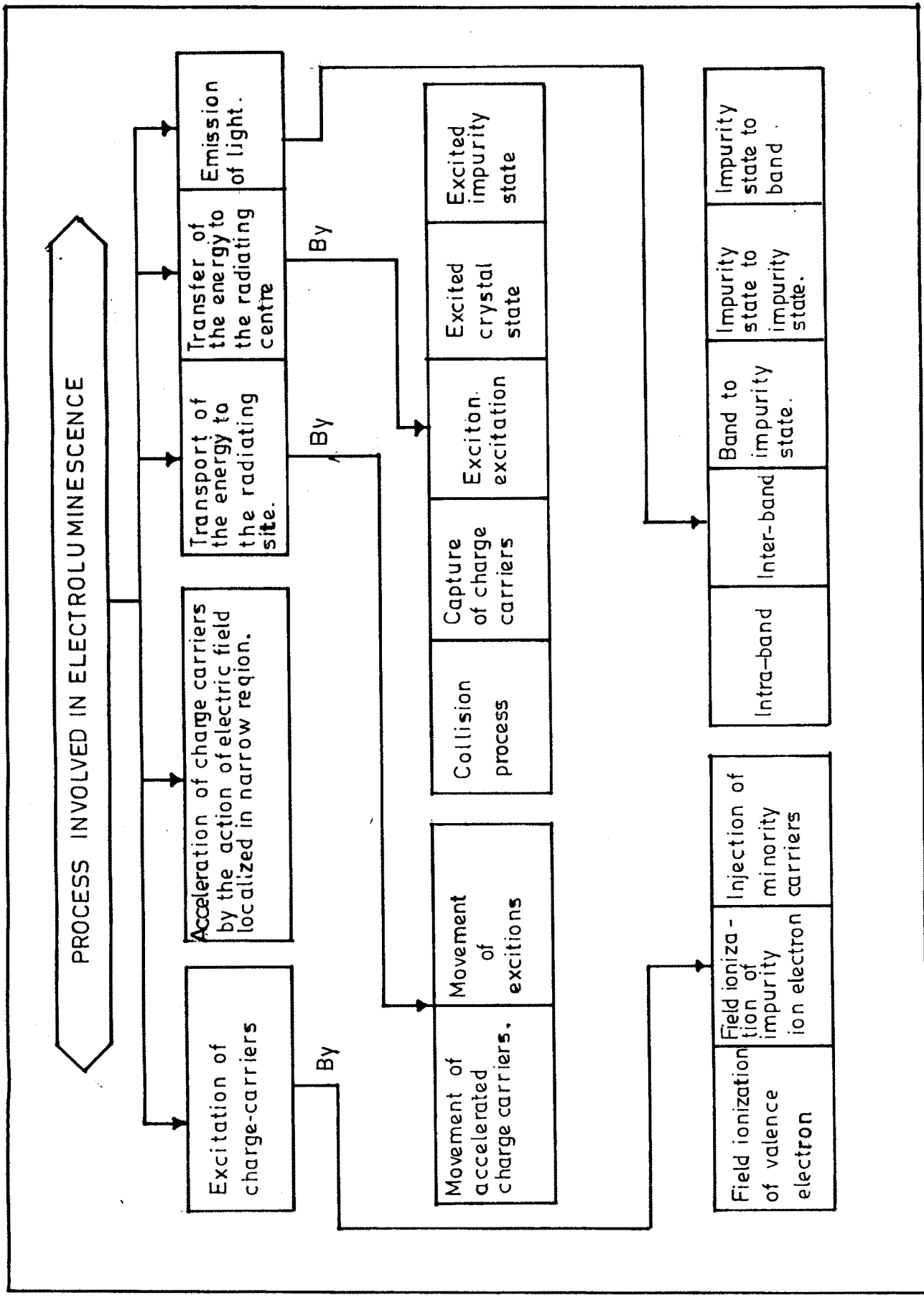


Fig.-4.1

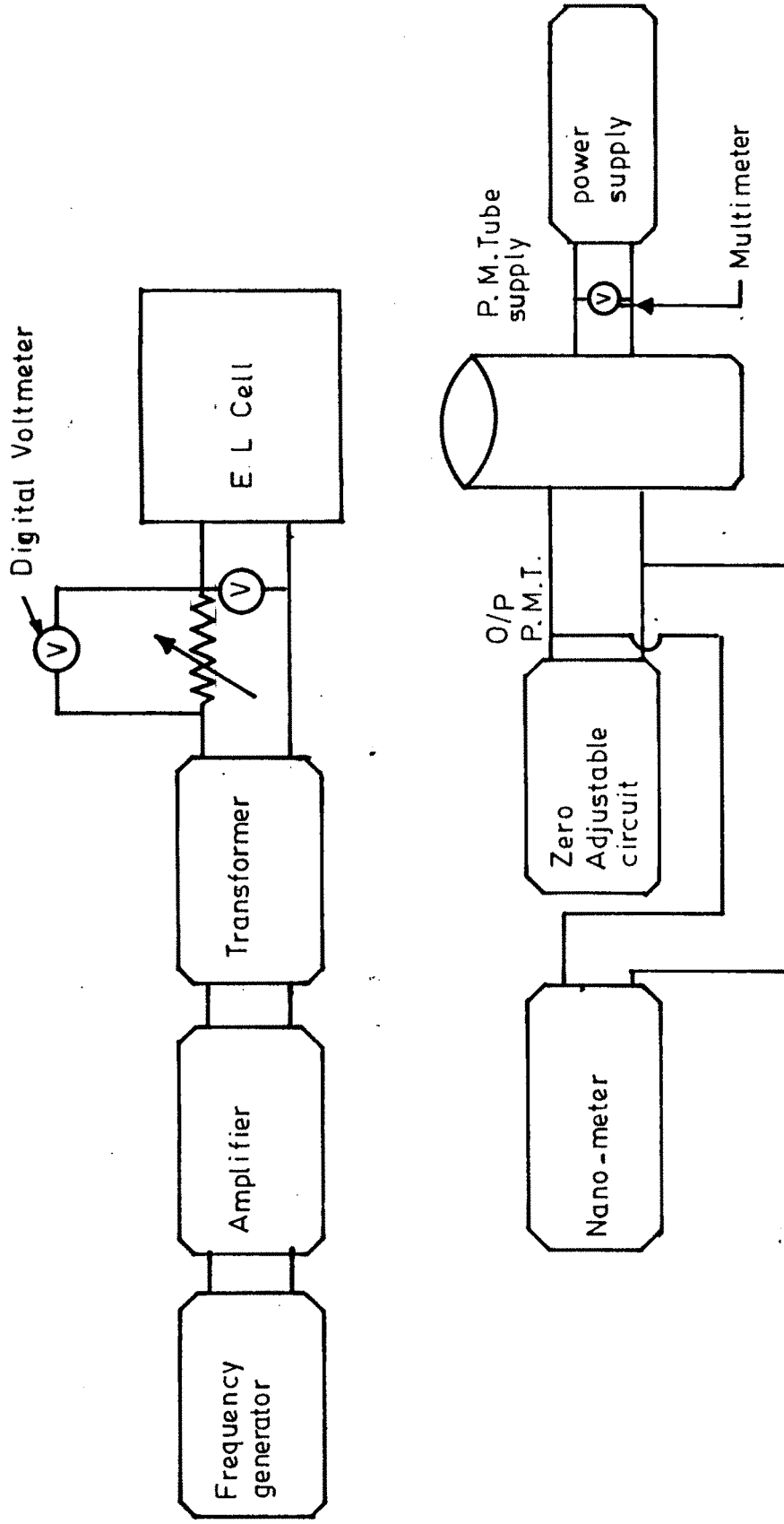
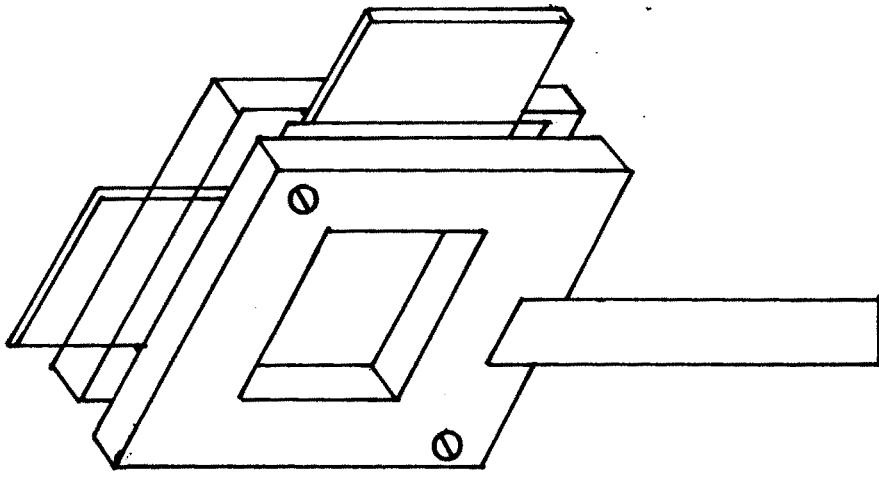
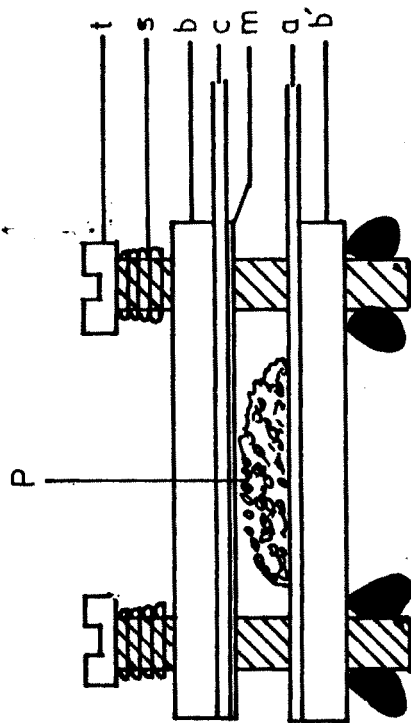


Fig - 4.2



(b)



P = Phosphor in dry powder form.

t = nuts to press the Phosphor between electrodes.

s = Spring.

b, b' = bakelite Plates.

c = Conducting glass.

m = mica sheet.

a = aluminium electrode.

(a)

Fig-4.3

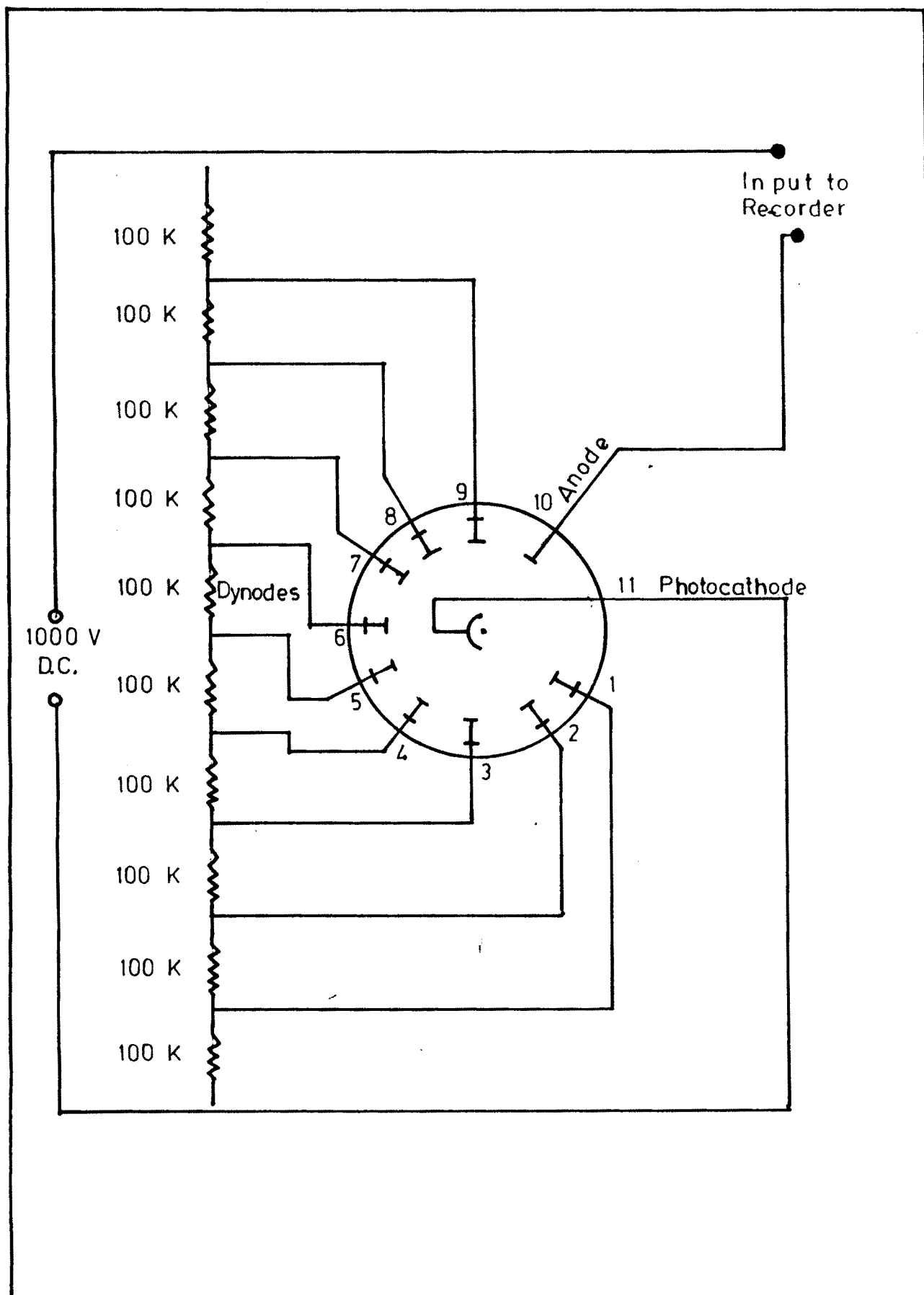


Fig 44 - ELECTRODE CONNECTION FOR A IP-21 PHOTOMULTIPLIER TUBE .

