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Synthesis and luminescence studies of Tb-doped MgO-$MgAl_2O_4$-Mg_2SiO_4 ceramic for use in radiation dosimetry

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HIGHLIGHTS

- Ceramic MgO samples with five different terbium concentrations were produced using the single mixture of components method.
- TL of ceramic MgO:Tb sample showed an intense and well defined peak at 210 °C and other less intense at 350 °C.
- The 210 °C TL peak presented a linear behavior for beta doses between 1 and 20 Gy and minimum detectable dose of ~40 mGy.
- OSL signal presented a linear behavior between 1 and 10 Gy and minimum detectable dose of ~600 mGy.
- The 210 °C TL peak presented a fading of ~20% during the first five hours after beta irradiation dose of 1 Gy.
- The luminescence of 210 °C TL peak was due to electron transitions of Tb^{3+} ions.

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ABSTRACT

In the present work, MgO ceramic samples with different terbium concentrations were produced and the Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) properties analyzed and discussed, aiming the use in radiation dosimetry. The samples were produced using MgO, $Mg(NO_3)_2{\cdot}6H_2O$, Al_2O_3, SiO_2 and $Tb(NO_3)_3{\cdot}6H_2O$ precursors in stoichiometric concentrations with five different terbium concentrations between 0.1 and 0.5 mol% and after, heat-treated at high temperature ~1500 °C. X-ray diffraction measurements on samples showed the formation of MgO as principal phase, and others in low concentration due to $MgAl_2O_4$, Mg_2SiO_4 and Tb_4O_7 phases. The TL glow curve of samples showed an intense and well-defined peak having the maximum at ~210 °C and other less intense at ~350 °C. The sample with 0.1 mol% of terbium concentration presented highest luminescence peak when compared to the other samples. The relationship between 210 °C TL peak intensity and dose was linear to doses between 1 and 20 Gy and the minimum detectable dose obtained by interpolation taking into account three times the standard deviation of the zero dose reading, was ~40 μGy. A fading of ~20% during the first 5 hours after irradiation of 210 °C peak was observed. TL emission spectra showed strong emission lines due to Tb^{3+} ion. The OSL signal presented a linear behavior to doses between 1 and 10 Gy using 532 nm wavelength stimulation.

1. Introduction

Magnesium oxide is an interesting material, which is used in different areas of science and technology. The material doped with transition metal ions was widely investigated in order to understand the formation and properties of point defects creation and their function in optical and electrical properties (Dunphy and Duley, 1990; Hirsch and Shankland, 1991; Timmer and Borstel, 1991), also has been investigated as a possible tunable laser (Chen et al., 1990).

In radiation dosimetry, (Thomas and Houston, 1964) suggested the use of material as a thermoluminescent dosimeter. However, it was not widely used due to some aspects, such as irregularity of Thermoluminescence (TL) properties (which depends on the sample source), radiation and thermal treatment histories, (McKeever et al., 1995). A review of impurity related centers, lattice defect structure and TL mechanism in the material was done by Las and Stoebe (1984)

Lately, the attention on MgO came back again, after the material has been proposed as Optically Stimulated Luminescence (OSL) dosimeter (Bos et al., 2006). As is known, at the moment there are only two OSL dosimeters for use in radiation dosimetry (Al_2O_3:C and BeO); and the lack of other OSL materials prevents the expansion and new applications of OSL technique, unlike TL technique, where there are numerous

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dosimeters for various uses and applications.

MgO has also been proposed for use in neutron dosimetry, more specifically, for fast neutron detection in a mixed radiation field with γ - radiation (Dolgov et al., 2002; Kvatchadze et al., 2011). Backscattered neutrons (albedo neutrons), it can be detected by a thermoluminescent dosimeter (LiF TLD chip), however, for fast neutron detection, MgO becomes an interesting dosimeter which can help extend the range detection in neutron dosimetry.

Usually, MgO single crystal is grown by arc fusion technique, but can also be produce by other methods such as sol-gel (Bokhimi et al., 1995; Kumar et al., 2011), solution combustion synthesis (Orante-Barrón et al., 2011) or single mixture of components (Bos et al., 2006).

