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LUMINESCENCE STUDY OF SPODUMENE

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INTRODUCTION

Spodumene is silicate whose chemical composition is $LiAlSi_2O_6$. There are many types of spodumene, each one reacting differently to the irradiation and annealing process (Claffy, 1953; Manoogian et al, 1965; Holuj, 1968; Holuj and Manoogian, 1968; Gait and Michoulier, 1973; Leckebusch et al, 1974; Schmitz and Lehman, 1975; Hassan and Labib, 1978; Ito, 1980; Fujii and Isotani, 1988).

The chronian spodumene, green variety of spodumene, does not show luminescence nor tenebrescence, and the absorption spectrum is not changed by heating nor by irradiation with ionizing radiation.

The color of non–chromian spodumene are colorless, lilac, yellow and green. Mn and Fe are present and the color is probably due to the absorption of light by the Mn and Fe cations. Lilac spodumene showed $Fe/Mn < 1$ ratio and green and yellow spodumene showed $Fe/Mn > 1$ ratio.

Lilac spodumene present luminescence and tenebrescence (Claffy, 1953). UV irradiation induces protracted phosphorescence (Millson and Millson, Jr., 1950) of exceptional duration.

Our main objective is to present a comparative study by luminescence of five kinds of spodumene from Minas Gerais, Brazil, studied previously by optical absorption spectroscopy (Fujii and Isotani, 1988). We used natural gemstones that, in the course of the experiments, were irradiated with X–rays.

EXPERIMENTAL DETAILS

The crystals used in this study have different colors: colorless I and lilac with $Fe/Mn \lesssim 1$ ratio and colorless II, yellow and green with $Fe/Mn > 1$ ratio.

The slices used in the experiments had thickness of 0.2 to 0.8 mm. They were cut either parallel or perpendicular to the c–axis.

The samples were irradiated with X–rays from a Phillips apparatus operating at 40 kV and 20 mA, at liquid N_2 temperature.

A home made device was used for the TL measurements. A Kanthal sheat was used for heating the samples, and the emission was detected in a EMI 978913 photomultiplier coupled to a current–voltage converter and recorded in a ECB xt–recorder. A Corning 4–70 filter (500 nm – 650 nm) was set between the sample and the photomultiplier. The heating rate was set in 2.8 K/s. The grain size were chosen in the interval of diameter between 0.074 mm and 0.177 mm. Possible triboluminescence produced by the grinding process was eliminated by treating the powder at 400°C by 24 h.

A Carls–Zeiss DMR21 spectrophotometer and a Perkin–Elmer MPF4 spectrofluorimeter were used for the phosphorescence decay measurements. The samples were cooled with a cold finger within a cryostat at lmPa (10^{-5} torr). Temperature was controlled using cryogenic substances: liquid N_2 (77K), dry ice (194K), water and ice (273K) and water (300K). A quartz window allowed the transmittance of the emitted light to the spectrometer or spectrofluorimeter.

RESULTS

Spodumene X–irradiated exhibit the characteristic orange phosphorescence, shown in Figure 1. The emission spectrum showed a band at around 1700 cm^{-1} (550 mm). The

INSERT FIGURE 1

phosphoresence intensity decreases as a function of Fe/Mn ratio. In lilac phosphorescence

is visible, while is not seen in green spodumene.

The $[Fe^{2+}]$ group stabilized by a neighbour Z^{2-} ion, have on electron excess. Thus $[Fe^{2+}]$ is able to capture one hole center in the oxygen ion around Fe^{2+}. The hole center, is possible localized around the three oxygen ions at opposite site from that of Z^{2+}. Due to this localization, the hole could couple with the $Fe-O$ vibrations. We estimate the EPR line width, ΔH, of the hole assuming the following assumptions: **(a)** each oxygen vibration promote spin relaxation; **(b)** the $Fe-O$ vibrations are at about = 500 cm^{-1} (Nakamoto, 1963; Ross, 1972); **(c)** the uncertainty relation $\Delta E \Delta \tau \sim h$, where $\Delta E = g\Delta H$ and $\Delta \tau \sim 1/c$, can be applied. The value obtained is 3×10^5 gauss, showing a big spin–vibration line broadening, which is beyond the usual range of measurements.

