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A study of photoluminescence and composition of amorphous As_2Se_3 films modified with Er (thd) $_3$ complex compound

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Photoluminescence and composition of amorphous As_2Se_3 films modified with an Er (thd) $_3$ complex compound have been studied. A band centered at 1.54 μm, characteristic of photoluminescence from Er embedded in amorphous matrices, has been revealed. The composition of thin amorphous As_2Se_3 films modified with an Er (thd) $_3$ complex compound has been examined by methods of nuclear microanalysis: Rutherford backscattering and nuclear resonant reactions. Dependences of the concentrations of Er ions, oxygen and carbon on the growth conditions of the films are obtained. It is shown that the Er concentration in a thin film nonlinearly grows as the relative concentration of the starting complex compound increases. In addition, the increase in the Er content of a film is accompanied by a simultaneous rise in the content of such light elements as oxygen and carbon. Comparison of nuclear microanalysis data and IR spectra demonstrates that, in the As_2Se_3 modification with the Er (thd) $_3$ complex compound, the nearest environment of Er in the complex compound is partly preserved.

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Keywords: As_2Se_3 films, Er $(thd)_3$ complex compound, Photoluminescence

1. Introduction

The interest in chalcogenide glassy semiconductors (ChGS) doped with rare-earth elements (REE) is determined by the possibility of their practical application in integrated fiber optics, medical IR lasers, etc. In the last decade, intensive research in this area has been conducted both abroad [1–5] and in Russia [6, 7]. This interest is based on the unique properties of ChGS: low phonon energies, high refractive index and transparence in the near- and mid-IR spectral ranges. These properties make ChGS a very good host for doping with REE from the standpoint of practical implementation of these devices. In particular, the absence of absorption bands associated with hydroxyl groups at 1.44 μm enables fabrication of a-As_2S_3: Er broadband amplifier operating in the 1.2–1.7 μm spectral range [4]. Bulk Ge –Ga–S glasses doped with Tm^{3+} / Ho^{3+}, which exhibit luminescence at a wavelength of 2.0 μm, are promising as materials for medical lasers [8].

A critical factor in the practical implementation of the above-mentioned devices is the choice of a host material (ChGS matrix), REE dopant, and its content (~1–2 at %) adequate to the goals to be achieved. Most of studies concerned with REE-doped ChGS have been performed with bulk ChGS produced by high-temperature synthesis (700–1000°C) in the course of 25 h [1, 3, 7, 9–11]. Among the wide variety of the existing ChGS, REE-doped As_2Se_3, As_2S_3, $As_{12}Ge_{33}Se_{55}$, and $Ge_{25}Ga_5S_{70}$ bulk glasses have been for the most part used as objects of study. In Ge–Ga–S glasses, such a deficiency as the low solubility of REE (< 0.4 wt %) can be eliminated, with the solubility brought to 2 wt % [10,11].

Er, Dy, and Pr have been used as REE dopants, with the photoluminescence (PL) from REE observed at room temperature [12,13]. The modern state of telecommunication technologies requires that various optical functions should be integrated in small-size devices, i.e., thin-film techniques are necessary. Recently, PL from REE has been observed in REE-doped ChGS and the possibility of fabrication of a planar optical amplifier has been demonstrated [2, 4]. In these studies, ChGS films were formed by thermal co-evaporation of ChGS and REE. However, deposition of thin REE-doped ChGS films by this widely used method leads to low REE doping concentrations because of the different evaporation rates of ChGS and REE atoms. Attempts have been made to introduce REE by ion implantation [4] and laser ablation [6]. It should be noted that both these techniques are rather expensive and have a number of shortcomings: implantation gives rise to defects whose removal requires additional thermal annealing, and laser sputtering cannot produce large-area films.

It has been shown previously that amorphous films of arsenic triselenide (As_2Se_3) can be doped with REE ions by modification with volatile complex compounds of REE (CC) and, in particular, with REE diethyldithiocarbamates Ln (ddtc) $_3$ and dipivaloylmerhanates Ln (thd) $_3$ (Ln = Pr, Nd, Eu, Sm) [14–16].

