

# Thermoluminescence of natural and synthetic diopside

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## Abstract

Diopside, a natural silicate mineral of formula  $\text{CaMgSi}_2\text{O}_6$ , has been investigated concerning its thermoluminescence (TL) and electron paramagnetic resonance (EPR) properties. Glow curves and TL vs.  $\gamma$ -dose were obtained irradiating natural samples to additional dose varying from 50 to 10,000 Gy. Except for a 410 °C peak found in the Al-doped artificial diopside, all the other peaks grow linearly with radiation dose, but saturate beyond  $\sim 1$  kGy. To investigate high-temperature effect before irradiation, measurements of TL intensity in samples annealed at 500–900 °C and then irradiated to 1 kGy  $\gamma$ -dose were carried out. Also the TL emission spectrum has been obtained. To compare with natural diopside, a synthetic pure polycrystal was produced and further those doped with iron, aluminum and manganese were also produced.

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## 1. Introduction

Diopside is a calcium and magnesium silicate of chemical formula  $\text{CaMgSi}_2\text{O}_6$ . Diopside is a mineral from the series of diopside–hedenbergite and forms solid solutions between  $\text{CaMgSi}_2\text{O}_6$  and  $\text{CaFeSi}_2\text{O}_6$ . It belongs to inosilicate class and to the group of calcic pyroxenes. The origin of the mineral name is from two Greek words, double and appearance, because the vertical zone of its prism can be oriented in two forms. This mineral is monoclinic (2/m) and belongs to the spatial group C2/c [1]. Diopside is common in metamorphic rocks, frequently found associated with calcite and phosphorite. The transparent varieties of diopside are used as gems.

The pyroxene structure consists of single chains of  $\text{SiO}_4$  tetrahedra extending along the *c*-axis of the unit cell. Cameron and Papike [2] described two types of cation positions, designated as M1 and M2. The M1 site is smaller

than the M2 site and lies between the apices of opposing tetrahedra forming an almost regular octahedron. The M2 site lies between the bases of the tetrahedra forming distorted six- or eight-fold sites. In the diopside, the positions M1 are occupied by Mg and M2 by Ca.

The position that  $\text{Mn}^{2+}$  can occupy in diopside has been the object of study for some authors. Vinokurov et al. [3] compared the orientation of electron paramagnetic resonance (EPR) axes in relation to the positions of the immediate neighborhood of the ions that can be substituted by  $\text{Mn}^{2+}$ . He concluded that  $\text{Mn}^{2+}$  cations can enter so either in M1 or in M2 sites; furthermore the  $\text{Mn}^{2+}$  in the position of  $\text{Ca}^{2+}$  is responsible for the most intense hyperfine structure. Ghose and Schindler [4] confirmed the constant of the spin Hamiltonian determined by Vinokurov et al. but they obtained an inversion in the position mentioned above.

Gaite [5] carried out very careful measurements of the EPR spectra of  $\text{Mn}^{2+}$ , interpreting each spectrum through the constants of the fine structure of the Hamiltonian. It was possible to distinguish the spectrum due to  $\text{Mn}^{2+}$  in

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M1 from that to  $\text{Mn}^{2+}$  in M2. He concludes that the neighborhood of  $\text{Mn}^{2+}$  in M1 has a pseudo-cubic symmetry, while  $\text{Mn}^{2+}$  in M2 is in a quite distorted neighborhood.

Michouler and Gaité [6] using the same method of determination of the site as for  $\text{Mn}^{2+}$  have shown that  $\text{Fe}^{3+}$  should occupy the M1 site, because it is smaller and more distorted in agreement with the crystallographic results.

No works on the thermoluminescence (TL) of natural or artificial diopside were found in the literature.

In the present work, TL and EPR properties of the natural diopside have been investigated.

Artificial polycrystals of pure and doped diopside produced by the devitrification method also were investigated. With this procedure, we hope to discover the intrinsic or extrinsic defects responsible for TL and EPR signals.

## 2. Experimental procedure

The white diopside samples used in the present work were provided by Mineração São Judas, São Paulo, SP, Brazil. A portion of the sample was crushed carefully using pestle and mortar and sieved to retain grains of size between 0.080 and 0.180 mm, which were used in TL and EPR measurements. Grains smaller than 0.080 mm were used in the X-ray fluorescence (XRF) analysis. XRF measurements were performed at the Geology Institute (IG/USP).

The TL measurements were carried out in a Daybreak TL reader, Model 1100, equipped with a bialkali photomultiplier EMI 9235QA for light detection with filters Corning 7–59 and Schott BG-39 used in front of the PMT. The heating rate used in the TL measurements was  $4^\circ\text{C}/\text{s}$  in nitrogen atmosphere. ESR measurements were performed in a Bruker EMX spectrometer with a rectangular cavity (ST ER4102) using a microwave frequency of 9.75 GHz (X-band), microwave power of 20 mW and modulation field of 100 kHz.

