CHAPTER FOUR

ELECTRO-THERMOLUMINESCENCE

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4-1 INTRODUCTION:

Light output during thermoluminescence is affected by application of constant electric field (1) and the phenomenon is termed as 'Electro-thermoluminescence (2). The pecularities of electro-thermoluminescence depend sensitively both on strength and frequency of applied field and rate of heating used during the study. Moreover, some maxima and minima, unlike to those found in glow curves; appear during heating of the phosphor with uniform heating rate. In this chapter are described the studies of electro-thermoluminescence carried with a view to gain the information about the following aspects:

1) effect of voltage and frequency on emission intensity;
2) effect of heating rate and activator concentration on brightness variation;
3) mechanism of electrothermoluminescence.

4-2 THEORETICAL BACKGROUND:

A literature survey presents that during last few decades a good number of workers (3-7) in the field of luminescence have studied the phenomenon under either a.c. or d.c. field excitation and have explained the results. A detailed and satisfactory theory is yet to take the shape. Some such explanations followed by different workers are as follows:

4-2.1 Explanation by Johnson et al. (8):

In a field dominated thermoluminescence, large variations in brightness may be expected, if one assumes that the electron traps responsible for thermoluminescence in certain temperature ranges alter the formation of high field region. The magnitude of field E in the exhaustion layer increases the number of shallow donors which can become thermally ionised during the half voltage cycle. The localised states may be neutral when occupied or may have the negative charge which is compensated by a nearby positive centre; such as an ionised activator. In either case, there will be an increase in the field in the exhaustion layer when an electron from trapping states is removed from the barrier region. The density, N, of the traps which ionise during the half voltage cycle (τ) is

$$N = N_o \left[-\exp. \left(-P_1 \tau \right) \right] \qquad \text{- - - -} \qquad (4.1)$$

Where N_o is the number of trapped electrons per unit volume and P_1 is the rate constant for thermal emptying of traps and is given by $P_1 = S_1 \exp. \left(-^{E_1}/kT \right)$. The magnitudes S_1 and E_1 are the frequency factor for untrapping and trap depth respectively.

The exact expression for brightness depends on the detailed knowledge of all localised levels in the phosphor system.

However, the following equation describes to a good approximation, the dependance of brightness on average field (9).

$$B_1 = A \exp. ({}^{-C}/E) \quad ---- \quad (4.2)$$

Where A is the proportionality constant and C is a constant which depends on the efficiency of excitation process and varies inversely with this efficiency. The average field $\bar{E}$ resulting from formation of exaustion barrier region is given by

$$\bar{E} = (\frac{2\pi e}{K} V_o)^{1/2} \quad (N + Nd)^{1/2} \quad ---- \quad (4.3)$$

Where V_o is the magnitude of applied voltage, N and Nd are the concentrations of empty traps and empty donors respectively; and K is the dielectric constant of the phosphor. Substitution of equations (4.1) and (4.3) into equation (4.2) gives,

$$B_1 = B_{10} \exp. [{}^{-\beta} \exp. ({}^{-P_1 \tau})] --- \quad (4.4)$$

The constants B_{10} and β result from the combination of constant terms and with an approximation $N < Nd$.

Even at low temperature, the traps may contribute to brightness by being field ionised in the region of high field, thereby producing the electrons which are accelerated to impact excitation. The traps may provide the charge carriers for acceleration to the extent that they are not thermally ionised during the half voltage cycle. This contribution to brightness is given by

$$B_2 = B_{20} \exp. (-P_1 \tau) \quad ---- \quad (4.5)$$

Where B_{20} is temperature independent and is proportional to N and is also a function of local field configuration. Thus the total contribution to the emission intensity from electron traps is the sum of the equations (4.4) and (4.5). Hence,

$$B = B_{10} \exp. [-\beta \exp.(-P_1\tau)] + B_{20} \exp.(-P_1\tau) \quad (4.6)$$

gives the temperature dependance of brightness.

Differentiating equation (4.6) with respect to temperature gives the following expression for the temperature, T_m of the minimum.

$$T_m = \frac{E_1}{K \log (S\tau/\alpha)} \quad ---- \quad (4.7)$$

with α as a constant given by,

$$\alpha = \log (\beta \log \beta \frac{B_{20}}{B_{10}})$$

An alternative mechanism for the effect of electron traps on the EL brightness requires a thermally activated process governed by trapping for removal of electrons from ionised activators, is followed by trapping in bulk of the crystal. The mechanism results in equation for brightness,

$$B = B_o \frac{(1- \exp. (P_1\tau)}{[(1- \exp.(- (P_1 + P_2)\tau]} \quad -- \quad (4.8)$$

where P_2 and P_1 are the rates for removal from and return to the activators respectively.

4-2.2 Explanation by Thornton (19):

The modifications in emission intensity may occur due to sensitiveness of traps to the field. The theory suggested by Thornton (10) assumes field controlled thermal release of electrons from trapping states. According to this theory, the return of electrons to excitation region is controlled by their thermal release from such traps. The number which are successful in returning is a function of release rate (voltage and temperature) and also of time (frequency) available. For sufficiently high voltage and low frequency all the traps may be depleted. The results of increasing voltage should be similar to those of lowering of frequency.

Here the probability of return of electrons in presence of field is given by,

$$P \propto \exp. \left({}^{-E^*}/kT \right) = \exp. \left[- \left(E - f(F) \right) /kT \right) \qquad (4.9)$$

Where E is the trap depth in absence of field, F the field strength and f(F) a function of strength and frequency of the applied field; such that it increases with the former and decreases with latter.

4-2.3 Explanation by Zalm (11):

Zalm (11) pointed out that the voltage dependence of the luminous emittance given by

$$B = B_O \exp. \left({}^{-C}/ \sqrt{V} \right) \quad ---- \quad (4.10)$$

is satisfied at all temperature in the range from $-190^{\circ}C$ to $400^{\circ}C$. The behaviour of B is a function of temperature. The constant C in equation (4.10) determines - among other things - the relation between applied voltage and the local field strength in the exhaustion barrier within the phosphor.

This constant is an intricate function of, for example, the thickness of the luminescent layer, the dielectric constant of insulator, the volume fraction of phosphor in insulator, the shape and dimensions of the grains and so on.

The existance of trapping states in a phosphor deviates the actual potential distribution within it considerably. In the case of trapping, a negative space charge is built-up inside the phosphor which prevents a further transport of electrons through the crystal. The voltage across the barrier and local field strength in barrier are thereby decreased.

It was also assumed that the positive space charge density in an exhaustion region arises from the ionised activator levels. As soon as the escape of holes manifests itself above certain temperatures, the positive space charge decreases and with it the field strength in the barrier.

