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Redox reactions and mechanism of luminescence in BaFCl:Eu

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Abstract. The phenomenon of stimutable luminescence of phosphors pre-irradiated with high-energy radiation is widely used in the field of imaging. Phosphors such as BaFX:Eu (X = Cl, Br) are extensively used in x-ray screens for digital image processing. There is, however, divided opinion regarding the mechanism responsible for the luminescence process in these materials. In this paper we have discussed the role of $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion in BaFCl:Eu phosphor using PL, TL, TL emission and ESR techniques.

1. Introduction

The phenomenon of stimutable luminescence of phosphors pre-irradiated with high-energy radiation has been known for a long time. Storage phosphors have found a wide range of applications in the field of dosimetry. One of the most interesting applications of storage phosphors is in the field of x-ray imaging (Sonada *et al* 1983). Various types of material have been considered for use as photostimulable x-ray storage phosphors. BaFCl and BaFBr activated with Eu^{2+} are most widely used as x-ray phosphors for medical imaging via photostimulated luminescence (PSL). BaFCl:Eu²⁺ was studied as early as 1974 (Blasse and Brill 1974) and its use for x-ray screens was proposed in 1975 (Stevens and Pingault 1975). BaFX:Eu²⁺ photostimulable phosphors for computed tomography were proposed by Takahashi *et al* (1984). These workers also proposed the mechanism of luminescence in this phosphor. They suggested that creation of F centres by x-rays due to filling of existing vacancies by electrons and the release of the trapped electron during photostimulation is involved in PSL (Takahashi *et al* 1984, Iwabuchi *et al* 1994). They also speculated that during irradiation Eu^{2+} is oxidized to Eu^{3+} . Decrease in Eu^{2+} luminescence and increase in that of Eu^{3+} were observed (Takahashi *et al* 1984, de Leeuw *et al* 1987) which support the hypothesis. Von Seggern *et al* (1988, Von Seggern 1989) proposed that the F centre electron is not released but tunnels to Eu^{3+} . Close association of F centres and Eu^{3+} was suggested. Later works refute $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ conversion (Meijerink and Blasse 1991, Hangleiter *et al* 1990, Crawford and Brixner 1991). In fact Sun and Su (1988) found evidence of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ conversion. Instead of Eu^{3+} , intrinsic hole trapping sites such as V_k centres were suggested (Crawford *et al* 1989). Reuter *et al* (1990) suggested that irradiation creates F centre interstitial pairs stabilized by Eu^{2+} at Ba substitutional sites. F centre stimulation destabilizes the interstitial halogen centre. Electron tunnelling from the F centre converts the pair into an $e + V_k$ pair which decays and the energy is transferred to a nearby Eu^{2+} ion. Crawford and Brixner (1991) pointed out that only samples fired in

nitrogen/hydrogen atmosphere show PSL, and thus speculated that the hole trap is a hydrogen anion at a fluorine substitutional site. Upon photostimulation the F centre electron and hole recombine by tunnelling and the energy of recombination is transferred to Eu^{2+} . The various models proposed have been recently reviewed (Harrison *et al* 1991, Lakshmanan and Rajan 1994, Lakshmanan 1996, Spaeth *et al* 1995, Dong and Su 1995). In recent years we have studied $\text{Eu}^{3+} \longleftrightarrow \text{Eu}^{2+}$ conversion in several phosphors using correlated TL, PL and ESR measurements (Upadeo *et al* 1994, Upadeo and Moharil 1995). These studies have helped in establishing the mechanism of thermoluminescence in $\text{CaF}_2:\text{RE}$ and $\text{CaSO}_4:\text{RE}$ phosphors. We have carried out similar studies on $\text{BaFCl}:\text{Eu}$ phosphor which throw light on the mechanism of TL and PSL in this phosphor.