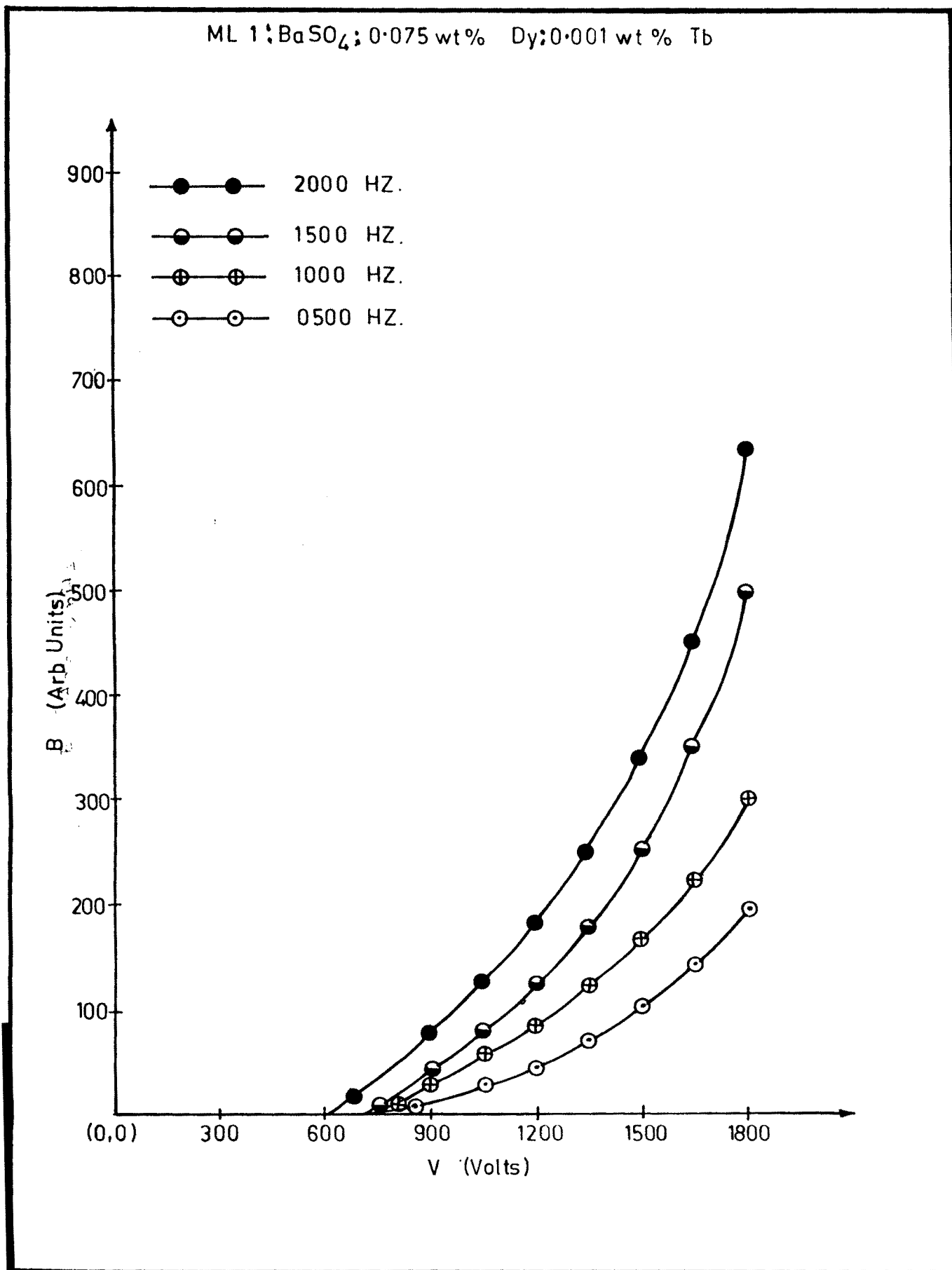


Fig 4.5

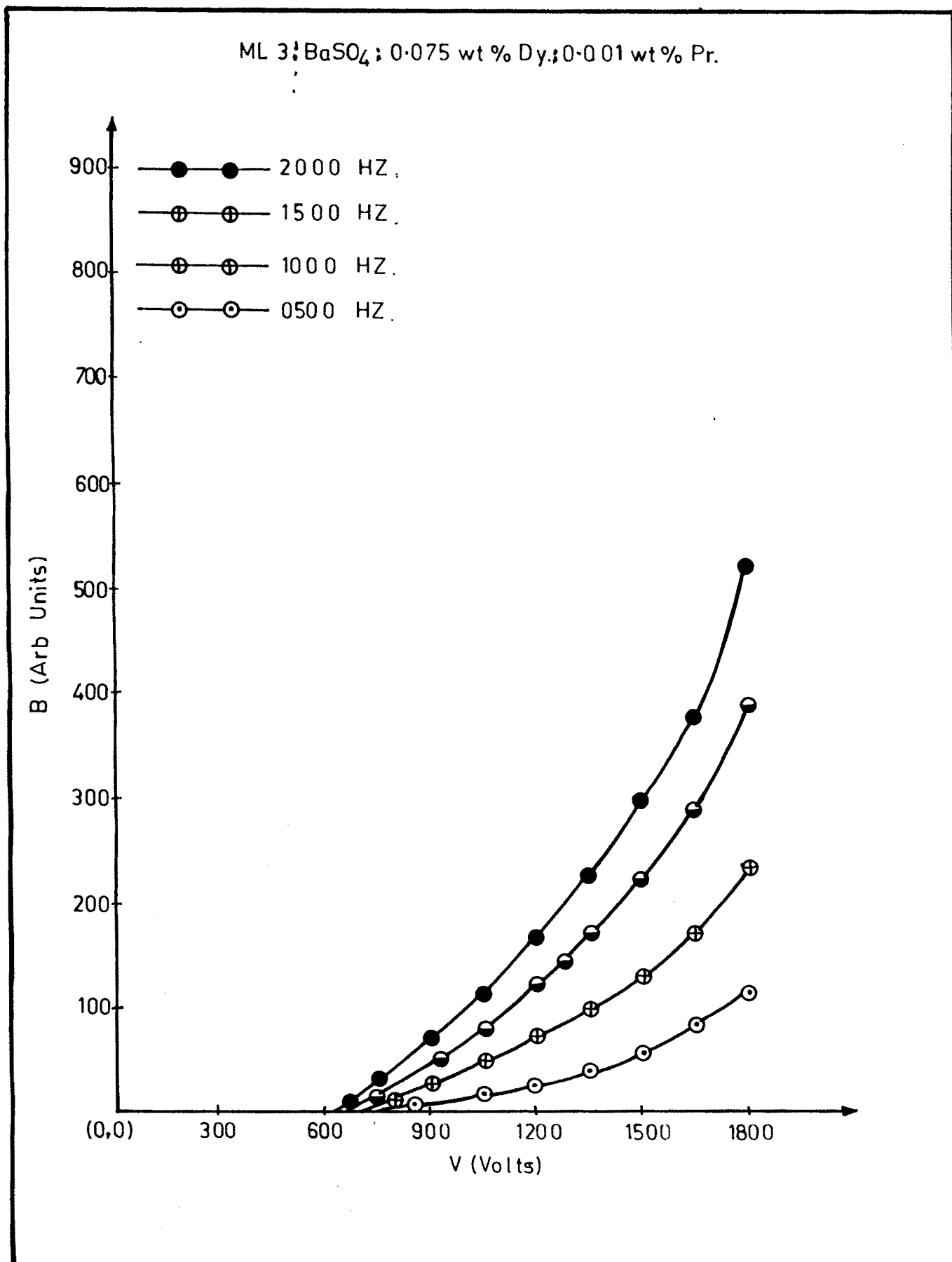


Fig. 4.6

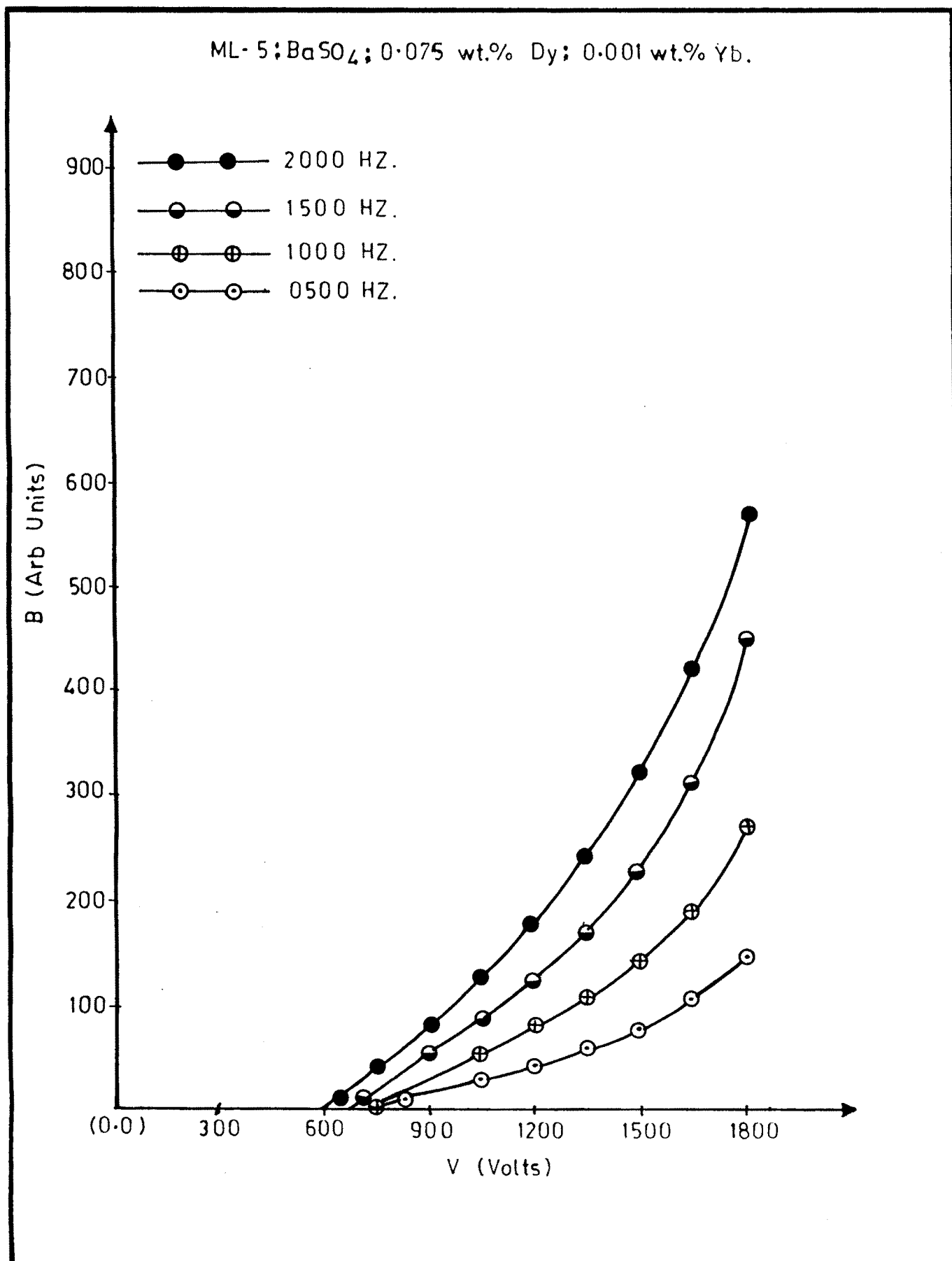


Fig. 4.7

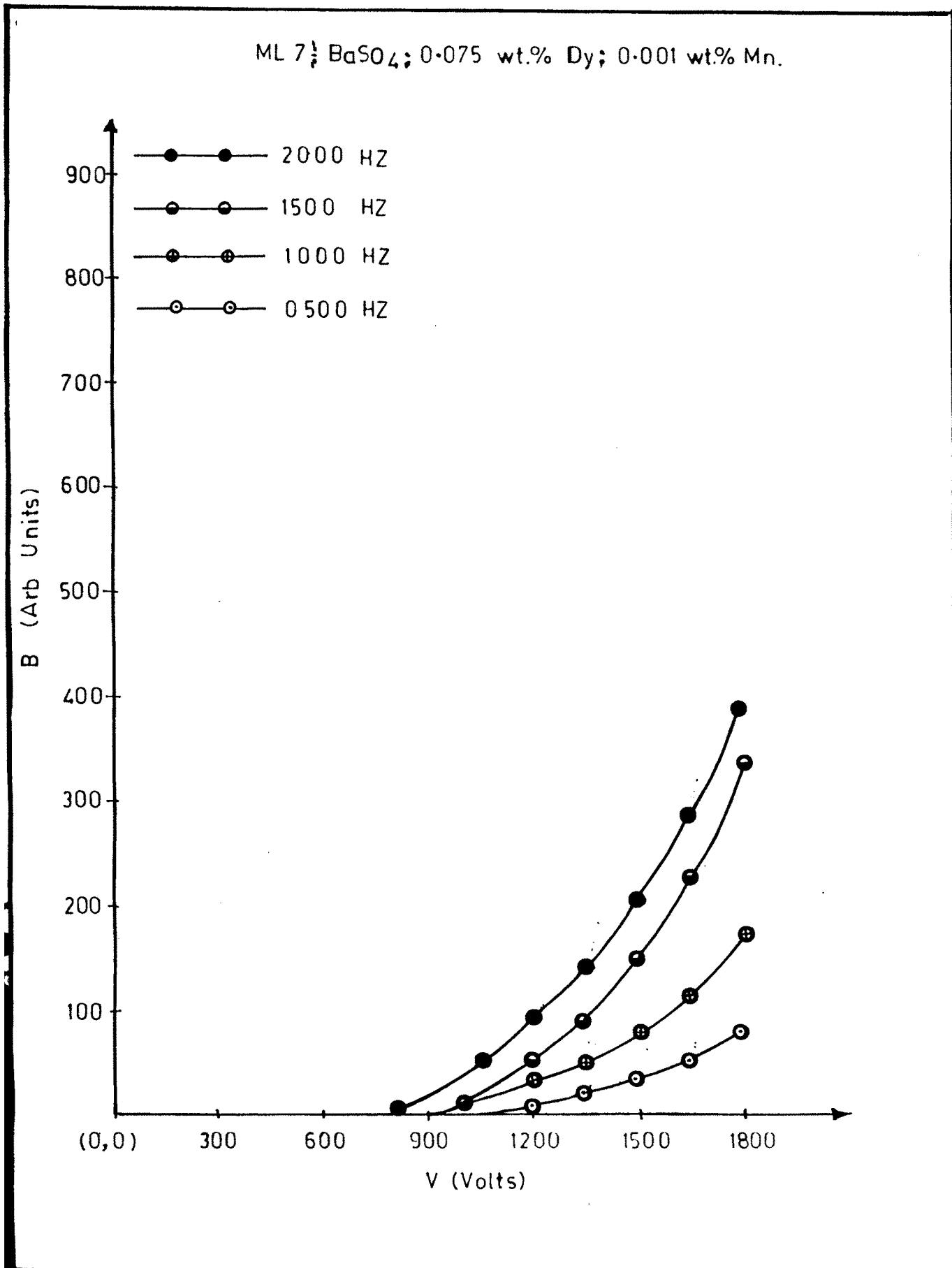


Fig. 4.8

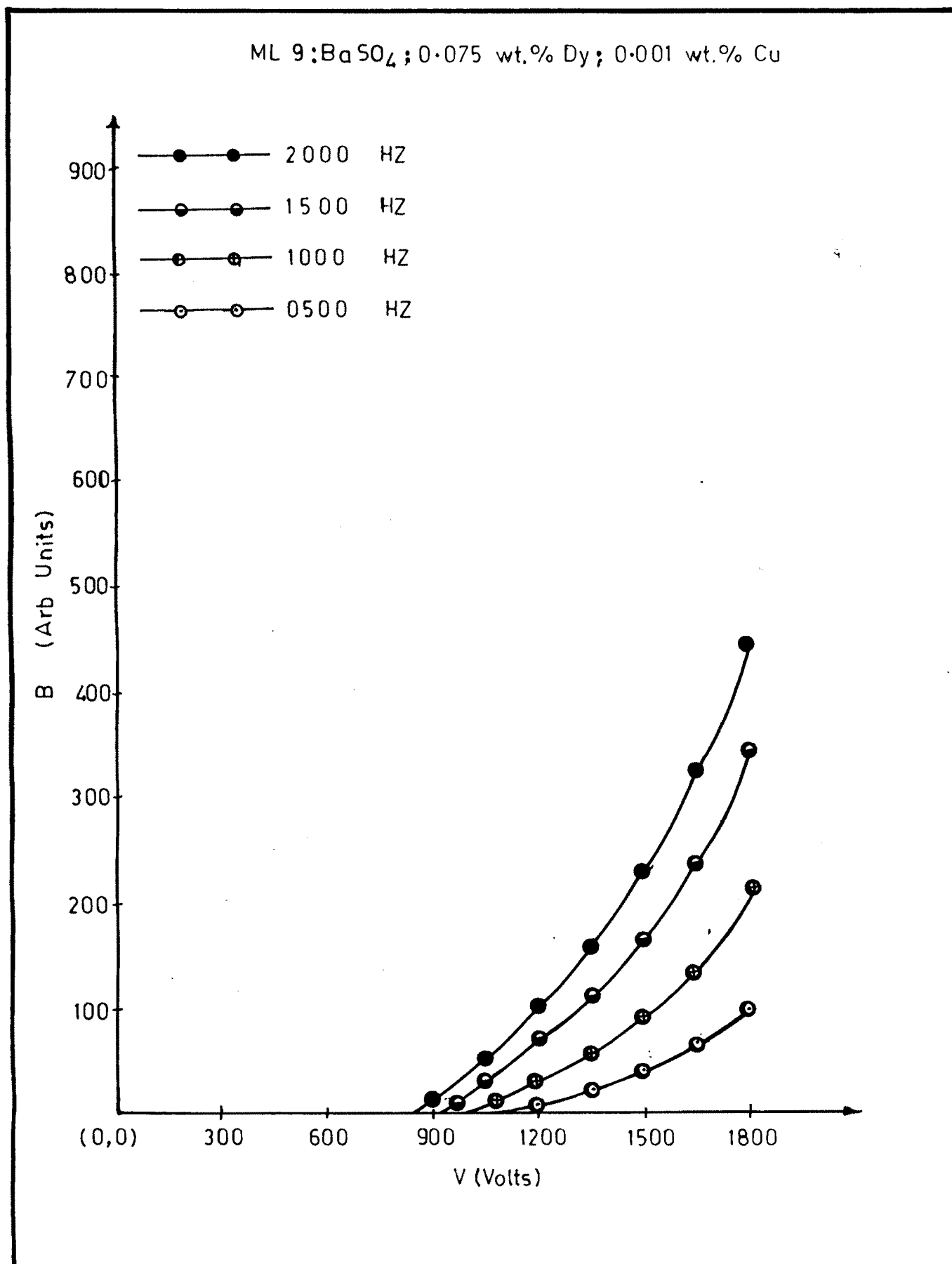


