

The Effect of Argon Pressure on the Photoluminescent Properties of Laser Ablated SrAl₂O₄:Eu²⁺, Dy³⁺ Thin Films

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Abstract: *The morphological, elemental composition and Photoluminescence (PL) properties of laser ablated SrAl₂O₄:Eu²⁺, Dy³⁺ thin films prepared at different Argon (Ar) pressures are reported. The Atomic Force Microscopy (AFM) and scanning electron microscopy (SEM) techniques were employed for the morphological data collection. The data for elemental composition were collected using the Energy Dispersive X-ray Spectrometer (EDS) and Fourier Transform Infra-Red (FTIR). The room temperature photoluminescence (PL) data collection was done by using Cary Eclipse fluorescence spectrophotometry. The films were excited by the UV light from the xenon lamp. The PL intensities of the films seem to vary proportionally with the Ar pressure, when other parameters are kept constant. The highest green emission PL peak for the films is at 526 nm wavelength, attributed to 4f⁶5d¹ → 4f⁷ Eu²⁺ transitions. AFM images with well defined grains are observed on the films deposited at higher Ar pressures. The EDS and FTIR elemental composition analysis reveals that the films consist of elements and groups of SrAl₂O₄.*

Keywords: SrAl₂O₄:Eu²⁺, Dy³⁺, thin film, PL, AFM, SEM, FTIR, PLD

1. Introduction

The long afterglow strontium aluminate doped with europium and dysprosium (SrAl₂O₄:Eu²⁺, Dy³⁺) is among the highly studied phosphor as can be substantiated by a number of published works [1-6]. SrAl₂O₄:Eu²⁺, Dy³⁺ phosphor is preferably prepared in thin film forms due to the fact that thin film phosphors have several advantages over powders, such as higher lateral resolution from smaller grains, better thermal stability, reduced out gassing and better adhesion to solid substrates [7]. Among the techniques employed in preparing SrAl₂O₄:Eu²⁺, Dy³⁺, pulsed laser ablation has distinguished itself as the most reliable and versatile technique. This is in part due to the fact that laser interaction with reactive gases is relatively weak and the deposition pressure range is extremely large, therefore electrostatic problems such as those encountered with sputtering are avoided. Additionally, the techniques can be applied in the growth of meta-stable phases and artificial structures which are impossible to stabilize by conventional means of synthesis [8]. The ability to easily change the deposited material in situ is another unique advantage to PLD which has enabled the development of new materials, including meta-stable phases and artificial super lattices, as well as the fabrication of novel device structures [9].

The deposition atmosphere during the PLD process has a great influence to the properties of the pulsed laser ablated particles as reported elsewhere [1, 4]. Nsimama and his co-workers [1] compared the photoluminescent properties of pulsed ablated SrAl₂O₄:Eu²⁺, Dy³⁺ thin films deposited by using oxygen, argon and vacuum deposition atmospheres. The gas pressures were fixed at 0.34 Torr and other parameters were kept constant. The film with best luminescence properties was the one deposited in the argon atmosphere. It is of great interest to investigate the changes of SrAl₂O₄:Eu²⁺, Dy³⁺ properties with the argon pressure, so as to establish the optimum range of argon pressure for the best PL properties of SrAl₂O₄:Eu²⁺, Dy³⁺ thin films. That can

provide a wider understanding of the PLD process in the argon atmosphere. Nonetheless, there is limited literature on the influence of argon pressures on the properties of pulsed laser ablated SrAl₂O₄:Eu²⁺, Dy³⁺ thin films. Ali and his co-workers [5] reported on the pulsed laser deposited SrAl₂O₄:Eu²⁺, Dy³⁺, Nd³⁺ thin films and investigated on the argon pressure and substrate temperature influences on the photoluminescent properties of the films. Only small ranges of substrate temperature [100-300 oC] and argon pressures [10-30 mTorr] were considered and the laser fluency was 0.2 Jcm⁻². The highest PL emission was recorded by the film that was deposited at low temperature (100 oC) and intermediate argon pressure of 20 mTorr.