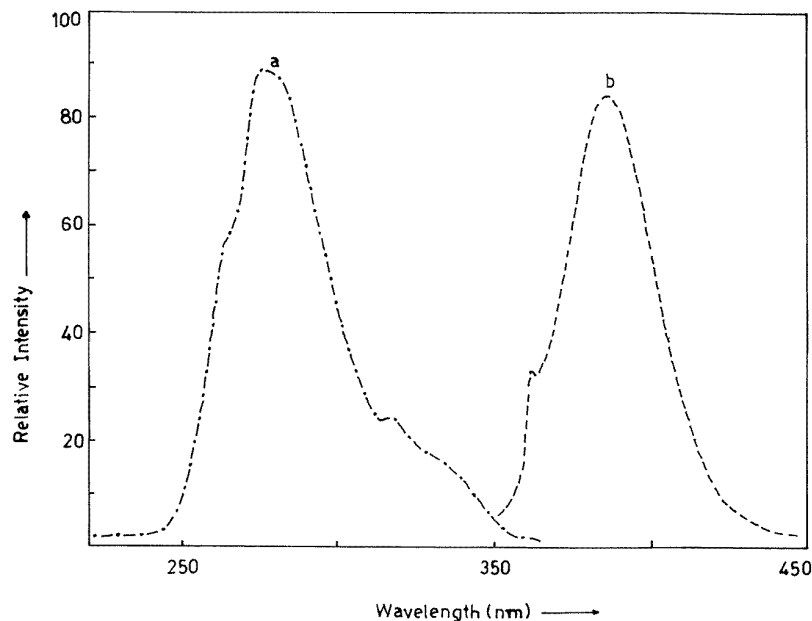


Figure 1. (a) The PL excitation spectrum of $\text{BaFCl}:\text{Eu}$ (sample II) for $\lambda_{em} = 385$ nm. (b) The PL emission spectrum of $\text{BaFCl}:\text{Eu}$ (sample II) for $\lambda_{ex} = 276$ nm.

2. Experimental details

$\text{BaFCl}:\text{Eu}^{2+}$ was synthesized by the precipitation method. A solution of NaF was added to a solution of BaCl_2 , NaCl and Eu salt in double-distilled water. The precipitate obtained was washed repeatedly and dried. It was then heated by two different methods. In the first method, the dried precipitate was heated in vacuum at 973 K for 1 h in a graphite crucible to reduce Eu to Eu^{2+} (sample II). Incorporation of Eu^{3+} needs charge compensation, which can be easily accomplished by diffusion of oxygen into the lattice. Such compensation does not take place during vacuum heating and hence sample II is expected to contain Eu in predominantly divalent form. In the second method the precipitate was heated in air at 973 K for 1 h in a porcelain crucible (sample III). In this sample, along with Eu^{3+} , an oxygen impurity, which acts as a charge compensator, is expected. Undoped BaFCl was also prepared; this will be denoted as sample I. The samples used in the experiments were in fine powder form (85–210 μm).

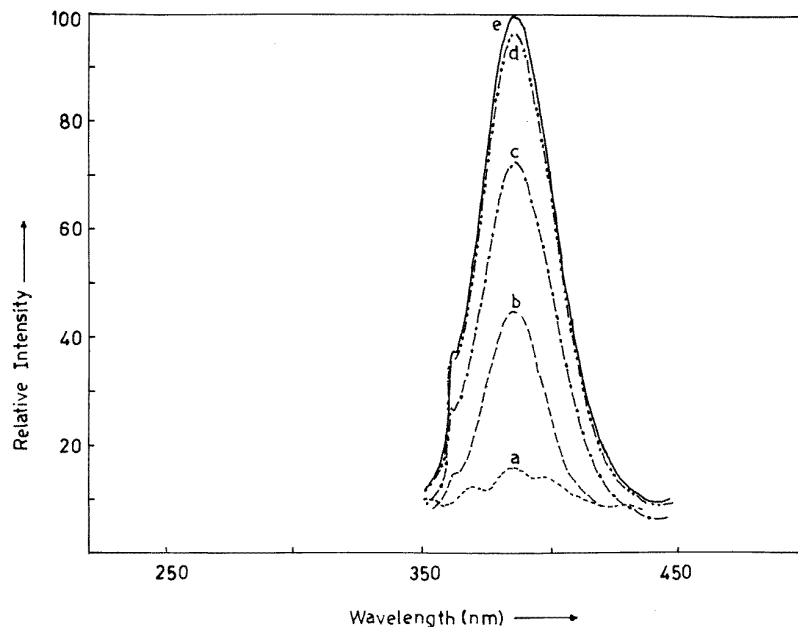


Figure 2. Eu²⁺ emission in BaFCl:Eu (sample III) exposed to gamma rays. Exposure in C kg⁻¹, (a) as prepared, (b) 0.39, (c) 2.51, (d) 6.73 and (e) 10.94.