Fig. 4.9

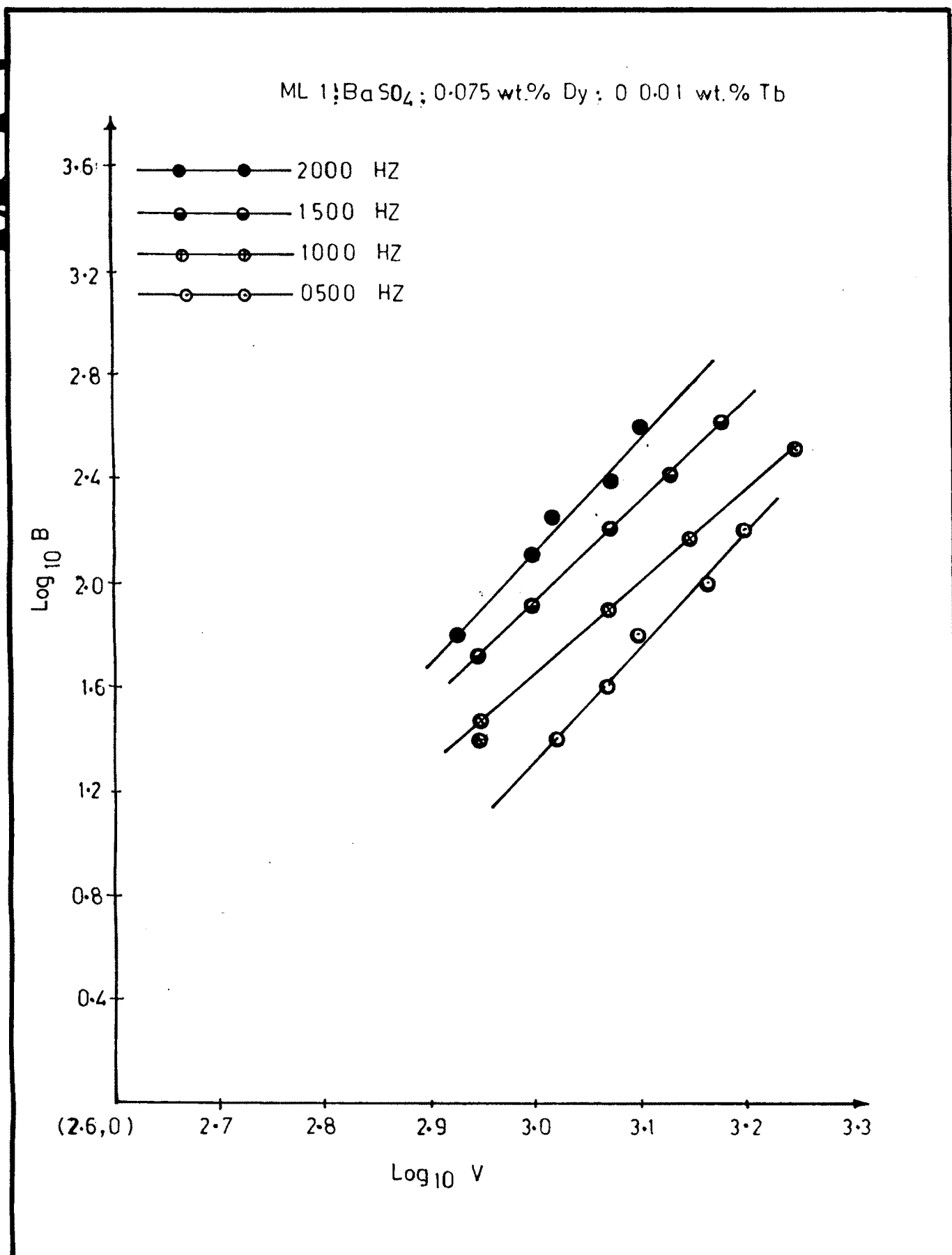


Fig. 4.10

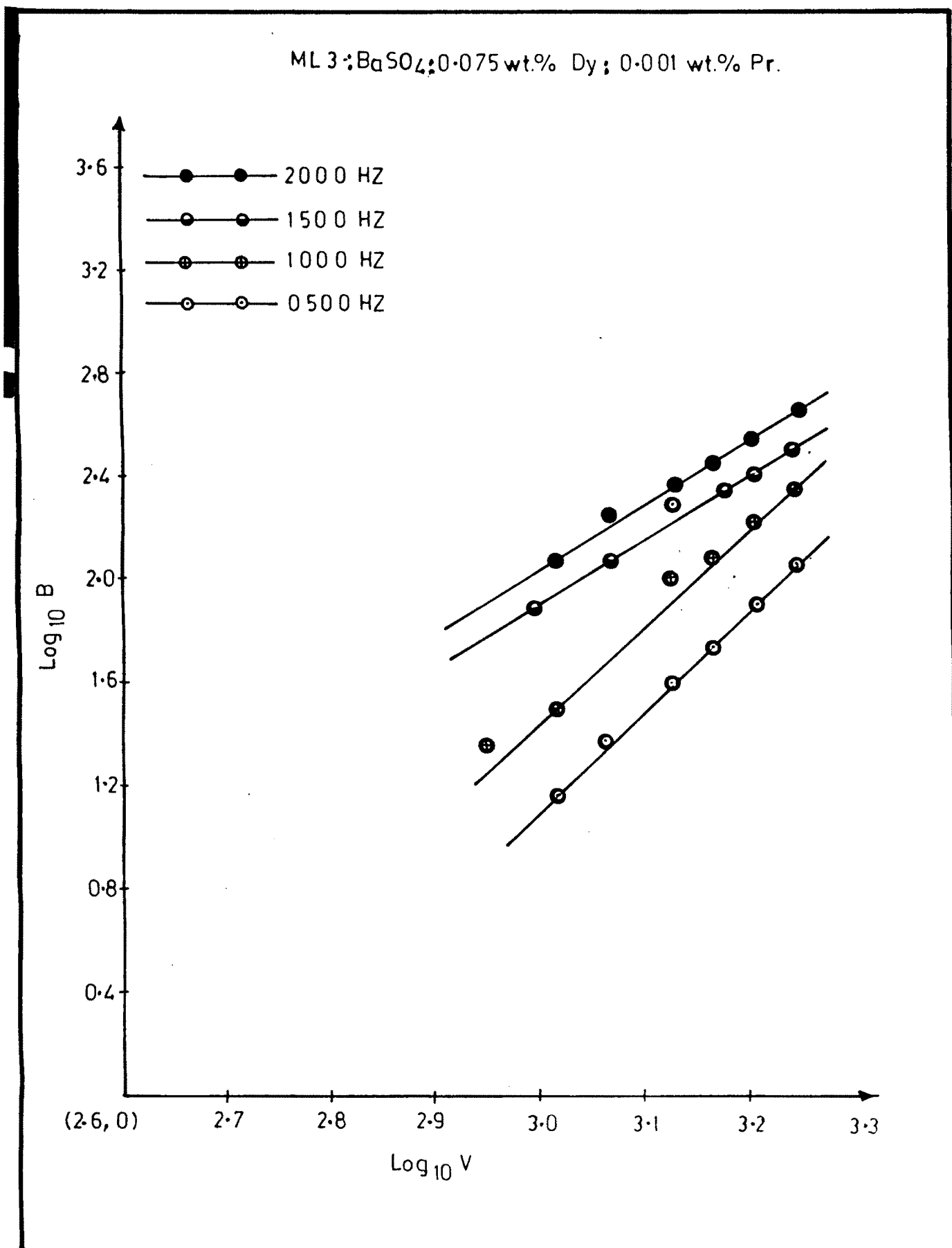


Fig. 4.11

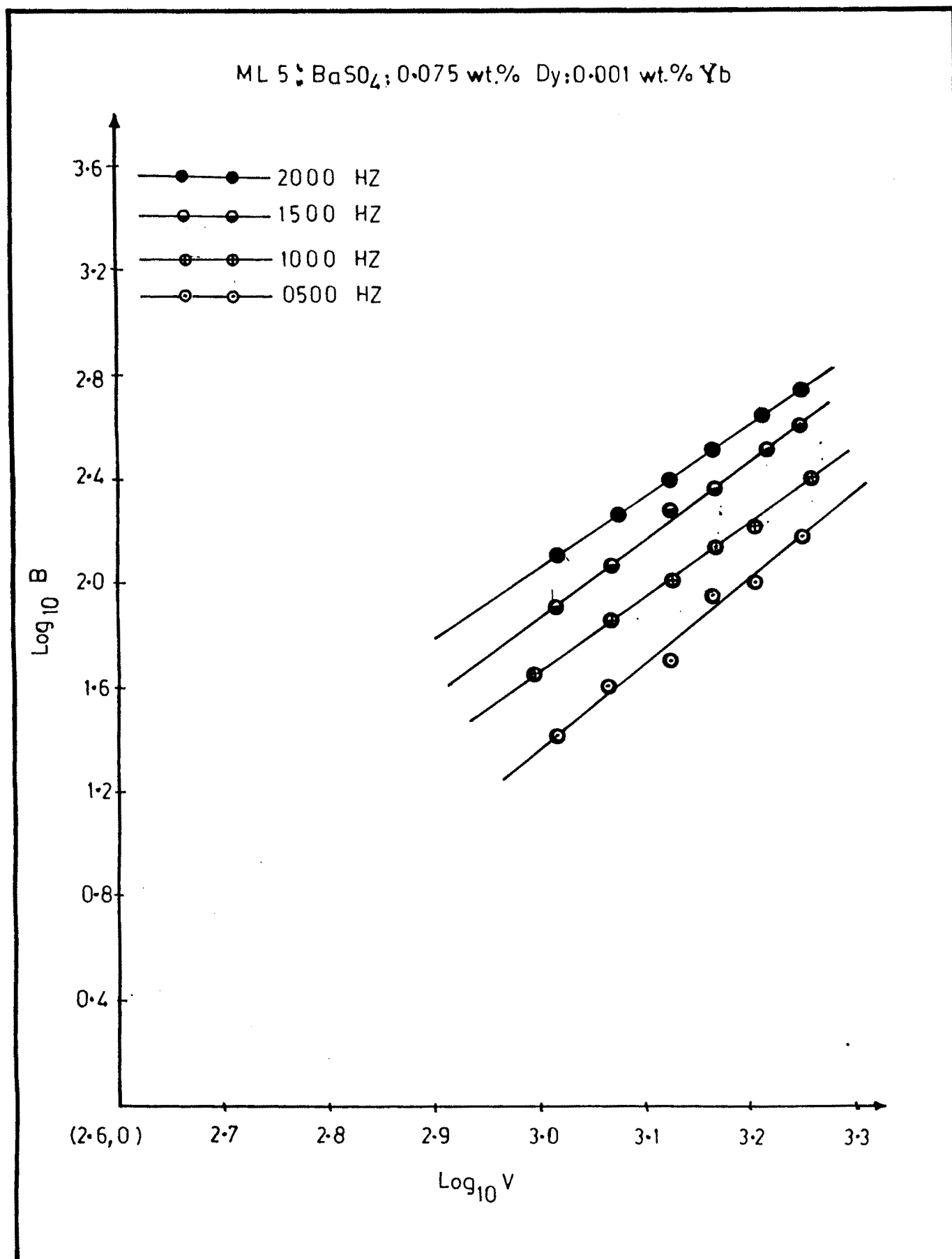


Fig. 4.12

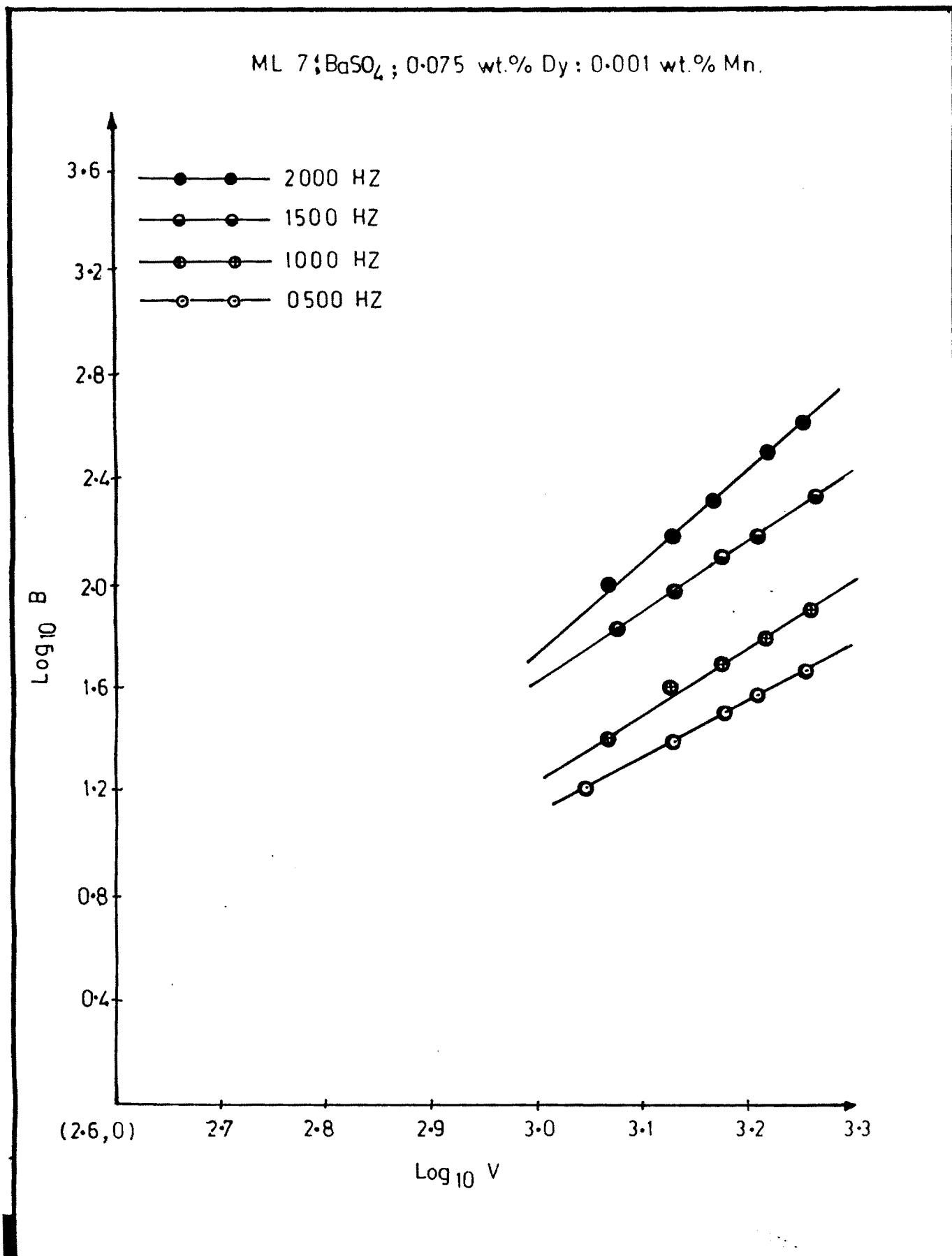


