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PHOSPHORESCENCE IN IRRADIATED SPODUMENE

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ABSTRACT

Kinetics of phosphorescence in ^{60}Co γ-rays irradiated spodumene with low [Mn]/[Fe] ratio is determined. It is interpreted through the Adirowitch's kinetic model in which trapped electrons are liberated thermally and are retrapped or captured by luminescent centres.

RESUMO

Determinamos a cinética da fosforescência em espodumênio irradiado com raios γ do ^{60}Co com baixa relação [Mn]/[Fe]. Interpretamos esta cinética através do modelo de cinética de Adirowitch em que elétrons armadilhados são liberados termicamente e são rearmadilhados ou capturados por centros luminescentes.

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INTRODUCTION

We report here a study of the kinetics of phosphorescence in lilac spodumene with a high ratio between the concentrations of Mn and Fe. The spodumene is a silicate belonging to the inosilicate class of the formula $LiA\ell Si_2O_6$ (Deer et al, 1966). Transparent and beautiful colored varieties constitute precious and semi-precious stones. These are known as kunzite (lilac), hiddenite (green) and spodumene (colorless or yellow). Color is changed by heating or by irradiation with γ-ray, X-ray, ultraviolet light, electrons and others ionizing radiations.

Color change and luminescence of kunzite have been studied by many authors (see Webster, 1975; Claffy, 1953). Luminescence produced by irradiation of kunzite with X-rays was observed by Baskerville in 1903 and with other radioactive sources by Baskerville and Kunz in 1904. These authors attributed this luminescence to the presence of Mn.

The luminescence of orange color observed during and after irradiation with ionizing radiation was found to be bigger for samples with high ratio between the concentration of Mn and Fe.

EXPERIMENTAL

The samples were obtained in Minas Gerais, Brazil. They showed cleavage planes (110) and 93^{o} angles between the planes $(\bar{1}10)$. This morphology together with the known growth direction along the c axis allowed us to identify all crystallographic axis.

We cut pieces in the form of parallelopipeds of ~ 5 ×5 × 10 mm with a 12" thickness low concentration diamond blade in the Buehler Isomet and polish in a Buehler Minimet.

The phosphorescence were induced by irradiation with γ-rays in a ^{60}Co source of EMBRARAD S.A. through an agreement between IFUSP-EMBRARAD. The doses were of 0.02 MGy.

The phosphorescence measurements were done in a Perkin-Elmer MPF4 spectrofluorimeter of IQUSP and in the Zeiss DMR 21 spectrometer of IFUSP.

The measurements at different temperatures were done in a cryostat with a cold finger (Fujii, 1981). The temperatures were varied using liquid N_2 (77°K), dry ice (194°K), water-ice (273°K) and room temperature (300°K).

RESULTS

After irradiation with γ-rays, phosphorescence of orange color was observed. Emission spectrum is shown in figure 1, the peak being around 17000 cm^{-1} (590 nm). This emission also takes place after irradiation with X-rays and ultraviolet light (lilac sample).

Insert Figure 1

The isothermal decay of phosphorescence is shown in figure 2. At room temperature we find isothermic decay kinetics of phosphorescence in the Perkin-Elmer MPF4 spectrofluorimeter at $\lambda = 590$ nm and for total emission in the Zeiss DMR 21 spectrometer. Both measurements agreed very well. So we conclude that the form of the emission band does not change during the decay, and used the Zeiss DMR 21 spectrometer for the low temperature measurements.

Insert Figure 2

The analysis of the isothermal decay curves of the phosphorescent emission is complex. We tried two models, say the coupled decay model (Fuller and Moran, 1976) and Adirowitch's model (1956).

The coupled decay model statesment are: (a) there exist electron traps, 1, with activation energy ΔE_1; (b) there are electron-hole recombination centres where the excess of energy is released in the form of phosphorescent light; (c) there are electron traps, 2, with very short half life and activation energy ΔE_2 near the recombination centre. The kinetic equations are:

$$\frac{dm_1}{dt} = - \beta_1 m_1 \quad ,$$

$$\frac{dm_2}{dt} = - \beta_2 m_2 - \frac{dm_1}{dt} \quad ,$$

where m_1 and m_2 are the populations of electrons in trapped in the traps 1 and 2, β_1 and β_2 are the Boltzmann factors associated to the traps 1 and 2. The intensity of the phosphorescence was shown to be:

$$I = - \frac{d}{dt}(m_1+m_2) = a_1 e^{-\beta_1 t} + a_2 e^{-\beta_2 t} \quad ,$$

where

$$a_1 = \frac{\beta_1\beta_2}{\beta_2-\beta_1} m_{10} \quad ,$$

$$a_2 = \left[m_{20} - \frac{m_{10}\beta_2}{\beta_2-\beta_1} \right] \beta_2 \quad ,$$

m_{10}, m_{20} = initial concentrations .