In the current work, the changes of SrAl₂O₄:Eu²⁺, Dy³⁺ PL properties with the argon pressure ranging from 0.2-0.9 Torr are reported. Other parameters were kept constant. The FTIR data for the brightest film is analyzed and discussed.

2. Materials and Methods

Silicon (100) wafer substrates were cleaned in an acetone for 5 min, in an ultrasonic water bath and then in methanol for the same time duration. Commercially available SrAl₂O₄:Eu²⁺, Dy³⁺ standard phosphor powders from phosphor technology (UK) were treated as reported elsewhere [1] before installing in the PLD system. The deposition chamber was pumped by a turbo molecular pump to a base pressure of 8 x 10⁻⁶ mbar before the system was backfilled with argon ambient gas (purity 99.99 %) with pressures of 0.2 Torr, 0.44 Torr and 0.9 Torr, while fixing other parameters. The Lambda Physic 248 nm excimer KrF laser was used to ablate the thin films. The number of pulses, laser fluency and repetition rate were fixed at 12000, 0.74 J cm⁻² and 8 Hz respectively. The substrate temperature and target-laser distance were fixed at 400 oC and 50 cm respectively. The ablated area was 1 cm² and the laser beam was focused using a 20 cm focal length quartz lens on a rotating target at 45 oC angle of incidence. A Shimadzu

Superscan SSX-550 system was used to collect the SEM data. AFM pictures were captured using Shimadzu SPM - 9600. The excitation source was from the Xenon lamp ($\lambda = 330$ nm) of the Cary Eclipse Fluorescence Spectrometer. The FTIR data was collected from SHIMADZU FTIR spectrometer.

3. Results and Discussion

3.1 AFM Results

The AFM images for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} thin films prepared at different argon pressures while keeping other parameters constant are shown in Figure 1. It is clear from the results that roughness of the films increased with the increase in the argon pressure. Films with larger and well defined particles were recorded by the films deposited at 0.9 Torr and the opposite was recorded by the sample deposited at the lowest argon pressure of 0.2 Torr.

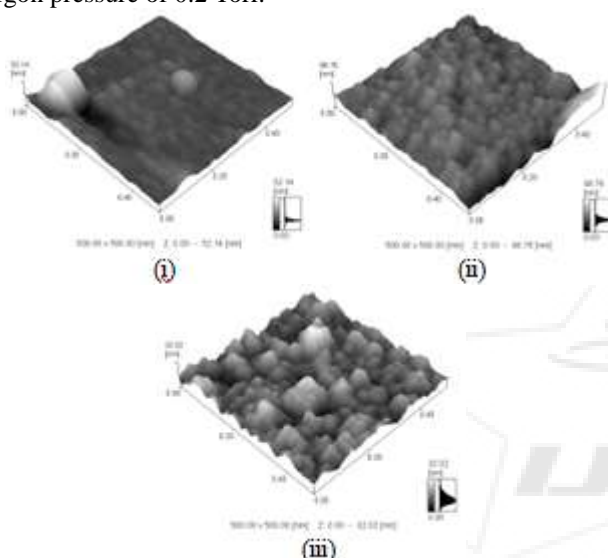


Figure 1: The AFM images for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} thin films deposited at (i) 0.2 Torr (ii) 0.44 Torr and (iii) 0.9 Torr while keeping all other parameters fixed.

Similar results were reported by Ali et al. [5], who studied the influence of argon pressure on laser ablated $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} thin films. The reason for this is that when the gas pressure in the chamber is low the mean free path (MFP) of the particles is longer hence yielding less effective collisions, whereas as the gas pressure increases the MFP decreases resulting in more effective collisions between the particles leading to nucleation and growth resulting in bigger particles [10,11]. The background gas of Ar has a higher mass density and therefore tends to reflect lighter atoms in the plume more, resulting into a film with big particles on the substrate [12].

3.2 The SEM Results

The SEM images with a unit micrometer scale for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} thin films deposited at different Ar pressures are shown in Figure 2. There is no significant difference among the images, except the presence of high density of spherical droplets on the surface of a film deposited at Ar pressure of 0.44 Torr. The re-sputtering of

atoms at the substrate surface due to high energetic atoms is the possible reason for the observed morphology.

