LOCAL STRUCTURE AND OPTICAL PROPERTIES OF HALIDE-TELLURITE GLASSES DOPED WITH RARE EARTH ELEMENTS

LOKÁLNA ŠTRUKTÚRA A OPTICKÉ VLASTNOSTI HALOGENIDO-TELURIČITÝCH SKIEL DOPOVANÝCH PRVKAMI VZÁCNYCH ZEMÍN

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Abstract

Tellurite glasses, $70TeO_2$•$30PbCl_2$ (7T3P), were prepared in Au and Pt crucibles. Pr^{3+} ions were added in different chemical forms (metals, chlorides, oxides), in concentrations of 500 – 1500 wt-ppm. Photoluminescence (450-700 nm) and Raman spectra (150-3000 cm^{-1}) were measured at room temperature. In the range of 640-700 nm, six photoluminescence (PL) peaks were observed, at 641.5, 647.1, 652.4, 660.8, 662.9, and 664.5 nm, both in "pure" and doped glasses. In the range of 200 – 1200 cm^{-1}, seven Raman scattering (RS) peaks were observed, at 184, 217, 321, 468, 654, 735 cm^{-1}, and a small peak at 650 cm^{-1}. Both spectra were deconvoluted using symmetrical Gaussian functions. Energies, amplitudes and half-widths of band maximums were free parameters. Relative intensities of PL bands and RS ones depend on the concentration of Pr^{3+} and on the material of the crucible.

Teluričité sklá $70TeO_2$•$30PbCl_2$ (7T3P) boli pripravené v zlatom (Au) a platinovom (Pt) kelímku. Ióny Pr^{3+} boli pridávané v rôznych chemických formách (kov, chlorid, oxid) v koncentrácii 500 – 1500 wt-ppm. Skúmala sa fotoluminiscencia (450 – 700 nm) a Ramanove spektrum (150 – 3000 cm^{-1}) pri izbovej teplote. V rozsahu 640-700 nm bolo spozorovaných šesť fotoluminiscenčných (PL) píkov pri 641.5, 647.1, 652.4, 660.8, 662.9 a 664.5 nm pre "čisté" aj dopované sklá. V rozsahu 200 – 1200 cm^{-1} bolo spozorovaných sedem píkov Ramanovho rozptylu (RS) pri 184, 217, 321, 468, 654, 735 a pri 650 cm^{-1}. Obe spektrá boli rozložené použitím symetrických Gaussových funkcií, kde voľné parametre boli energia, amplitúda a pološírka. Relatívna intenzita PL a RS píkov závisela na koncentrácii Pr^{3+} a materiáli kelímku.

Key words

photoluminescence (PL), Raman spectra (RS), crucible, Gaussian deconvolution of PL and RS spectra

fotoluminiscencia, Ramanove spektrum, kelímok, gaussovský rozklad Ramanovych a fotoluminiscenčných spektier.

1. Introduction

Tellurite glasses have a great scientific and technological interest. Their most important advantages are:

- wide transmission range (≈400 nm to 6 μm),

- lack of toxicity, good glass stability and strength, good corrosion or moisture resistance,
- low phonon energy (≤ 800 cm^{-1}), high density (≈5.5 g/cm^3),
- high refractive index (≈2).

The glasses can be used in optical components (windows, prisms, laser glasses) or in fiber optics communications [1, 2].

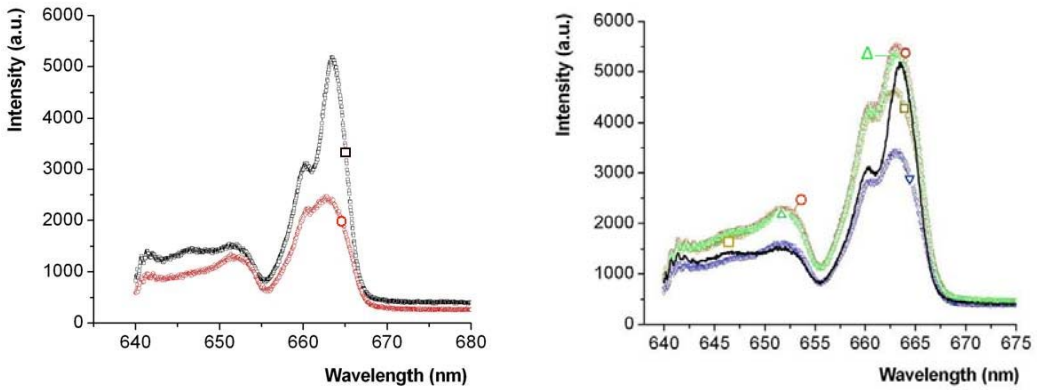
The aim of this work is to present the photoluminescence and Raman spectra of halide-tellurite glasses, $70TeO_2 \cdot 30PbCl_2$, doped with Pr^{3+} ions in various concentrations and chemical forms, which are prepared in Pt or Au crucibles. The aim of this work was focused on microstructure and optical properties of glasses.

