

## Optical Absorption and Electron Paramagnetic Resonance Studies of Colorless and Pink Beryl

ANA REGINA BLAK, SADA O ISOTANI and SHIGUEO WATANABE

Instituto de Física, *Universidade* de São Paulo, São *Paulo, Brasil*

Recebido em 25 de Março de 1982

The results of the Optical Absorption (OA) and Electron Spin Resonance (EPR) measurements of colorless and pink beryl, heated and ultraviolet (UV) irradiated are presented. In the UV region of the OA spectra, it is observed bands at  $36000\text{ cm}^{-1}$  and  $42000\text{ cm}^{-1}$ . The UV irradiation produces atomic hydrogen, stabilized in the crystal lattice at room temperature. This was revealed by the presence of  $\text{H}^0$  lines in the EPR spectrum.

Neste artigo são apresentados os resultados de medidas de Absorção Ótica (AO) e Ressonância Paramagnética Eletrônica (RPE) em berilo rosa e iricolor. Na região espectral do ultravioleta são observadas duas bandas respectivamente em  $36000\text{ cm}^{-1}$  e em  $42000\text{ cm}^{-1}$ . A irradiação ultravioleta produz na rede cristalina, hidrogênio atômico, estável à temperatura ambiente. A presença das linhas do  $\text{H}^0$  nos espectros de RPE evidenciam esse fato.

### 1. INTRODUCTION

In the present paper, OA and EPR studies on natural colorless and pink beryl heated and UV irradiated are reported. The structure of beryl was described in detail by Bragg and West<sup>1</sup>. Beryl,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , is a silicate with hexagonal crystal structure. It is formed from six  $(\text{SiO}_4)^{4-}$  tetrahedra that are stacked above each other in different spa-

tial orientations forming hollow columns (channels) parallel to the crystallographic c-axis. These channels are joined by  $Al^{3+}$  and  $Be^{2+}$  ions.

The Infrared (IR) spectra of water in beryl were reported by Wood and Nassau<sup>2</sup> but so far, no AO measurements were reported for the UV region of the spectra in colorless and pink beryl. Water molecules occupy two sites in the channels. The water in site I has its  $C_2$  symmetry axis perpendicular to crystal c-axis and the water in site II has its  $C_2$  symmetry axis parallel to the crystal c axis and has an alkalide ion in its neighbourhood.

EPR spectra of beryl, showed that: in green beryl<sup>3</sup>  $Fe^{3+}$  is found in channels midway between adjacent silicate rings. X-ray irradiated beryl<sup>4</sup> shows the presence of atomic hydrogen, stable at room temperature, and methyl radicals. Both  $H^0$  and  $CH_3$  were assigned to sites in the channels and were assumed to arise from irradiation induced decomposition of water and methane molecules respectively. It was also observed<sup>5</sup> that  $H^0$  is unstable above  $200^{\circ}C$ .

## 2. EXPERIMENTAL METHODS

Natural colorless beryl from the Claire Azadian collection and pink beryl from A.Halba Co., both from Minas Gerais - Brazil, of near gem-quality were studied. Slices of 0.3 to 1.0 mm thickness were cut, with the crystal  $C_6$  axis perpendicular and parallel to the plane of the slices, for OA and IR measurements. Slices of  $2 \times 2 \times (5 - 10)$  mm were used in the EPR measurements.

The OA spectra were recorded with a Carl-Zeiss DMR 21 spectrophotometer for the UV - vis-near IR range, and with a Perkin-Elmer IR-180 spectrophotometer for the IR range. The EPR spectra were obtained with a Varian X-band type spectrometer. Both the thermal treatments and the UV irradiation were carried out in air.

### 3. RESULTS

In table 1, a semi-quantitative spectrographic analysis is given in ppm units. The alkalimetals are determined only qualitatively and the frequency of the (+) sign estimates the relative alkali content from sample to sample. As compared to blue and green beryl, the alkali content in colorless and pink beryls is large. This high content is also shown in the IR spectrum in Fig. 1, though water bands in the IR spectrum show us that water of type II predominates in colorless and pink beryls.

Table 1 - Semi-quantitative spectrographic analysis in ppm units. The frequency of the (+) sign estimates the relative alkali content from sample to sample.