A  $^{60}\text{Co}$  source was used for  $\gamma$ -irradiation with a dose rate of 5.5 kGy/h. The powder sample was divided into portions irradiated in the range of dose varying from 50 to 50,000 Gy. The  $\gamma$ -irradiation was performed at room temperature.

A mixture (25.89 wt% of CaO, 18.61 wt% of MgO and 55.49 wt% of  $\text{SiO}_2$ ) well homogenized was melted in a platinum crucible in an oven at high temperature up to 1450–1500  $^\circ\text{C}$ . The sample was kept in the oven for 2 h at 1450  $^\circ\text{C}$  and then for 30 min at 1500  $^\circ\text{C}$ , temperature that melts the mixture. After that it was maintained inside the oven for slow cooling during 48 h until reaching room temperature. Polycrystalline diopside is then obtained. To produce doped samples with different impurities, the same procedure of preparation was used, now mixing MnO,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in concentrations that are found in the natural diopside.

## 3. Results and discussions

The diffractograms of the natural and artificial diopside are shown in Fig. 1, together with that of a standard diopside crystal. Except for the lines around  $21.6^\circ$  due to cristobalite in Al- and Mn-doped synthetic diopside, all the others lines in the spectra are coincident.

In a paper published in Phys. Stat. Sol. (c) [7], here referred to (I), TL glow curves of 600  $^\circ\text{C}$  heat-treated diopside samples for 1 h have been irradiated to  $\gamma$ -doses from 50 to 50,000 Gy. A broad and intense TL peak around 160  $^\circ\text{C}$  and weaker but still broad peak around 360  $^\circ\text{C}$  have been found (Fig. 2(a)). The peak around 160  $^\circ\text{C}$  grows linearly with  $\gamma$ -dose up to about 1 kGy and then becomes sublinear (Fig. 2(b)). To compare with these glow curves from natural diopside, in Figs. 3(a–d), the glow curves of synthetic samples irradiated to 1 kGy were presented. The pure sample has shown peaks around 160 and 260  $^\circ\text{C}$ , this second one being very broad and intense. This result indicates that these two TL peaks are due to intrinsic defects, although the 260  $^\circ\text{C}$  peak is not seen in the natural sample. The undoped sample and the Mn-doped one presented very similar glow curves to each other. It is possible that Mn did not affect the TL emission. As it is shown in Fig. 4, the EPR spectrum of both natural and Mn-doped synthetic diopside displayed the typical six  $\text{Mn}^{2+}$  hyperfine lines. The Al-doped sample presented almost same 160  $^\circ\text{C}$  TL peak of the natural sample, but peaks around 290 and 410  $^\circ\text{C}$  are additionally present. Finally, the Fe-doped sample presented very weak TL, from 100 to 400  $^\circ\text{C}$ . A peak around 440  $^\circ\text{C}$  is visible,

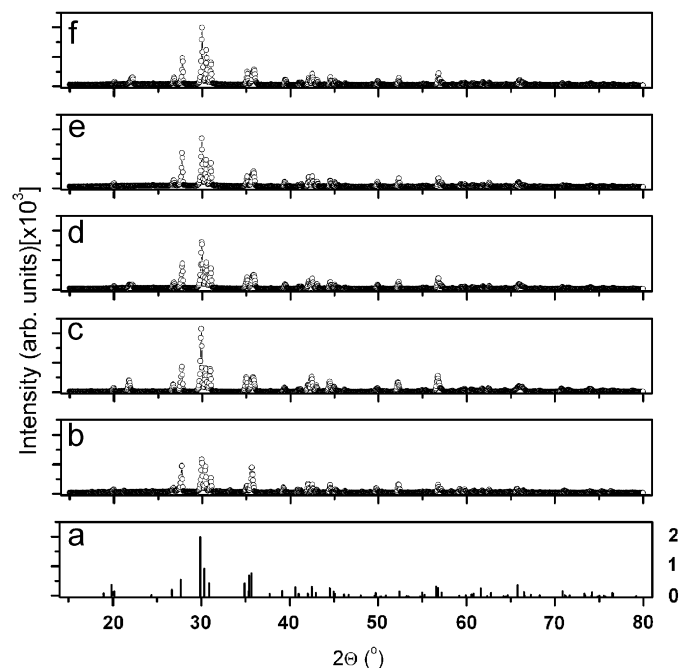


Fig. 1. X-ray diffraction of diopside samples: (a) standard, (b) natural, (c) synthetic non-doped, (d) synthetic doped with Al, (e) with Fe and (f) with Mn.

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