4-3 RESULT AND DISCUSSIONS:

4-3.1 ELTL Curves:

The variation of emission intensity as a function of temperature under different field conditions is illustrated in the Figs. from (4.1) to (4.9). The measurements are carried out above the threshold voltage with the heating rates of $0.053^{o}K$/Sec., $0.1^{o}K$/Sec. and $0.167^{o}K$/Sec. in the temperature range of $300^{o}K$ to $433^{o}K$. The results obtained can be summarised as:

1. An ELTL curve initially increases with temperature, reaches to a maximum and then decreases to exhibit a minimum.

2. An increase in voltage, keeping the frequency constant, shifts the maximum and minimum towards the lower temperature side (Figs. 4.1 to 4.3).

3. At higher voltages, broadening of maximum occurs with a sharp rise in brightness level (Figs.4.1 to 4.3).

4. At constant voltage, increase in frequency causes to shift the maximum towards the higher temperature.

5. When frequency is made high, broadening of the maximum takes place (Figs.4.4 to 4.6).

6. An increase in heating rate, under the same field condition, causes to shift the maximum towards the low temperature side (Figs.4.7 to 4.9).

As mentioned earlier, no detailed and satisfactory theory is available to account the above said behaviour. Different workers, who have studied the phenomenon either by heating the phosphor with an uniform heating rate or holding the phosphor at a temperature and then noting the intensity, obtained non-coherent results. In the studies of temperature dependence of EL brightness. Zalm (11), on ZnS:Cu,Al phosphors, observed initial decrease in brightness followed by a minimum and then a maximum in ELTL curves. ~~Also he observed that an increase in ELTL curves.~~ Also he observed that an increase in frequency shifts the position of maximum and minimum towards higher temperature side. The findings of Patil (12) and Hahn (2) on ELTL behaviour of CaS:Ag,Dy and ZnO;Zn phosphors respectively also indicated the occurence of minimum and maximum in ELTL curves. However, in these studies the increase in frequency causes to shift the maximum towards the high temperature side while minimum towards the low temperature side. Johnson et al,(8) in studying the temperature dependence of EL brightness for ZnS:Cu,Al phosphors, observed initial increase in brightness followed by a minimum and then continuous increase. They found maximum to shift to higher temperature with increase in frequency of excitation while change in voltage has no effect on the peak position. In contrast to this, Bhushan and Saleem (13) observed maximum to shift to lower temperature side with increase in voltage. The findings of Johnson et al. and Bhushan and Saleem are more or less similar to our investigations in this chapter. These workers have interpreted their results on theories based on different assumptions. In the light of these the results of present investigation can be accounted for as follows:

Figs. 4.1 to 4.9 illustrate the ELTL curves exhibitting a maximum followed by a minimum and then a continuous increase. Comparision of these curves with a normal glow curve (Fig.4.1), it seems that the emitted intensity is sensitively modified on application of field during heating. A normal glow curve exhibits two maxima in the temperature region studied while

ELTL curve the single one. Moreover, the temperature of maximum of ELTL curve is seen to be less than that of first glow peak temperature of a normal glow curve. This is expected since EL is a field dominated phenomenon and large variation in brightness with temperature may occur if electron traps responsible for TL can, in certain temperature range, alter significantly the formation of high field region (8).

Johnson (8) and Zalm (11), considering the exhaustion mechanism and effect of electron traps, tried to explain the nature of the ELTL curves. According to Johnson (8), at lower temperatures the traps may contribute to the EL output by being field ionised in the region of high field, thereby producing the electrons which are accelerated to impact excitation. The traps may provide the charge carriers for acceleration to the extent that they are not thermally ionised during the half voltage cycle. This contribution to the brightness increases the ELTL brightness at the lower temperatures (Portion AB, Fig.4.1).

Considering the effect of filled traps, Zalm (11) assumed creation of positive space charge in an Mott-Schottky type exhaustion barrier and explained the decrease of EL brightness with temperature (portion BC, Fig.4.1). According to him, application of an electric field ionises the donor levels with transfer of electrons to traps leaving behind the holes to the donor sites within the exhaustion barrier. At moderate temperatures, migration of holes from these donor sites takes place. This decreases the positive space charge and consequently the field strength in the exhaustion barrier, which results in decrease in the brightness.

The increase in brightness (portion CD, Fig.4.1) at higher temperatures is caused by thermal excitation of electron traps (8).

4-3.2 Effect of Voltage and Frequency:

From the Figs.4.1 to 4.3, it appears that the increase of voltage, at constant frequency and constant heating rate, causes to shift the position of maximum and minimum towards the low temperature side. The frequency change at constant voltage and constant heating rate has the reverse effect, except that the position of minimum shifts towards lower temperature (Fig.4.4 to 4.6). The observed behaviour can be accounted on the basis of Thornton's theory (10). As per theory, the number of electrons which are successful in returning to the excitation region is a function of release rate (voltage) and time (frequency) available. At sufficiently high voltages and low frequencies, all the traps are depleted and the result of increasing voltage is similar to that of lowering of frequency. Here the probability of return of electrons in presence of field is given by equation (4.9), viz.,

$$P \propto \exp. \left(^{-E^*} / KT \right) = \exp. \left(E - f(F) \right) / KT)$$

Where E is the trap depth in absence of the field, F the field strength and f(F) is a function of strength and frequency of the applied field such that it increases with the former and decreases with the later. Therefore, in presence of field, the trap depth E* should increase with increasing frequency and decreases with increasing field strength. Thus higher temperatures are required at higher frequencies to get these traps emptied and lower ones that at higher voltages (3,13,14), hence the effect. The theory, however, does not account for the observed variation of minimum with voltage and freqnency.

The apparent increase and decrease in trap depth respectively with increasing frequency and voltage appears because of change in effective drift mobility of electrons (11). With increase in frequency effective drift mobility is reduced and the effect is as good as trapping of electrons in traps of higher energy. Reverse is the case with variation of voltage.

The broadening of maximum both at higher voltages and frequencies might be due to ionisation of luminescence centres at thermal energies available in that region, whereas the effect of emptying of traps is negligible.

4-3.3 <u>Effect of Heating Rate:</u>

Figs.4.6 to 4.9 shows the effect variation of heating rate of ELTL curve under the same field conditions. As may be seen from the figures, the minimum and maximum in the brightness shift towards the lower temperature side with enhanced intensities with increase in heating rate. Strikingly enough, the observation is contradictory to the one usually seen with thermoluminescence. However, the result is similar to that observed by Bhushan and Saleem (13). They have explained the shift in the light of existing theories as: Faster heating rates deplete the traps earlier and hence cause a shift towards the lower temperature side.