In this communication, we report on a study of amorphous arsenic triselenide (As_2Se_3) films modified with an Er (thd) $_3$ complex compound. The scientific novelty of our study consists in that the new doping technique we suggest overcomes the above-mentioned disadvantages of the thermal co-evaporation method. The originality of our approach is in that co deposition of an inorganic component (glass) and a complex compound with organic ligands, which have close evaporation points, is used for modification, and this opens up wide prospects for development of structures with unique and, in particular, luminescent properties.

2. Experimental

Films were deposited in a vacuum installation from two independent sources at a residual pressure in the chamber $p = 10^{-4}$ Pa and deposition rate of 2–3 nm/s. The temperature mode and time schedule were chosen so as to provide uniform films with reproducible compositions. We took as an input technological parameter the relative mass content of the complex compound (CC) taken for deposition:

$\omega = [CC]/[CC] + [glass]\ 100\%$

As the material of substrates served KDB-10 silicon (p-Si: B with a resistivity of 10 ohm × cm). The starting As_2Se_3 glass was synthesized by the standard method at T = 750°C from semiconductor-purity reagents. The complex compound Er (thd) $_3$ was synthesized and identified at the chemical department of Moscow State University.

In this study, we made quantitative determinations by nuclear microanalysis with the use of fast deuterons from an electrostatic accelerator: Rutherford backscattering spectroscopy (RBS) and nuclear resonant reactions (NRR). The elemental composition of the samples was determined by RBS of deuterons with energies $E_d = 0.9$ and 1.0 MeV and NRR with deuterons with $E_d = 1.0$ MeV at a scattering angle of 135°. Oxygen and carbon were determined using nuclear reactions with deuterons: $^{16}O(d, p)\,^{17O}$ and $^{12}C(d, p)\,^{13C}$.

In the method of nuclear reactions, the particle detector was protected from backscattered deuterons with an 11-μm-thick aluminum filter, which completely absorbed deuterons scattered by the target but passed protons produced in the nuclear reactions.

The application of nuclear physical methods to compositional analysis of materials, including semiconductors, was described in detail in [17]. It should be noted that the NRR method cannot be used to detect and evaluate the hydrogen content of the starting CC. IR spectra were measured on a FTIR-8400S Fourier spectrometer. A Hitachi TM-1000 scanning electron microscope (SEM) (15 kV, 15 mPa, 10000×, 30 nm) and Solver Pro-NT-MDT atomic-force microscope (AFM) (50×50×2.5 μm scanning field) were used to analyze the surface morphology of the films. PL spectra were measured at room temperature. The PL was excited with light of a halogen lamp, passed through an SZS-24 glass band-pass filter (0.3–0.8 μm). The power of light focused by a set of lenses onto a sample was the same in all the experiments (~50 mW). The PL was recorded using a monochromator with a resolution of 7 nm and an InGaAs photo detector working at room temperature. The light flux from the halogen lamp was modulated with a chopper (36 Hz). Photocurrent pulses from the detector were converted into an ac voltage recorded with a selective voltmeter.

3. Results and discussion

3.1. Composition and Structure of the Films

As mentioned above, Rutherford backscattering was used to determine the content of the heavy element erbium. Fig. 1 shows experimental spectra of deuterons scattered by thin As_2Se_3: Er films, measured at different relative mass contents ω (wt %): (1) 1.0, (2) 13.0, and (3) 23.1. The spectra show peaks of deuterons scattered by silicon (substrate), arsenic, selenium, and erbium. Because the atomic masses of arsenic and selenium are close (75 and 79, respectively) and light particles (deuterons) are used for RBS, the spectra of arsenic and selenium superimpose on each other. In other words, the energy resolution of the RBS with deuterons is insufficient for experimental determination of the As/Se atomic ratio, and the formula of the stoichiometric compound, As_2Se_3, was taken in our calculations.

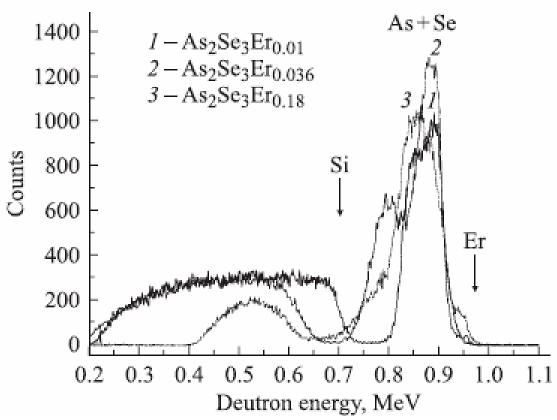

Fig. 1. Experimental spectra of deuterons scattered by As_2Se_3: Er thin films.ω (wt %): (1) 1.0, (2) 13.0, and (3) 23.1. Deuteron energy $E_d = 1$ MeV. Scattering angle 135°.