Thermoluminescence glow curves were recorded with the usual set-up consisting of a small metal plate heated directly using a temperature programmer, photomultiplier (PMT; 931 B), d.c. amplifier and a millivolt recorder. 5 mg phosphor was heated every time at the rate of 150 K min⁻¹.

Thermoluminescence emission spectra and the monochromatic glow curves were recorded by inserting the monochromator between heater plate and the PMT. The monochromator (central electronics) used a 25 cm grating having 1200 grooves mm⁻¹ providing resolution of 3 nm. Heavily irradiated (43.2 C kg⁻¹) samples were used for recording the emission spectra. 50 mg sample was heated at the rate of 300 K min⁻¹ to the desired temperature, which was then held constant. A Hamamatsu R-955 PMT having a flat response over a wide spectral range was used.

Exposure to gamma rays was performed using a Co⁶⁰ source. Fluorescence from various irradiated and unirradiated samples was studied on a Hitachi F-4000 fluorescence spectrophotometer. 300 mg sample was used every time. Emission and excitation spectra were recorded with a spectral slit width of 1.5 nm.

ESR measurements were carried out on a Varian E-112, E-line Century Series, X-band ESR spectrometer, which utilizes 100 kHz field modulation. TCNE ($g = 2.00277$) was used as a standard for g -factor measurements.

3. Results and discussion

3.1. Photoluminescence (PL)

PL studies can be used to decide, at least qualitatively, the valence state of the Eu impurity. Divalent Eu exhibits strong PL arising from the transition of the 4f⁵5d¹ configuration to

the $^8S_{7/2}$ ground state of the $4f^6$ configuration. The emission is in the form of a band, the position of which is strongly influenced by the host. In BaFCl, Eu^{2+} emission is in the form of a band centred around 385 nm. Emission of Eu^{3+} , in general, is in the form of lines around 595 and 610 nm originating in the parity forbidden transitions $^5D_0 \rightarrow ^7F_1, ^7F_2$. The intensity is very small unless some sensitization or charge transfer excitation process is operative.

In BaFCl: Eu^{2+} (sample II), strong Eu^{2+} luminescence was observed (figure 1) in the form of a broad band with a maximum at 385 nm and a shoulder around 362 nm. The corresponding excitation spectrum was in the form of a broad band centred around 276 nm with several shoulders. The maximum intensity of Eu^{2+} luminescence was obtained for 0.2 mol% concentration. No Eu^{3+} emission was observed in this sample. No changes were detected in PL spectra following irradiation of the sample. In particular, there was no Eu^{3+} emission observed.

In BaFCl:Eu (sample III) heated in air no emission was observed, which could be attributed to either Eu^{2+} or Eu^{3+} , but this sample showed considerable Eu^{2+} emission after irradiation with ionizing radiations. The Eu^{2+} emission increased with increase in irradiation time (figure 2). When the irradiated samples were heated, there was no decrease in Eu^{2+} PL until 673 K. For post-irradiation annealing treatment of sample III for 1 h at 923 K, Eu^{2+} emission decreased by about 70%, but it did not vanish completely.

PL measurements thus show that there is radiation induced $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ conversion in sample III. Thus, the 'reduction' seems to be more probable than the oxidation as proposed by Takahashi *et al* (1984). However, even the reduction does not seem to be correlated to TL and PSL as there is no back-conversion up to at least 673 K. As maximum PL was observed for BaFCl:Eu sample II with 0.2 mol% Eu, ESR and TL measurements were carried out on samples containing this concentration of Eu.