4-3.4 Mechanism of ELTL Process:

There are different views regarding the ELTL process. Rabotkin (15) concluded that the mechanism of thermal extinction in TL is similar to that of photoluminescence. Thornton (10) suggested the release of electrons from trapping states and their return to excitation region is controlled by electric field and hence the intensity. Zalm (11) considered the presence of exhaustion barrier inside the phosphor and field strength across and within it is considerably altered by the presence of trapping states. According to him, filling of traps builds up negative space charge inside the phosphor, which affects the potential across and inside the barrier. Further he assumed that the ionisation of donor states increases the positive space charge density within the exhaustion region. The heating of the phosphor changes negative as well as positive space charge densities; which has an effect on the field strength of exhaustion barrier and hence on the emitted intensity.

In the present study, it is believed that, as traps and Mott-Schottky type exhaustion barrier are present, the filling and emptying of traps contribute to the exhaustion mechanism. The electrons released from traps get transferred to exhaustion region where they are accelerated to optical energies ionise luminescence centres by impact ionisation, which in turn emit radiation. The intensity of radiation is being controlled by field across and within the barrier.

4-4 SUMMARY:

1. An ELTL curve exhibits a maximum followed by a minimum.
2. An increase in voltage, keeping the frequency constant, shifts the maximum and minimum towards the lower temperature side.
3. At higher voltages, broadening of maximum occurs with a sharp rise in brightness level.
4. At constant voltage, increase in frequency causes to shift the maximum towards the higher temperature side while minimum towards the lower temperature side.
5. When frequency is made high, broadening of the maximum takes place.
6. An increase in heating rate, under the same field condition, causes to shift the maximum a towards the low temperature side.

7. The probable mechanism of ELTL process is exhaustion mechanism which involves the transfer of electrons, released from traps, to exhaustion barrier where they are accelerated to optical energies, to ionise luminescence centres by impact ionisation, which in turn emit the radiation.

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REFERENCES

1. Henisch,H.K., International Series of Monographs on Semiconductors 'Electroluminescence' edited by H.K.Henisch (Pergamon Press, 5,150 (1962).

2. Hahn,D., Le Journal de Physique et le Radium, 17, 748 (1956).

3. Haake,C.H., J.Electrochem. Soc.,104,291 (1957).

4. Neumark,G. Phys.Rev.,98,1546(1956).

5. Ceva,T., Intl.Symp.Lumin.Phys.Chem.Scintill, Munich,1965, 398 (1966).

6. Hahn,D. and Kernchen,W., Z.Physik,1973 (3),300 (1963).

7. Subrahmanyam,A. and Rao,K.V., Indian J.Pure Appl. Phys.,17, 469 (1979).

8. Johnson,P.D., Piper,W.W. and Williams,F.E., J.Electrochem.Soc., 103, 221 (1956).

9. Piper,W.W. and Williams,F.E., Phys.,Rev.87, 151 (1952), Brit, J.Appl.Phys.,Rev.,98,1809 (1955).

10. Thornton,W.A., Phys.Rev.,102, 38 (1956): Ibid, 103, 1585 (1956).

11. Zalm,P., Philips,Res. Repts., 11, 417 (1956).

12. Patil,M.G., Ph.D.Thesis, Shivaji University, Kolhapur (1981).

13. Bhushan,S. and Saleem,M., Indian J.Pure Appl. Phys.,14, 530 (1976).

14. Prakash,S.G., Indian J.Phys.,51,A, 121, (1977).

15. Rabotkin,V.L., Abrosivano Izv., Vuz. Fig.(No.4), 131, (1976).

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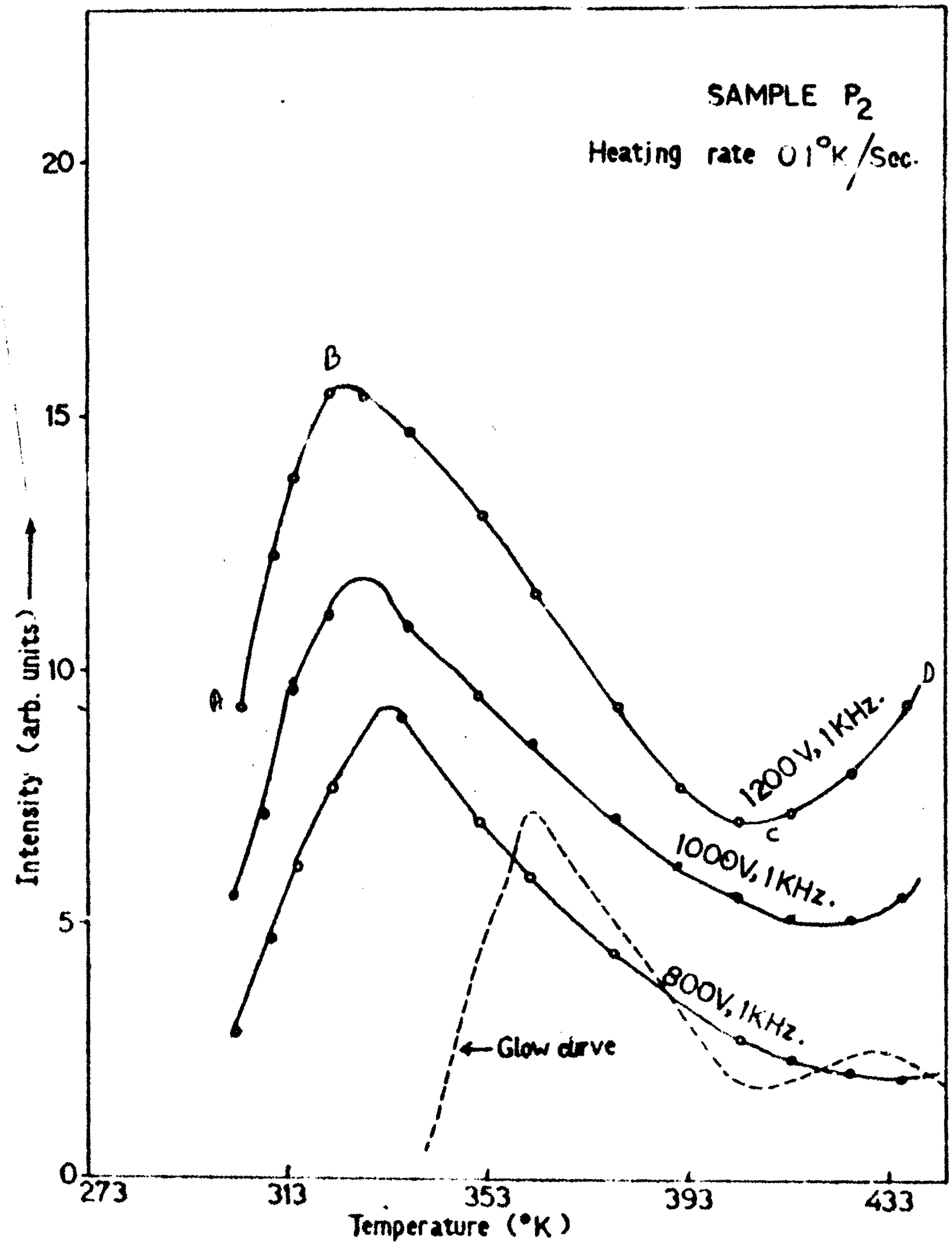