Impurity	sample			
	green	blue	pink	colorless
Fe	2000-2500	1500-2000	≤ 750	~ 750
Mn	< 150	<< 150	< 150	< 150
Mg	~ 200	~ 100	~ 100	~ 100
Ca	~ 500	~ 600	~ 700	~ 700
Na	+++	+++	++	+
Li	+	+	++	+++
Cs	+	+	+	++
K	+	+	+++	++

The OA spectrum of the pink and colorless beryl (Fig. 2) shows a high absorbance in the UV region. There are three maxima at 36000, 42000 and > 50000  $\text{cm}^{-1}$ . This last maximum is beyond the range of de-

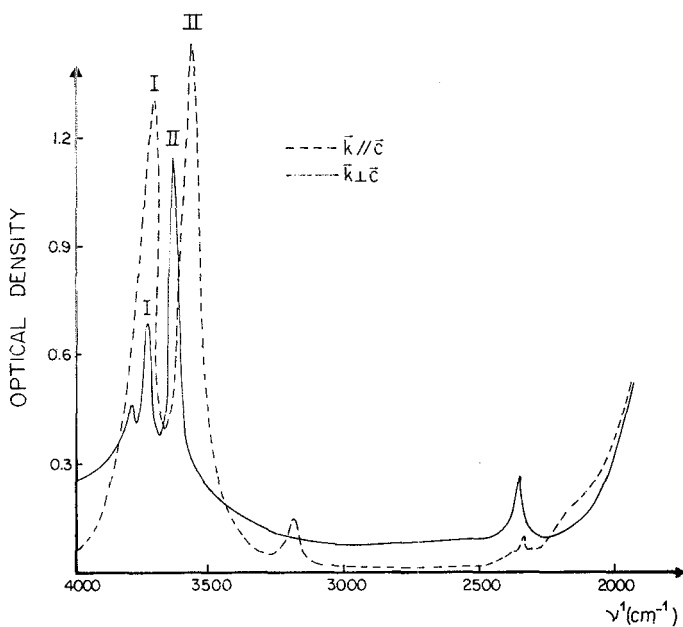


Fig.1 - Infrared spectrum of pink beryl showing predominance of type II water molecules.

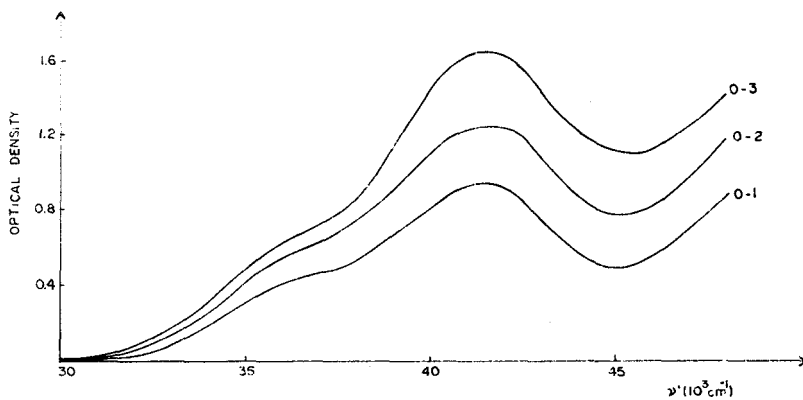


Fig. 2 - The curves represent differences between the OA of the untreated pink beryl (curve 0) and heated for 3 hours (curve 1), 6 hours (curve 2) and 15 hour (curve 3) at 700°C.

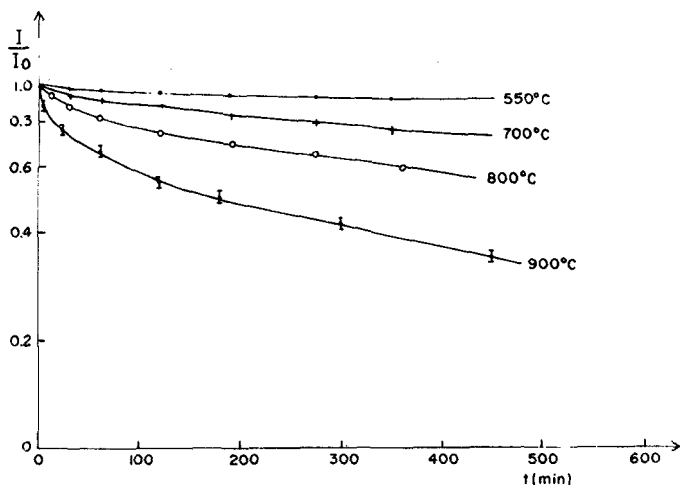


Fig. 3 - Thermally induced decrease in intensity of the 42000  $\text{cm}^{-1}$  OA band obtained by heating at 550, 700, 800 and 900°C.