The lowest transition energy in Fe^{2+} is around 6000 cm^{-1} and the highest phonon energy is around 600 cm^{-1} (Imbush, 1978, p.65). Therefore if non–radiative transition occurs across this 6000 cm^{-1} gap, it involves the creation of around 10 phonons. As the order of perturbation needed is not so high, non–radiative decay can occur easily, and so crystal luminescence in Fe^{2+} rich samples is expected to be hardly seen. Accordingly, we observed at present that UV excited luminescence and phosphorescence in X–ray and γ–irradiated samples are weaker in Fe richer samples.

Figure 2 shows the TL spectrum for lilac spodumene. We observed two peaks at

INSERT FIGURE 2

200°C and 400°C. The 200°C TL peaks is associated to the bleaching of the green color. So we call the 200°C peak by G–peak. The 400°C TL peak is associated to the belaching of the lilac color. Thus we call the 400°C peak by L–peak.

A series of measurements was carried out to obtain the isothermal decay of the phosphorescence in lilac spodumene, using the following procedure: the same sample of lilac spodumene was X–irradiated at 77K for 4h. The phosphorescence was measured by 20

minutes after the end of irradiation. The temperature was raised to a given temperature T_1 and maintained constant with appropriate cryogenic substance. After the measurement at T_1 was completed, the sample was annealed at 400°C for 24h and X–irradiated again.

The process was repeated at a second temperature T_2 and so on.

The room temperature phosphorescence decay curve observed with Perkin–Elmer MPF4 spectrofluorimeter at $\lambda = 590$ mm agreed very well with the decay curve determined for the total emission with the Carl Zeiss DMR21 spectrometer. This behaviour shows that the emission band does not change through the thermal decay process. As the intensity of the total emission is bigger than the emission at $\lambda = 590$ mm, we used the Carl Zeiss DMR21 spectrometer for the low temperature measurements.

Experimental values for the isothermal decay at 77K, 194K, 273k and 300k are shown in Figure 3.

INSERT FIGURE 3

The analysis of the isothermal decay curves of the low temperature X–ray irradiation induced phosphorescence is complex. First we applied two empirical models: the coupled decay model (Füller and Moran, 1976) and the Adirowich's Method (Curie, 1963).

The coupled decay model statement are: **a)** there are electron traps, 1, with activation energy ΔE_1 ; **b)** there are electron–hole recombination centers where the excess of energy is released in the form of phosphorescence; **c)** there are electron traps, 2, with very short half life and activation energy, ΔE_2 , near the recombination center. The kinetic equations are:

$$\frac{dn_1}{dt} = -\alpha_1 n_1 \quad , \tag{1a}$$

$$\frac{dn_2}{dt} = -\alpha_2 n_2 - \frac{dn_1}{dt} \quad , \tag{1b}$$

and the phosphorescence intensity is

$$I = -\frac{d}{dt}(n_1 + n_2) \quad , \tag{1c}$$

where α_1 and α_2 are the untrapping parameters of the centers 1 and 2; n_1 and n_2 are the concentration of the electrons trapped in the deffects 1 and 2. The phosphorescence is given by:

$$I = a_1 e^{-\alpha_1 t} + a_2 e^{-\alpha_2 t} \quad , \tag{2}$$

where

$$a_1 = a_1 a_2 n_{10}/(\alpha_2 - \alpha_1)$$

$$a_2 = [n_{20} - (\alpha_2 - \alpha_1)]\alpha_1$$

n_{10} and n_{20} are constants.

The fit parameters for equation (7) are shown in table I. The value of n_{10} and n_{20} change

INSERT TABLE I

with the temperature showing that this model is not suitable for the analysis of phosphorescence in spodumene.