FIG. 4.1 PLOTS OF INTENSITY V/s TEMPERATURE AT DIFFERENT VOLTAGES.

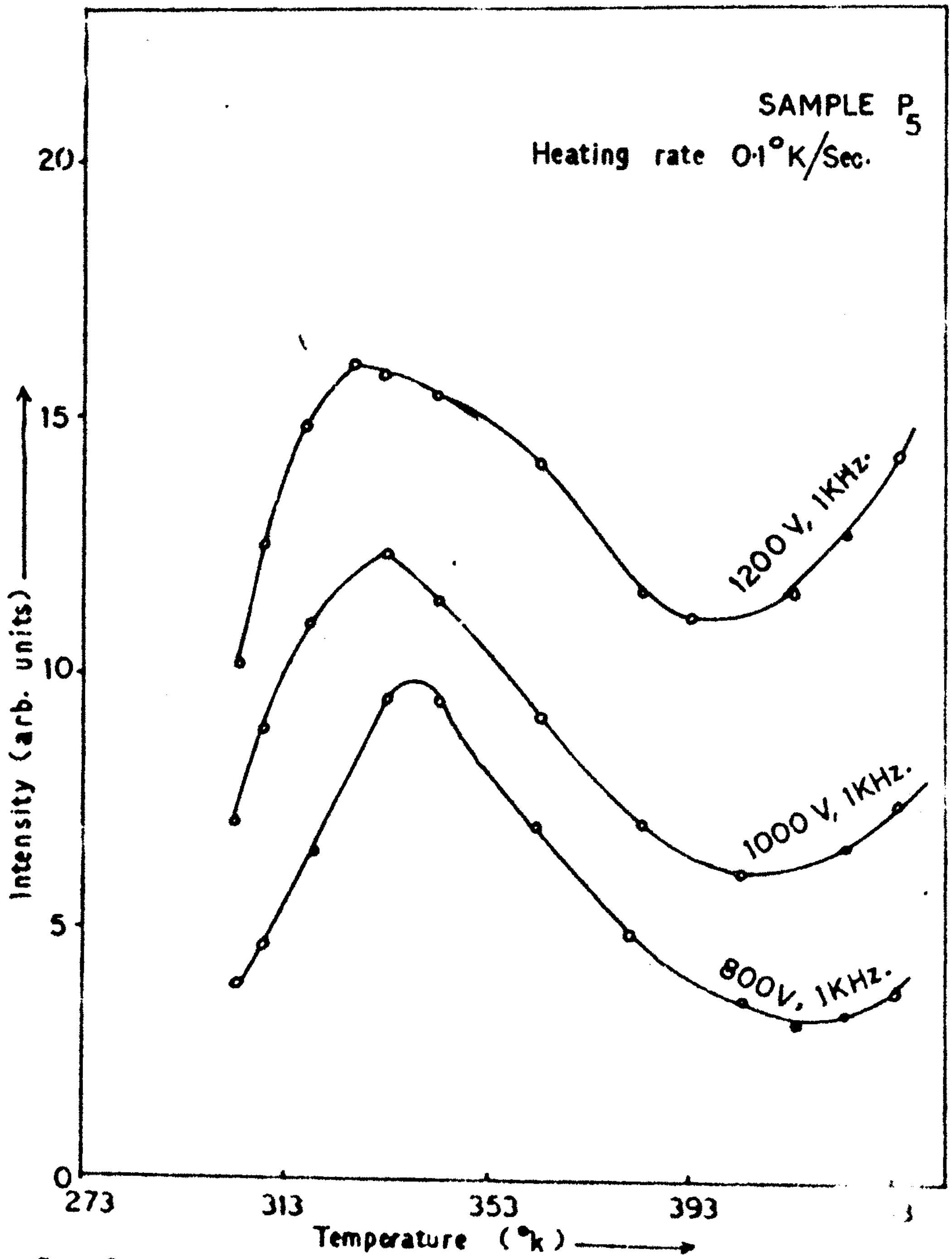

FIG.42 – PLOTS OF INTENSITY V/s. TEMPERATURE AT DIFFERENT VOLTAGES.