3.2. ESR measurements

Radiation induced $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ conversion in sample III could also be confirmed by the ESR measurements. The Eu^{2+} was monitored by measuring ESR. Figure 3 shows that the ESR signal which could be attributed to Eu^{2+} ions goes on increasing with the increase in the exposure, for sample III. All the fine-structure lines are not seen, possibly due to low concentration of Eu^{2+} . It should be mentioned that no ESR lines were observed in unirradiated BaFCl:Eu (sample III) indicating that Eu ions are not in the divalent state. The ESR signal did not decrease until the samples were heated at temperatures exceeding 673 K. Even after the post-irradiation annealing at 923 K for 1 h, the ESR signal due to Eu^{2+} did not vanish completely. The ESR measurements are consistent with the PL measurements for sample III.

3.3. Thermoluminescence (TL)

The TL glow curve for both the samples is shown in figure 4. The TL glow curve for sample II shows prominent peaks at 425 K and 590 K. It also shows shoulders around 470 K and 540 K. In sample III there is an intense peak at temperature as low as 385 K and a shoulder around 495 K. TL intensities in the two samples are comparable, total area under the glow curves being almost equal. In contrast, TL in undoped BaFCl was very weak and barely detectable. It is weaker by at least two orders of magnitude compared to that in the doped samples.

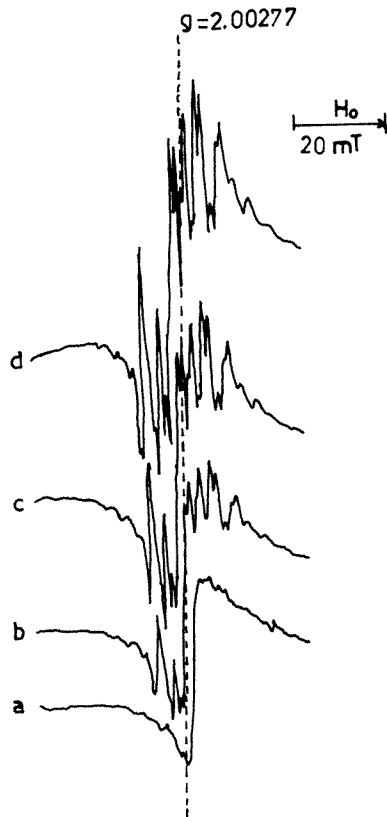


Figure 3. ESR of Eu^{2+} in BaFCl:Eu (sample III) exposed to gamma rays. Exposure in C kg^{-1} , (a) 0.39, (b) 2.51, (c) 6.73 and (d) 10.94.

The TL emission spectra (figure 5) could be recorded in both the BaFCl:Eu²⁺ samples as the TL was intense enough for this purpose. In both the cases TL emission spectra contained a peak around 385 nm, similar to that observed for Eu²⁺ PL emission. No TL emission corresponding to Eu³⁺ could be seen. This is not due to any limitation of the experimental set-up. In CaSO₄:Eu, using the same set-up, Eu³⁺ emission was detected in the TL emission spectrum (Upadeo *et al* 1994). There is also an additional, weaker band at longer wavelengths. Following Koschnik *et al* (1991) and Radzhabov and Otroshok (1995), this may be attributed to oxygen impurity.

It is thus seen that there is intense TL in both the BaFCl:Eu samples. Radiation induced valence changes are observed only in sample III. In this sample also, there is no correlation between TL and $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ back-conversion. The TL glow peaks lie at temperatures lower than 600 K; there is hardly any TL above 650 K. On the other hand there is no $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ back-conversion in this temperature range. The Eu impurity is thus not directly involved in trapping or recombination. TL in undoped BaFCl is very weak, indicating that the trapping efficiency is increased by Eu doping, irrespective of its valence state, and even though Eu^{2+} or Eu^{3+} is not directly involved in the trapping. TL emission in both samples is in the form of characteristic Eu^{2+} emission. One might have expected the TL emission in the form of Eu^{3+} in sample III, as Eu^{2+} concentration in this sample is