We determined the parameter a_1, a_2, β_1 and β_2 using the method of gaussian linearization (Bevington, 1969). These parameters are shown in table 1. The values of m_{10} and m_{20} varies

Insert Table 1

with temperature of the isothermal decay.

The Adirowitch's model statesment are: (a) there are electron traps with activation energy ΔE; (b) there are recombination electron-hole centres where the excess energy is released in the form of phosphorescent light; (c) conduction band electrons can be captured by empty electron traps as by centres. The kinetic equations are:

$$\frac{dn}{dt} = - sn + a_t \nu[N-n] \quad ,$$

$$\frac{d\nu}{dt} = sn - a_t \nu[N-n] - a_c \nu h \quad ,$$

$$\frac{dh}{dt} = - a_c \nu h = I \quad ,$$

where n, ν and h are the populations of trapped electrons, electrons in the conduction band, and holes; N is the number of traps; a_t and a_c are the effective cross-sections of conduction electrons with empty traps and holes, multiplied by the thermal velocity of the electrons; s is the frequency factor which varies with temperature as $s = s_0 \exp(-\Delta E/kT)$; ΔE is the activation energy.

The approximate solution obtained by Adirowitch is of the form:

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

where I_0, a and p are constants. Here p is a constant which depends on the ratio a_t/a_c. The correlation between p and a_t/a_c were obtained numerically.

The constants I_0, a and p for each isothermic decay curve were obtained using a iterative method based on four experimental points (Isotani et al, 1982). We showed that:

$$\frac{1 + a t_1}{1 + a t_2} = \left(\frac{1 + a t_3}{1 + a t_4}\right)^\gamma \quad ,$$

where

$$\gamma = \frac{\ell n[I(t_1)] - \ell n[I(t_2)]}{\ell n[I(t_3)] - \ell n[I(t_4)]} \quad .$$

The value of a were evaluated through the iterative equation:

$$a_{n+1} = \frac{\beta_{n-1}}{t_1 - \beta_n t_2} \quad ,$$

where

$$\beta_n = \left(\frac{1 + a_m t_3}{1 + a_n t_4}\right)^\gamma \quad .$$

The four points must be chosen in such a way to include different decay rates to allow good convergence.

In table 2 we show the parameters I_0, a and p. The

Insert Table 2

solid lines in figure 2 show the result of the fit. The activation energy as obtained from $s = s_0 \exp(-\Delta E/kT)$ is:

$$\Delta E = 0.009 \pm 0.001 \text{ eV} \quad .$$

CONCLUSION

The kinetics of phosphorescent decay in ^{60}Co γ-rays irradiated kunzite was determined at the temperatures 77, 194, 273 and 300°K. The best fit of the decay curves using the coupled and Adirowitch's models give good results. The parameters m_{10} and m_{20}, the initial population at the sites 1 and 2, were found to be temperature dependent. This shows that the coupled decay model is not appropriate for the explanation of the present data. On the other hand the Adirowitch's decay model gives $a_t/a_c = 50$, which is consistent with the slow decay of the phosphorescent decay in kunzite. The parameter $p=1$ indicates that $a_t/a_c = 50$, i.e., the capture cross-section for conduction band electrons by traps is fifty time bigger than that for recombination centres.

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TABLE 1 - Parameters for the coupled model.

T(K)	a_1	a_2	b_1	b_2	m_{10}	m_{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	-0.0040	-0.0447	8337	2276

TABLE 2 - 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

FIGURE CAPTIONS

Figure 1 - Phosphorecent emission of lilac spodumene after X-rays irradiation.

Figure 2 - Decay of the phosphorescent emission of lilac spodumene after X-ray irradiation. Dots are experimental data: ● - obtained in the Zeiss DMR 21 spectrometer; ▲ - obtained in the Perkin Elmer MPF4 spectrofluorimeter. Solid lines were evaluated using the Adirowitch's model.

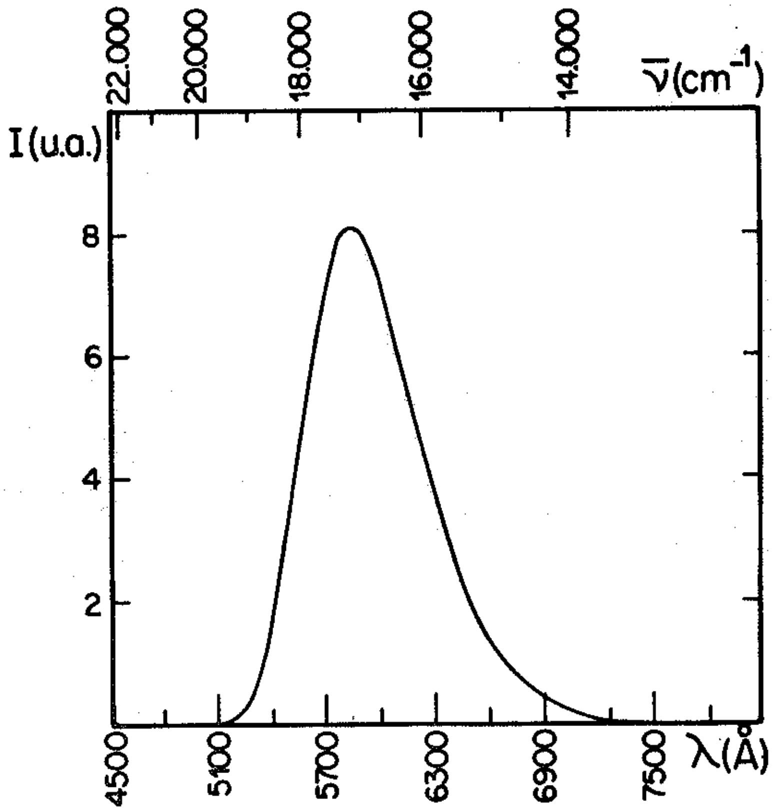
22.000
20.000
18.000
16.000
14.000
$\bar{\nu}$(cm^{-1})
I(u.a.)
8
6
4
2
4500
5100
5700
6300
6900
7500
λ(Å)