Fig. 4.13

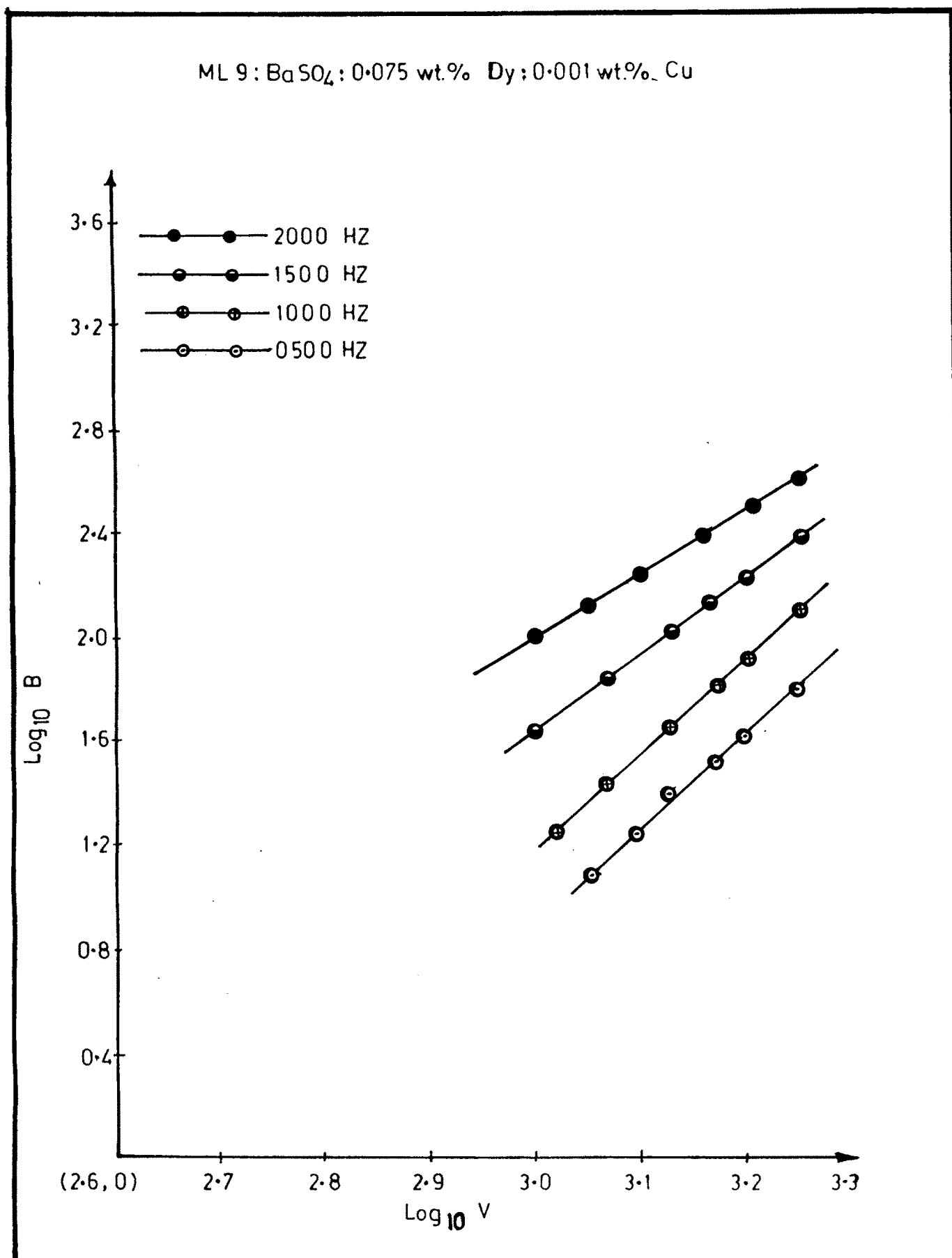


Fig. 4.14

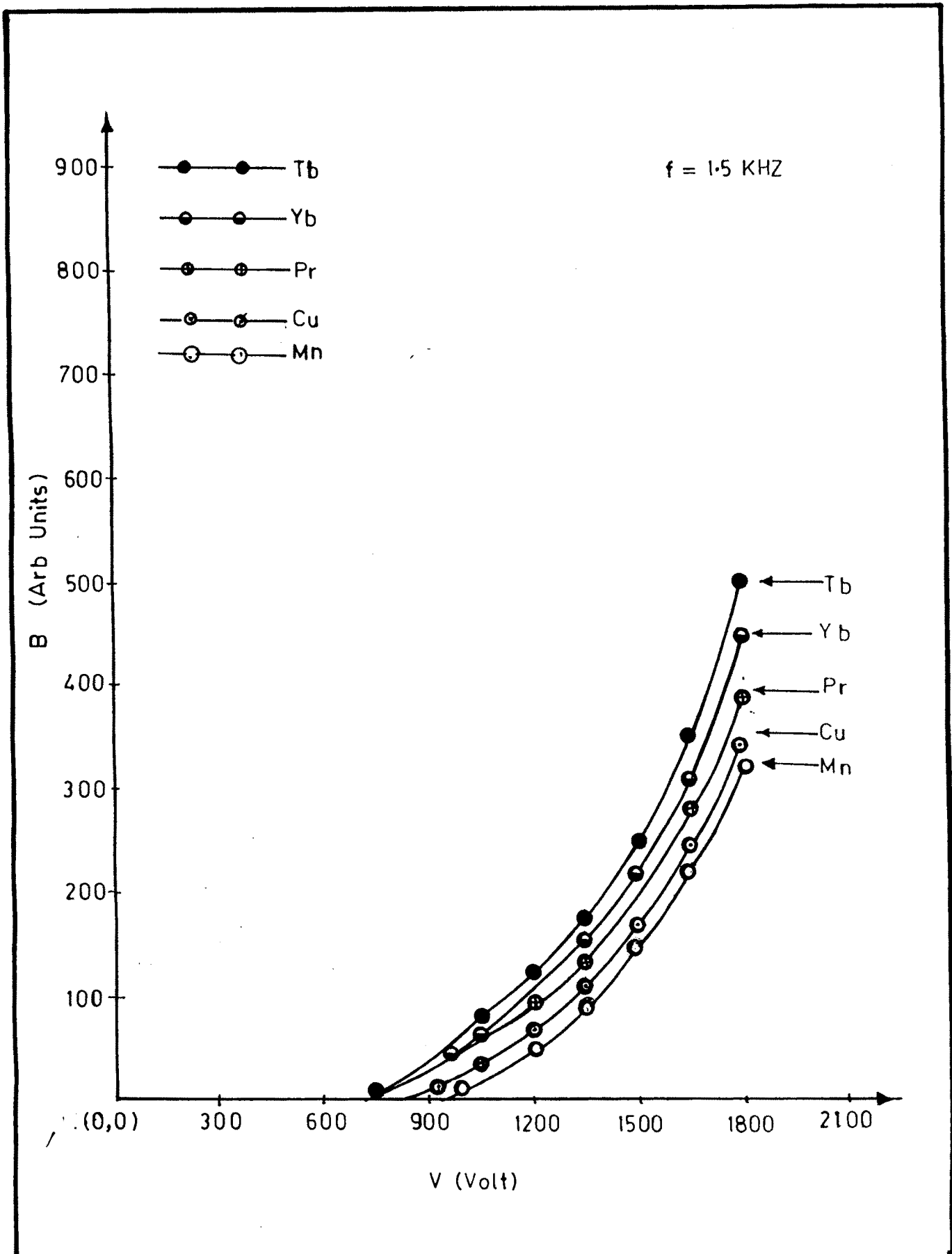


Fig. 4.15

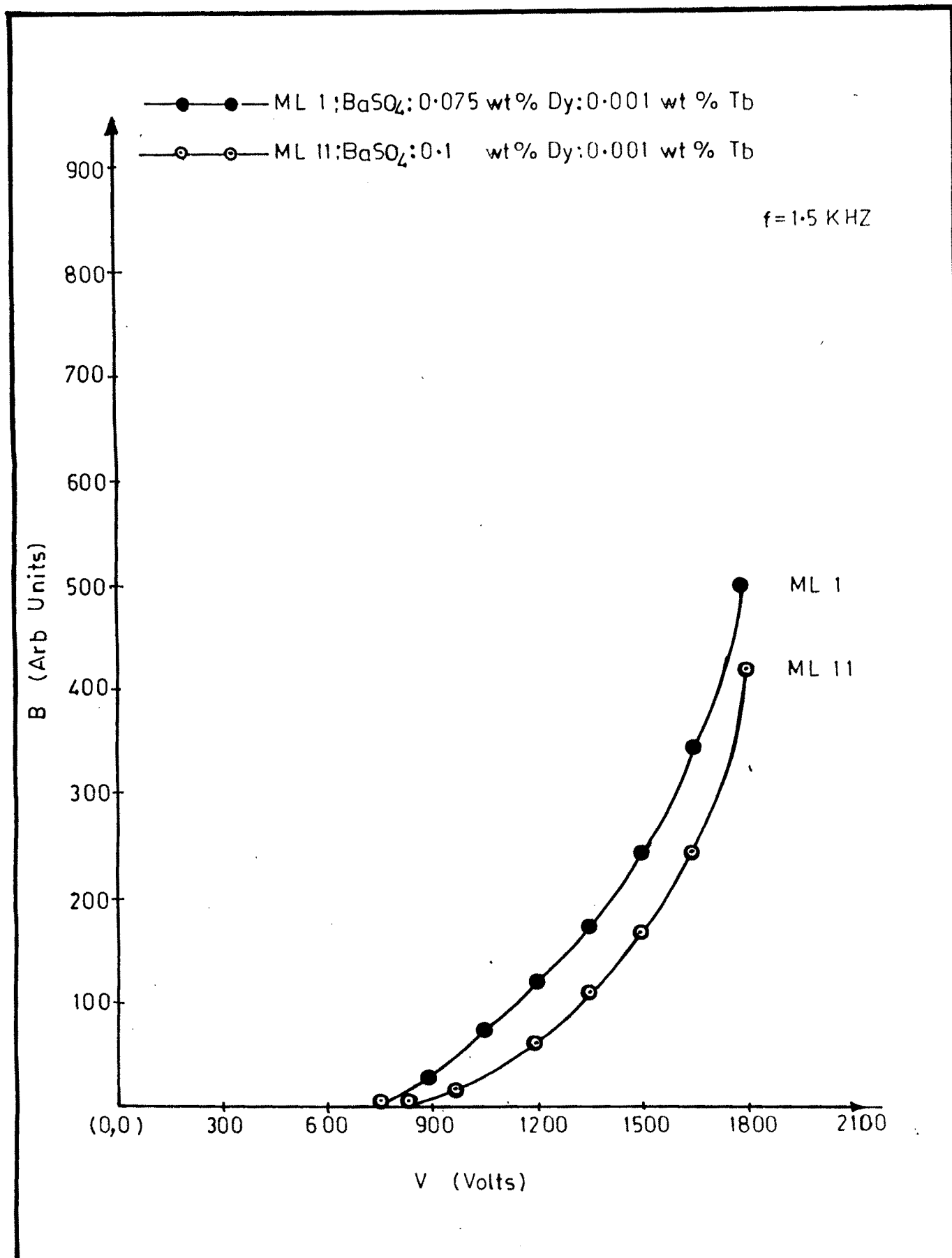


Fig. 4.16

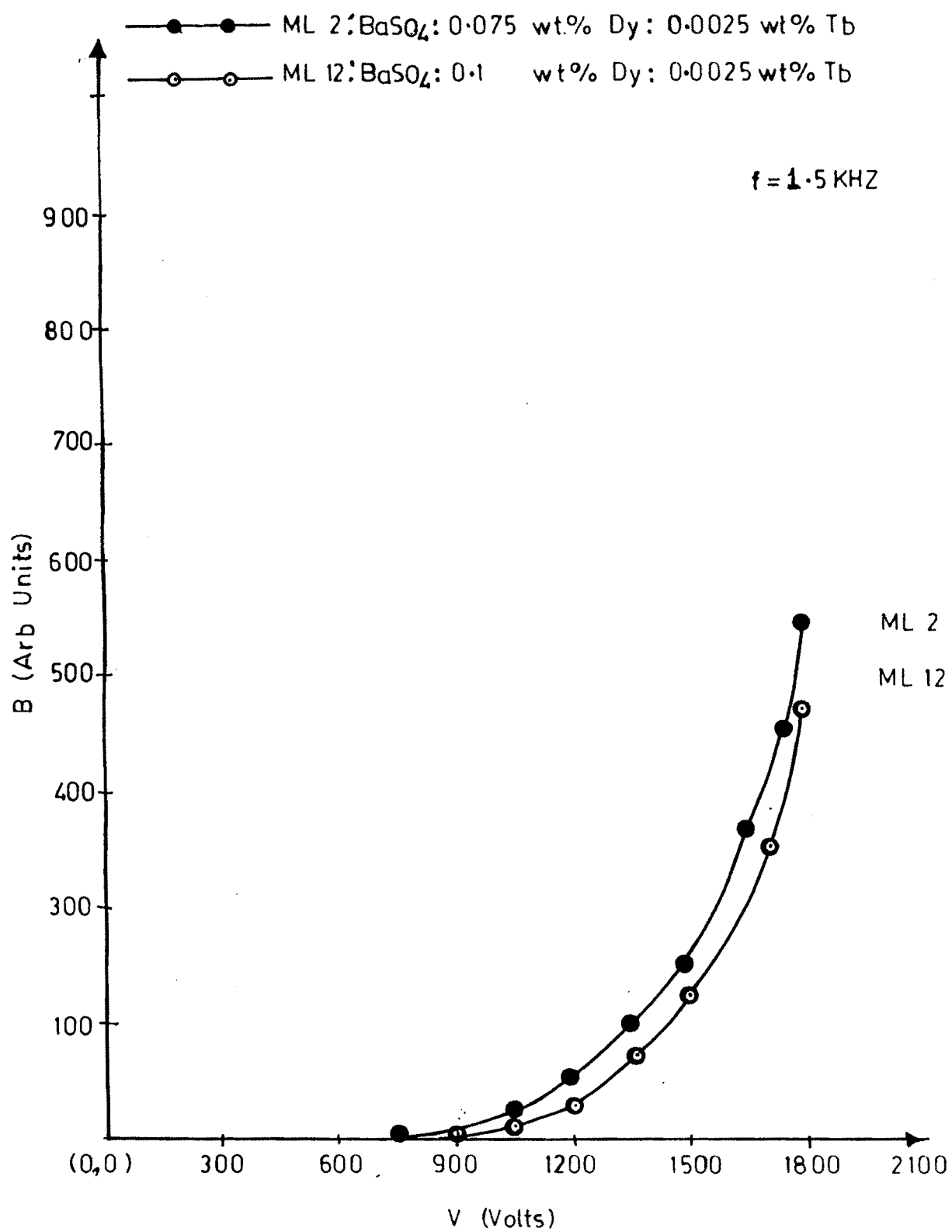


Fig. 4.17