The Adirowitch's method statement are: **a)** there are electron traps with activation energy, ΔE ; **b)** there are recombination electron–hole centers, where the excess of energy is released as phosphorescent light; **c)** conduction electrons can be retrapped by empty electron traps or by recombination centers. The kinetic equations are:

$$\frac{d}{dt} = -an + \alpha_t n^*(N-n) \quad , \tag{3a}$$

$$\frac{dn^*}{dt} = -an - \alpha_t n^*(N-n) - a_c n^* h \quad , \tag{3b}$$

$$I = \text{ctte}\, a_c\, n^* h \quad , \tag{3c}$$

where n, n^* and h are the concentrations of trapped electrons, conduction electrons and trapped holes, respectively; N is the concentration of electron traps; a_t and a_c are the effective cross–section of capture of conduction electrons by traps and holes, multiplied by the speed of the conduction electrons; α is the untrapping parameter, which obeys the Arrhenius law, i.e., $\alpha = \alpha_0 \exp(-\Delta E/kT)$. The approximate solution of the equations was obtained by Adirowitch in the form:

$$I = I_0/(1 + at)^p \quad , \tag{4}$$

where $p = a_t/a_c$, I_0 and a are parameters depending on T.

In table II we show the fit parameters for the Adirowitch's method. We see that p

INSERT TABLE II

is constant, roughly, the speed dependence on T in a_t and a_c cancel each other. The activation encergy ΔE cannot be determined from the Adirowitch's method, because the dependence of I_0 and a on T and ΔE is unknown. Otherwise the good fit shown by this method, suggest the possibility of analysis of the kinetic decay of phosphorescence using a microscopic model. This model must be consistent with the above analysed optical absorption results.

The EPR spectra of spodumene showed the presence of Mn^{2+} (Holuj and Manoogian, 1968), at the Al^{3+} ion–site. The charge stabilization can be achieved through a Z^{2+} neighbour to $[Mn^{2+}]$ forming a $Z^{2+}:[Mn^{2+}]$ defect (H–defect). This defect, have $Z^{2+} - Mn^{2+}$ axis along the c–axis. A trapped hole in the oxygens fartest from $Z^{2+}-$like ion, as in $Z^{2+}:[Fe^{2+}]$, will not be seen in the EPR spectra. The recombination of the hole

with an electron in the oxygens around Mn^{2+} promote Mn^{2+} to excited states, through energy transfer. The excess of energy is dissipated through phonons to the first excited state $^4T_{1g}$ and so to the ground state through $^4T_{1g} \longrightarrow {}^6A_{1g}$ luminescence (Marfunin, 1979, p. 195–196). The observation of the orange luminescence in lilac spodumene agrees with the present consideration. The EPR Mn^{2+} line remains unchanged (Ito, 1980) in irradiated samples, reinforcing the present model for stabilization of holes and subsequent luminescence froms electron–hole recombination.

The TL intensity is bigger for higher Mn concentration and TL killing is bigger for higher Fe concentration. As, both process of raising and killing of TL occur simultaneously, the electron–hole recombination cannot be a localized process. Thus the TL process should occur through conduction electrons, rather than metastable states. Thus we suggest here that the high temperature TL arises from electron–hole recombination of conduction electrons with holes trapped at H–defect. The conduction electrons are untrapped from G–center and L–center associated to the TL G–peak and L–peak.

ANALYSIS OF THE KINETIC OF LUMINESCENCE

We analyse in this thermal decay kinetics of phosphorescence. The previous developments in the analysis of optical absorption, luminescence and chemical kinetics were taken in account (Curie, 1953).

Here we assumed that phosphorescence in X–ray irradiated spodumene is due to the electron hole recombination at the H–defect ($Z^{2+}:[Fe^{2+}]$ defect) with the conduction electron coming from the untrapping of electrons trapped in a shallow P–defect.

The kinetic rate equations of untrapping of trapped electrons are giving by:

$$\frac{d}{dt}[P^*] = -\alpha_1[P^*] \quad , \tag{5a}$$

$$\frac{d}{dt}[P] = \alpha_1[P^*] \quad , \tag{5b}$$

$$\frac{d}{dt}[e] = \alpha_1[P^*] \quad , \tag{5c}$$

where the brackets referred to concentrations of trapped electrons, $[P^*]$, electron trapping defects, $[P]$, and conduction electrons, $[e]$. Here α is a constant which obeys Arrhenius' law.