tection of our spectrophotometer. The results for pink and colorless crystals are similar. After heating pink and colorless beryl samples at temperatures above 400°C one observes a decrease in the intensity of the UV bands. The decay kinetics of the 42000  $\text{cm}^{-1}$  band at several temperatures is shown in Fig. 3. The best fit for the curves describing the kinetics were obtained by a sum of two exponentials:

$$I(t) = a_1 e^{-b_1(T)t} + a_2 e^{-b_2(T)t} \quad (1)$$

where  $b_1$  and  $b_2$  are the decay rates,  $t$  is the annealing time and the  $a_i$  are decay rates. The values of  $b_i$  obtained in this way obey the Arrhenius law

$$b_i = b_{0i} \exp \left[ \frac{-\Delta E_i}{RT} \right] \quad (2)$$

giving the activation energies  $\Delta E_i$ , shown in Table II. The kinetics decay of the 42000  $\text{cm}^{-1}$  band is completely different from the  $\text{Fe}^{2+}$  band increase in the green beryl<sup>2</sup> suggesting that the former is not connected with processes of charge transfer  $\text{O}^{2-} \text{Fe}^{3+}$ . The 36000  $\text{cm}^{-1}$  band was assigned by Platanov *et al*<sup>6</sup> to  $\text{Fe}^{3+}$  in a  $\text{Be}^{2+}$  site.

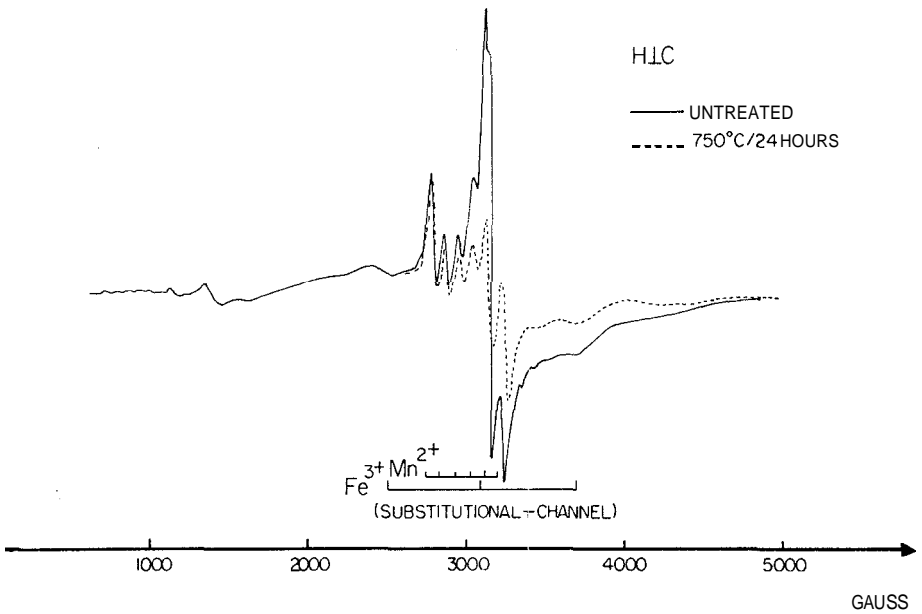
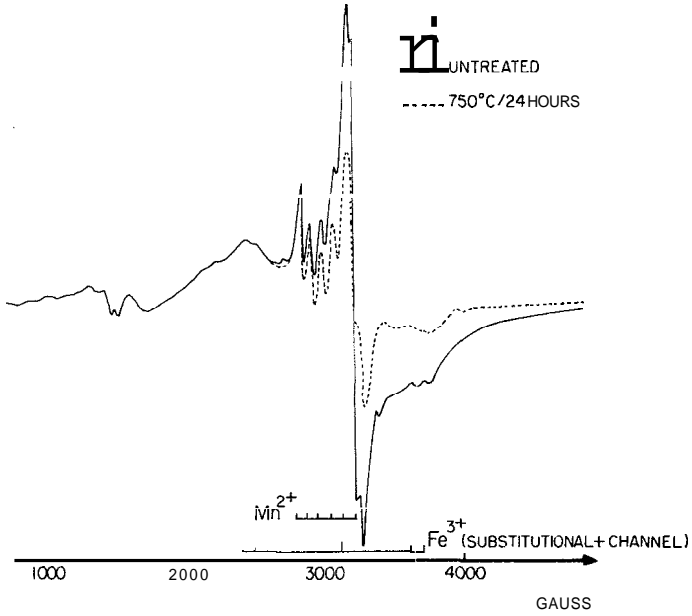


Fig. 4 - RPE spectra of pink Beryl.  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  lines are marked in the figure. Full line represents untreated samples and the dashed line the heated ones.

