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Comparative study of TL and EPR properties of four solid solutions of garnets

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In the present work four solid solutions of peralspite garnets indicated PP, PS, R and A have been investigated as to their TL properties. The glow curves of PP, PS, R and A irradiated by gamma rays with dose from 10 to 1000 Gy (2000 in A) presented peaks around 150, 200, 260 and 360-370 °C, but the response of these peaks to radiation doses varies from sample to sample. Also we present glow curves when samples were annealed at 500 °C for 30 min and irradiated to UV light. In other experiments samples irradiated to 1000 Gy were exposed to UV light; the TL intensity decreases under UV exposure. OSL measurements show a linear growth with radiation dose below 200 Gy. Almost straight line signal is obtained for EPR spectrum of natural PS sample. The change in the shape of EPR spectrum of PS sample annealed at high temperature in the range 800 to 1000 °C indicates that Fe^{2+} converts to Fe^{3+}. This is confirmed by Molecular Absorption Spectroscopy measurements.

1 Introduction The Garnet group is composed of six silicate minerals divided into the subgroup of piralspite (pyrope, almandine and spessartine) $X_3Al_2Si_3O_{12}$ (X=Mg, Fe^{2+}, Mn) and the subgroup of ugrandite (andradite, grossular and uvarovite) $Ca_3Y_2Si_3O_{12}$ [Y=Al, (Fe^{3+},Ti), Cr]. In nature very rarely a pure pyrope or almandine, etc can be found but mixture of them in solid solutions. Usually such solid solution is a mixture of two or three minerals inside each subgroup, except for grossular that has chemical components similar to those of the first subgroup, therefore one find mixture of garnets of the first group plus grossular [1].

Two grossular samples have been investigated by Yauri et al. [2, 3] as to its TL, optical absorption, and EPR properties. The sample containing 4.11% of iron presented an intense EPR signal around g=2.0 plus signal at g=4.3 whereas the sample with 0.75% of iron presented all the signals much weaker. The TL behaviour differed much between two samples.

Mittani and Watanabe [4] investigated a solid solution of almandine, grossular and spessartine. Most of published papers on garnet are about mineralogical nature.

No other published papers in the literature were found related to study here carried out. Furthermore, Yauri et al. [2, 3] tried to produce artificial grossular using devitrification method, starting with CaO, Al_2O_3 and SiO_2 in appropriate proportion, instead of grossular it was obtained gehlenite. Hence for a while we did not try to obtain synthetic pyrope or almandine, etc

In this work we obtained four solid solution of piralspite subgroup to investigate some of their physical properties.

2 Materials Gartnets with commercial names pyrope salvador (PS), rodolite (R), pink pyrope (PP) and almandine (A) have been purchased for comparative study of their TL and EPR properties. The X-rays fluorescence

Table 1 Composition of the four materials studied in this work (pyrope salvador, rodolite, pink pyrope and almadine).

Sample	Almandine (%)	Spessartine (%)	Pyrope (%)	Grossular (%)
PS	52.9	46	0.27	0.76
R	79	6.3	13	1.63
PP	75.89	6.8	11.94	5.4
A	71.26	7.96	10.4	10.46

analysis revealed that all samples are a mixture as we can see on Table 1.

Since in the nature it is almandine garnet that is found more abundantly, all PR, R, PP and A samples here investigated contain predominantly Fe_2O_3, although they are not "pure almandine" (more than 85% purity).

3 Experiments All TL measurements have been carried out on Daybreak 1100 TL reader; 4 $^{o}Cs^{-1}$ heating rate used for TL read out.

OSL measurements have been carried out in a Risoe TL/OSL reader at 120 ^{o}C, stimulating with 470 nm blue light during 40 s.

All samples have been crushed and sieved to retain grains size between 0.080 and 0.180 mm diameters.

γ-irradiation has been carried out using Co-60 γ-source at IPEN-Institute of Energy and Nuclear Researches, for ultraviolet irradiation a calibrated 60 W Hg lamp was used. EPR measurements have been carried out in the Bruker spectrometer.