The kinetics rate equations of retrapping of untrapped electrons (conduction electrons) are given by:

$$\frac{d}{dt}[P^*] = \gamma_1[e][P] \quad , \tag{6a}$$

$$\frac{d}{dt}[P] = -\gamma_1[e][P] \quad , \tag{6b}$$

$$\frac{d}{dt}[e] = -\gamma_1[e][P] \quad , \tag{6c}$$

where γ_1 is a constant.

The electron–hole recombination reaction at the H–defect gives the rate equations:

$$\frac{d}{dt}[H^*] = -\beta[e][H^*] \quad , \tag{7a}$$

$$\frac{d}{dt}[H] = \beta[e][H^*] \quad , \tag{7b}$$

$$\frac{d}{dt}[e] = -\beta[e][H^*] \quad , \tag{7c}$$

where $[H^*]$ and $[H]$ referred to concentrations of trapped holes and hole trapping defect ($Z^{2+} : Mn^{2+}$) and β is a constant.

Considering that all reaction are independent, the rate equations are the sum of all rates giving:

$$\frac{d}{dt}[P^*] = -\alpha_1[P^*] + \gamma_1[e][P] \quad , \tag{8a}$$

$$\frac{d}{dt}[P] = \alpha_1[P^*] - \gamma_1[e][P] \quad , \tag{8b}$$

$$\frac{d}{dt}[H^*] = -\beta[e][H^*] \quad , \tag{8c}$$

$$\frac{d}{dt}[H] = \beta[e][H^*] \quad , \tag{8d}$$

$$\frac{d}{dt}[e] = \alpha_1[P^*] - \gamma_1[e][P] - \beta[e][\beta^*] \quad . \tag{8e}$$

In the above system the equations have connected solutions.

If there are $[P]_0$ electron traps in the material, we have the relation:

$$[P]_0 = [P] + [P^*] \quad . \tag{9}$$

If there is $[G^*]$ and $[L^*]_0$ concentrations of electrons trapped in the $[G]$ and $[L]$ defects, respectively, the neutrality of the charge in the crystal gives the relation:

$$[H^*] = [e] + [P^*] + [G^*]_0 + [H^*]_0 \quad . \tag{10}$$

From equations (9) and (10) we can disconnect two of the equations (8). The resultant system of connected equations is:

$$\frac{dy_1}{dt} = -\alpha_1 y_1 + c_1 y_2 (P_0 - y_1) \quad , \tag{11a}$$

$$\frac{dy_2}{dt} = -\alpha_1 y_1 + c_1 y_2 (P_0 - y_1) - b y_2 (y_1 + y_2 + 1) \quad , \qquad (11b)$$

where $y_1 = [P^*]/K_0$, $y_2 = [e]/K_0$, $c_1 = \gamma_1 K_0$, $b = \beta K_0$, $P_0 = [P]_0/K_0$ and $K_0 = [G^*]_0 + [L^*]_0$. The equations were solved by the Runge–Kutta method (Milne, 1970). The phosphorescence is proportional to the rate equation for $[H^*]$:

$$I = \text{ctte}\, y_2 (y_1 + y_2 + 1) \quad . \qquad (12)$$

The samples were X–ray irradiated at liquid N_2 temperature. When the irradiation stopped at $t = 0$ there is $y_1(0)$ and $y_2(0)$ concentrations of trapped and conduction electrons, respectively, which were assumed to be fit parameters. The phosphorescence measurements begin after a time BT from the moment that irradiation was stopped. Thus we compare the calculated BT shifted decay curves with those obtained experimentally. These parameters are shown in table III. The fit is good as shown by the solid lines in Figure 3.

INSERT TABLE III

Recently, Antonini et al. (1989) fit the decay of the 15600 cm^{-1} using the present proposed defects. In Figure 4 we show that the values of α obtained by Antonini et al.

INSERT FIGURE 4

(1989) for temperatures between 401 and 483K and those obtained here fit the Arrhenius' law given an activation energy of $\Delta E_1 = 0.043$ eV and frequency factor $\alpha_1 = 30.6\ s^{-1}$. The small value for ΔE_1 agrees well with the small value expected for the P–defect.