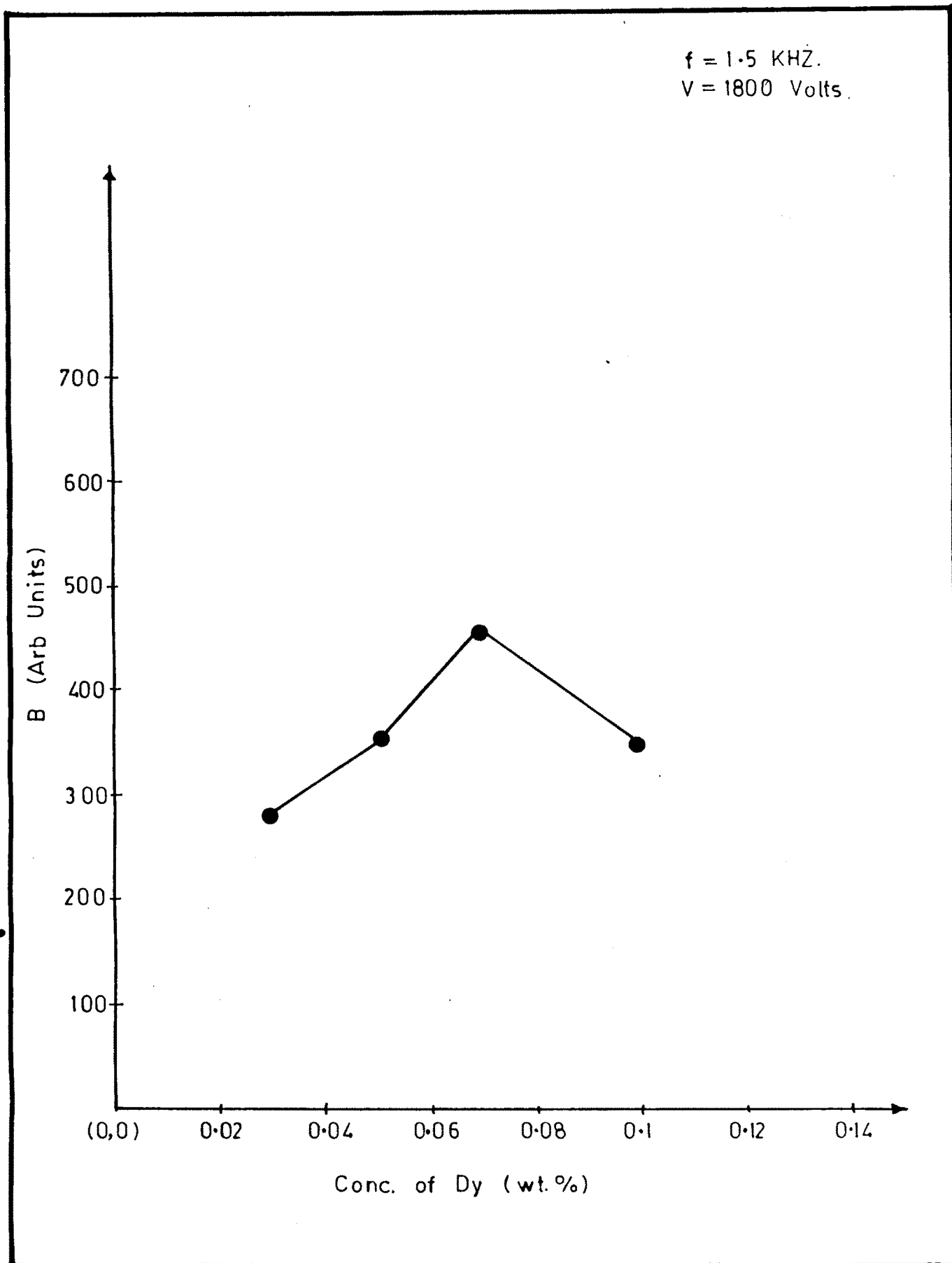


Fig. 4-18

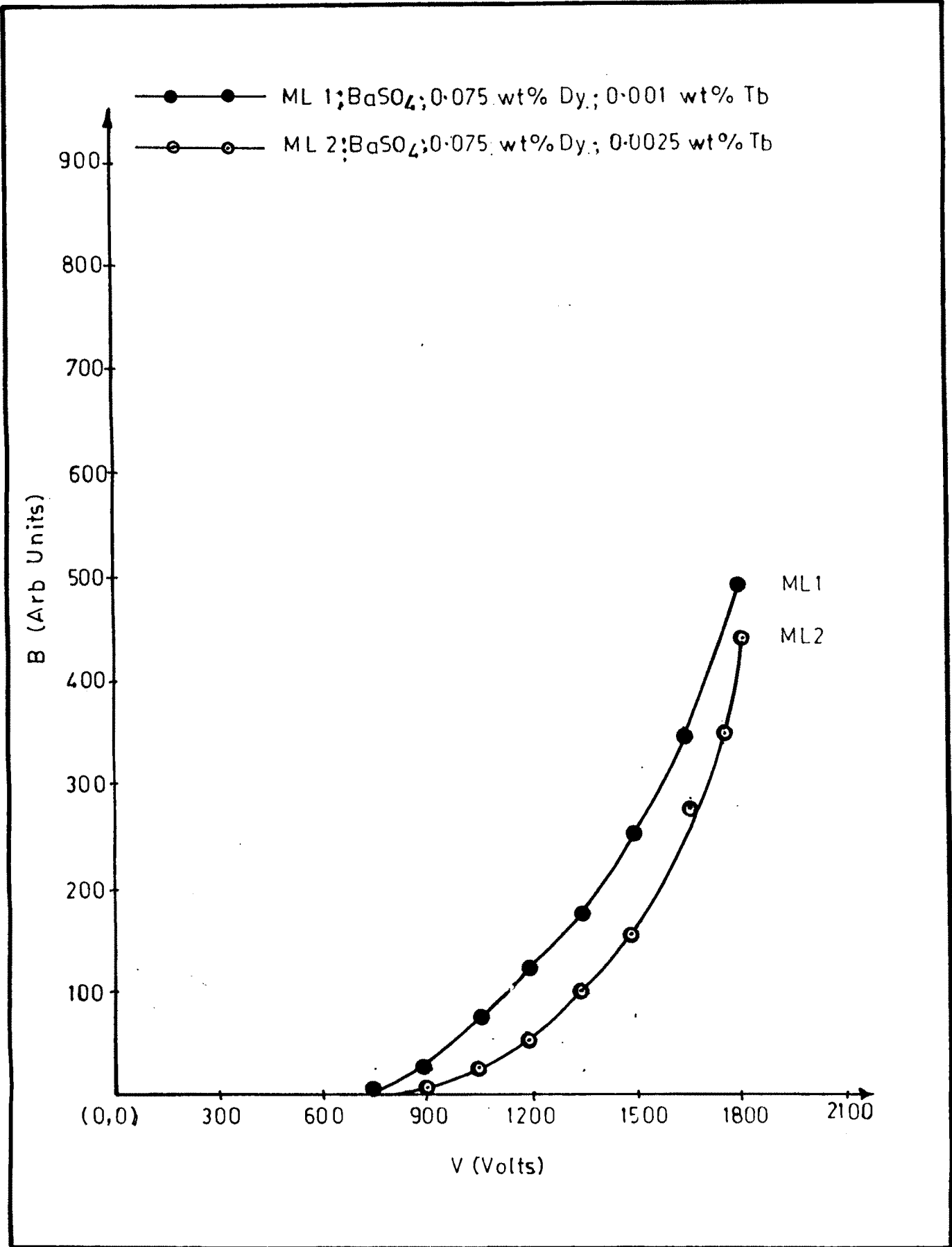


Fig. 4-19

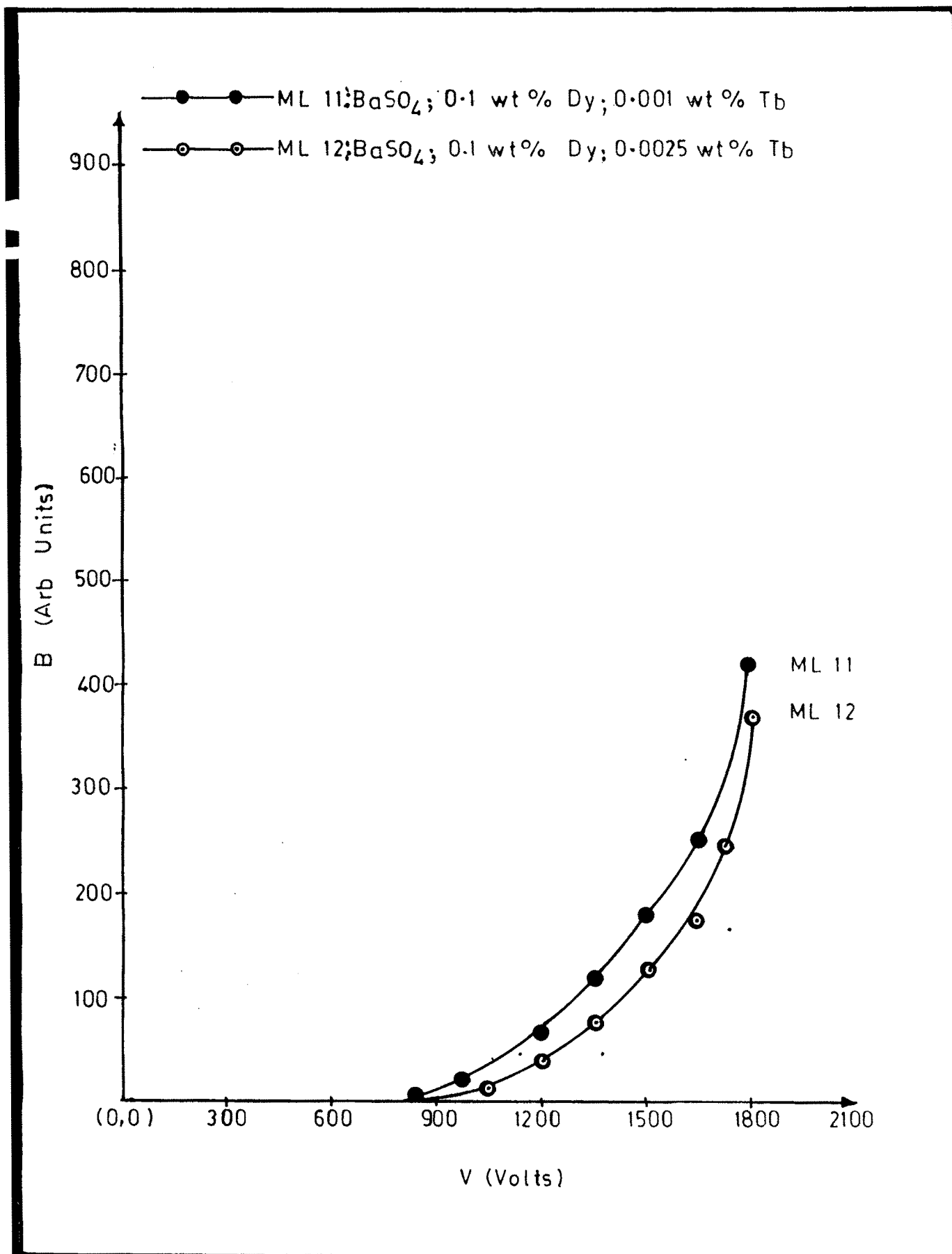


Fig. 4.20

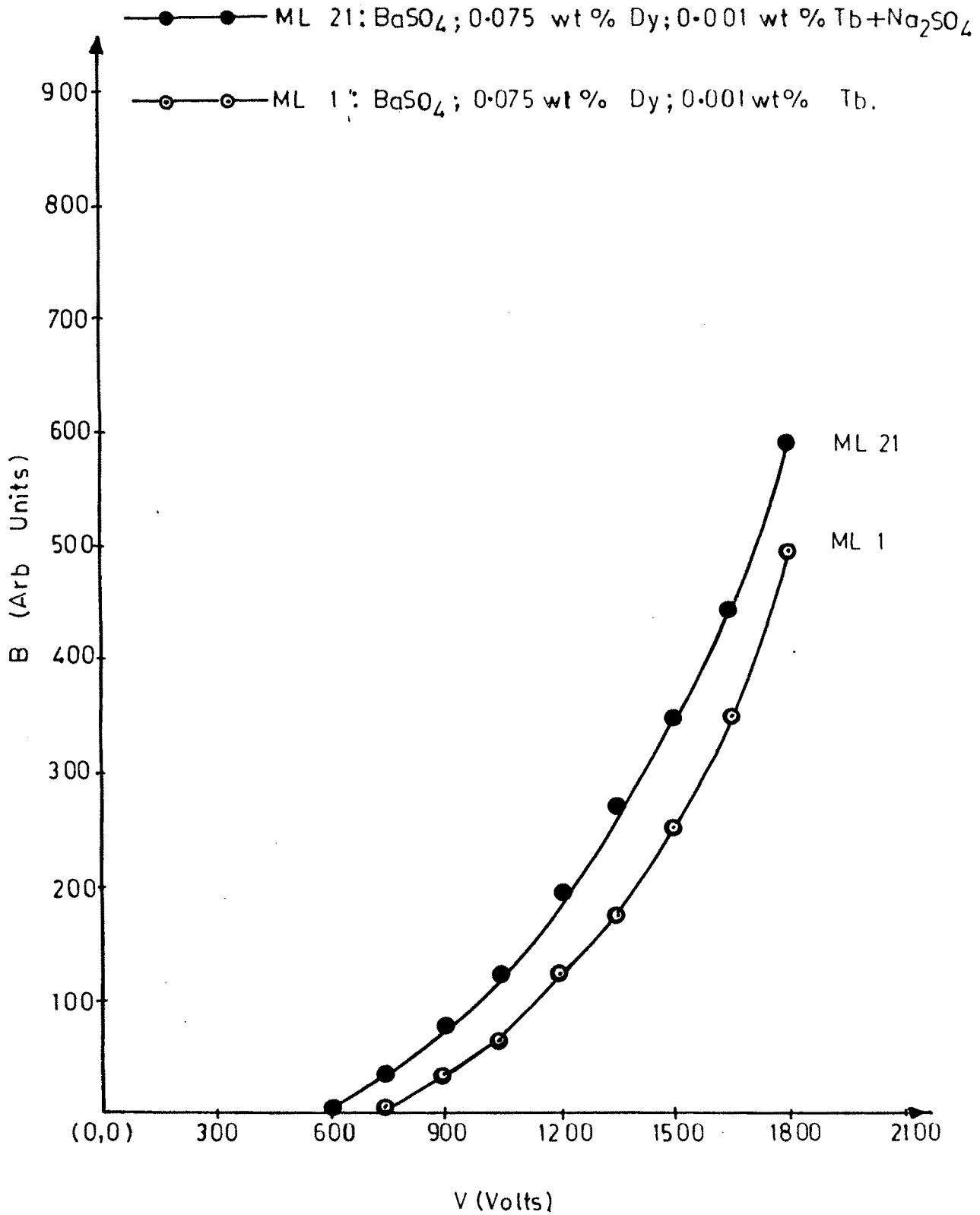
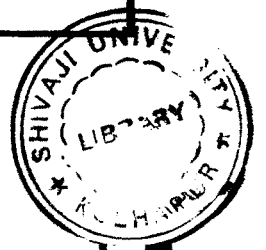