4 Results Figure 1(a, b, c and d) shows glow curves of irradiated PS, R, PP and A garnets, respectively, PS and

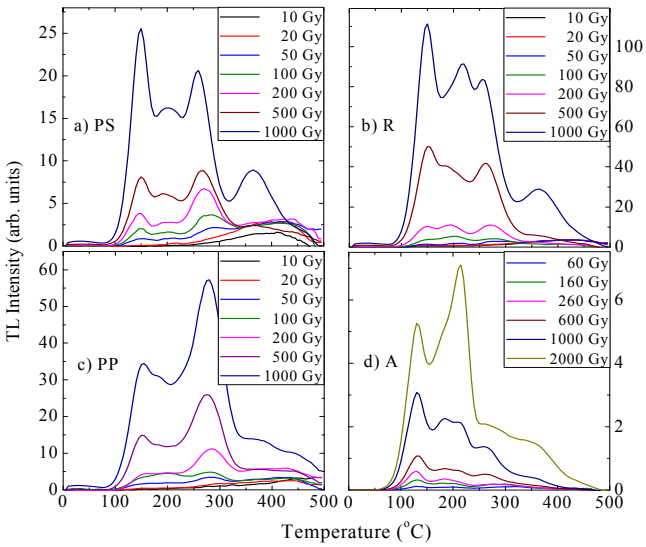

Figure 1 Glow curves of Garnet Group: (a) Pyrope Salvador; (b) Rodolite; (c) Pink Pirope and (d) Almandine samples; all of them pre-annealed at 500 ^{o}C for 30 min and irradiated at several γ-doses from 10 Gy up to 1 kGy.

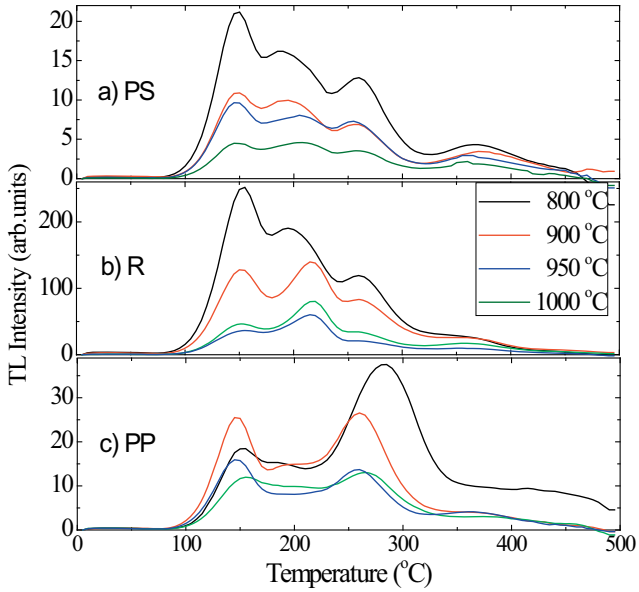

Figure 2 Glow curves of PS, R and PP samples which were annealed at 800, 900, 950 and 1000 ^{o}C for one hour and then irradiated to 1 kGy.

R glow curves presented TL peaks at about 150, 190~210, 260 and 360 ^{o}C; PP: 150, 185, 280, 380 and 440 ^{o}C; A: 130, 170, 220, 260 and 360 ^{o}C. The peak growth with radiation dose also differs from one sample to the other, for example 150 ^{o}C peak grows fast in PS and R, but slower in PP and A, 220 ^{o}C peak in A grows very fast, much slower in others.

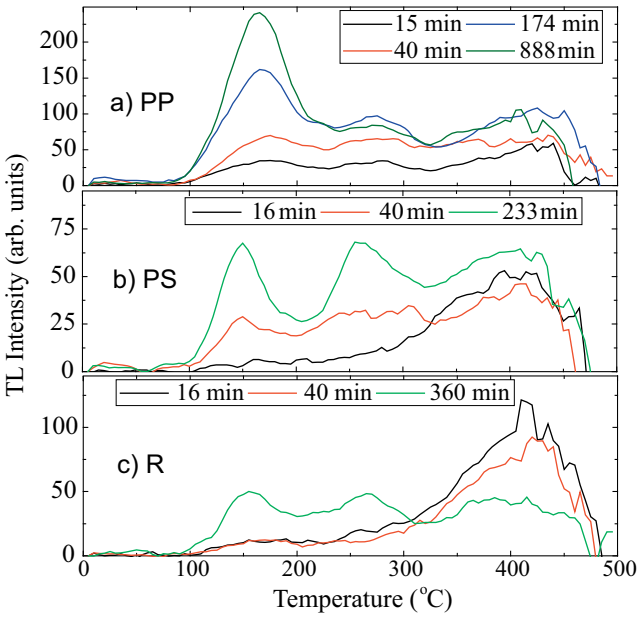

Figure 3 Glow curves of UV induced TL in: a) PP; b) PS and c) R samples.