ACKNOWLEDGMENTS

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TABLE I – Parameters for the coupled model.

T(K)	a_1	a_2	b_1	b_2	n_{10}	n_{20}
77	14.09	34.11	−0.0033	−0.0306	3808	1489
194	18.44	36.88	−0.0038	−0.0415	4412	1317
273	18.89	46.69	−0.0039	−0.0440	4414	1506
300	36.60	56.70	−0.0440	−0447	8337	2276

TABLE II – Parameters for the Adirowitch's model.

T(K)	I_0	a	p
77	51.4	0.029	1
194	65.2	0.047	1
273	68.67	0.042	1
300	85.61	0.041	1

TABLE III – Fit parameters of isothermal phosphorescence of lilac spodumene.

P \ T(K)	77	194	237	300
α_1	0.46 ± 0.0006	2.2 ± 0.8	4.86 ± 0.04	5.8 ± 0.2
β	0.235 ± 0.005	1.32 ± 0.02	1.875 ± 0.02	2.04 ± 0.06
c_1	8.0 ± 0.2	46 ± 10	65 ± 20	71 ± 30
$y_1(0)$	1.7 ± 0.1	1.9 ± 0.1	1.7 ± 0.1	1.7 ± 0.1
$y_2(0)$	6.9 ± 0.1	6.8 ± 0.1	6.9 ± 0.1	6.7 ± 0.1
P_0	8.0 ± 0.1	8.0 ± 0.1	8.0 ± 0.1	8.0 ± 0.1
BT(min)	30 ± 1	10.5 ± 1	10 ± 1	9 ± 1

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$y_1(0)$	1.7 ± 0.1	1.9 ± 0.1	1.7 ± 0.1	1.7 ± 0.1
$y_2(0)$	6.9 ± 0.1	6.8 ± 0.1	6.9 ± 0.1	6.7 ± 0.1
P_0	8.0 ± 0.1	8.0 ± 0.1	8.0 ± 0.1	8.0 ± 0.1
BT(min)	30 ± 1	10.5 ± 1	10 ± 1	9 ± 1

FIGURE CAPTIONS

Figure 1 – Phosphorescent emission of lilac spodumene after X–rays irradiation.

Figure 2 – Thermoluminescent (TL) spectrum of lilac spodumene after X–rays irradiation.

Figure 3 – Isothermal decay of phosphorescent emission of lilac spodumene after X–ray irradiation. Dots are experimental data: • – obtained in the Zeiss DMR 21 spectrometer; Δ – obtained in the Perkin Elmer MPF 4 spectrofluorimeter. Solid lines were evaluated from equations (11).

Figure 4 – Arrhenius law applied to the parameters α for lilac spodumene.