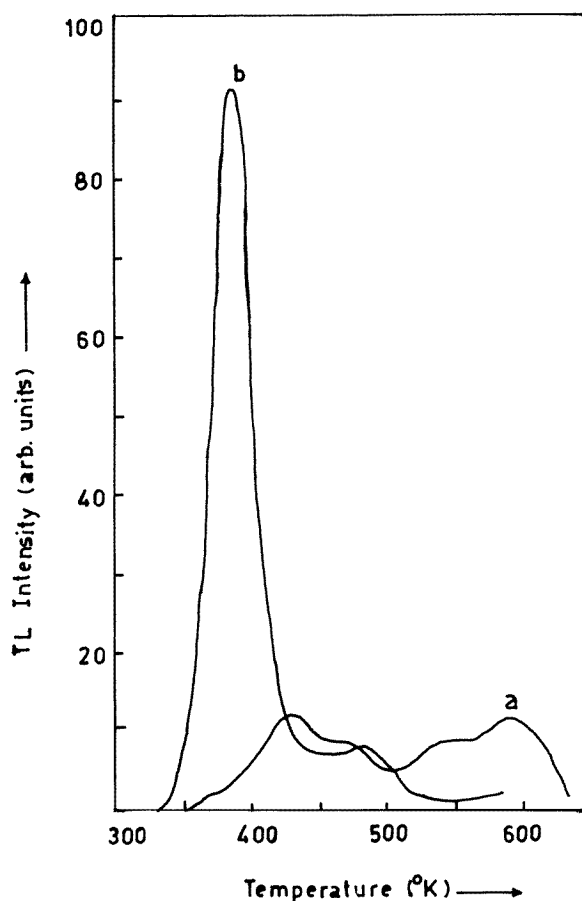


Figure 4. TL glow curves for BaFCl:Eu exposed to (0.39 C kg^{-1}) gamma rays: (a) sample II and (b) sample III.

very small. (Irradiation is known to cause $\text{RE}^{3+} \rightarrow \text{RE}^{2+}$ conversion of the order of 1% (Mathewes and Stoebe 1982, Morgan and Stoebe 1989); thus Eu^{2+} in a concentration of the order of 0.002 mol% exists in irradiated sample III. This is consistent with the fact that the PL intensity in this sample is about 30 times weaker than that in sample II containing about 0.2 mol% Eu^{2+} .) Apparently, Eu^{2+} even in such a small concentration acts as an efficient luminescence centre. An efficient energy transfer from the recombination site to Eu^{2+} is indicated. One may speculate that in sample III, Eu^{2+} created by radiation induced reduction of Eu^{3+} is located close to recombination centres.

It may be noted from well known results that good PSL sensitivity for excitation by He-Ne laser is observed only in samples containing Eu^{2+} in concentrations of the order of 0.2 mol%. The PSL emission spectrum is in the form of characteristic Eu^{2+} emission (Lakshmanan and Rajan 1994, Lakshmanan 1996). Thus, the concentration of irradiation induced Eu^{2+} is sufficient to enable it to act as an efficient luminescence centre for TL but not for PSL.

From the above discussions the following picture for the luminescence in BaFCl:Eu emerges. The radiation creates electron deficient centres (such as trapped hole centres or