Fig. 4.21



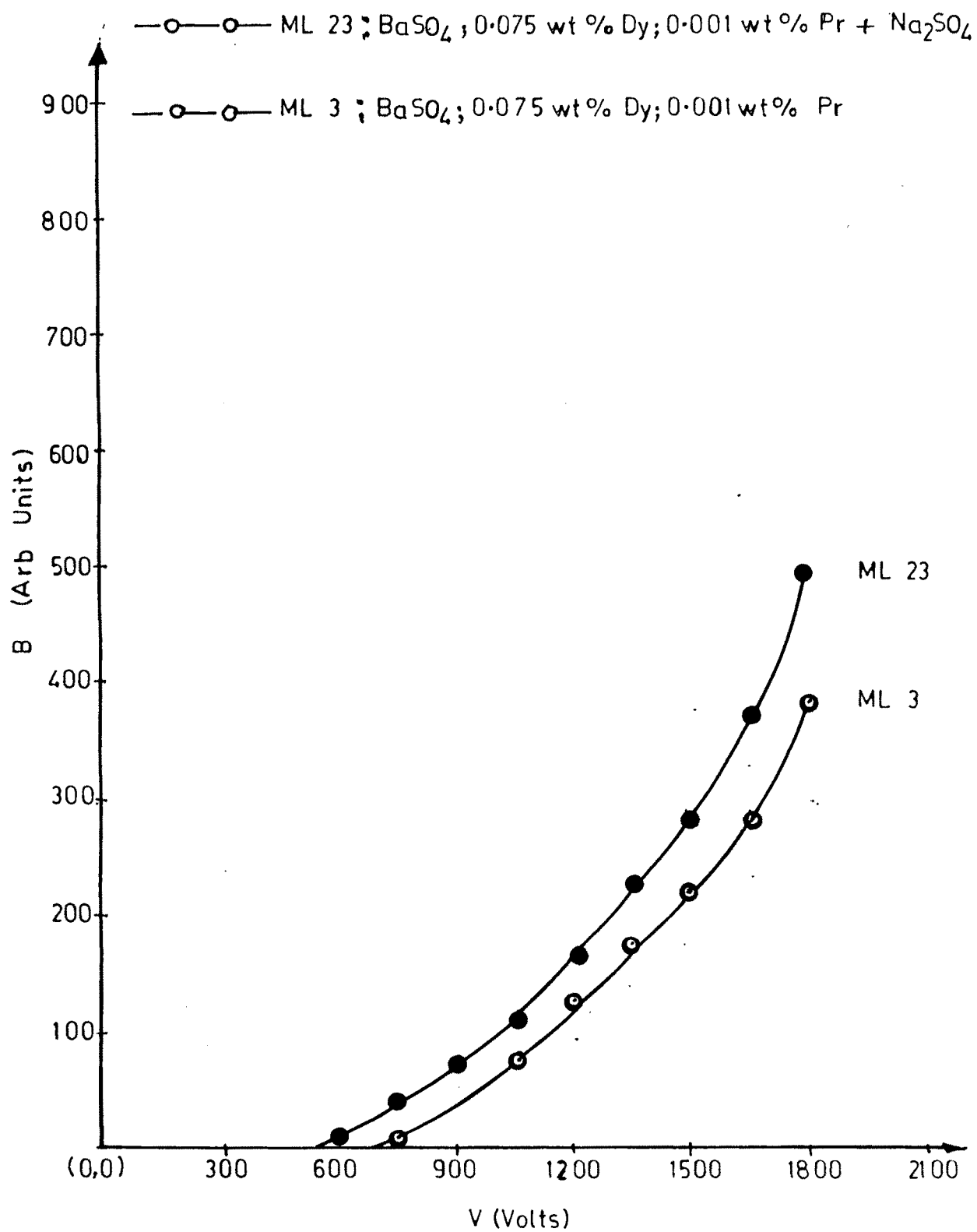


Fig. 4.22

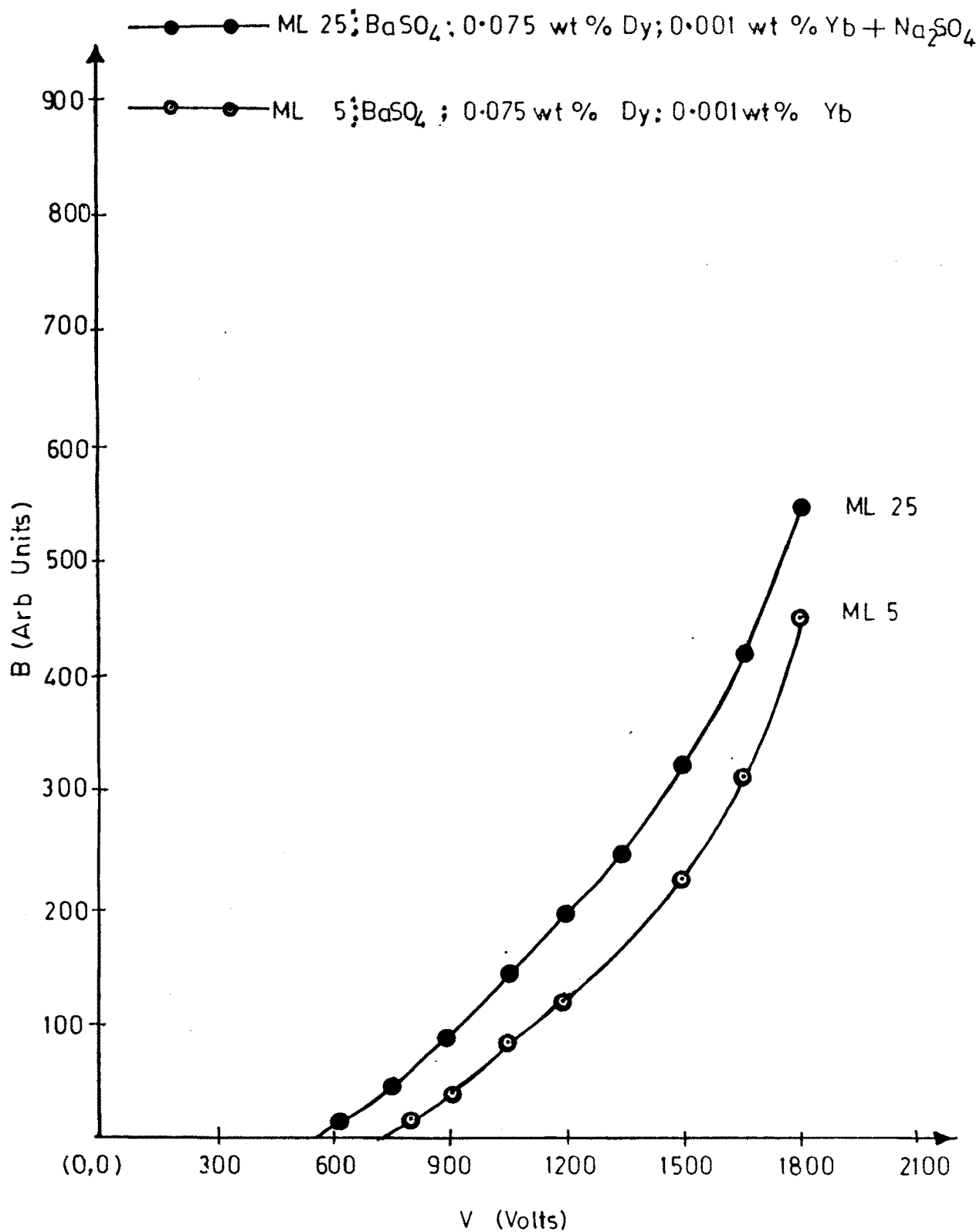


Fig. 4.23

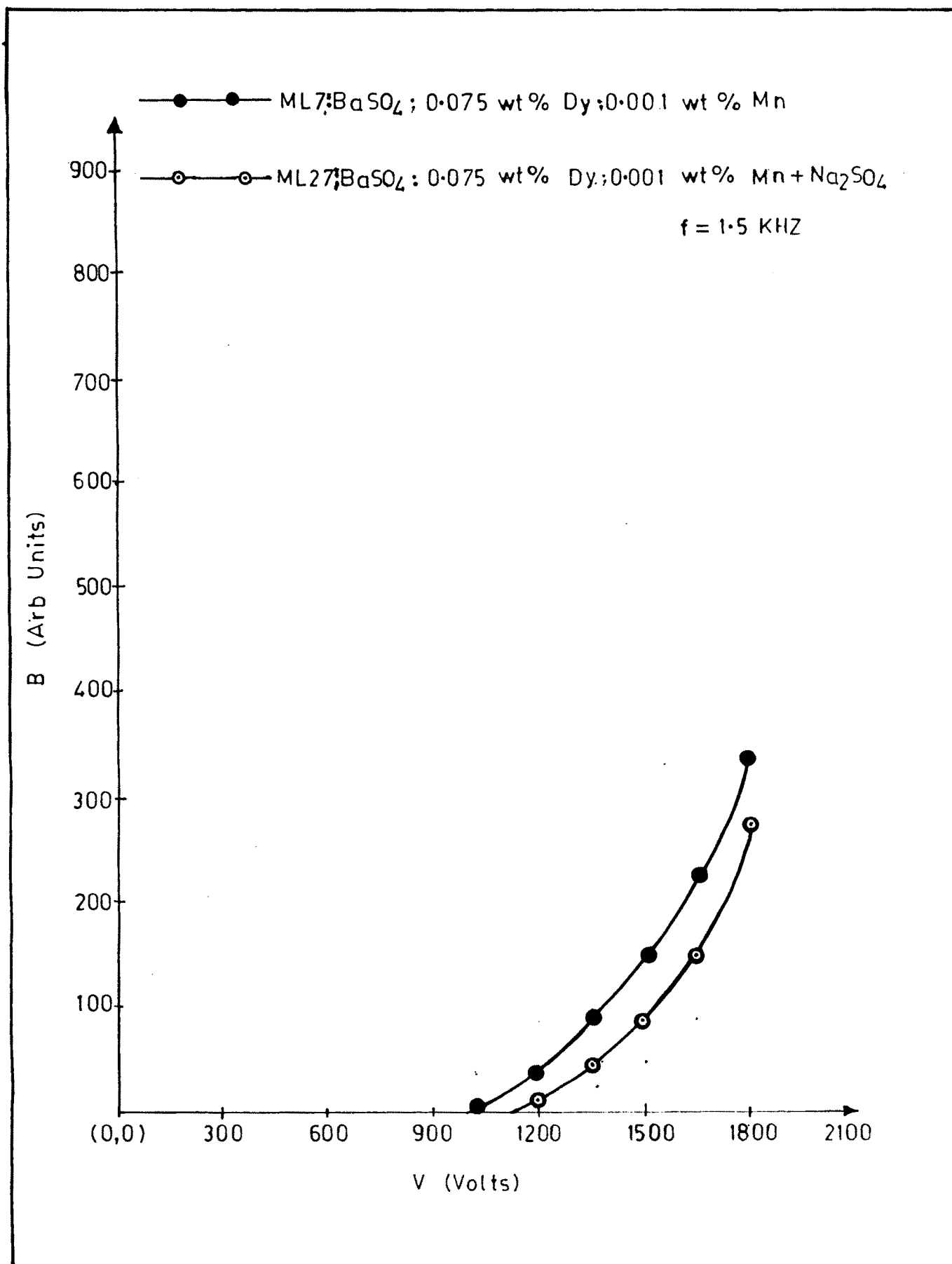


Fig 4.24

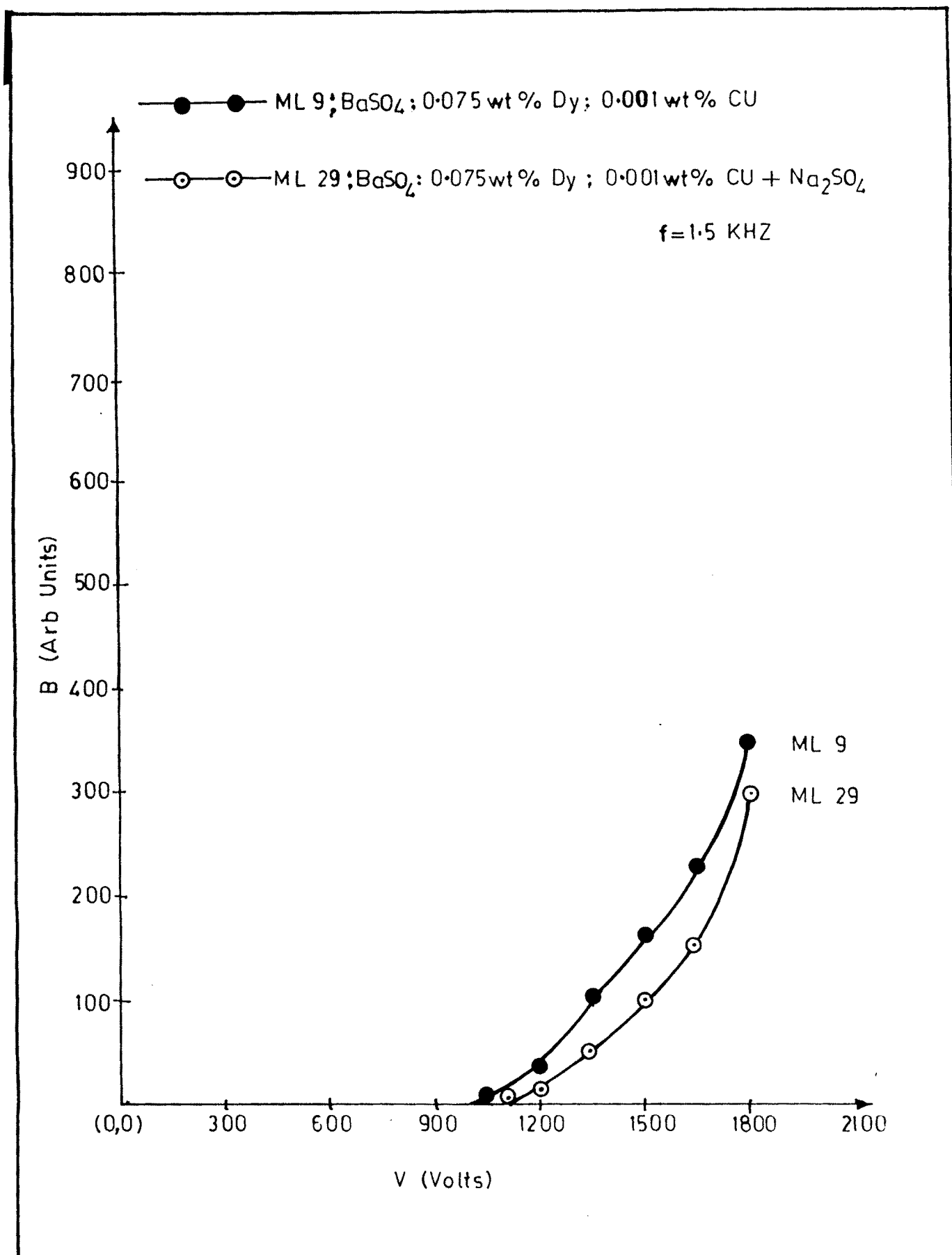