Of all the mentioned methods, the most simple and easiest to produce MgO is the single mixture. In this method, the compounds are mixed in stoichiometric amounts and heat-treated at high temperatures. Some advantages of this method compared the others are the short steps to produce the final material, it is not necessary a rigid stoichiometric control for fuel-oxidizer mixture (solution combustion) or rigid control of pH in the mixture (sol-gel).

In the present work, ceramic MgO doped with five different terbium concentrations were produced using the single mixture of compounds and their TL, OSL and TL spectra properties analyzed and discussed. Terbium (Tb) was used as a dopant in the samples due to the various luminescence components in the visible region. The aim of the work was to study the TL and OSL dosimetric properties of ceramic MgO doped with terbium.

2. Experimental

2.1. Synthesis

All the ceramic samples were produced by single powder mixture using MgO (produced in laboratory from Magnesium Nitrate), $Mg(NO_3)_2{\cdot}6H_2O$ (Sigma Aldrich), Al_2O_3, (ALCOA), SiO_2 (Carlo Erba) and $Tb(NO_3)_3{\cdot}5H_2O$ (Sigma Aldrich) precursors in stoichiometric amounts, with five different terbium concentrations between 0.1 and 0.5 mol% and one sample without terbium. After mixing, the samples in powder form were heat-treating at ~800 °C during one hour using a heating rate of 3 °C/min in alumina crucible to eliminate components as water, nitrogen, etc. from precursors. After this first heat-treatment, the samples were ground using a mortar and pestle and the resulting powder was made pellets with 12 mm of diameter and 3 mm thickness. Then, the pellets were heat-treating again, but at this time to ~1500 °C during one hour in alumina crucible using a heating rate of 3 °C/min. Finally, the pellets were crushed and sieved (90 − 150 μm) for TL and OSL measurements.

2.2. X-ray diffraction

The crystalline phases of the ceramic samples were investigated by X-ray diffraction using the MiniFlex 300 from Rigaku, with Cu Kα radiation (λ = 1.5418 Å), and the data collected by scanning 2θ from 3° to 80° at room temperature. The powder size used for the measures was less than 50 μm.

2.3. Thermoluminescence (TL) measurements

TL measurements were carried out using Risø TL/OSL reader (model DA-20). The luminescence of samples was detected using the photomultiplier (PMT) tube EMI 9235QB (Electron Tubes Inc.) together a set of optical filters composed of Schott BG-39 (~2 mm thick) and Corning 7–59 (~4 mm thick) in front of the PMT. The heating rate used in the measurements was 5 °C s^{-1} from room temperature to 450 °C. For dose response, the samples were irradiated to different doses between 1 and 20 Gy using a beta source ($^{90}Sr/^{90}Y$) coupled to the Risø TL/OSL reader with a dose rate of ~ 0.1 Gy/s. Aliquots of 5 mg of sample in stainless steel cups were used for the readouts.

2.4. Optically Stimulated Luminescence (OSL) measurements

The Risø TL/OSL reader mentioned above is used for OSL dating, therefore, it is equipped with blue light LEDs (470 nm) for optical stimulation and the luminescence detected in UV region using the optical filter Hoya U-340 (transmission between 270 − 380 nm). The prepared samples of this work have the luminescence in the visible region, thus, it was necessary to use other equipment with green laser as optical stimulation and the luminescence detected in the visible region.

So, OSL measurements were carried out in Daybreak TL/OSL system reader (model 1100 series) equipped with photomultiplier EMI 9235QB (Electron Tubes Inc.) with the same set of optical filters used in TL measurements. For optical stimulation, it was used a low power green laser (532 nm) which was taken to the sample using the optical fiber attached to the TL reader. With this optical stimulation arrangement, all the measurements were carried out at room temperature being the power at sample position ~2 mW cm^{-2}. For these measures were used 60 channels with count time per channel of 10 s, this long time was used due to the low power of the optical stimulation at the sample position. Aliquots of 5 mg of sample in aluminum disk were used for the readouts, previously irradiated in the beta source ($^{90}Sr/^{90}Y$) coupled to the Risø reader with doses between 1 and 20 Gy.