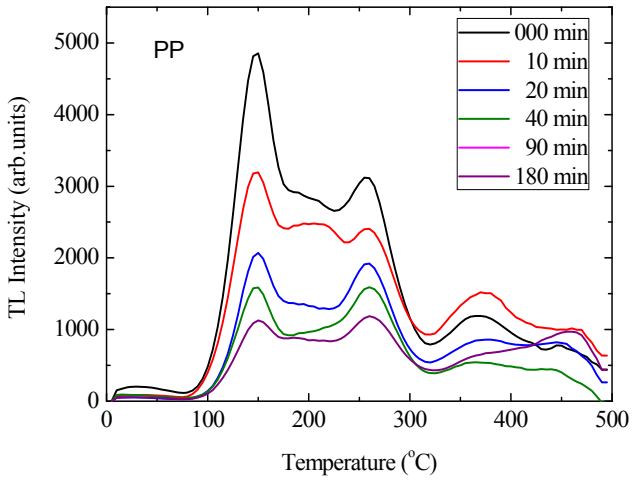

Figure 4 Glow curve for pink pyrope, the sample was irradiated with 1 kGy then irradiated with UV light in order to observe how the UV light change the TL glow curve.

In the following the PS, R and PP samples were annealed at 500, 800, 900, 950 and 1000 °C for one hour and then irradiated to 1000 Gy. The respective glow curves are shown in the Fig. 2(a, b, c), those results are opposite to that found in several other silicate minerals, for which in general the TL sensitivity grows with pre-irradiation annealing temperature, however, here it decreases.

It is known that the ultraviolet light induces TL in silicates minerals. Figure 3(a, b, c) shows glow curves of UV induced TL in PP, PS and R, respectively. On the other hand, UV light causes bleaching of the existing TL peaks as shown in Fig. 4 for PP sample. Figure 5 presents OSL decay curves for PP irradiated by different γ-doses and Fig. 6 shows OSL intensity vs. dose curve for PP, PS and R, respectively.

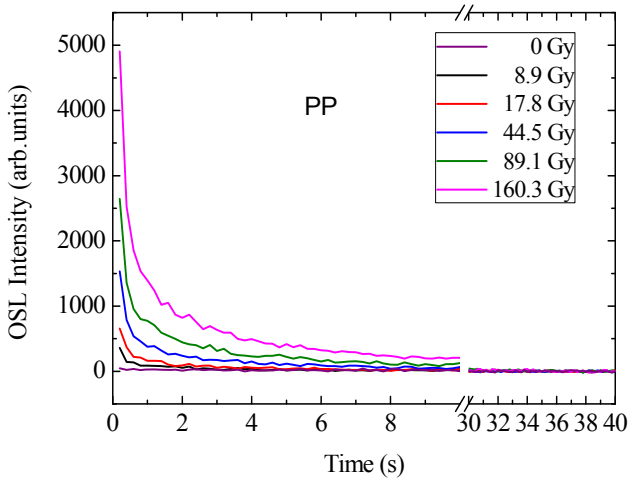

Figure 5 OSL decay curve for pink pyrope, irradiated with different doses of γ-rays.

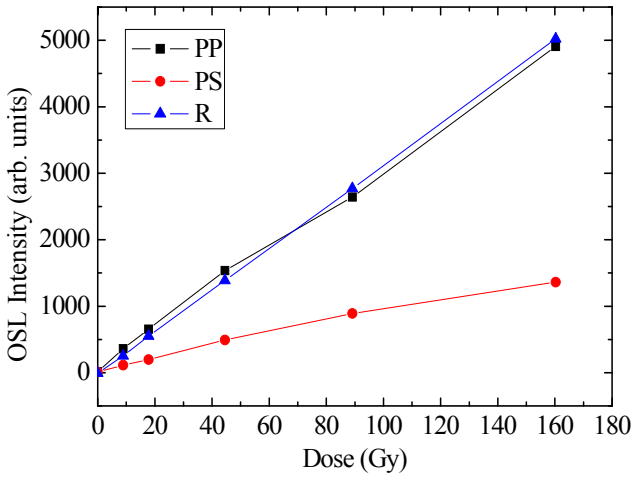

Figure 6 OSL grow curve for samples PP, PS and R.

Figure 7 shows the EPR spectrum of PS samples; showing a huge background signal obviously extending beyond the available region of magnetic fields with a smaller and narrower signal superposed near g=2.0 which is increasing upon annealing while the background disappears. Figure 8 shows the change in the spectrum when the samples are annealed from 600 to 1000 °C; the straightline like shape gradually changes to known form of signal around 3400 G. Observe the intense growth of EPR intensity going from 900 °C to 1000 °C annealing.

It is possible that the EPR spectrum of non treated sample is due to something like ferromagnetic cluster [5, 6] and under high temperature annealing such cluster is substituted by individual Fe^{3+}-magnetic dipole (S=3/2) interacting with neighboring magnetic dipole [7]. Beyond 900 °C annealing, by $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$, the number of Fe^{3+} increases strongly and the signal due to Fe^{3+} increases.