The content of light elements, oxygen and carbon, was found by the method of nuclear resonant reactions. Fig. 2 shows experimental spectra of protons produced in nuclear reactions for thin As_2Se_3: Er films with different relative mass contents ω (wt %): (1) 0.2 and (2) 1.0.

The measurements were made at a deuteron energy $E_d = 1$ MeV and a thickness of the absorbing aluminum filter on the detector of 11 μm.

As can be seen from Fig. 2, peaks of reactions on oxygen and carbon are observed. The results of these measurements made it possible to determine the composition of the films under study (see table). It should be noted that the last sample in the table is a film deposited by thermal evaporation of Er (thd) $_3$ (without As_3Se_3) onto a crystalline silicon substrate.

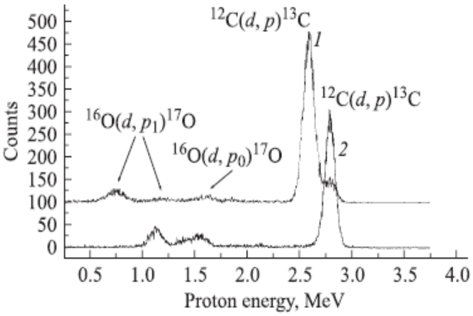

Fig. 2. Experimental spectra of protons, products of nuclear reactions, for thin As_2Se_3: Er films.ω (wt %): (1) 0.2 and (2) 1.0.Deuteron energy E_d = 1 MeV. Thickness of the absorbing aluminum filter on the detector 11 μm.

Table 1. Elemental composition of thin amorphous As_2Se_3: Er films

Film	Thickness t, μm	ω, wt %	Composition
As_2Se_3	0.5		As_2Se_3
As_2Se_3: Er (*thd*) $_3$	2.3	0.2	As_2Se_3: (Er $_{0.012\pm 0.004}$ O $_{0.4\pm 0.2}$ C $_{0.5\pm 0.1}$)
As_2Se_3: Er (*thd*) $_3$	1.1	1.0	As_2Se_3: (Er $_{0.010\pm 0.003}$ O $_{0.3\pm 0.1}$ C $_{0.6\pm 0.1}$)
As_2Se_3: Er (*thd*) $_3$	0.44	13.0	As_2Se_3:(Er $_{0.036\pm 006}$ O $_{0.9\pm 0.1}$ C $_{1.1\pm 0.1}$)
As_2Se_3: Er (*thd*) $_3$	0.65	23.1	As_2Se_3: (Er $_{0.18\pm 0.02}$ O $_{3.2\pm 0.4}$ C $_{3.9\pm 0.4}$)
As_2Se_3: Er (*thd*) $_3$	0.3	33.3	As_2Se_3: (Er $_{0.09\pm 0.01}$ O $_{1.9\pm 0.2}$ C $_{7.0\pm 1}$)
Er (*thd*) $_3$	0.3	100	($Er_1O_5C_{16}$)

The concentrations obtained were used to plot the dependence of the content of Er, O, and C for modified thin films on the relative mass content of Er. These results are presented in Fig. 3. It can be seen that the content of the REE in the thin film nonlinearly grows as the relative content of the starting complex compound increases. In addition, the increase in the REE content of the film is accompanied by a simultaneous rise in the content of such light elements as carbon and oxygen. The compositional analysis suggests that oxygen, carbon, and, probably, hydrogen are present in the local environment of REE in a ChGS film. The same figure shows the dependence for a thermally evaporated Er (thd) $_3$ film. An analysis of the chemical composition of this film demonstrated that oxygen and carbon remain in the Er environment, but the methyl groups CH_3 present in the starting complex compound are split-off.