2. Experimental details

Samples were prepared using the method of a „divided ampoule“ [3, 4]. They were doped with praseodymium (0 - 1500 wt-ppm), which was added as metal (Pr), chloride ($PrCl_3$) or oxide (Pr_2O_3). Samples prepared in Pt and Au crucibles were orange or yellowish, respectively. Photoluminescence and Raman spectra were measured at room temperature. Photoluminescence (450-700 nm) and Raman (150-3000 cm^{-1}) spectra were measured using Raman spectrometer, Dilor-Jobin Yvon-Spex, type LabRam. He-Ne laser (632.8 nm) was used as the excitation source.

3. Results and discussion

Influence of the crucible on the PL spectrum of 7T3P glasses is shown in Fig. 1 a. Influence of the Pr^{3+} concentration (in a metallic form) on the PL spectrum is in Fig. 1 b. The influence of a chemical form of Pr^{3+} on the PL spectra is shown in Fig 2. The experimental dependences were fitted by a sum of symmetrical Gaussian distributions (Fig.3 a,b, Fig. 4 a, b). Energies of band maximums, amplitudes and half-widths were free parameters. In the range of 640-700 nm, six PL peaks, centered at 641.5(1), 647.1(4), 652.4(1), 660.8(2), 662.7(4), 664.5(2) nm were observed. Relative intensities of these bands depended on the chemical form, concentration of Pr^{3+}, and material of the crucible.



a/ **b/**

Fig. 1. *Photoluminescence spectra of 7T3P glasses a)"pure" glasses, prepared in Pt (□□□, black) or Au (○○○, red) crucibles; b) prepared in Pt crucibles, doped with Pr in a metallic form (500 wt-ppm, □□□ (brown), 800 wt-ppm, ○○○ (red), 1000 wt-ppm, ΔΔΔ (green), 1500 wt-ppm, ∇∇∇ (blue), "pure" - full line)*

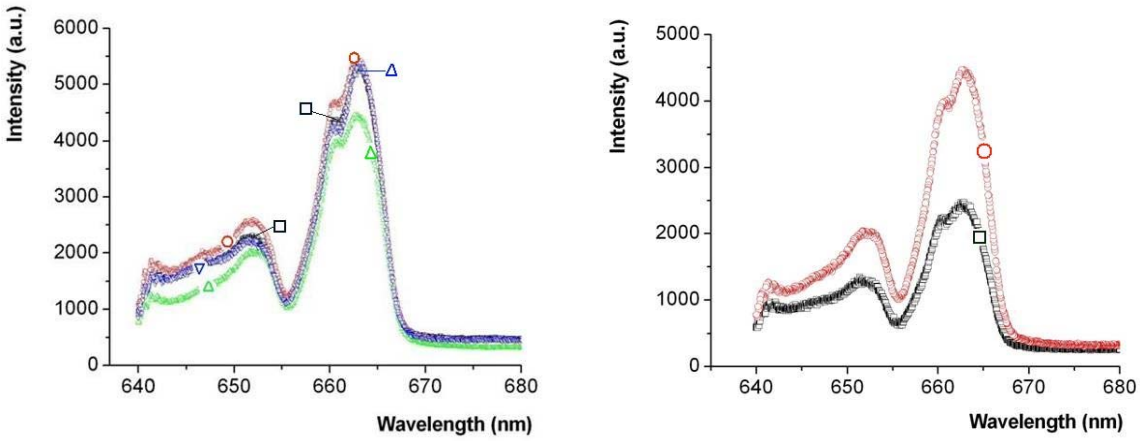


Fig. 2. *Influence of the chemical form of Pr on the PL spectra of 7T3P glasses prepared in a/ Pt crucibles (1000 wt-ppm Pr_2O_3, □□□ (black), 1000 wt-ppm $PrCl_3$, ○○○ (red), 1000 wt-ppm Pr, ∇∇∇ (blue), and in an Au crucible (1000 wt-ppm $PrCl_3$, ΔΔΔ (green),) b/ Au crucibles ("pure", □□□ (black), 1000 wt-ppm $PrCl_3$, ○○○ (red))*