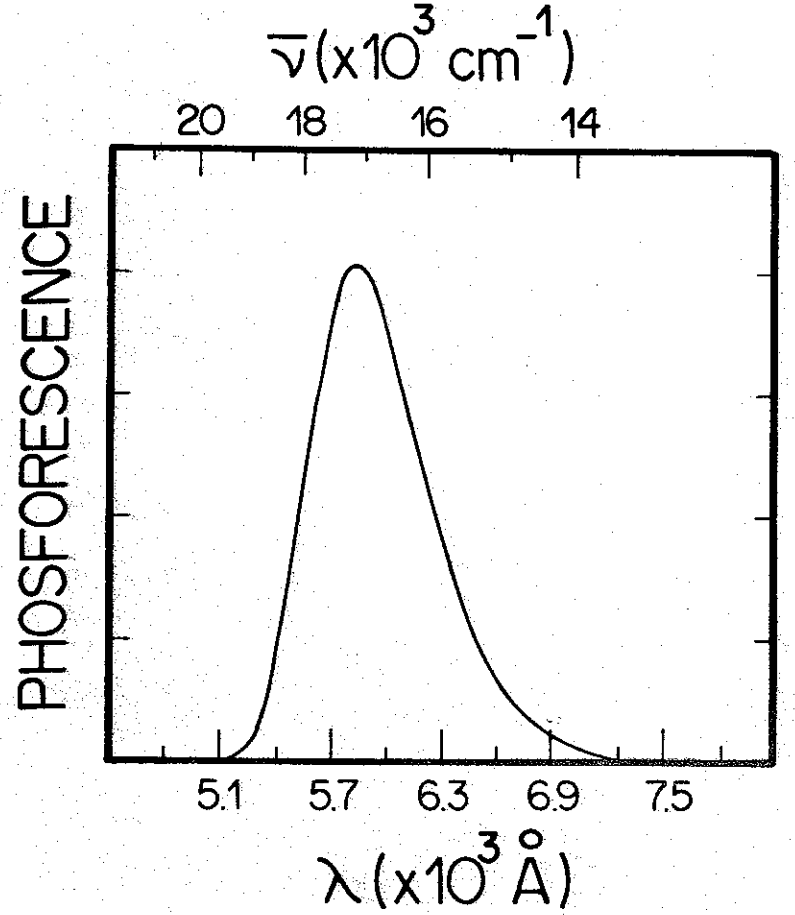

Figure 1

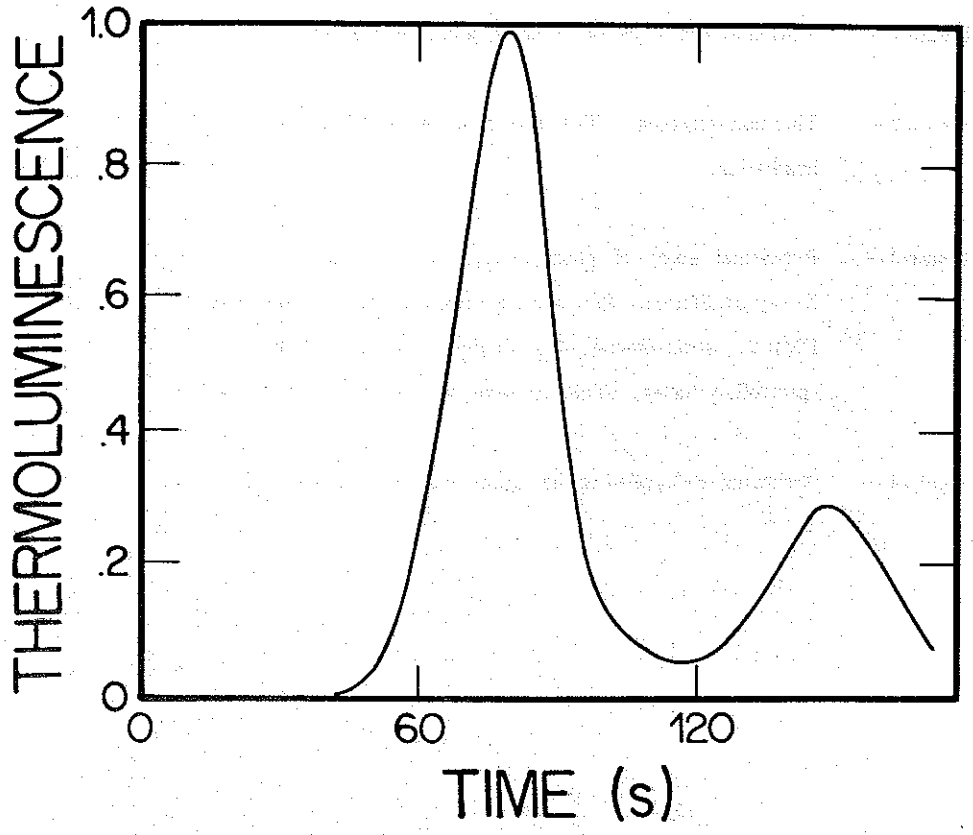

Figure 2