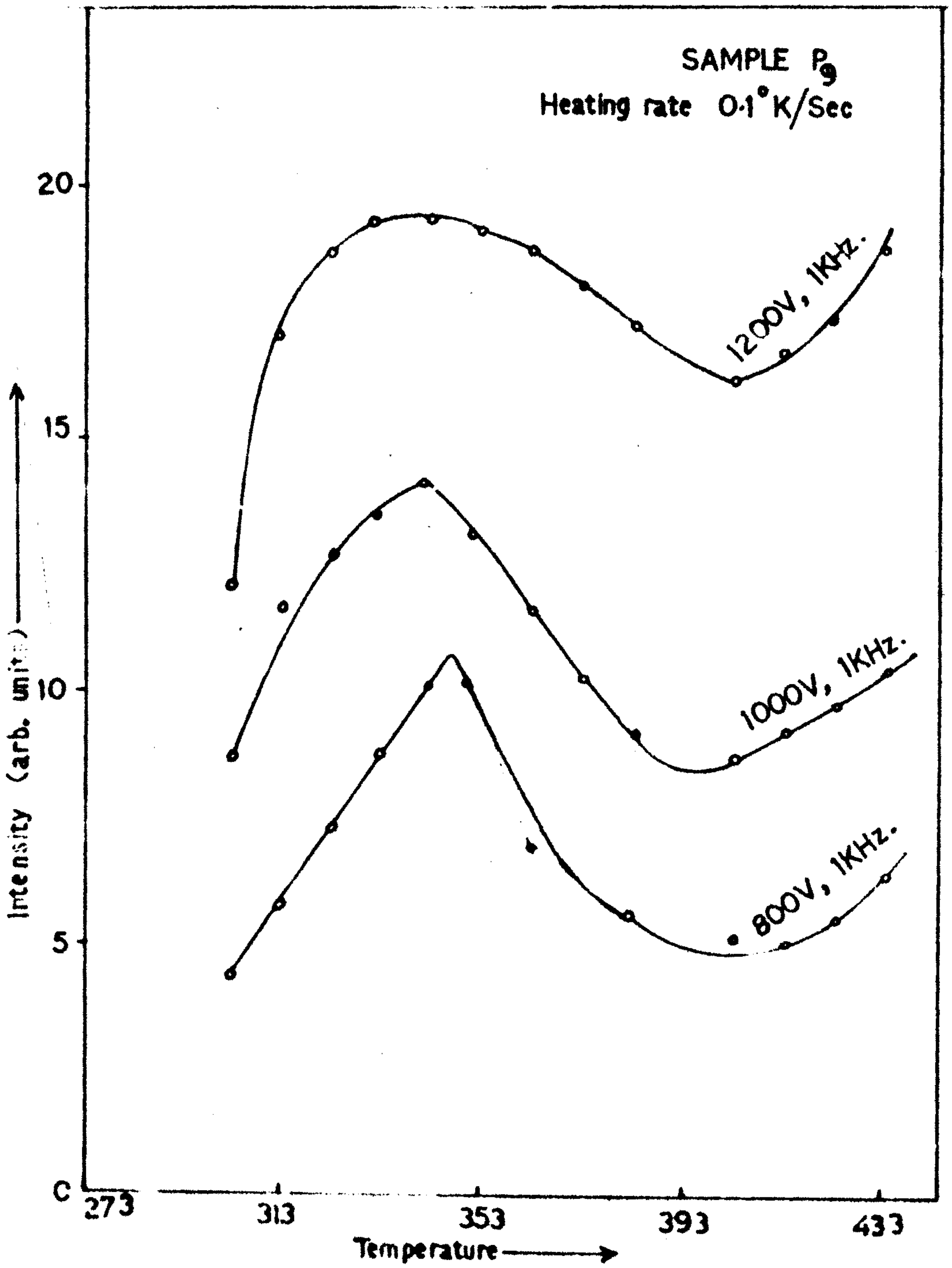

FIG.4·3—PLOTS OF INTENSITY Vs. TEMPERATURE AT DIFFERENT VOLTAGES.

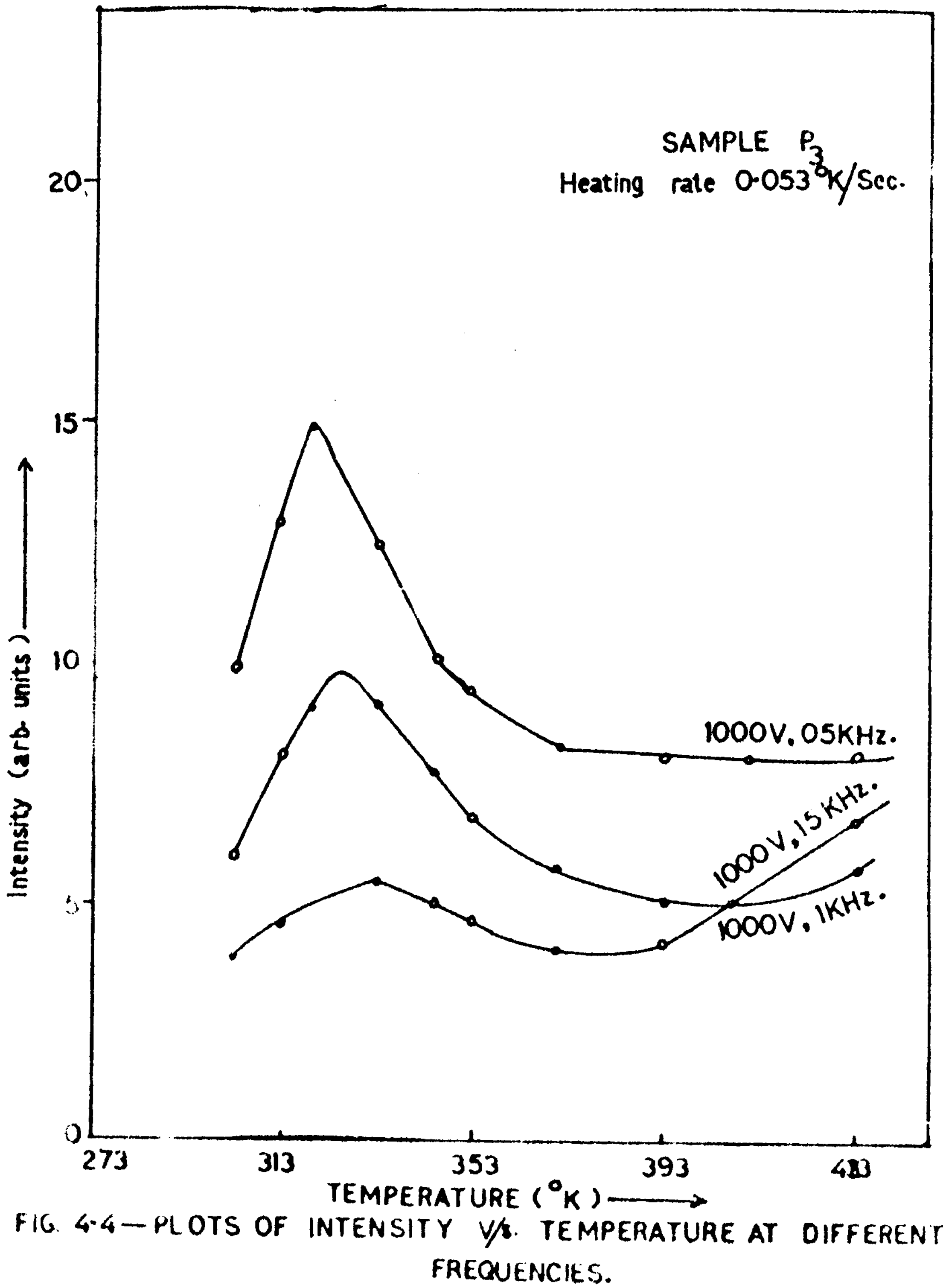

FIG. 4·4 — PLOTS OF INTENSITY V/s. TEMPERATURE AT DIFFERENT FREQUENCIES.

