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THERMOLUMINESCENCE, ELECTRON PARAMAGNETIC RESONANCE AND OPTICAL ABSORPTION PROPERTIES OF ANDRADITE

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ABSTRACT

Andradite is one of six members of Garnet Group. Together with grossular and uvarovite form the subgroup of ugrandite. A sample of andradite obtained from a stone dealer has been investigated as to its thermoluminescence optical absorption and electron paramagnetic resonance properties. Peaks at 150, 220, 260 and 350 °C have been observed. Except for high temperature peak, the others grow linearly up to about 6-7000Gy and then saturate. The 350 °C peak has low dose supralinearity up to about 200 Gy then linear and saturation. Up to 700 °C the pre-irradiation annealing increases the TL response but above this temperature the effect is to diminish the TL output. High temperature annealing has an effect to darken the sample. The optical absorption spectra show a strong UV absorption, weaker absorption in the visible but enough to make the sample somewhat dark. Due to large concentration of Fe^{3+}, the EPR signal is a strong and very broad around g=2.0. All other signals are hidden.

1. INTRODUCTION

Andradite of chemical formula $Ca_3(Fe_2Ti)(SiO_4)_3$ is one of six members of Garnet group; it belongs Andradite of chemical formula $Ca_3(Fe_2^{2+}Ti)(SiO_4)_3$ is one of six members of Garnet group; it belongs also to the subgroup called *ugrandite* [1]. In the nature very rarely is found pure andradite of the above formula, however andradite containing more than 90% of the andradite molecules is fairly common. The main solid solution series is that of andradite-grossular.

The unit cell of any garnet contains eight $X_3Y_2Si_3O_{12}$ formula units. Alternating SiO_4 tetrahedral and YO_6 octahedral which shares corners forming a three-dimensional network, Fig. 1. Within this these are cavities that can be described as distorted cubes of light oxygens which contain X cations.

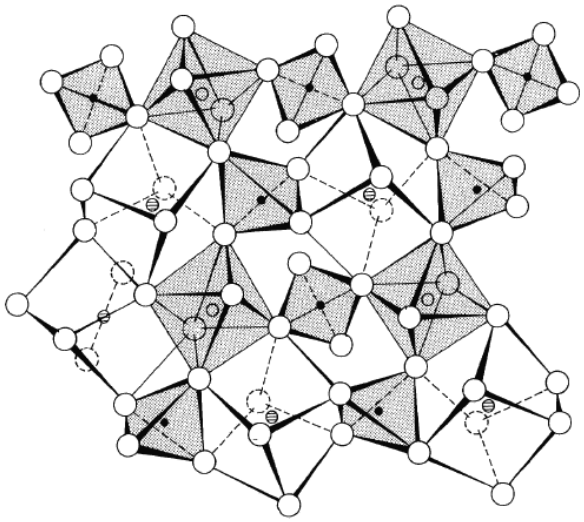

Figure 1. Projection on a plane perpendicular to z-axis of a part of a garnet. Large open circle is oxygen, smaller open circles, Y-cations, solid circle- Si, hatched circle- X cations.

Fig. 1 presents a projection of a plane perpendicular to z-axis of a portion of a garnet. SiO_4 tetrahedral (shaded) alternate with YO_6 octahedral (shaded) eight-fold triangular dodecahedral (drawn as distorted cubes) coordinating X-cations. Large open circle is O, smaller open circles, Y-cations, solid circle, Si, hatched ones, X cations (Novak and Gibbs, 1971). In the andradite mineral, X=Ca, Y=Fe [2].

Except for uvarovite, all the members of Garnet group are found in Brazil. The study on spessartine has already been reported [3].

Due to its gemological importance, several authors [4,5] measured optical absorption spectra of grossular and discussed crystal field effect on energy levels of transition ions, usually found in silicate minerals, including garnet minerals.

For the best of our knowledge, however, no report on luminescence thermally stimulated (TL) in grossular was found in the literature.

Therefore, the present work was focused on the investigation of TL properties. Since EPR measurements usually add some information on defects related to TL and/or OA properties, some EPR measurements have been carried out.

2. MATERIAL AND EXPERIMENTAL

As shown in Fig. 2, a bunch of about a dozen small crystals of andradite encrusted in a piece of rock not identified, was a bunch of small crystals fastened together on a seat formed, maybe by quartz grains perhaps.

Purchased from a stone dealer Luiz Meneses Minerals Ltd in Belo Horizonte, MG, it was extracted from a mine at S. José de Barreiro, State of Minas Gerais. These crystal samples are of dark brown color, but willowish green varieties have been found elsewhere.