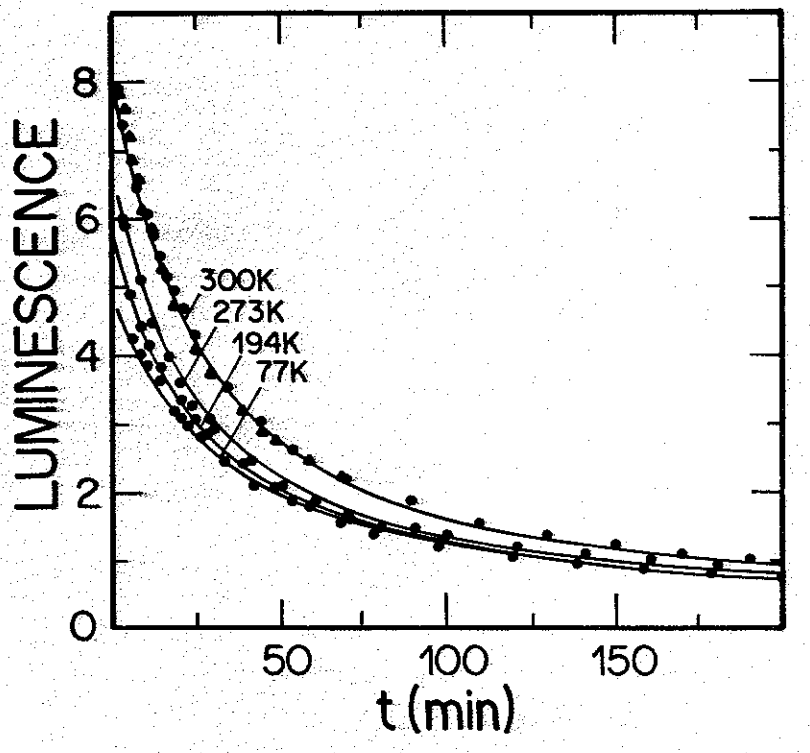

Figure 3

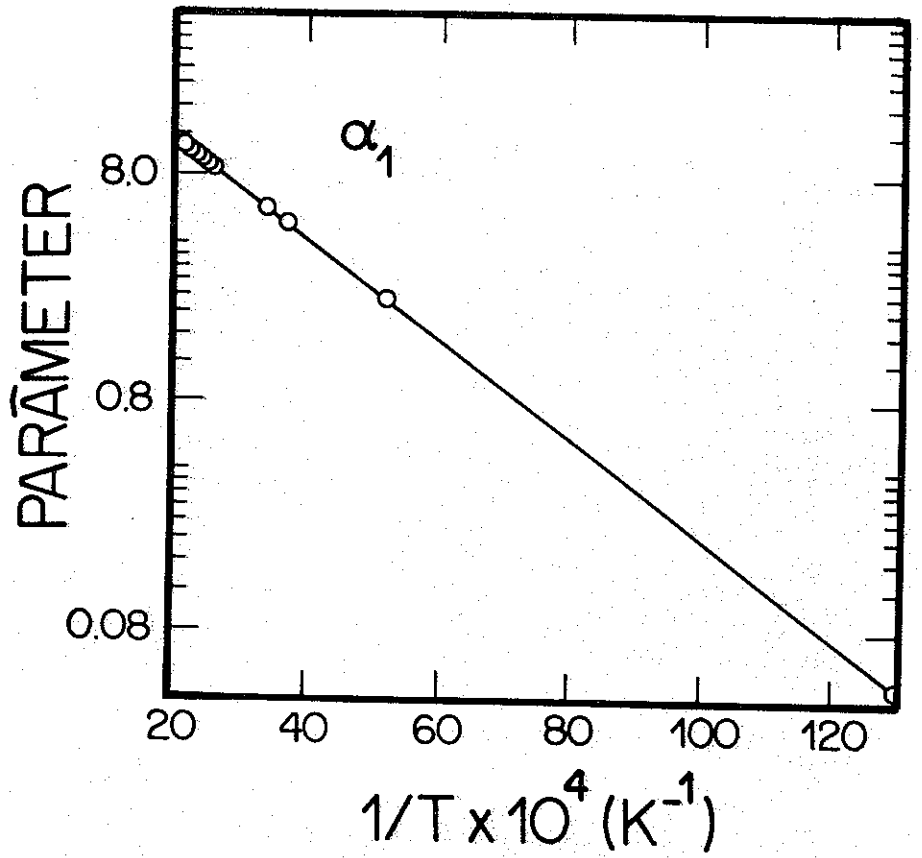

Figure 4