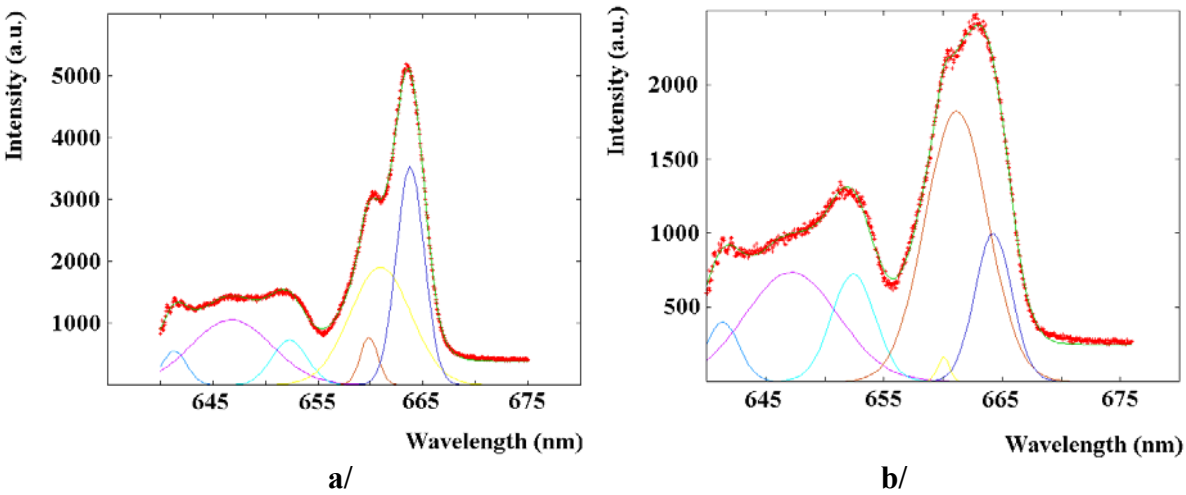


Fig. 3. *Deconvolution of PL spectra in undoped 7T3P glasses prepared in a/ Pt, b/ Au crucibles*

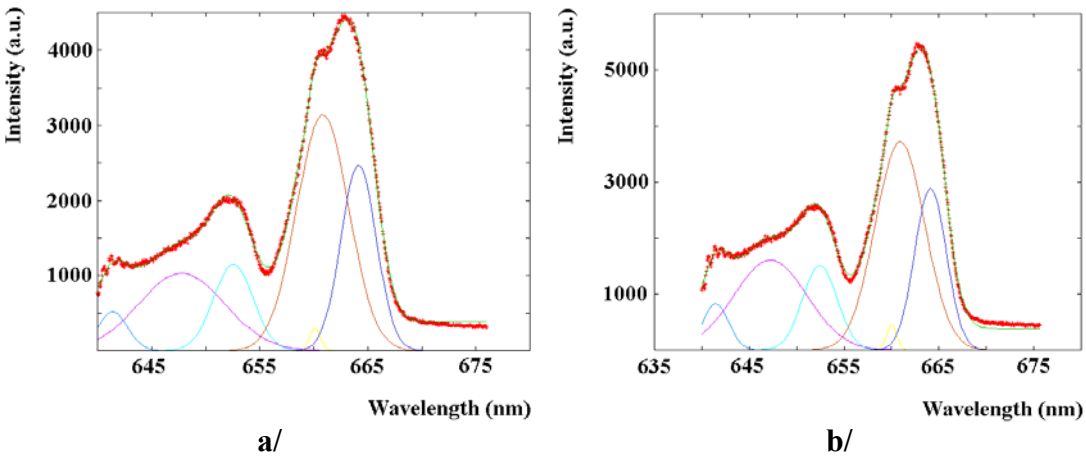


Fig. 4. *Deconvolution of PL spectra in 7T3P glasses doped with 1000 wt-ppm $PrCl_3$, prepared in a/ Au, and b/ Pt crucibles*