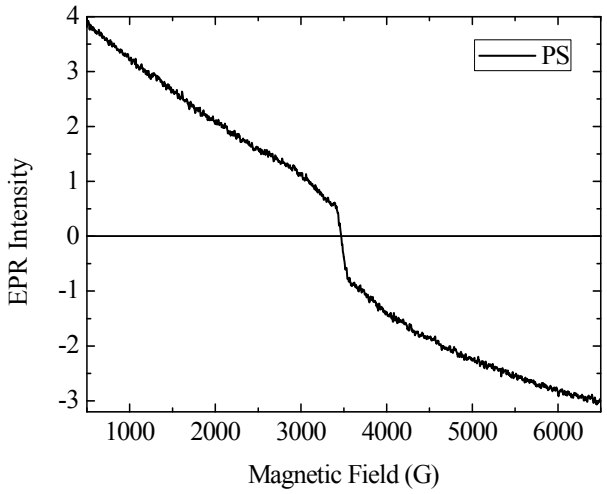

Figure 7 EPR spectrum for natural PS sample.

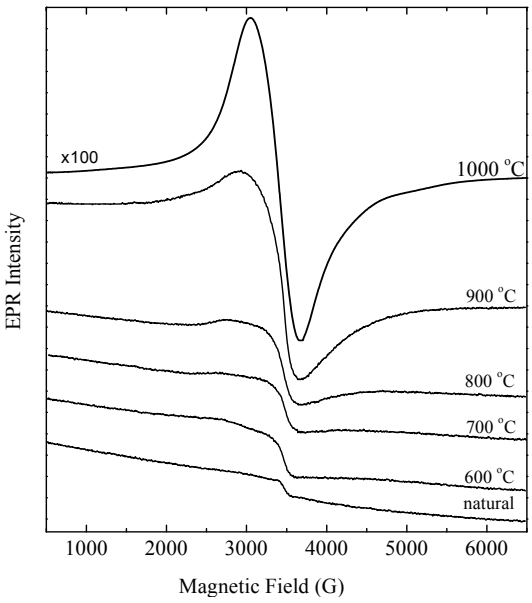

Figure 8 EPR spectrum for natural PS sample, then annealed at 600, 700, 800, 900 and 1000 °C.

We used Jeffrey (1975) [8] method to follow Fe^{2+} concentration change as the annealing temperature varies from 600 to 1000 °C. Initially, the sample is mixed to "ortophenanthroline (Phen)" both solids, and then in a polypropylene vials 10% solution of HCl and 48% solution of HF are added. Following reaction takes place:

$$Fe^{2+} + 3PhenH^{+} \rightarrow Fe(Phen)_3^{2+} + 3H^{+}$$

A molecular absorption spectrophotometer is used to find concentration of Fe^{2+}. Table 2 shows the decrease in Fe^{2+} concentration as the annealing temperature varies from 600 to 1000 °C.

5 Conclusions Although all four minerals belonging to the piralspite subgroup all of them have more than 71% almandine, except for PS sample with 52.9% almandine and 46% spessartine, their peaks at 150 , 185-210 , 260-280, 360-370 °C grow differently with the γ-doses.

Table 2 Variation of Fe^{2+} concentration (weight %) in PS, R and PP samples.

Annealing (°C)	PS	R	PP
Natural*	0.038±0.0011	0.040±0.0012	0.046±0.0013
600	0.031±0.0009	0.036±0.0011	0.042±0.0014
800	0.030±0.0011	0.023±0.0004	0.032±0.0010
900	0.020±0.0006	0.019±0.0003	0.031±0.0009
1000	0.018±0.0005	0.009±0.0002	0.013±0.0004

* Sample without annealing.

The fact however, that all of them presents TL peaks at around same temperatures indicate that the same kind of defects centres are responsible for these peaks, By all means, Al- and Ti- hole centres and oxygen vacancy related centre and E´ centres are responsible for the TL peaks.

With pre-irradiation annealing at high temperatures between 800 °C and 1000 °C, The TL sensitivity decreased steadily. These results indicate that the either electron traps or hole centres diminished concentration with the temperature.

The glow curve of TL induced by ultraviolet radiation on PP, PS and A samples differ in shape from each other and differ also from those due to γ-ray. It is interesting to note that relatively intense 400 °C peak is induced in all of them.

The EPR spectrum of PS, one of the samples here investigated, without any treatment is a straight line extending from 500 G to 6500 G.

The straight line has an inclination. We attributed these results to ferromagnetic like cluster of Fe^{3+}, which is dissolved under high temperature annealing in the region of 800 to 1100 °C. The spectrum changed gradually to the typical magnetic dipoles (due to Fe^{3+}) interaction.

Beyond 900 °C annealing the conversion of Fe^{2+} into Fe^{3+} plus an e^{-}, increases the concentration of Fe^{3+} such that the signal around g=2.0 of Fe^{3+} increases considerably.

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