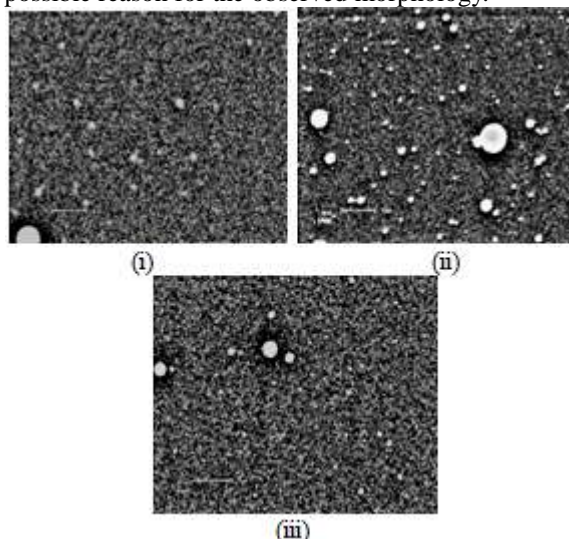


Figure 2: The AFM images for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} thin films deposited at (i) 0.2 Torr (ii) 0.44 Torr and (iii) 0.9 Torr while keeping all other parameters fixed.

3.3 The EDS Results

The EDS results for the thin films deposited at different argon pressures are shown in Figure 3. The prominent peak for all films was coming from the substrate (Si) as revealed in Figures 3 (i) and (ii). The Sr peaks were embedded on Si peaks as it shown in Figure 3 (ii) of the directly recorded EDS data for the optimum film. The in-set figure of Figure 3 (i) shows the variations of O and Al for the same films. The film that was deposited at highest argon pressure gave highest O composition. The compositions of Al were comparable for films deposited at 0.2 and 0.9 Torr, while the sample deposited at 0.44 Torr gave the highest Al compositions. It seems at such intermediate amount of Ar atoms favoured the reflections of Al atoms whose atomic mass (27 g) doesn't differ much with that of Ar (39 g). However, at higher Ar pressures, the lighter element, O is possibly reflected at higher rates and deposited on the substrate. The O composition increased three times as the Ar pressure was increased from 0.2 Torr to 0.9 Torr and the Al/O ratio variation with the Ar pressure shown in Figure 3 (iii) is basically brought by the changes in the O composition since the Al composition didn't vary much.

It is worth noting that the directly recorded EDS data for the sample deposited at highest Ar pressure, has some traces of C, possibly coming from the atmospheric contamination, since similar traces were reported in our previous results [1].

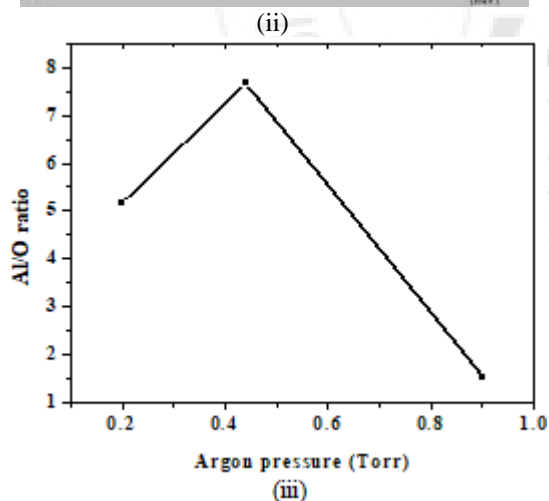
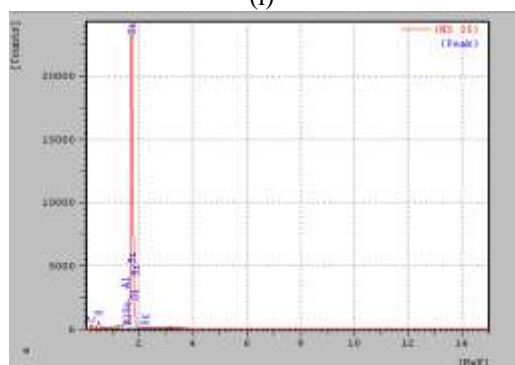
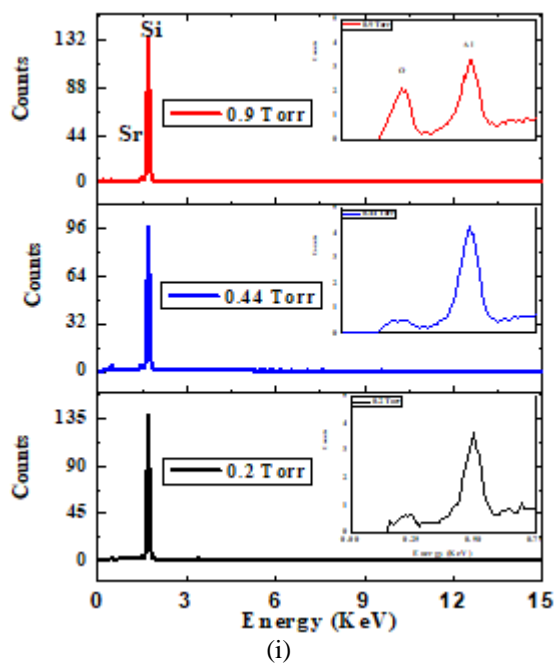