Fig. 4.25

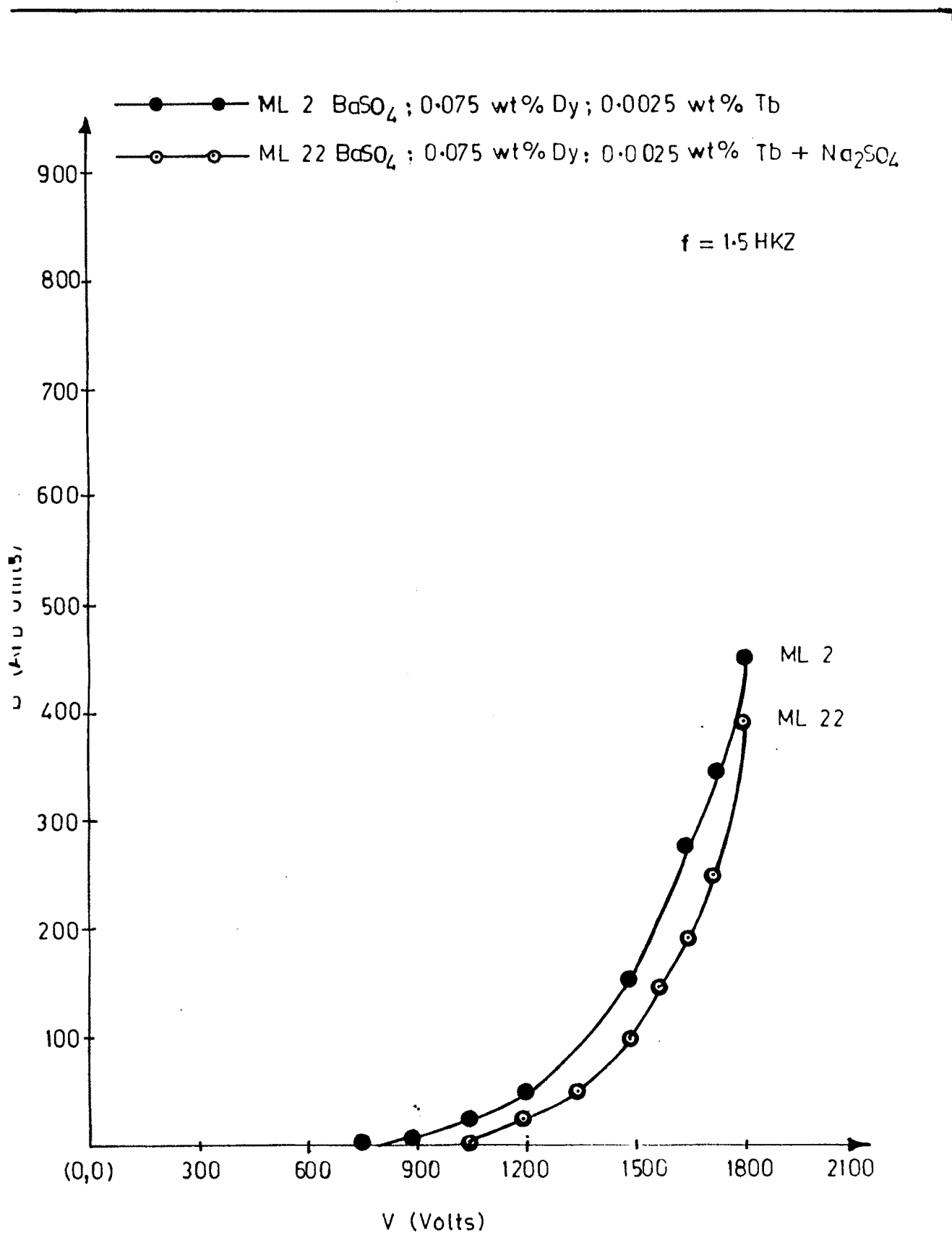


Fig. 4-26

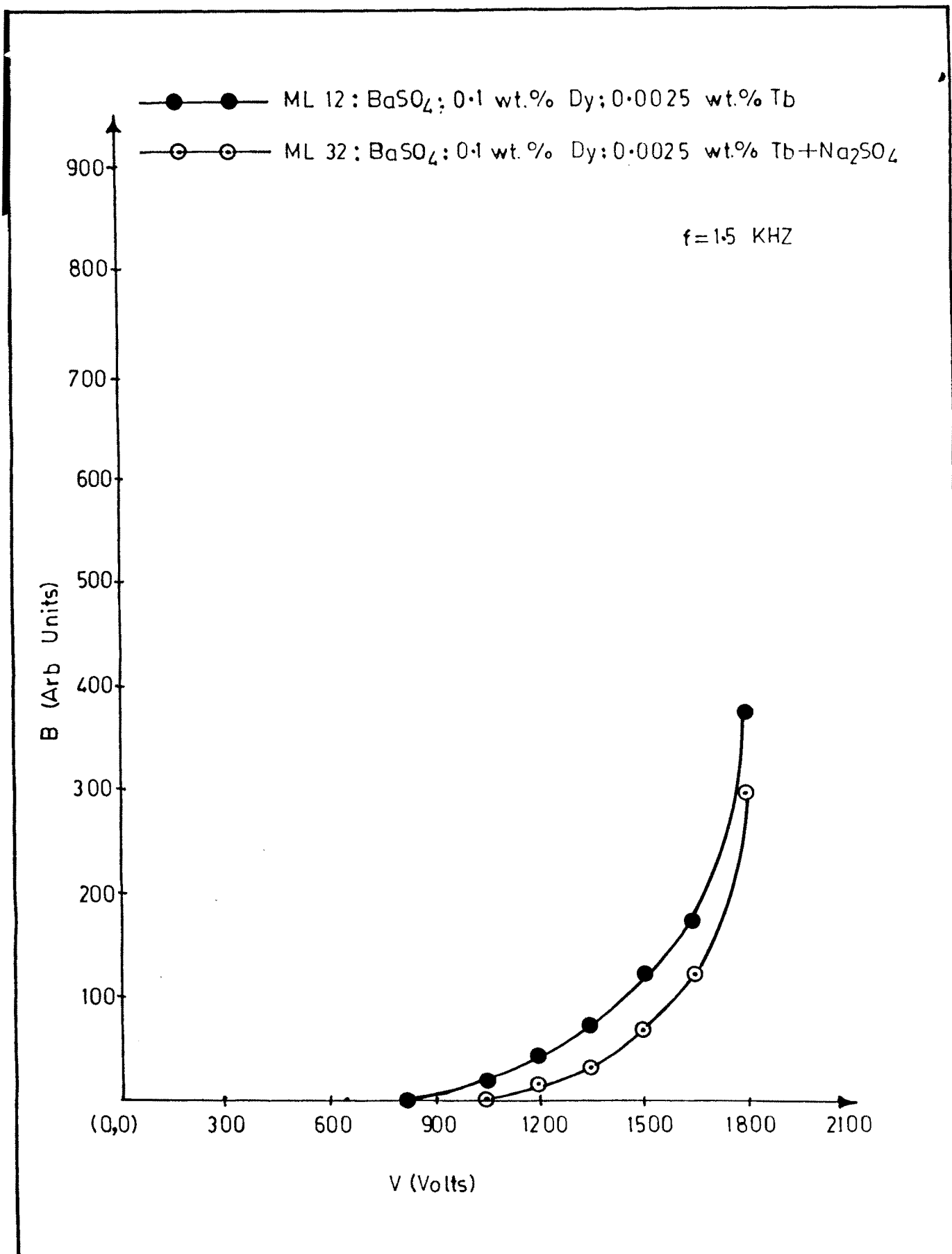


Fig. 4.27

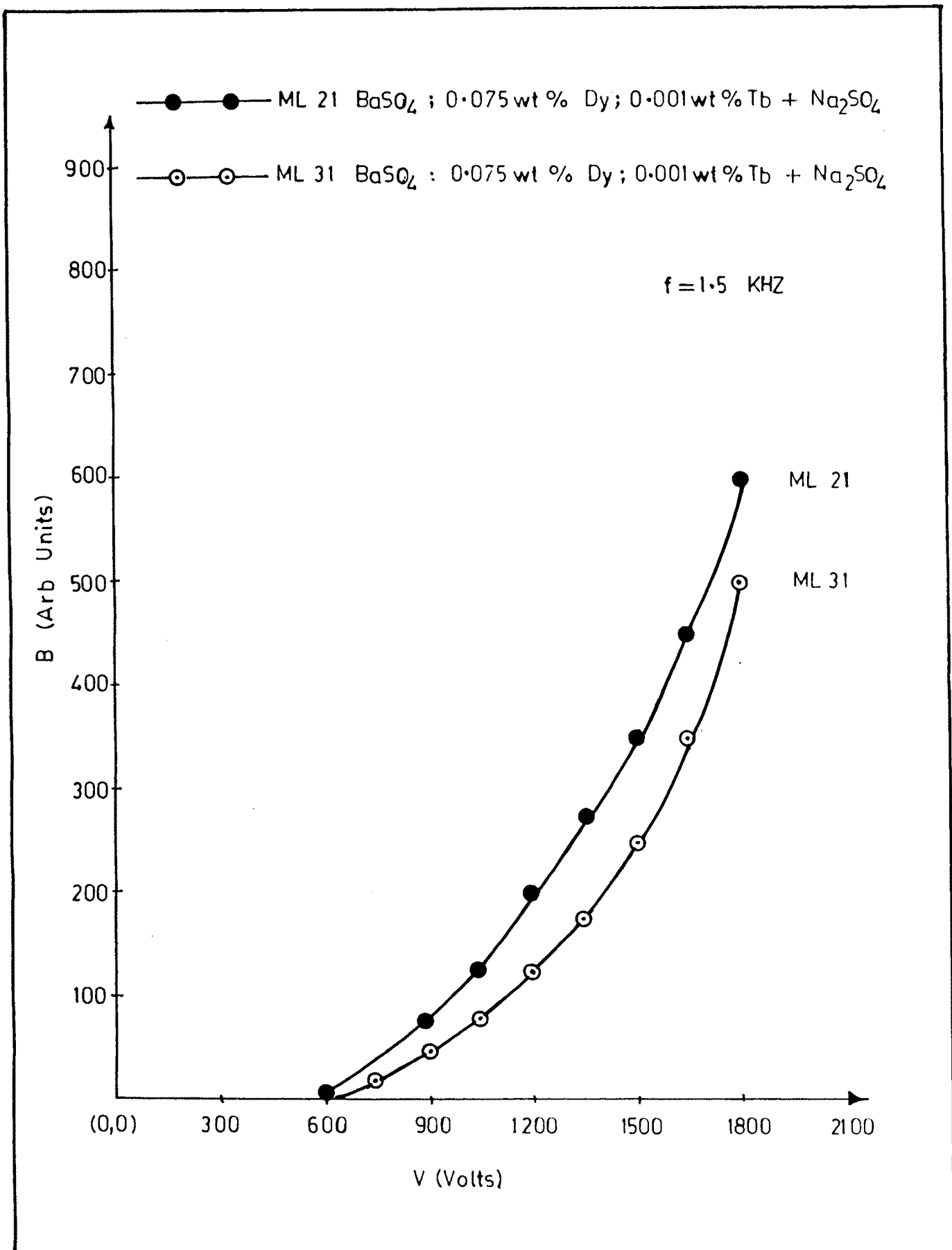


Fig. 4.28