In figs. 5 and 6, Raman spectra of the T7P3 glasses are presented. Experimental dependences were fitted by a sum of Gaussian bands. Six Gaussian bands, centered at 184(2), 217(7), 321(2), 468(2), 654(9), 735(5) and 650 cm^{-1}, were determined (Fig. 7 a,b,). In the range of 350 - 900 cm^{-1}, the spectra are similar to those of pure and binary TeO_2 glasses [10-12]. The structural unit making up TeO_2 glass is an asymmetrical [TeO_4] trigonal bipyramid (tbp) in which one of the equatorial sites is occupied by a lone pair of electrons. Upon inclusion of modifiers or intermediates, the coordination state of Te changes from TeO_4 trigonal bipyramids (tbp) by means of an intermediary [TeO_{3+1}] polyhedron to [TeO_3] trigonal pyramids (tp), and concentration of non-bridging oxygen increases [13]. Peaks at 735 and 654 cm^{-1} are attributed to stretching vibrations of TeO_3 trigonal pyramids (tp) or those of TeO_4 trigonal bipyramids (tbp), respectively. The small peak at 650 cm^{-1} probably comes from

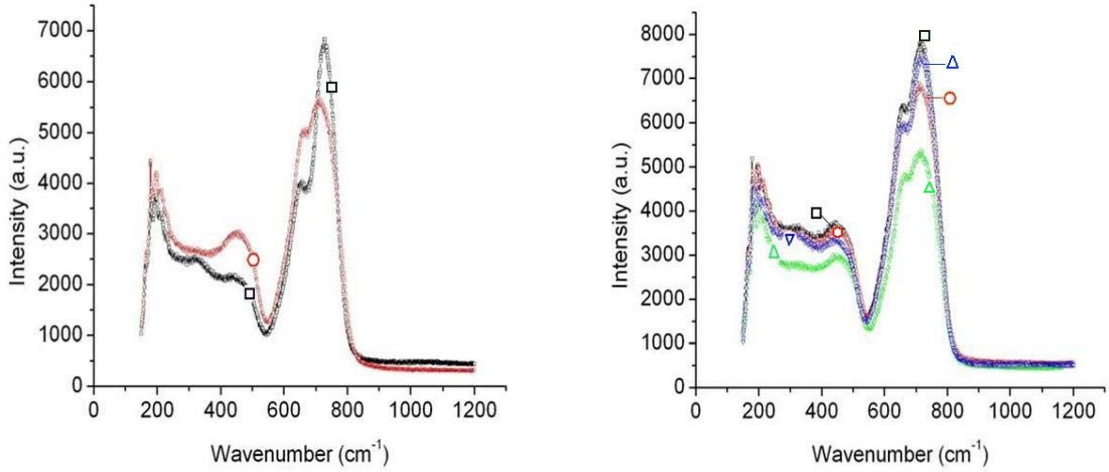


Fig. 5. *Raman spectrum of 7T3P glasses, a) "pure" glasses, prepared in a Pt (□□□, black) or Au (○○○, red) crucible, b) doped with 1000 ppm Pr_2O_3 (□□□, black), 1000 ppm $PrCl_3$ (○○○, red), 1000 ppm Pr (∇∇∇,* blue*), prepared in Pt crucibles, and 1000 ppm $PrCl_3$ (ΔΔΔ, green), prepared in Au crucibles*

intermediate TeO_{3+1} polyheders. Its intensity increases significantly in "pure" glasses prepared in Pt crucibles. These three structural units are connected each other with their corners into linear or ring chains. The peak at 468 cm^{-1} is assigned to bending vibrations of Te-O-Te [9-16]. Pb^{2+} increases the number of non-bridging oxygens [17,18]. The peak at 322 cm^{-1} can be probably assigned to Pb-Cl vibrations. Relative intensities of the peaks depend on doping and on the material of the crucible. In glasses prepared in gold crucibles, the peak at 468 cm^{-1} is more pronounced than that in glasses prepared in Pt crucibles. It indicates a better connectivity of the glass network. Also the tbp (654 cm^{-1}) peak is more pronounced, in comparison to the tp (735 cm^{-1}) peak, in glasses prepared in gold crucibles. It seems that presence of PbCl2, in "pure" glasses prepared from Pt crucibles, increases the number of TeO3 structural units and decreases the number of Te-O-Te linkages [20].