Figure 3: (i) The EDS results for SrAl₂O₄:Eu²⁺, Dy³⁺ films deposited at different argon pressures. The in-set graph is displaying the levels of Al and O in the deposited films. (ii) The variation of Argon pressures with the Al/O ratios for the three films

3.4 The Photoluminescence Results

The variation of room temperature PL intensity with the argon pressure is shown by Figure 4. All films gave a symmetrical green peak at 526 nm resulting from the 4f⁶5d¹ → 4f⁷ Eu²⁺ transitions luminescent center [13] with a prominent peak resulting from a film that was deposited at 0.9 Torr Ar pressure. The brightest film also has a small blue

peak at 448 nm, likely due to Eu²⁺ center activated by different crystallographic sites of SrAl₂O₄ crystal host as reported elsewhere [2] for lower temperature (200 K) laser ablated film. Apart from the peak at 526 nm, the film deposited at lower argon pressures of 4.4 Torr and 0.2 Torr had PL peaks at wavelengths 572 nm and 580 nm. The peak at 572 nm is likely coming from the characteristic emission of Dy³⁺ ion [14]. In general, there are two factors that influence the emission radiation of a phosphor. The first one is the strength of the crystal field at the sites of the luminescent ions, and the second is the degree of covalence (or coordination number) of these ions with the surrounding oxygen ions [15]. It is possible that the PL peak at 580 nm is arising from the degree of covalence of Dy³⁺ ions.

So, generally, the PL peaks are found to increase with the increase of Ar pressures. As a result, the film deposited at Ar pressure of 0.9 Torr gave the highest green intensity and the lowest intensity was recorded by the film that was deposited at 0.2 Torr Ar Pressure.

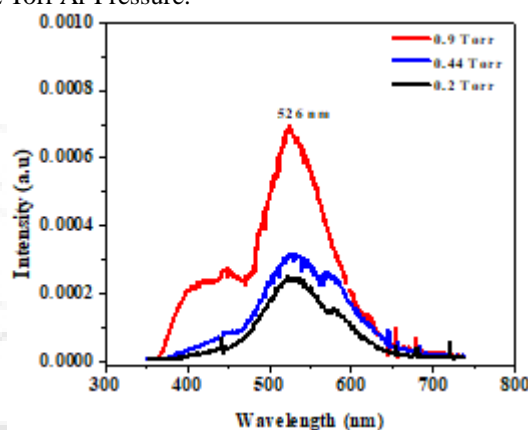


Figure 4: The PL properties of SrAl₂O₄:Eu²⁺, Dy³⁺ films ablated at different argon pressures, while fixing all other parameters.