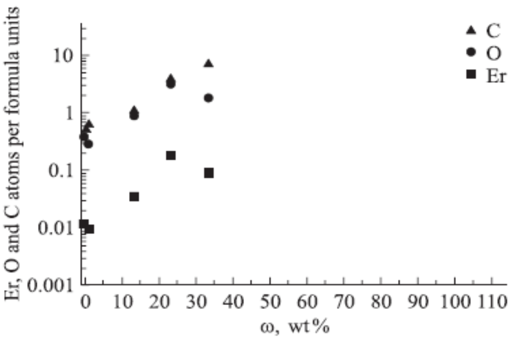

Fig. 3. Er, O, and C content of As_3Se_3: Er films vs. ω.

However, the ratio of the oxygen and carbon contents to erbium ion is somewhat smaller than the same ratio in the starting Er (thd) 3. The structure of Er (thd) $_3$ CC used for modification is constituted by the central Er ion coordinated to six oxygen atoms of the chelate ligands and contains

Er – O, C–O, C (sp^2) –C (sp^2), C (sp^2) –C (sp^3) bonds and C–H bonds at methyl carbons [18]. Of interest was an IR spectroscopic study of the films we obtained, because it is known that stretching vibrations of these bonds give rise to a set of bands in IR spectra [19]. The measurements were made at room temperature. The results obtained are presented in Fig. 4.

It can be seen in Fig. 4 that the spectra of the initial unmodified As_2Se_3 films (spectra 1) contain bands of various intensities at 609, 739, 1108, 2350, and 3700 cm^{-1}. According to the data of [20,21], these bands are due to stretching vibrations of the As–Se bond and deformation vibrations of the As–Se–As bond, to arsenic oxide As_2O_3 present in the starting glass, and to carbon oxide and water dissolved in the starting glass. Additional, compared with those in the starting composition, bands appear in films upon their modification (spectra 2, 3), which can be attributed to hydroxyl groups OH, C–O bonds (strong bands at 1600 cm^{-1}), and C–H bonds [2854 cm^{-1} (sp^3 $CH_{2\ sym}$), 2923 cm^{-1} (sp^3 $CH_{2\ asym}$), and 2954 cm^{-1} (sp^3 $CH_{3\ asym}$)] [16]. It should also be noted that lines at 418–420, 456, and 472–474 cm^{-1} are observed. It is known that bands at 400–500 cm^{-1} are characteristic of metal – oxygen bonds in coordination compounds of the given type [19] and the results of a nuclear microanalysis unambiguously indicate that both REE and oxygen are incorporated into the amorphous matrix. Therefore, these bands can be attributed to stretching vibrations of the Er–O bond in the amorphous matrix. This result confirms the previous assumption [14] that, with the modification method described above, the local environment of REE is mostly preserved upon its incorporation into the amorphous matrix of arsenic chalcogenides. At present, it cannot be concluded with certainty whether this result is a consequence of the properties of the amorphous matrix of arsenic chalcogenides by itself or it is predetermined by the method used to fabricate thin films.

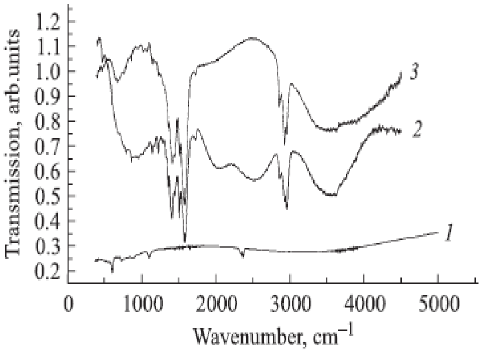

Fig.4. IR spectra of films: (1) initial undoped As_2Se_3, (2) As_2Se_3: Er (ω = 33.3 wt %), and (3) Er (thd) $_3$.

SEM and AFM studies of the surface of the films demonstrated that unmodified As_2Se_3 films have a smooth surface with an average size of irregularities (roughness) of 3–5 nm. The surface of the films has the form of hillocks with base diameter of several tens of nanometers to a hundred of nanometers. The modified films also have a smooth surface; however, the size of irregularities exceeds that in unmodified As_2Se_3 films. SEM and AFM surface topographs of the As_2Se_3: Er film (3D images) are shown in Figs. 5a and 5b. This result indicates that chemical modification with complex compounds can modify the surface of a film on the nanoscale level, and this may be due to presence of intermediate structures (possibly, agglomerates or clusters) in the amorphous matrix.