Glasses prepared in Pt crucibles and doped with various concentrations and forms of Pr3+ increases intensities of peak at 468 cm-1 and 654 cm-1. Spectra of doped glasses prepared in different crucibles are more similar one another than spectra of "pure" glasses. It seems that reactions with crucibles and a fast diffusion of Au into the glass result in serious structural changes in tellurite polyhedrons. The influence of Pr^{3+} and Au^{+} on the structure of glasses is similar [16].

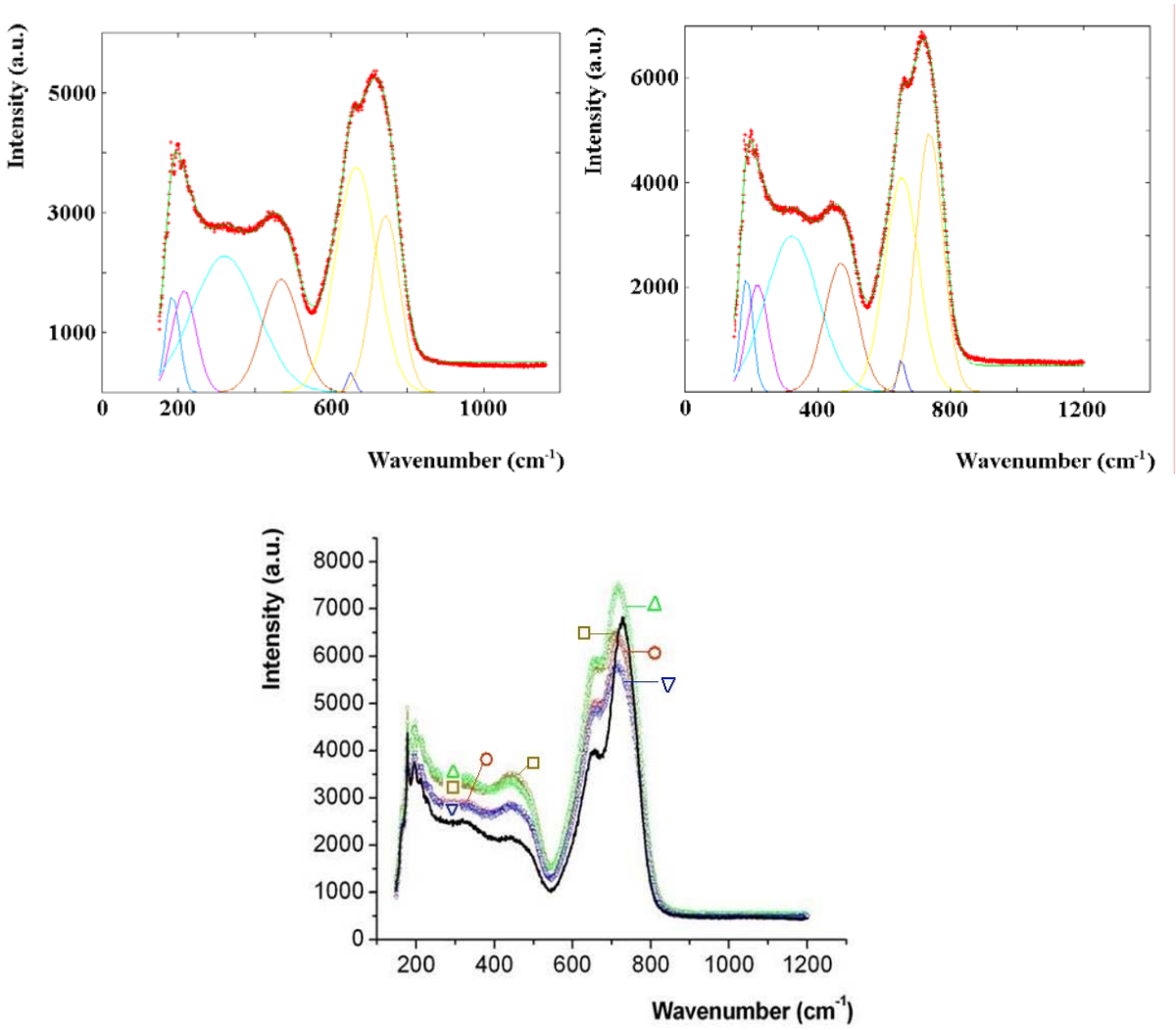
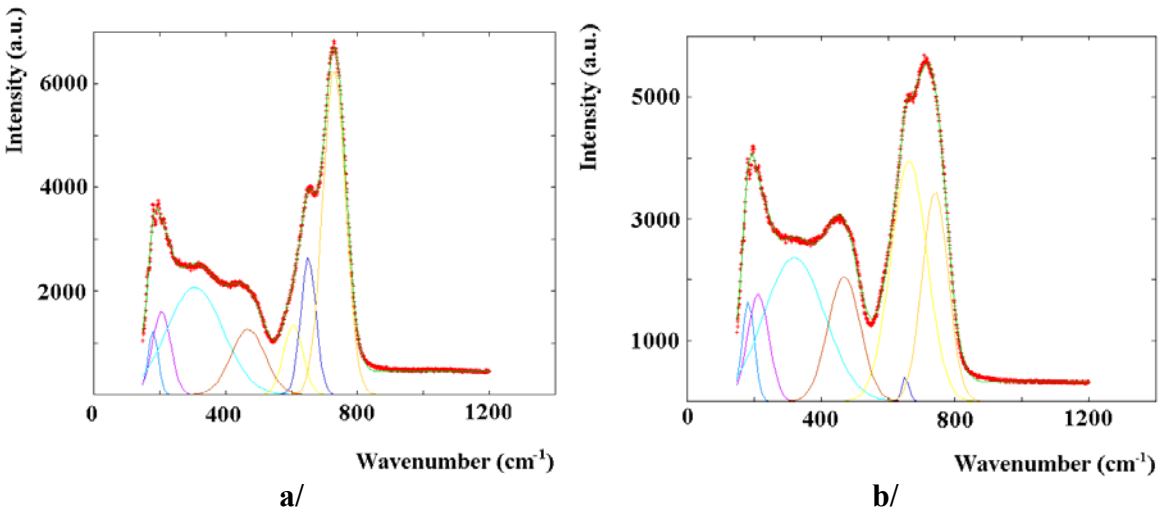