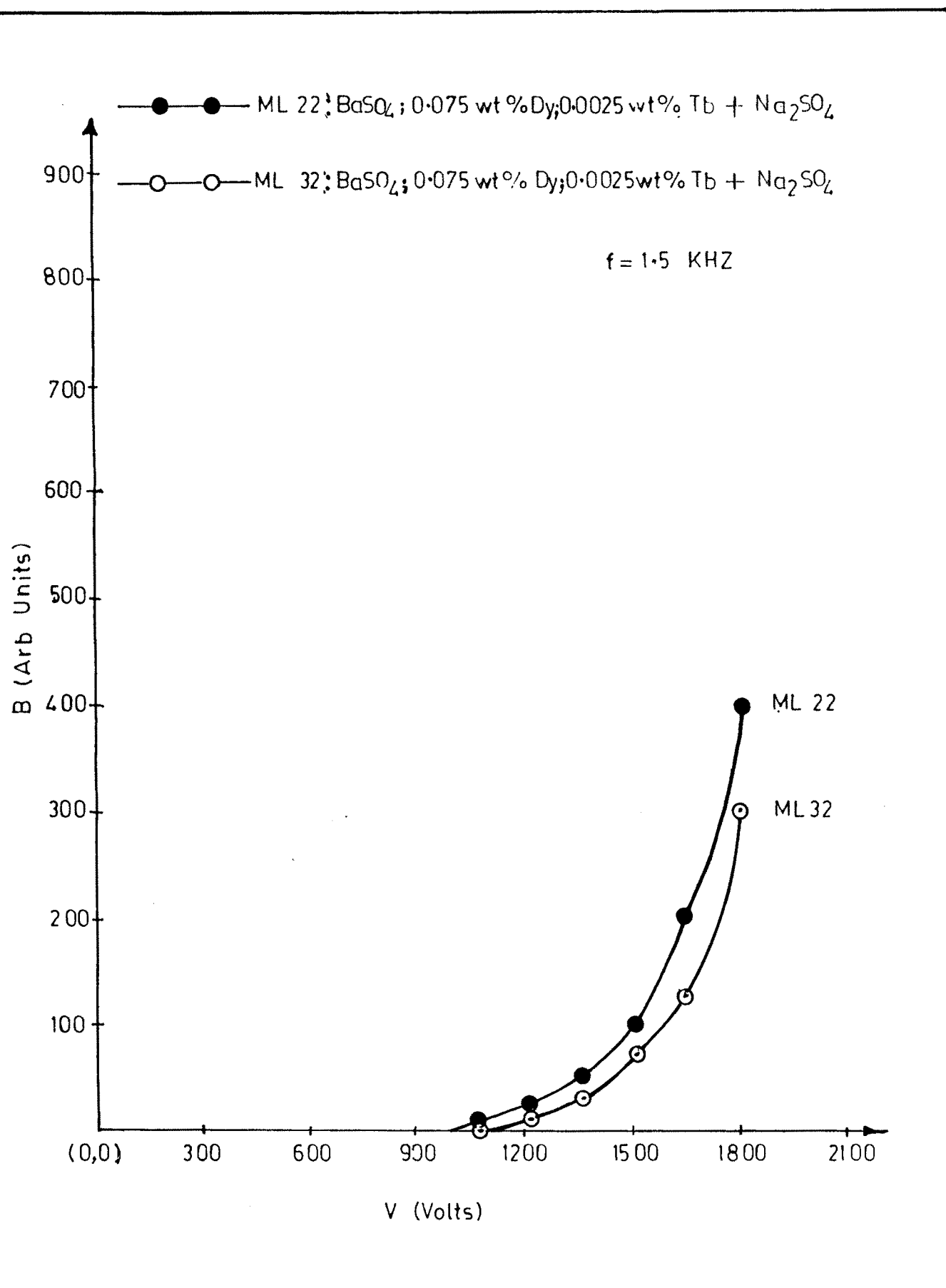


Fig. 4.29

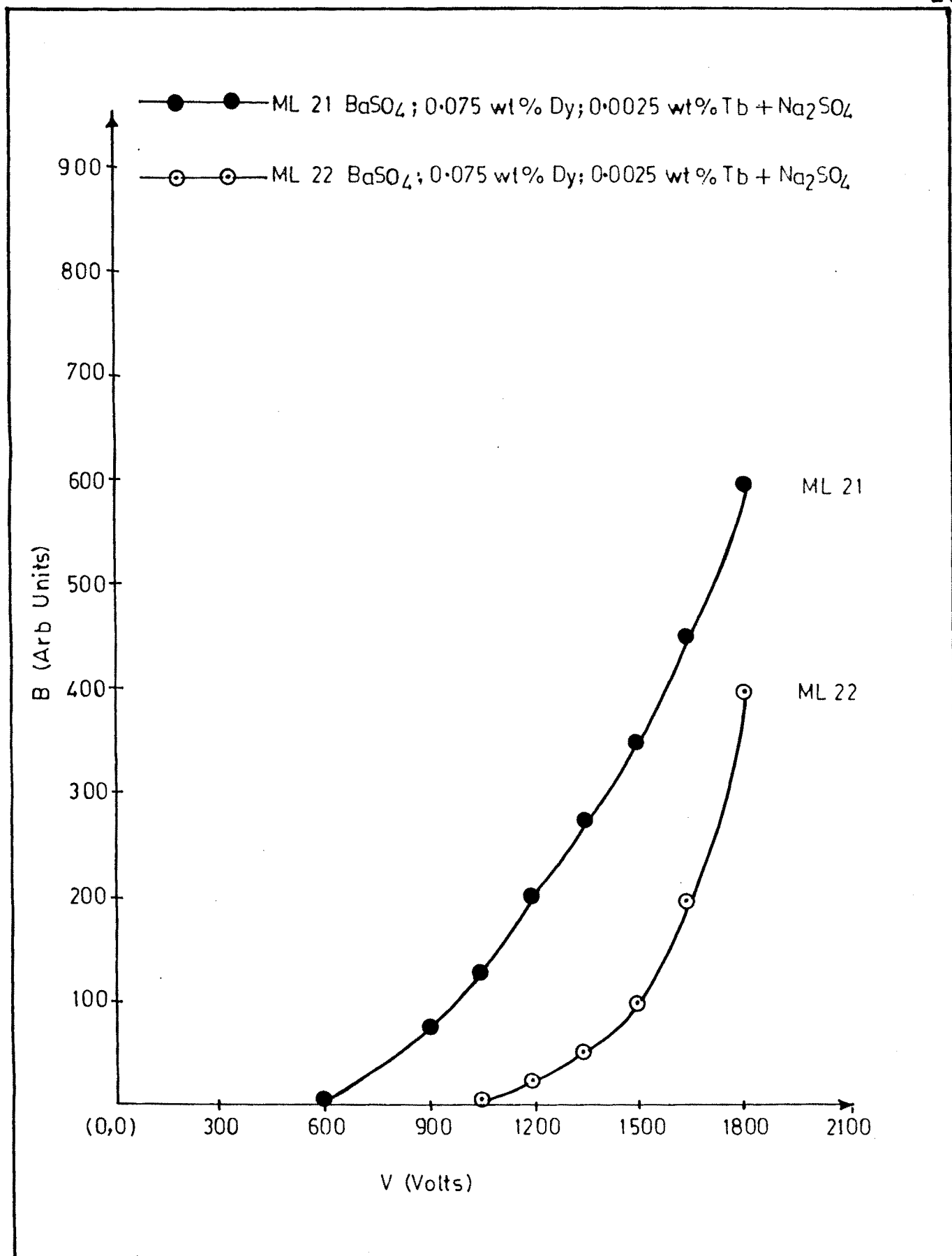


Fig. 4.30

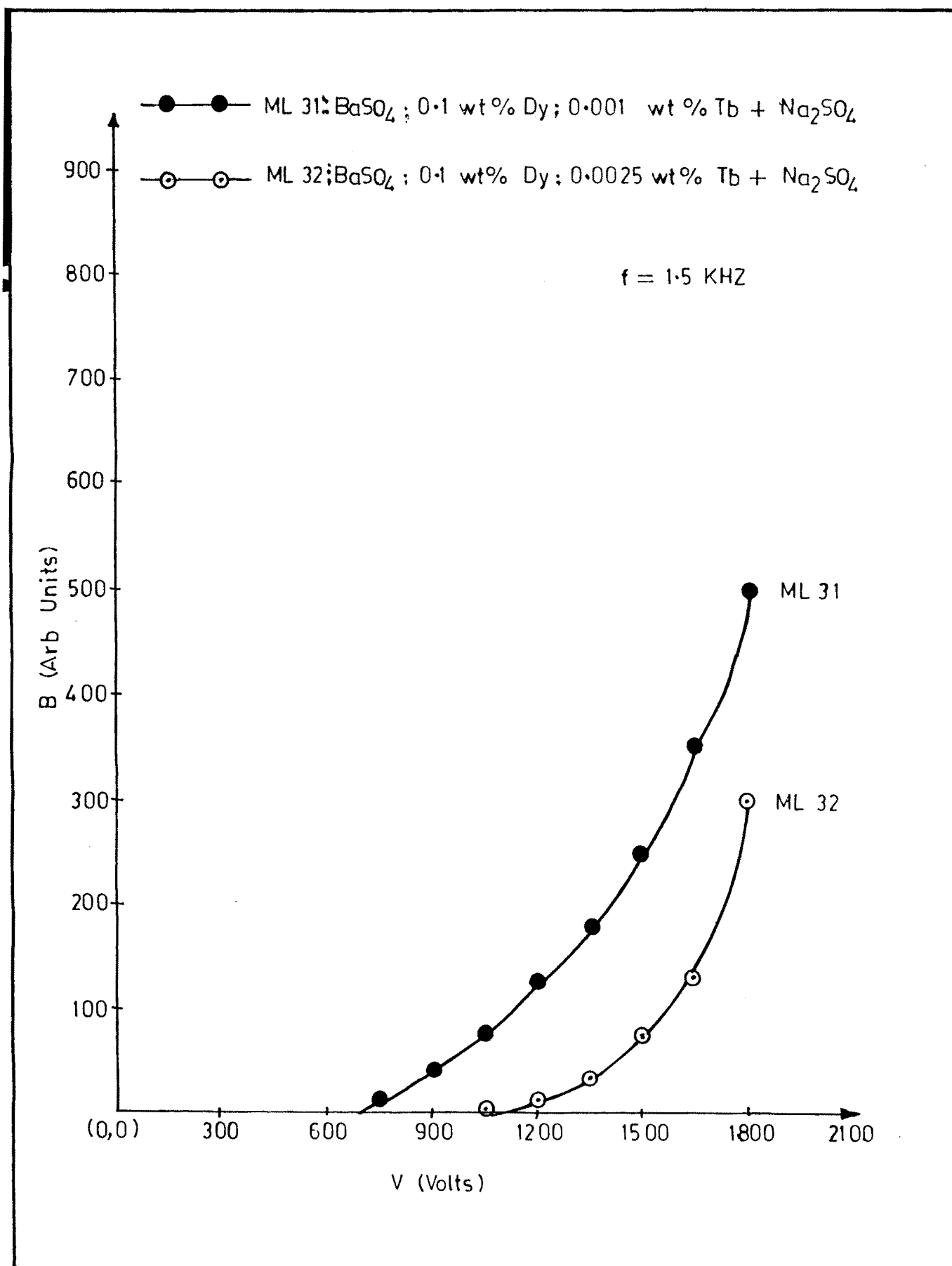


Fig. 4.31

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