2.5. TL spectra

TL spectra measurement was done using the Varian CARY 500 spectrophotometer through an optical fiber attached to Daybreak TL/OSL system reader. For measures, it was used high irradiation dose to get high luminescence from samples, thus, the sample was irradiated for two days with dose of ~ 23 kGy in a ^{60}Co gamma source. The heating rate for the measurement was 1 °C s^{-1} from room temperature to 450 °C and the aliquot mass of 10 mg. During the heating, the spectra were recording from 300 to 800 nm and not correction for the response of the system was performed.

3. Results and discussion

X-ray diffraction (XRD) measurements of samples without and with terbium concentration are shown in Fig. 1. From figure and after matching with reported pattern (Fig. 2), it was verified the formation of the principal phase due to MgO (cubic structure, space group Fm-3 m) in all the ceramic samples. Mg_2SiO_4, (orthorhombic structure, space

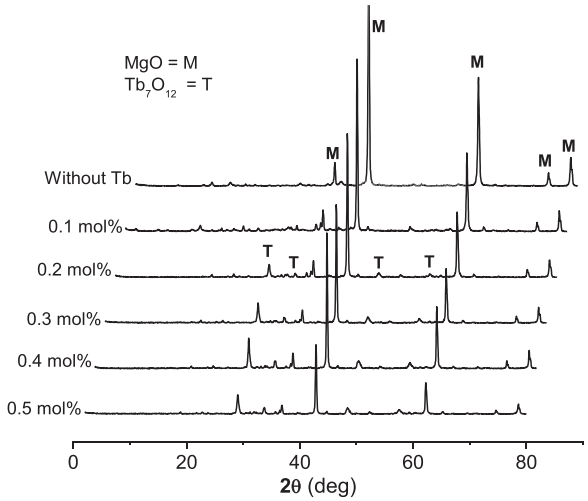

Fig. 1. X-ray diffraction measures of MgO ceramic samples without and with terbium concentration (1 and 5 mol%).

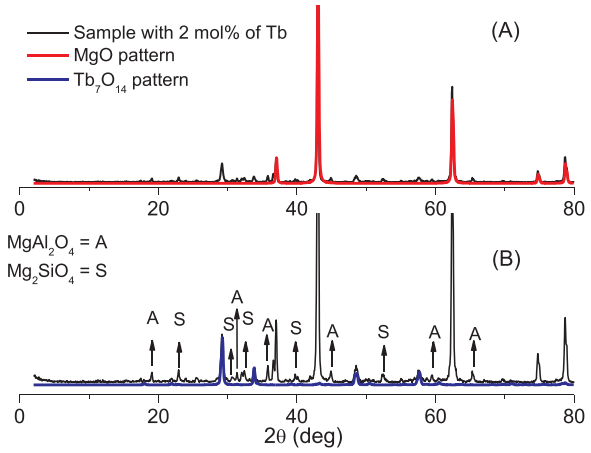

Fig. 2. X-ray diffraction of sample with 2 mol% of Tb concentration and principal peaks of each phase after match with ICSD 088058 (MgO, cubic structure, space group Fm-3 m), ICSD 026374 (Mg_2SiO_4, orthorhombic structure, space group Pbnm), ICSD 024766 (Al_2MgO_4, cubic structure, space group Fd-3 m) and ICSD 073822 (Tb_7O_{12}, rhombohedral, space group R-3). Fig. 2 (B) is the same as Fig. 2 (A) but enlarged × 2,6 to show the small peaks of Mg_2SiO_4, Al_2MgO_4 and Tb_7O_{12}.

group Pbnm) and $MgAl_2O_4$ (cubic structure, space group Fd-3 m) phases were also observed in all the samples (Fig. 2), however, the peak intensities of both phases were very low compared to the MgO phase indicating in this way the low concentration of both phases in the ceramic samples. The Tb_7O_{12} (rhombohedral structure, space group R-3) phase was verified only in samples with terbium content (Fig. 2) and an increment of peak intensities of the phase according to the terbium increment was observed.