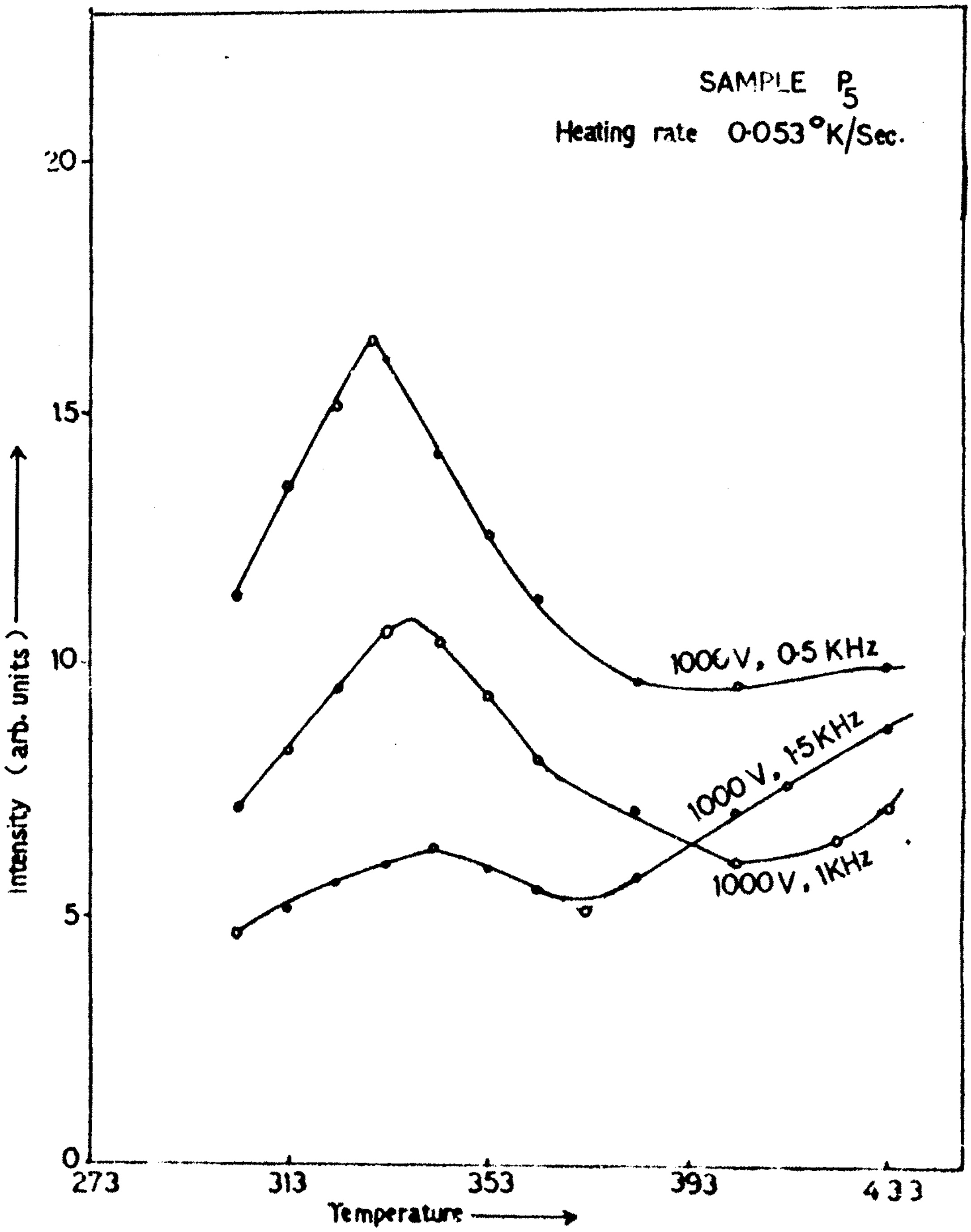

FIG. 4·5–PLOTS OF INTENSITY Vs TEMPERATURE AT DIFFERENT FREQUENCIES.