Figure 2. Crystal of andradite investigated in this work.

The main purpose is to characterize andradite samples by four following techniques: (1) X ray fluorescence, (2) thermolumnescence (TL), (3) optical absorption (AO) and (4) electron paramagnetic resonance (EPR). A synthetic andradite will be produced to compare with the properties of natural mineral.
X ray fluorescence measurements are carried out at Escola Politecnica, Univ. de São Paulo. For TL measurements Daybreak TL reader model 1100, for AO measurements Cary Spectrophotometer and for EPR Bruker Spectrometer in X-band have been used. Both TL and EPR properties study require gamma irradiation which was done at the Institute of Energy and Nuclear Researches.
For AO spectrum experiment slates 1.0 mm thickness with faces well polished were prepared.
To compare with natural sample TL glow curve synthetic policrystals have been produced at laboratory, using devitrification process with controlled cooling.
For TL and EPR measurements enough amount (about four grams) of crystal has been crushed and sieved to retain grains with diameters between 0.080 mm and 0.180 mm. Powder grains smaller than 0.080 mm were used for X-ray fluorescence analysis.

3. RESULTS

Table 1 presents oxides in (weight %), both components of the crystal and impurities. It indicates that this sample is a fairly pure andradite since grossular is found less than 3 %. It is relatively pure in the other sense too. The number of impurities is smaller than that found in other natural garnet.

Table 1. Composition of natural andradite using X-ray fluorescence analysis

Compound	Fe_2O_3	CaO	SiO_2	Al_2O_3	MnO	K_2O	SO_3
mass %	36±2	34±2	27±2	2.1±0.8	0.27±0.03	0.19±0.02	0.03±0.01

Fig. 3 shows glow curves of andradite irradiated to 50, 200, 1000, 5000 and 50000 Gy.

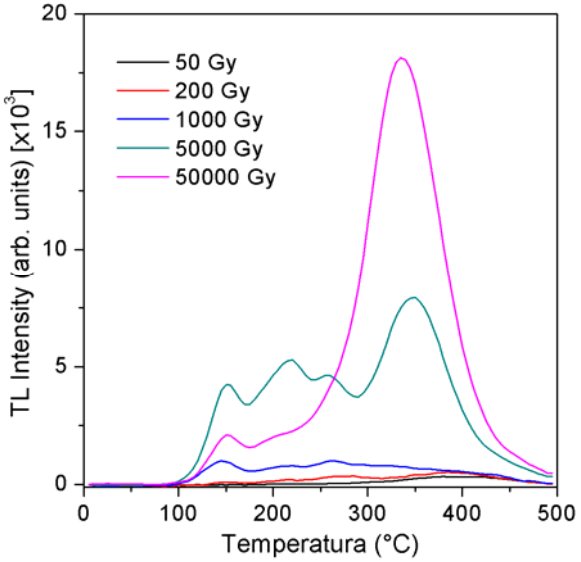

Figure 3. Glow curves of andradite irradiated to 50, 200, 1000, 5000 and 50000 Gy.

Fig. 4 shows TL intensity as function of dose of TL peaks at 150, 220, 250 and 340 °C.

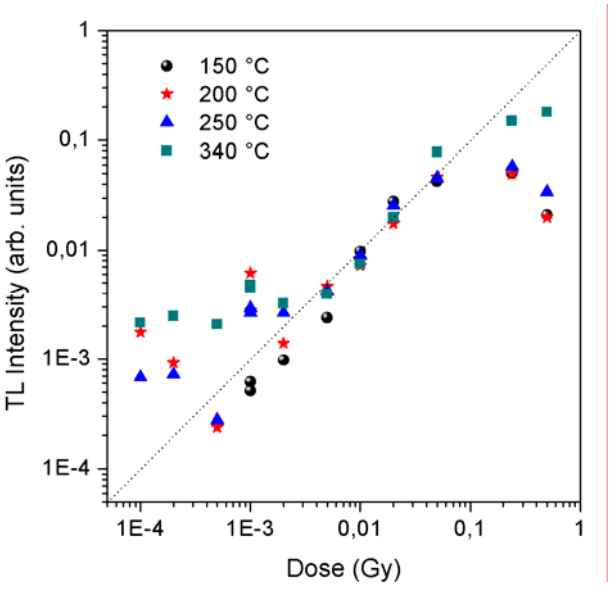

Figure 4. TL response as function of dose.