In general, all the samples (without and with terbium concentrations) shown the same glow curve with two TL peaks (Fig. 4), one intense at ~210 °C and other less at ~350 °C. Fig. 3 shows the 210 °C peak intensity as a function of terbium concentration after 1 Gy of beta dose irradiation. Among all the samples, that with 0.1 mol% of terbium had the highest intensity when compared to the other samples. The increment of terbium concentration produces luminescence diminution of peak intensity due to quenching concentration phenomena already; the sample without terbium had the lowest intensity, thus showing that the addition of terbium enhances the luminescence of samples.

As the sample with 0.1 mol% of terbium concentration MgO:Tb (0.1 mol%) had the highest luminescence, it was used to analyze and discuss the TL and OSL dosimetric properties with the main attention on 210 °C TL peak because, it seems appropriate to be used in radiation dosimetry.

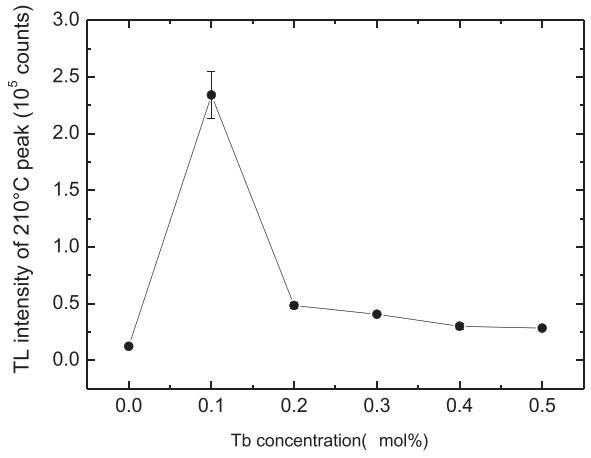

Fig. 3. TL intensity of 210 °C peak as function of Tb concentration after 1 Gy of beta irradiation.

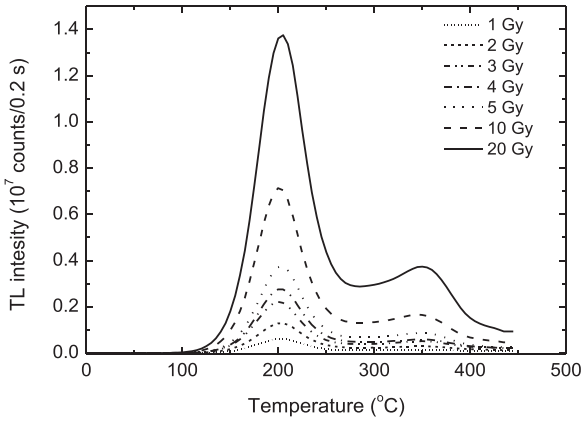

Fig. 4. TL glow curves of MgO:Tb (0.1 mol%) sample for different beta doses between 1 and 20 Gy (heating rate 5 °C s^{-1}).

Initially, it was analyzed the TL dose response and for this the MgO:Tb (0.1 mol%) sample was irradiated with different beta doses between 1 and 20 Gy. TL glow curves for the irradiation doses are shown in Fig. 4. An increment in the glow curve according to radiation dose addition is observed. As the attention is in 210 °C TL peak, the behavior with the dose was analyzed and the peak intensity was used. Fig. 5 shows the 210 °C peak intensity as a function of dose (where each point is the average of five aliquots measured). The peak shows a linear behavior for beta doses between 1 and 20 Gy. Knowing the linearity, the minimum detectable dose (MDD) was then calculated. Normally, the MDD value is obtained intercepting the linear fit behavior of TL peak with three times the standard deviation of zero dose TL reading ($3\sigma_{TL}$), in this way, a MDD of ~40 μGy was obtained. It is necessary to mention that the fading was not considered for these measurements because TL readout was done immediately after irradiation in Risø reader.

In order to evaluate the reproducibility of TL intensity, a set of 10 measure cycles (annealing / irradiation / readout) was done. Fig. 6 shows the reproducibility for 1 Gy beta dose irradiation. In all the cases, it was verified that the TL intensity suffers a variation less than 1.5%, according to the standard deviation of the 10 measure cycles.