The result from this work differs from the results reported elsewhere [10], who found best SrAl₂O₄:Eu²⁺, Dy³⁺, Nd³⁺-phosphor films at Ar pressure of 20 mTorr, which was the intermediate value in their work. The difference is possibly attributed to the differences in the laser fluency values for the two works and the introduction of Nd³⁺ rare earth dopant in their work. The laser fluency is one of the critical deposition parameters in PLD experiments. This is due to the fact that, the energy absorbed in the target material per unit surface area depends on the laser fluency implying that the ablation rate is a function of fluency [8]. The laser fluency for the current work is 0.74 Jcm⁻², while Ali et al. [5] work was 0.2 Jcm⁻². The results suggest a linear variation between the laser fluency and argon pressures for brightest laser ablated SrAl₂O₄:Eu²⁺, Dy³⁺ thin films. However, further studies on the effect of Ar pressure on SrAl₂O₄:Eu²⁺, Dy³⁺ thin films ought to be done to get more understanding of the scientific processes responsible for the differences.

3.5 The FTIR Results

The FTIR spectrum, for the brightest film, which was deposited at Ar pressure 0.9 Torr is shown in Figure 5. The bands on the range 350-1000 cm⁻¹ can all be assigned to

infra red active vibration modes of SrAl₂O₄ phosphor and associated with the vibrations of Al=O, Sr=O and Sr-O-Al bonds [17]. The band at 403 cm⁻¹ is due to a symmetric bond of O-Al-O, while the anti symmetric stretching bands range from 588-845 cm⁻¹ is due to the Sr-O vibrations, implying that the band at 836 cm⁻¹ is likely representing Sr-O. The band at 1454 cm⁻¹ is possibly due to C-O vibration band [18]. The carbon impurity was recorded in the EDS results (Figure 2) of the sample deposited at Ar pressure 0.9 Torr in Figure 3 (ii) above. There is also a peak at 1641 cm⁻¹ possibly coming from the C=O vibration [19]. The band located at about 3660 cm⁻¹ is from -OH group symmetric vibration [20] whose source is not yet clear. Regarding the FTIR peak at 2310 cm⁻¹, it is likely that it is representing the impurity from CH₃ group [20].

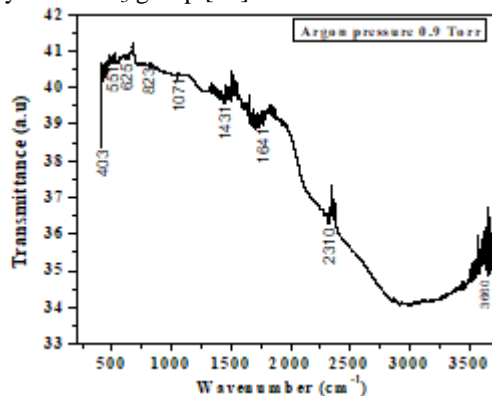


Figure 5: The FTIR result for a highly emitting laser ablated SrAl₂O₄:Eu²⁺, Dy³⁺ thin film deposited at Ar pressure of 0.9 Torr.

So, in general, the FTIR data proves that the sample reported in this work is a SrAl₂O₄ phosphor.

4. Conclusion

Pulsed laser ablated SrAl₂O₄:Eu²⁺, Dy³⁺ thin films have successfully been prepared and it evident that the argon pressure has a significant influence on the morphological and PL properties of the films. AFM images with well defined grains are observed on the films deposited at higher Ar pressures. The PL intensities of the films seem to vary proportionally with the Ar pressure, when other parameters are kept constant. The highest green emission PL peak for the films is at 526 nm and is attributed to 4f⁶5d¹ → 4f⁷ Eu²⁺ transitions. The EDS and FTIR elemental composition analysis reveals that that the films consist of elements and groups of SrAl₂O₄