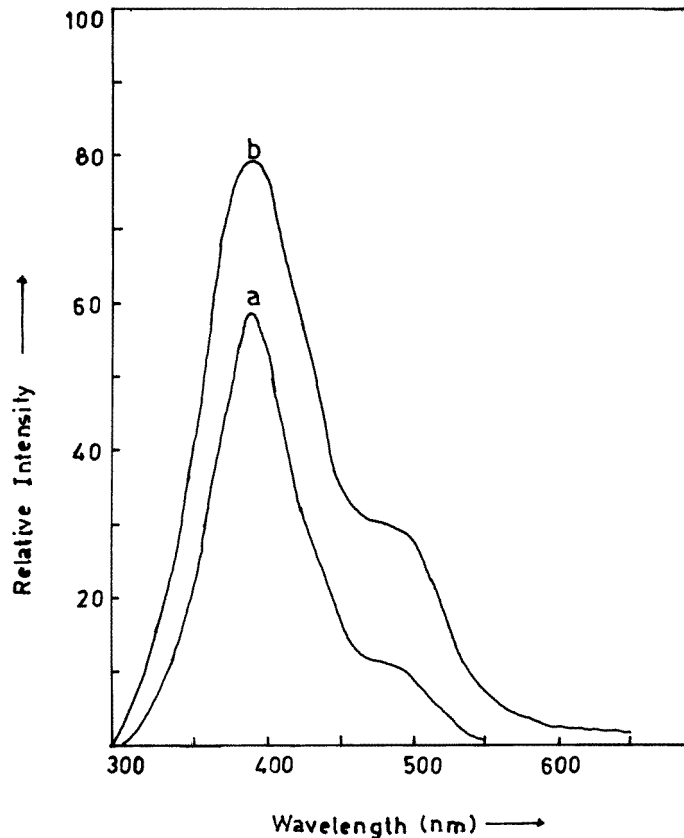


Figure 5. TL emission spectra for BaFCl:Eu samples: (a) sample II—425 K peak; (b) sample III—385 K peak.

interstitial halogen atoms and aggregates), and F centres. Eu impurity helps stabilization of the electron deficient centres. During TL, holes (or halogen atoms) are released from the traps and recombine (either by migration or via the conduction band) with F centres. The energy of recombination is transferred to nearby Eu^{2+} ions. During PSL, light is absorbed by F centres and they recombine with hole centres (again, either by migration or via the conduction band), and the recombination energy is transferred to nearby Eu^{2+} ions (Eu^{2+} ions being abundantly present in sample II, the probability of finding Eu^{2+} ions near the recombination site is high). Thus, both PSL and TL involve characteristic Eu^{2+} emission. Both PSL and TL are intense in sample II.

In the case of sample III, the only Eu^{2+} available is in the form of that obtained by reduction of Eu^{3+} which preferentially takes place close to F centres (i.e. at sites from which the charge compensator for Eu^{3+} is removed); such reduction at preferential sites is well known in CaF_2 (Hayes and Twidell 1963). During TL, electron-hole recombination takes place at F centres. Energy transfer to Eu^{2+} is efficient as Eu^{2+} ions are in the vicinity of F centres. During PSL, recombinations take place at trapped hole centres (or interstitial halogen atoms). There are no Eu^{2+} ions present in the vicinity of the recombination site and hence PSL intensity in sample III is poor. This explains the good TL sensitivity but poor PSL sensitivity of sample III.

It may be argued that the poor PSL efficiency of sample III could be due to a decrease in F centre formation efficiency arising from charge compensating defects. It would be desirable to compare F centre concentrations in samples II and III by, say, making reflectance measurements. However, the sensitivity of the reflectance technique is low compared to the TL or PSL detection efficiency. It will be necessary to use high exposures of the order of 25 C kg^{-1} , while TL and PSL measurements are made at exposures which are at least two orders of magnitude lower. Again, during the reflectance measurements, the samples will be exposed to F light and F centres will decay by photostimulated recombinations with hole centres. TL measurements provide indirect evidence about the F centre concentrations. TL is due to recombination of holes with F centres. It is not due to recombination of electrons with Eu^{3+} . Such a recombination would result in an increase in Eu^{3+} concentration by about 1%. PL is not sensitive enough to measure this increase. However, Eu^{2+} PL would also decrease, which for sample III can be detected by PL, as well as ESR, because we do not find any increase in Eu^{2+} concentration in PL or ESR for post-irradiation annealing up to 675 K. Comparable TL intensities in samples II and III suggest that F centre concentrations in the two samples are also comparable.

4. Conclusions

From the results presented here and the already established facts in the context of PSL, the following can be concluded.

(1) $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ reduction is more probable than the $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ oxidation, when BaFCl:Eu phosphor is exposed to radiation. The reduction takes place preferentially at sites lying close to F centres.

(2) The redox reactions are not involved in TL or PSL processes.

(3) An Eu impurity (irrespective of its valence state) increases the trapping efficiency of BaFCl .

(4) Eu^{2+} acts as an efficient luminescence centre.

(5) Mechanisms of TL and PSL are different. The former most probably involves migration of holes to F centres, while the latter involves the opposite process (migration of F centres to hole centres).

(6) Though the results presented and the model proposed are in the context of BaFCl:Eu , they may be applicable to BaFBr:Eu phosphor as well.

Acknowledgments

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