To know the fading behavior of ~210 °C peak, TL measurements to different times for a period of 24 h were carried out and, it is shown in Fig. 7. It was used a short time of 24 h only to know the critical fading occurring during the first hours after irradiation. For these measurements a beta dose of 1 Gy was used and the samples stored at room temperature in Risø equipment. According to the Risø equipment manual, the irradiation cross-talk for adjacent positions from principal

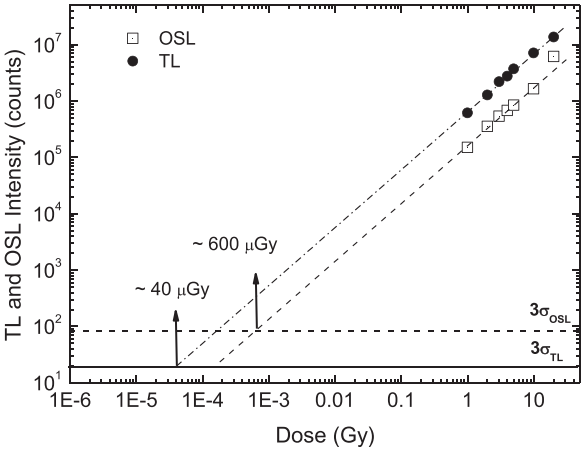

Fig. 5. TL intensity of 210 °C peak and OSL intensity using the first point of decay signal of MgO:Tb (0.1 mol%) sample as a function of dose and minimum detectable dose (each point in figure is the average of 5 measures).

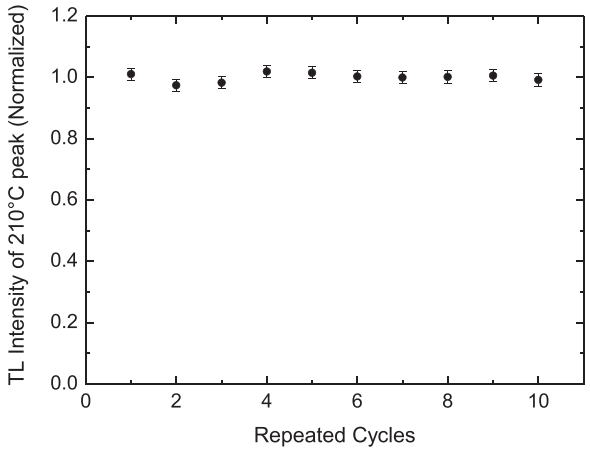

Fig. 6. Reproducibility through 10 repeated cycles (annealing / irradiation / readout) for 1 Gy beta dose irradiation.

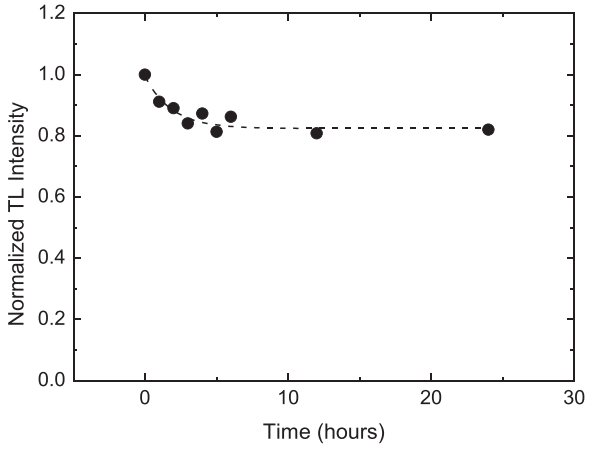

Fig. 7. Fading measures of 210 °C TL peak after beta irradiation of 1 Gy (each point is the average of 5 measures).

irradiation position is 0.250% ± 0.003%, which is very low dose, but for precaution, the stored sample was kept away from the radiation source. From Fig. 7, it is observed that the peak intensity has a critical fading of ~20% during the initial five hours and after it seems to have a constant behavior.