We see in the glow curves of andradite sample irradiated to 50, 200, 1000, 5000 and 50000 Gy shown in Fig. 3 peaks at 90, 150, 220, 265, 330-340 °C are observed. Actually high temperature peak seems to start around 385 °C for 2000 Gy and moves down to 330 °C for 20000 to 50000 Gy. The TL intensity growth curves as function of dose is presented in Fig. 4(a, b, c, d).

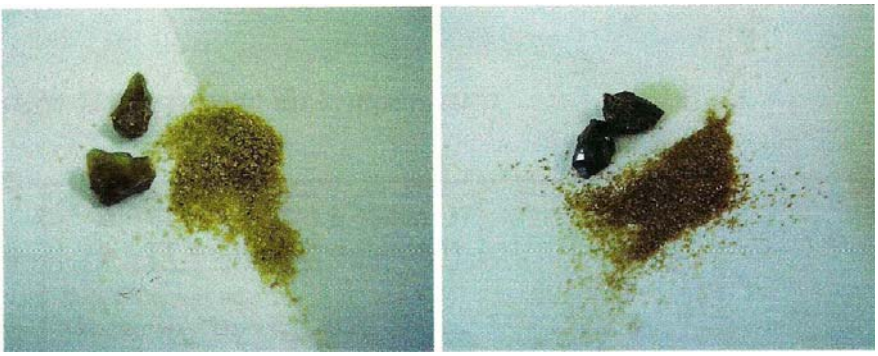

Figure 5. Color change due to annealing. (a) at 700 °C, (b) at 900 °C.

The color change is shown in Fig. 5(a) after annealing at 770 °C and in Fig. 5(b) after heat treatment at 900 °C. Natural sample has golden-yellow color; after heat treatment it becomes darker. One sees that in powder form after 900 °C annealing it is darker than under 700 °C heat treatment.

Fig. 6 shows that 900 °C annealing before 1000 Gy irradiation has an effect to reduce TL intensities compared to that due to 700 °C pre-annealing.

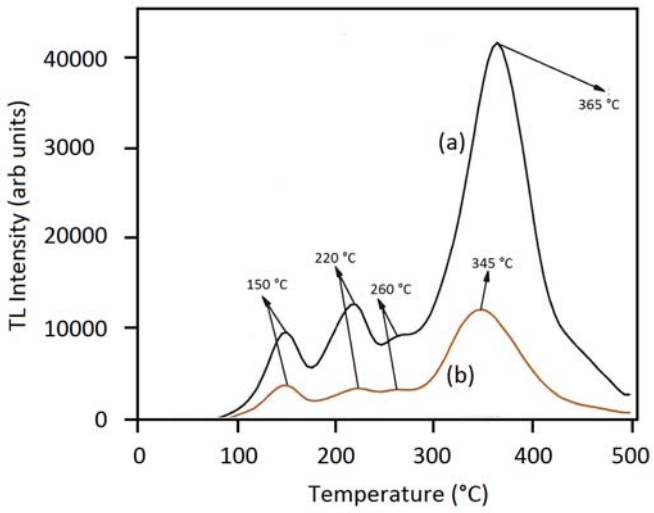

Figure 6. Pre-irradiation annealing. (a) at 700 °C, (b) at 900 °C.

Synthetic andradite has been produced indigenously using devitrification method namely an appropriate mixture of CaO, FeO, Ti_2O_3, and SiO_2 was melted in a platinum crucible in an oven heated to about 1400 °C. The melt is kept on the oven for longer than 60 min and then cooled to room temperature using temperature controller. After about 48h cooling the polycrystal of andradite is obtained.

Fig. 7 shows a glow curves of the synthetic andradite irradiated to 1000, 2000 and 10000 Gy γ-ray. TL peaks at 140, 220, 260, 300 and 380 °C are observed. All the peaks grow with radiation dose.

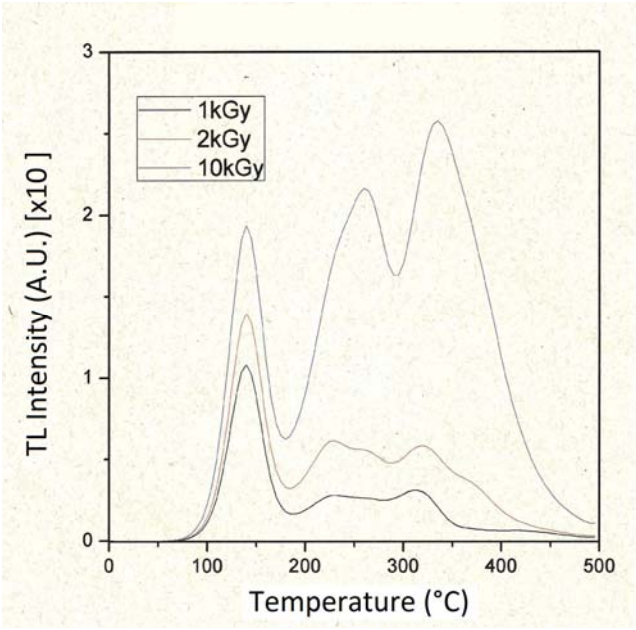

Figure 7. Glow curves of the synthetic andradite irradiated to 1000, 2000 and 10000 Gy.