Figure 1

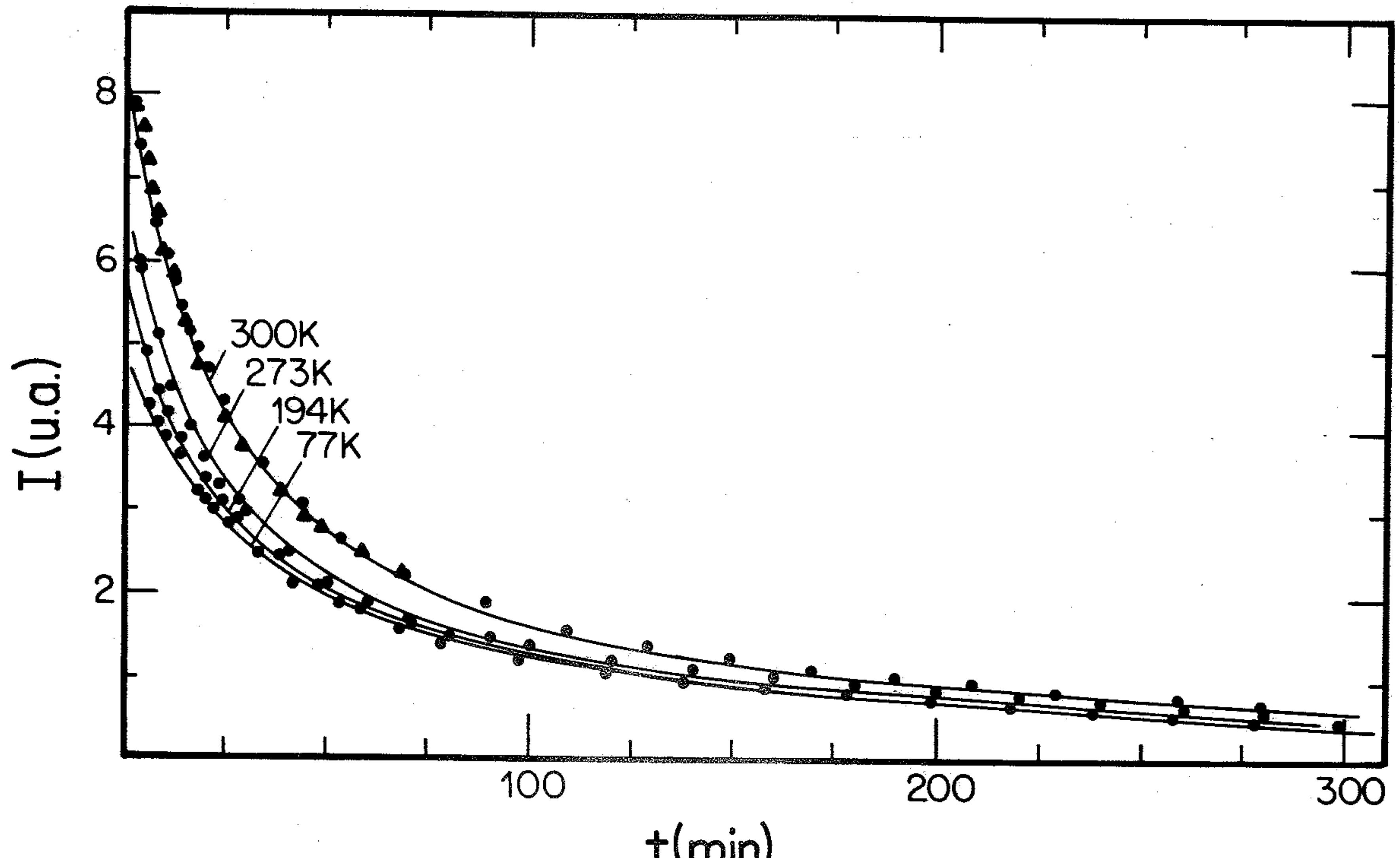

Figure 2