TL emission spectra of MgO:Tb (0.1 mol%) sample after high gamma dose irradiation is shown in Fig. 8. In general, the spectra shows emission lines peaking at 418, 438, 489, 545, 588 and 622 nm due to electron transitions of $^5D_3 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, and $^5D_4 \rightarrow {}^7F_3$ levels from Tb^{3+} ion respectively, plus an emission band between 650 and 800 nm due to crystal point defects in the sample. However, it is necessary to emphasize some interesting aspects which are observed in the spectra, such as i) only emission lines with high intensity due to Tb^{3+} ion are observed for temperatures between 170 and 230 °C, indicating that the luminescence of ~210 °C TL peak is due only to terbium and ii) for temperatures above 230 °C, Tb^{3+} lines start to decrease while the band between 650 and 800 nm begins to increase having the maximum at ~280 °C and after diminishing significantly at 320 °C.

The OSL decay curves for the same beta doses as TL is shown in Fig. 9, and the behavior of OSL intensity as a function of the dose in Fig. 5 (it was used the first point of the OSL signal and each point in figure is the average of five measures). Unlike TL, the OSL signal shows only a linear behavior to the gamma doses up to 10 Gy and after supralinearity. The minimum detectable dose for OSL in this case was ~600 μGy which was calculated in the same way as TL. This high value of minimum detection dose compared to that of TL was due to use of low power green laser in the measurements.

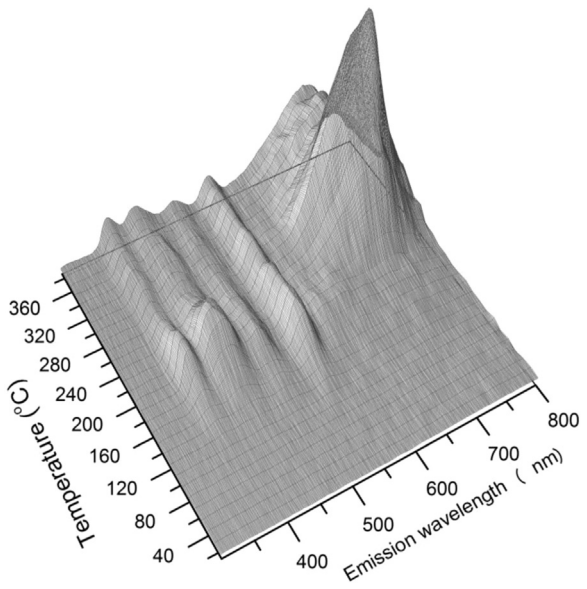

Fig. 8. TL spectra of MgO:Tb (0.1 mol%) sample after high gamma dose irradiation.

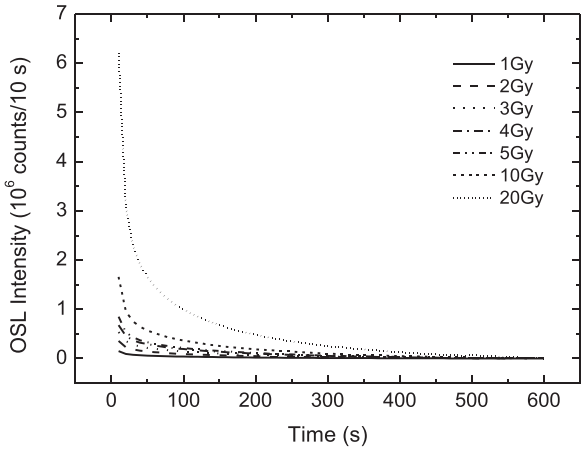

Fig. 9. OSL signal of MgO:Tb (0.1 mol%) sample using 532 nm laser stimulation for different beta doses between 1 and 20 Gy.

4. Conclusions

From the results, we can conclude that the single mixture method seems suitable for preparation ceramic MgO:Tb due to the advantages, such as low cost, easy to handle, short steps to produce the final material, it is not necessary a rigid stoichiometric control for fuel-oxidizer mixture (solution combustion) or rigid control of pH in the mixture (sol-gel). The MgO:Tb (0.1 mol%) shown high luminescence when compared with the other terbium concentrations. The glow curves of the samples showed two TL peaks, one intense at ~210 °C and other less at 350 °C. The ~210 °C TL peak showed a linear behavior for beta doses between 1 and 20 Gy, minimum detectable dose of ~40 μGy and fading of ~20% during the initial five hours. The OSL signal showed a linear behavior for doses between 1 and 10 Gy and minimum detection dose of ~600μGy. According to these previous results, the material has a potential to be used in radiation dosimetry.

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