Fig. 8 shows the optical absorption spectrum of natural andradite. Relatively strong and broad UV absorption band, a weak but broad band around 600 nm and a broad band around 850 nm are observed.

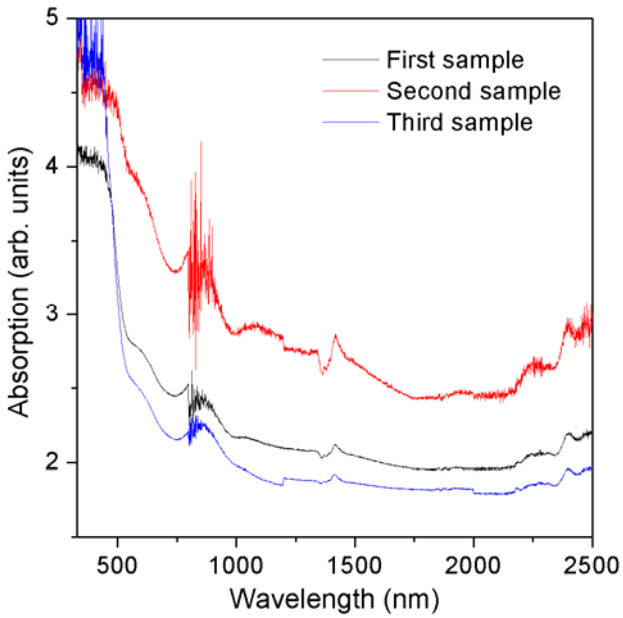

Figure 8. Optical absorption spectra for three samples of andradite.

Fig. 9 shows a broad and very intense EPR signal around g=2.0. This is due to iron dipole-dipole interaction. It is so strong that no other signal can be observed.

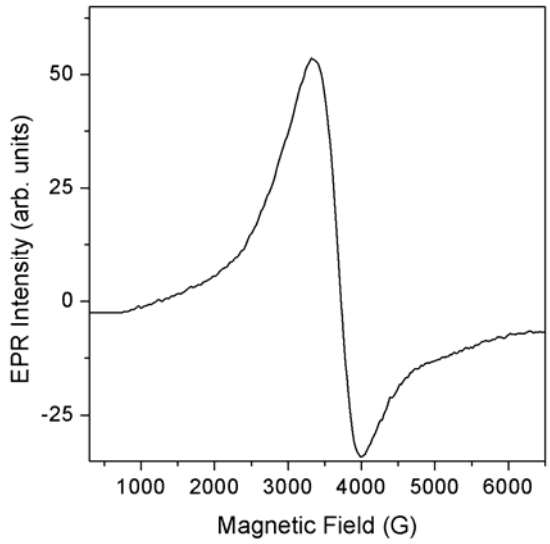

Figure 9. A strong and broad EPR signal around g=2.0

3. CONCLUSIONS

The glow curve of andradite is composed of TL peaks at 150, 220, 250 and 340-365 °C. Actually, high temperature peak shifts to lower temperature as the radiation dose increases: 340 °C peak for 5000 Gy irradiation moves to 350 °C and after 50000 Gy irradiation to 340 °C. TL intensity of any peak below 300 °C grows linearly up to about 8000 to 9000 Gy, but decreases for doses larger than 10000 Gy. The high temperature peak grows supralinearly at low doses up to about 1000 Gy, then grows linearly saturating beyond 10000 Gy. TL intensities of all the peaks increase for annealing from 300 to 700 °C, before irradiation, but for larger temperatures the TL intensities become less intense. With heat treatment the color becomes darker; at 900 °C annealing it becomes very black The glow curve of the synthetic policrystal has shown all four TL peaks found in natural andradite; this means that these peaks are due to intrinsic defects. The optical absorption spectra show relative high absorption at any wave length, a fact that is expected since the natural crystal is dark. The EPR signal is just a strong and broad one around g=2.0; this is due to dipole-dipole interaction since any andradite contain large concentration of Fe^{3+}.

ACKNOWLEDGMENTS

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