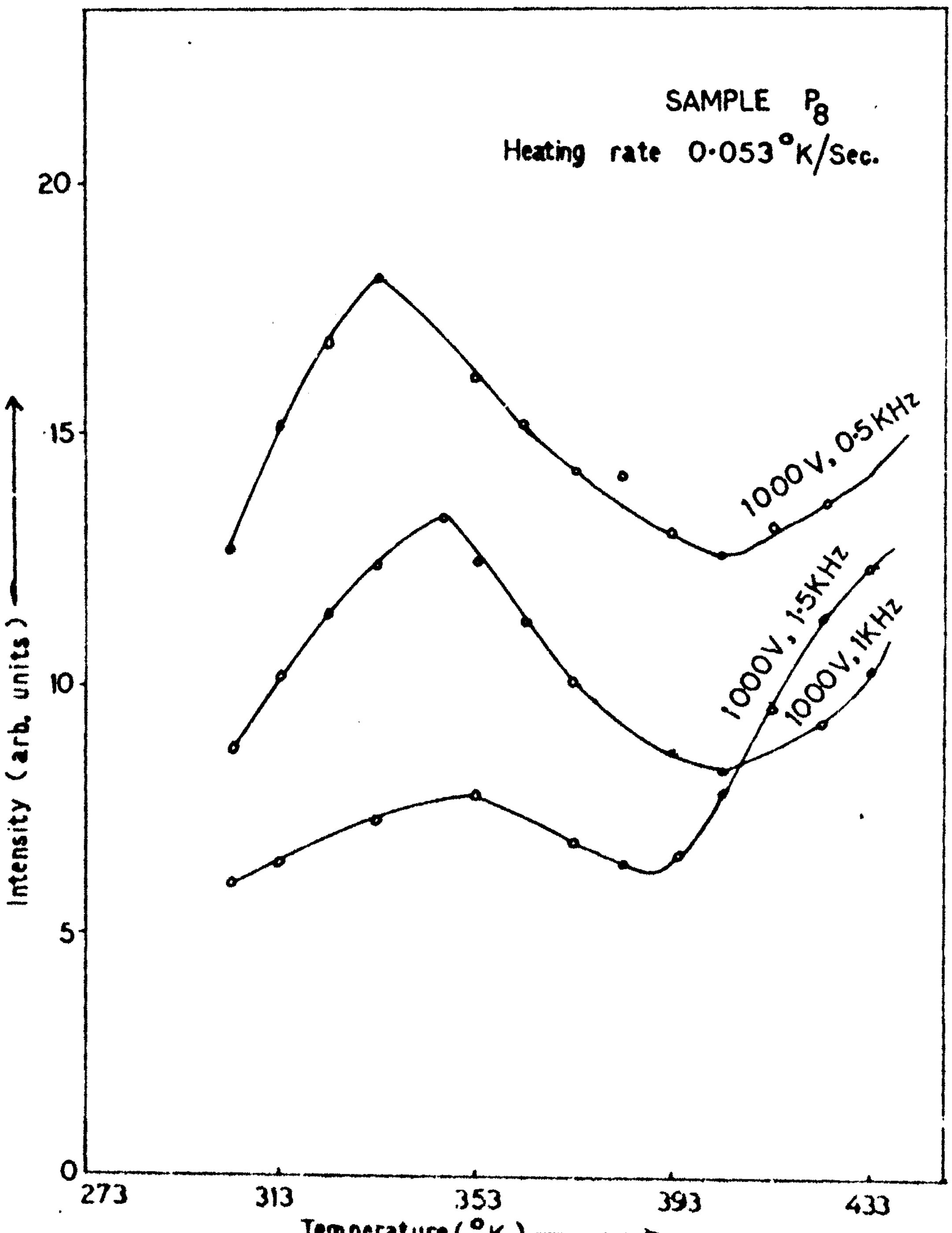

FIG. 4·6 PLOTS OF INTENSITY Vs. TEMPERATURE AT DIFFERENT FREQUENCIES

This is not following any pattern unlike B.