Table II - Activation energies and relaxation times for the thermal decay of the OA 42000  $\text{cm}^{-1}$  band.

SLOW DECAY		RAPID DECAY	
$E(\text{eV})$	$\tau_0(\text{seg})$	$E(\text{eV})$	$\tau_0(\text{seg})$
0,46	435	0,41	29,3

The EPR spectrum of pink beryl is shown in Fig. 4. One observes a single line due to the presence of  $\text{Fe}^{3+}$  in the channels<sup>2</sup> and weak lines of  $\text{Fe}^{3+}$  at the  $\text{Al}^{3+}$  sites<sup>7</sup>. In addition one sees the six characteristic lines of  $\text{Mn}^{2+}$ . By heating the pink beryl at temperatures above  $400^\circ\text{C}$ , the  $\text{Fe}^{3+}$  line is completely annealed. No modification in the  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  ( $\text{Al}^{3+}$  sites) lines was observed.

It was found that the UV irradiation produces stable  $\text{H}^0$  i.e. atomic hydrogen, as shown in the EPR spectrum of figure 5, represented

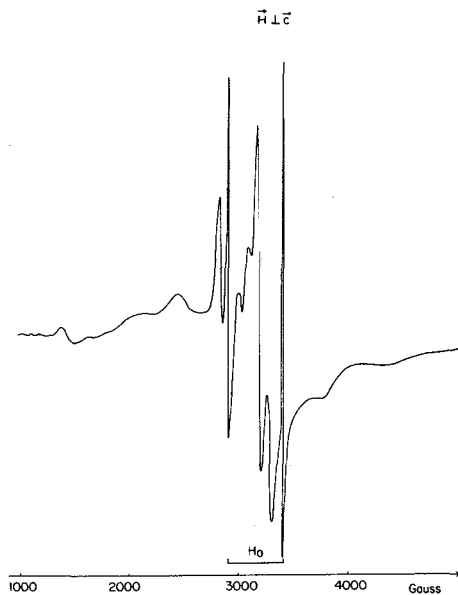


Fig. 5 - RPE spectrum of pink beryl showing the appearance of the  $\text{H}^0$  lines at 2900 and 3400 Gauss.

by two lines at 2900 and 3400 Gauss. The X-ray irradiation also showed to produce stable  $H^0$  centers as it was previously reported<sup>5</sup>. The  $H^0$  lines disappear completely when the crystal is heated above 120°C. Here we suggest that the  $H^0$  center is produced from the dissociation of type II water molecules  $\{H_2O.M^+\}$ , where  $M^+$  represents an alkali ion, producing a  $U_{2\alpha}$  center<sup>8</sup> with the configuration  $\{H^0.(OH^-.M^+)\}$ .

We wish to thank Dr. S.P. Morato for many useful discussions. This work was partly supported by grants from the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and from the Financiadora de Estudos e Projetos (FINEP).

## REFERENCES

1. Bragg, W.L. and West, J., Proc. Roy. Soc. (London) *A111*, 691 (1926).
2. Wood, D.L. and Nassau, K., J.Chem.Phys. *47*, 2220 (1967).
3. Blak, A.R., Isotani, S. and Watanabe, S., To be published in Phys. Chem. Minerals.
4. Bershov, L.V., Geochemistry *7*, 853 (1970).
5. Edgar, A. and Vance, E.R., Phys. Chem. Minerals *1*, 165 (1977).
6. Platanov, A.N., Tarau, M.N., Minko, O.E. and Polshyn, E.V., Phys. Chem. Minerals *3*, 87 (1978).
7. Dvir, M. and Low, W., Phys. Rev. *119*, 1587 (1960).
8. Morato, S. and Gomes, L., J. de Physique, colloque *C6*, *7*, C6-155 (1980).