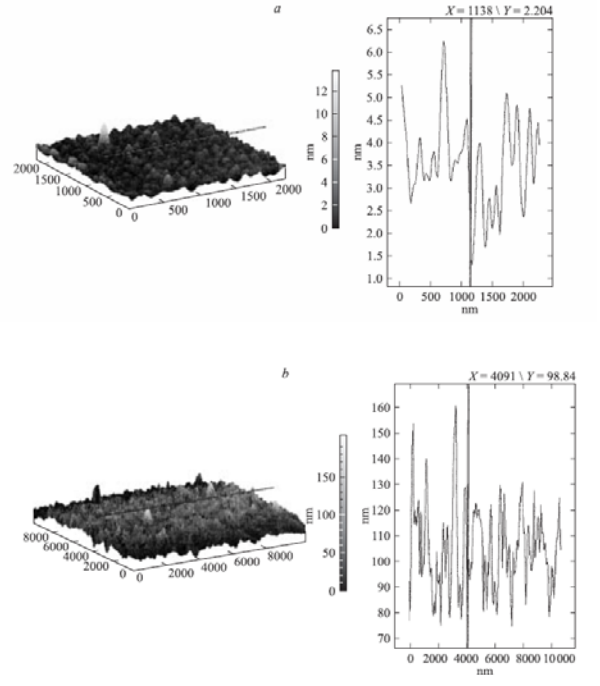

Fig. 5. (a) 3D AFM image of an unmodified As_2Se_3 film and its SEM micrograph; (b) 3D AFM image of a modified As_2Se_3: Er (ω = 13.0 wt %) film and its SEM micrograph.

3.2. Photoluminescence

We carried out PL measurements at room temperature with thin films of the As_2Se_3 chalcogenide glassy semiconductor, both doped via modification with complex compounds of a rare-earth element erbium and undoped. The PL spectra obtained are shown in Fig. 6.

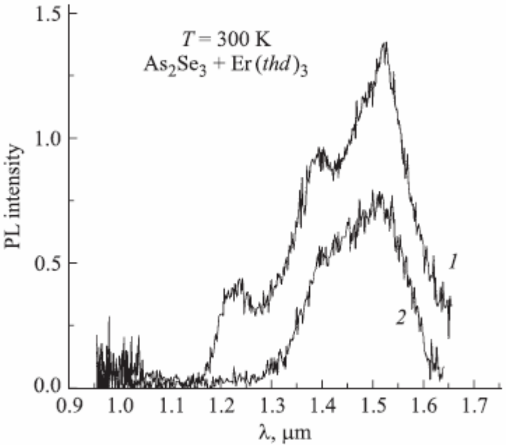

Fig. 6. PL spectra of As_2Se_3: Er films at T = 300 K. ω (wt %): (1) 1.0 and (2) 23.1.

The PL spectra of Er-doped films show a PL band at 1.54 μm, characteristic of PL from ER in an amorphous host (Fig. 6). It should be noted that the band at 1.54 μm is not found for the initial As_2Se_3 films (undoped with REE CC) at room temperature. The fact that this band is observed both in films deposited onto a glass substrate and in those formed on a crystalline Si substrate suggests that it is related to erbium, rather than being associated with defects in the crystalline Si substrate. The Er-related PL band is comparatively broad (full width at half-maximum, FWHM ≈ 0.1 eV), which may be due to a nonuniformity of the local environment of Er introduced into the composition of the complex compound. It is known that the intrinsic PL spectrum of As_2Se_3 is a broadened peak with a FWHM of several tenths of an electron volt, centered at an energy that is considerably lower than the optical band gap ($1/2E_g^{opt} \approx 0.88$ eV). The intensity of the intrinsic PL is strongly temperature dependent: it decreases by several orders of magnitude as we go from liquid-nitrogen temperature to room temperature. A model has been suggested by Street, Mott, and Davis for describing the mechanism of the intrinsic PL [22]. This model assumes that native defects of the host are involved in the intrinsic PL. It should be noted that the intrinsic PL band of As_2Se_3, associated with transitions between defect states, is commonly not observed at room temperature.