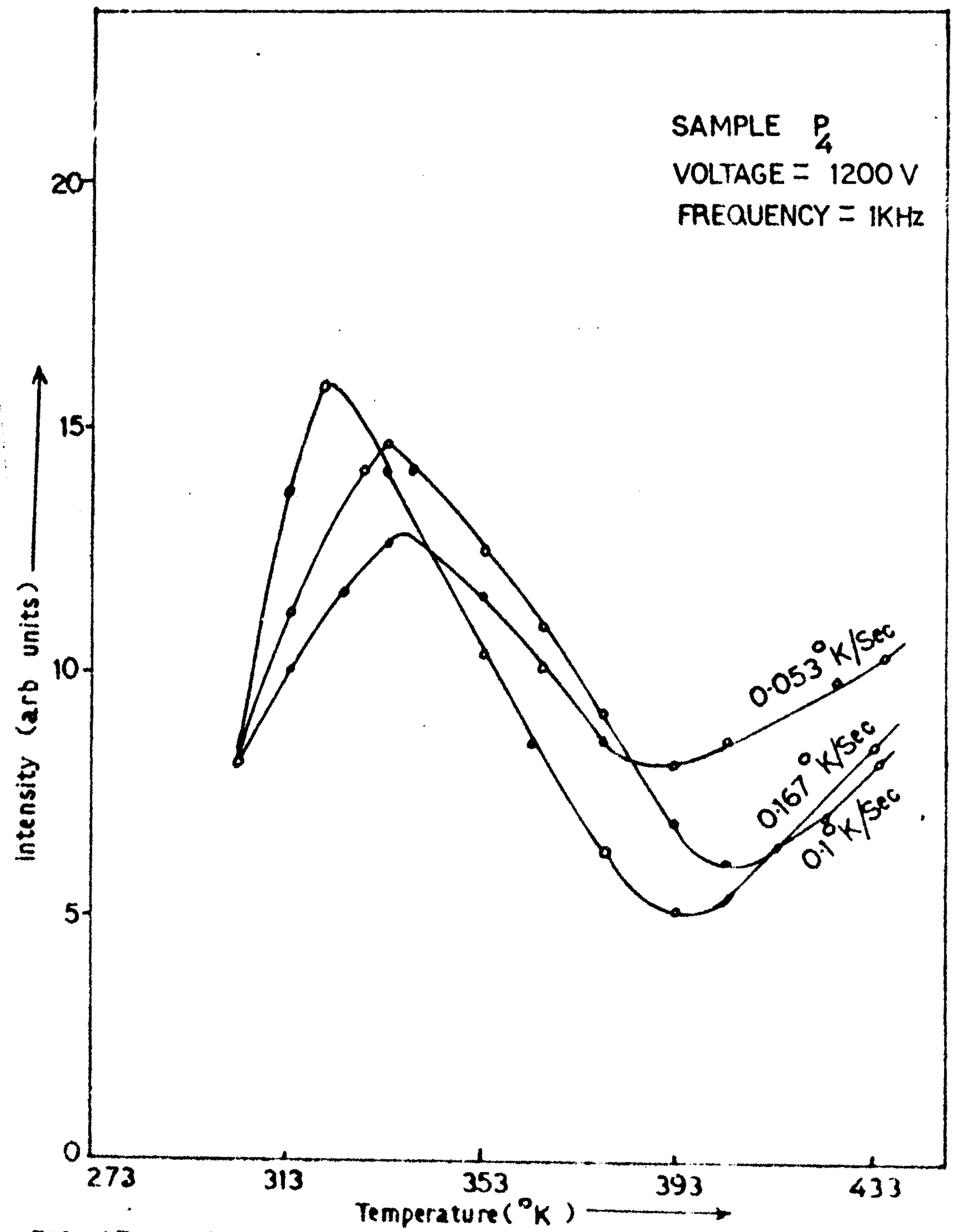

FIG. 4·7—PLOTS OF INTENSITY Vs TEMPERATURE AT DIFFERENT HEATING RATES

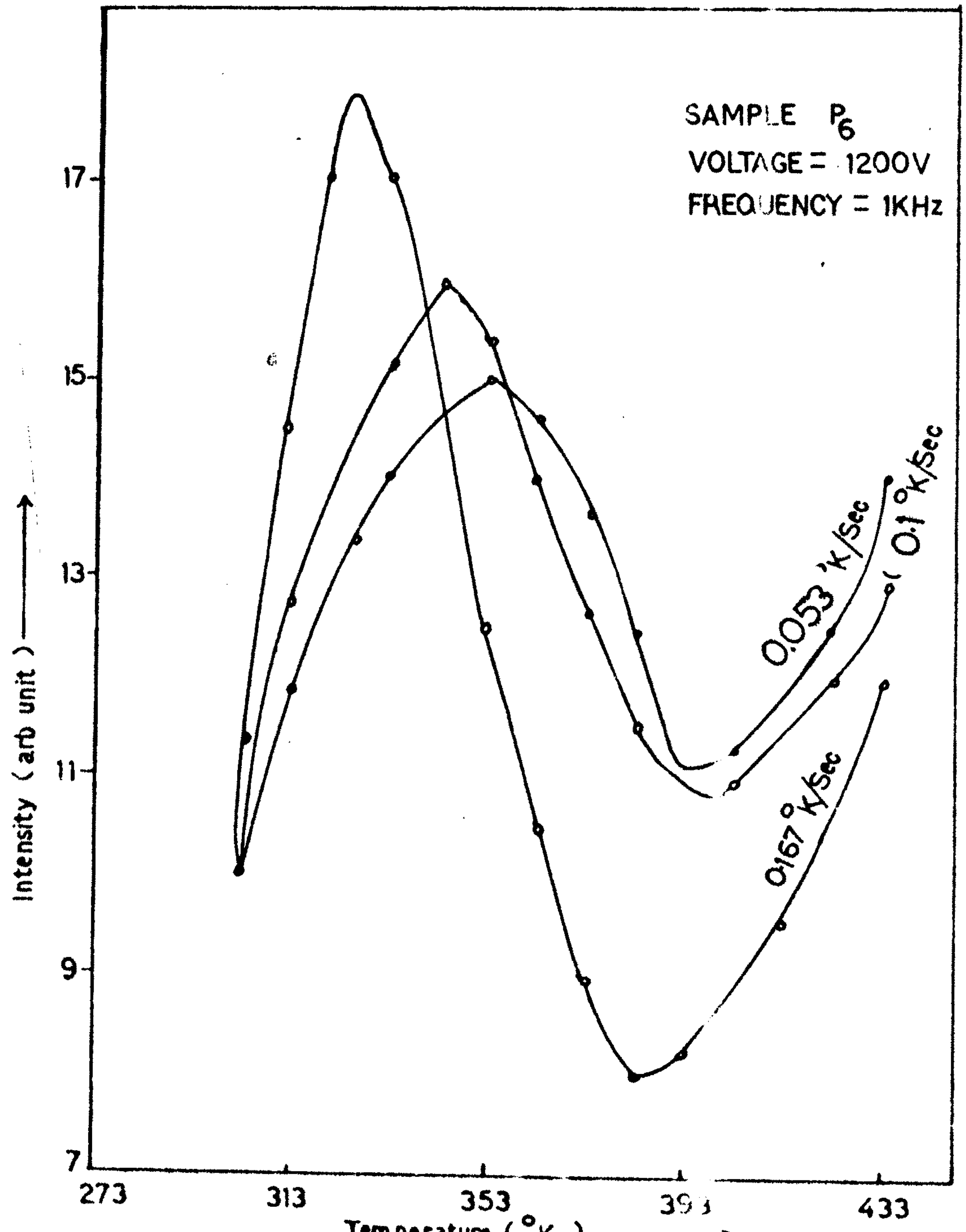

FIG. 4.8—PLOTS OF INTENSITY Vs. TEMERATURE AT DIFFERENT HEATING RATES

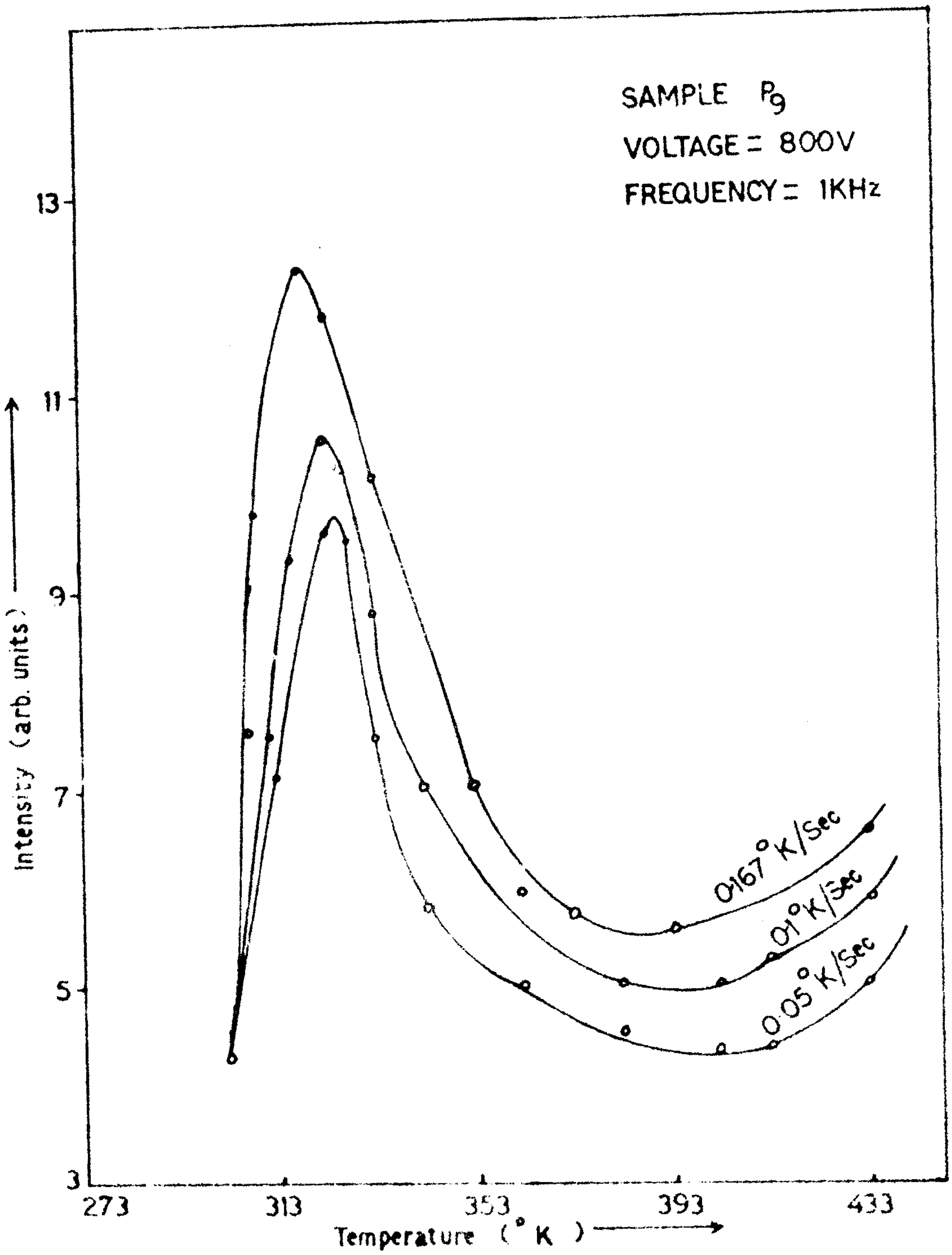

FIG. 49—PLOTS OF INTENSITY Vs TEMPERATURE AT DIFFERENT HEATING RATES