Fig. 6. *Raman spectra of 7T3P glasses, prepared in Pt crucibles, doped with metallic Pr (500 wt-ppm (□□□, brown), 800 wt-ppm (○○○, red), 1000 wt-ppm, (ΔΔΔ, green), 1500 wt-ppm, (∇∇∇, blue), "pure" glass (full black line))*



a/ **b/**

Fig. 7. *Deconvolution of Raman spectra in undoped tellurite glasses (70 TeO_2·30$PbCl_2$) prepared in a/ Pt, b/ Au crucibles.*

4. Conclusions

Doping with rare earth elements and reactions with crucibles result in serious changes in tellurite polyhedrons. Influence of Pr^{3+} and Au^{+} admixtures on the glass structure is similar. In the range of 600-700 nm, six PL peaks, centered at 641.5(1), 647.1(4), 652.4(1), 660.8(2), 662.7(4), 664.5(2) nm, were observed, both in pure and doped glasses. Relative intensities of these peaks depend on the concentration of Pr and on the material of the crucible. In the range of 200 – 1200 cm^{-1}, seven Raman bands, centered at 184(2), 217(7), 321(2), 468(2), 654(9), 735(5) and 650 cm^{-1}, were determined. Three peaks at higher frequencies are assigned to vibrations of TeO_4 or TeO_3 polyhedrons, and Te-$_{eq}O_{ax}$-Te linkages. The peak at 322 cm^{-1} can be probably assigned to Pb-Cl vibrations. Influences of Pr^{3+} and Au^{+} on the glass structure are similar. Relative intensities of both PL and RS peaks depend on the concentration of Pr and on the material of the crucible.

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