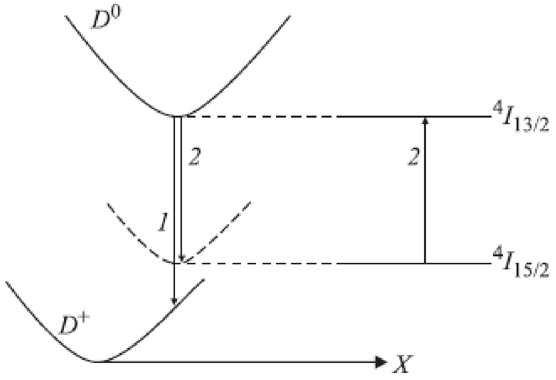

Fig. 7. Configuration diagram for D^0 – e → D^+ transitions: (1) radiative transition responsible for the intrinsic PL in ChGS and (2) Auger transition responsible for the excitation of the erbium ion.

One of the key issues in the PL study is that of excitation of erbium ions. According to [23], erbium ions in a-Si: H (Er) are excited via an Auger process in which an electron from the conduction band is captured by a neutral defect, a dangling bond D ^{0}, to give a D^- state. The transition energy is imparted via Coulomb interaction to the inner 4f-shell of the erbium ion, with this ion transferred from the ground state $^4I_{15/2}$ to the first excited state $^4I_{13/2}$. The efficiency of this process is due to the closeness of the $D^0 + e \rightarrow D^-$ transition energy to that of erbium oxidation. In our case, we can suggest a similar mechanism for Er-doped As_2Se_3. For a qualitative description of the excitation mechanism of Er ions, we use the model suggested by Street, Mott, and Davis [22]. Fig. 7 shows a configuration diagram used in this model to describe the intrinsic PL band in undoped As_2Se_3. The difference from the interpretation used in [23] consists in the following. In ChGS, one of the main states of defects is the D^+ state, and both the radiative and Auger transitions occur by the scheme $D^0 - e \rightarrow D^+$. It is important to note that the energy of the optical transition associated with the intrinsic PL band (0.88 eV, radiative transition 1) is close to that of transition from the ground state $^4I_{15/2}$ of the erbium ion to the first excited state $^4I_{13/2}$ (~0.8 eV). This suggests that the Auger process in which the energy of the $D^0 - e \rightarrow D^+$ transition nearly resonantly excites the erbium ion and transfers it from the ground state $^4I_{15/2}$ to the $^4I_{13/2}$ state (Auger transition 2 in Fig. 7) will occur with a higher probability. A minor disagreement between the energies can be easily compensated for by local phonons [23].

The conclusion that the PL band under discussion is associated with the mechanism we suggest is also confirmed by the FWHM of the PL line, equal to 0.1 eV. It is approximately 4–5 times the FWHM of the corresponding PL line of erbium in a-Si: H (Er), which points to a strong interaction of the electron shell of erbium with the neighboring atoms in the case of As_2Se_3: Er. At the same time, it is considerably lower than the FWHM of the intrinsic PL band in undoped As_2Se_3 (equal to 0.33 eV at low temperature), which does allow us to identify it as a band of PL from erbium. To confirm this interpretation, it is necessary to measure both intrinsic and Er-related PL at low temperatures.

4. Conclusion

The photoluminescence and composition of amorphous As_2Se_3 films modified with a complex compound Er (thd) $_3$ were studied. A photoluminescence band at 1.54 μm, characteristic of photoluminescence from Er embedded in amorphous materials, was observed at room temperature. Methods of nuclear microanalysis, Rutherford backscattering and nuclear resonant reactions, were used to study the composition of amorphous As_2Se_3 films modified with the complex compound Er (thd) $_3$. The concentration dependences of the content of ER ions, oxygen, and carbon in the films obtained were determined. It was shown that the content of Er in a thin film nonlinearly grows as the relative content of the starting complex compound increases. In addition, the increase in the ER content is accompanied by a simultaneous rise in the content of such light elements as carbon and oxygen. Also, the thin films were studied by IR spectroscopy. Comparison of the results of a nuclear microanalysis and IR spectra suggests that, with As_2Se_3 modified with the complex compound Er (thd) $_3$, the local environment of Er in the complex compound is partly preserved.

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