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References

- [1] P.D. Nsimama, O.M. Ntwaeaborwa, H.C. Swart, "The effect of different gas atmospheres on luminescent properties of pulsed laser ablated SrAl₂O₄:Eu²⁺,Dy³⁺ thin films", *Journal of Luminescence*, (131), pp 119-125, 2011.
- [2] K. Sato, S. Komuro, T. Morikawa, H. Aizawa, T. Katsumata, S. Harako, X. Zhao, (2005), "Long afterglow characteristics of thin film phosphor fabricated by laser ablation" *Journal of Crystal Growth*, (275), pp e1137-e1141, 2005.
- [3] P.D. Nsimama, O.M. Ntwaeaborwa, E. Coetsee and H.C Swart, "The influence of the number of pulses on the morphological and photoluminescence properties of SrAl₂O₄:Eu²⁺,Dy³⁺ thin films prepared by pulsed laser deposition", *Physica B*, (404), pp 4489-4492, 2009.
- [4] P. D. Nsimama, "The influence of oxygen pressure on the Photoluminescent properties of pulsed laser ablated SrAl₂O₄:Eu²⁺,Dy³⁺ thin films", *American Journal of Optics and Photonics*, (4), pp 25-31, 2016.
- [5] A. H. Wako, F.B. Dejene, H.C Swart, "Structural and luminescence properties of SrAl₂O₄:Eu²⁺, Dy³⁺ phosphor thin films grown by pulsed laser deposition", *Physica B*, (480), pp 116-124, 2015.
- [6] Sang-Do Han et al. "Preparation and characterization of long persistence strontium aluminate phosphor", *J. of Luminescence*, (128), pp 301-305, 2008.
- [7] D.P. Norton, "Synthesis and properties of epitaxial electronic oxide thin film materials" *Materials Science Engineering R* (43), pp 139-247, 2004.
- [8] Jean-Francois Hamet and Bernard Mercey, "Laser ablation for the growth of materials" *Current Opinion in Solid State & Materials Science*, (3), pp 144-146, 1998.
- [9] Chun Zhao, C. Z. Zhao, M. Werner, S. Taylor, and P. R. Chalker, "Advanced CMOS Gate Stack: Present Research Progress", *ISRN Nanotechnology*, 2012, pp 1-35, 2012.
- [10] P.D. Nsimama, "The surface analysis and photoluminescence properties of SrAl₂O₄:Eu²⁺,Dy³⁺ thin films prepared by the pulsed laser deposition technique", *Tanzania Journal of Applied Science*, (2), pp 268-276, 2011.
- [11] H.C. Swart, O.M. Ntwaeaborwa, P.D. Nsimama, J.J. Terblans, "Surface characterization and luminescent properties of SrAl₂O₄:Eu²⁺,Dy³⁺ nano thin films", *Phys. B Condensed. Matter*, (407), pp 1660-1663, 2012.
- [12] S.T.S. Dlamini, H.C. Swart, J.J. Terblans, O.M. Ntwaeaborwa, "The effect of different gas atmospheres on the structure, morphology and photoluminescence properties of pulsed laser deposited Y₃(Al,Ga)₅O₁₂:Ce³⁺ nano thin films", *Solid State Science*, (23), pp 65-71, 2013.
- [13] Pooja Sharma, D. Haranath, Harish Chander, Sukhivir Singh, "Green chemistry-mediated synthesis of nanostructures of afterglow phosphor", *Applied Surface Science*, (254) pp 4052-4055, 2008.
- [14] Ishwar Prasad Sahu, D. P. Bisen, N. Brahme, Raunak Kumar Tamrakar, "Generation of white dysprosium-doped strontium aluminate phosphor by a solid-state reaction method", *Journal of. Electronic Materials*, (45), pp 2222-2232, 2016.

- [15] D. Haranath, Virendra Shanker, Harish Chander and Pooja Sharma, "Tuning of emission colours in strontium aluminate long persisting phosphor", *Journal of Physics D: Applied Physics*, 36, pp 2244-2248, 2003.
- [16] R. Eason (Editor), *Pulsed laser deposition of thin films, "Applications-led growth of functional materials"*, Hoboken, USA, Wiley Interscience, pp 3- 28, 2006.
- [17] S. Angappan, L.J. Bechermans, C.O. Augustin, "A sintering behaviour of $MgAl_2O_4$ - a prospective anode material", *Material Letters*. (58), pp 2283-2289, 2004.
- [18] H.G Ahalya, B. H. Doreswamy, B. M. Nagabhusana, "Synthesis and characterization of $SrAl_2O_4:Sm$ phosphor by low temperature synthesis", *International Journal of Research in Engineering and Technology*, (3), pp 553-557, 2014.
- [19] <https://webspectra.chem.ucla.edu/irtable.html>, Visited on 04th November 2017.
- [20] <https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/infrared/infrared.htm>, Visited on 04th November 2017.

Author Profile



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