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## Synthesis of boron carbon nitride oxide (BCNO) from urea and boric acid

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### ABSTRACT

A solid state synthesis of boron carbon nitride oxide (BCNO) material was carried out starting from urea and boric acid treated at 600°C. The X-ray diffraction pattern corresponded to amorphous BCNO with an interlayer distance of 3.49 Å. The material had a layered structure similar to that of graphite and hexagonal boron nitride (h-BN). Infrared spectroscopy (IR) showed bands which were similar to those typical of BN and carbon nitride. The presence of boron was also confirmed by energy dispersive spectroscopy in an amount compatible with the IR spectrum. The spectra obtained by X-ray photoelectron spectroscopy (XPS) corresponded to those of a BCNO family with a considerable content of oxygen too. The optical band gap was estimated to be 3.22 eV, typical of a wide band-gap semiconductor. The particle size was very dispersed from micro to nanosize. The material dispersed in polar solvents formed stable suspensions due to the presence of hydroxyl groups.

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boron carbon nitride oxide; semiconductor; boron nitride; carbon nitride; carbon materials

### Introduction

The synthesis of boron nitride (BN) and polymeric (also known as graphitic) carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) have been objects of many efforts in order to synthesize a new family of materials (e.g., 1–3), whose properties seem to be ideal for applications in many fields, such as chemical sensors, nano-transistors, flame retardants, and photocatalysts for reactions, such as Friedel-Crafts, water splitting, etc. (1–4). The simultaneous doping of carbon structures, such as graphene, with boron and nitrogen (5, 6) have been regarded with interest because of the new properties that can arise by means of the introduction of these two elements, which are located in groups III and V of the periodic table, respectively, just before and after carbon.

According to McMillan et al. (7), and Lotsch et al. (8), graphitic (polymeric) carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) can be synthesized by utilizing several different reagents: either melamine (C<sub>3</sub>N<sub>6</sub>H<sub>6</sub>) or a combination of melamine with other triazine, such as cyanuric chloride (C<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub>), respectively. Niu et al. (9), Zheng et al. (10), and Zhang et al. (4) employed diaminomaleonitrile (DMNA) and dicyandiamide (DCDA) at temperatures around 600°C. In addition, Dante et al. have synthesized carbon nitride using melamine cyanurate (3, 11, 12), and mixing melamine with uric acid (2). The range of temperatures used for the reaction process was between 450 and 700°C.

Hexagonal boron nitride (h-BN) is a compound whose properties can be useful for several applications, including an

effective adsorbent for metals ions (13), a white solid lubricant as an alternative to the black graphite, and in high power semiconductor devices. Bonizzi et al. (1) deposited thin films of cubic boron nitride (c-BN) on Si wafers in order to analyze its effect on nanohardness and electronic properties. In addition, Li et al. have employed porous h-BN because of its structural defects, low density, chemical durability, oxidation resistance to quantify its interaction with organic pollutants (tetracycline, methyl orange and congo red) and metal ions (Cr<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>) (13). The results reported by Li showed that h-BN is effective as an adsorbent of metal ions and organic molecules. Moreover, the quasi-direct band-gap energy of h-BN was determined as 5.96 ± 0.04 eV (14, 15), which allows it to combine low electrical conductivity with lubricant properties due to sliding layers as for graphite.

This research report is focused on the intermediate material between polymeric carbon nitride and boron nitride, i.e. boron carbon nitride oxide (BCNO). The basic idea was to combine a reagent rich in nitrogen and carbon with one rich in boron. Lei et al. reported the synthesis of boron carbon nitride (BCN) by means sodium borohydride as the boron source and urea (NH<sub>2</sub>)<sub>2</sub>CO or guanidine hydrochloride (CH<sub>5</sub>N<sub>3</sub>HCl) as the carbon–nitrogen source (6). BCNO is a semiconductor with a band gap considerably lower than h-BN, able to behave as a metal free phosphor and could be applied in lightning

technology for its low cost and nontoxicity, and because of the wide range of fluorescence emissions from ultraviolet to blue depending on the particle size (6, 16). In this research, the BCNO was obtained by thermally treating a blend of urea and boric acid at 600°C, and was characterized through several techniques such including infrared spectroscopy (IR), scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS), and UV-vis spectroscopy to determine its main chemical and physical characteristics.

## Methodology, materials and equipments

The synthesis of BCNO was carried out by heating mixtures of urea (25 g) and boric acid (5 g) inside a capped ceramic crucible with two temperature plateaus and a heat rate of 25°C/min. The first plateau was at 300°C for 10 min, so as to homogenize the sample temperature. The second heating plateau was at 600°C for 30 min to complete the chemical reaction. The furnace employed during the synthesis process was a Vulcan 3-550 (power: 1.440 kW, 120 V, 12 A,  $T_{\max} = 1200^\circ\text{C}$ , USA) with programmable ramps.

The chemical characterization of the samples was accomplished by a FT-IR spectrometer Spectrum one, Perkin Elmer (USA). The tablets were prepared mixing dry KBr and small portions of BCN. The structural analysis of the BCN samples was carried out by XRD with a Philips PW 1710 (NL) reflection diffractometer operating with  $\text{Cu K}\alpha_1$  and  $\text{K}\alpha_2$ .

The morphological analysis of BCNO was performed by SEM Phenom ProX Desktop (NL) with backscattered electrons' detector, maximum image magnification up to 100000 $\times$  and acceleration voltages from 5 to 15 kV. An elemental analysis was also executed by means of energy dispersive X-ray spectroscopy (EDS).

A comparison among the IR spectra of BN,  $\text{CN}_x$  (polymeric carbon nitride) and the obtained BCNO was carried out in order to better assign the absorption bands and make a hypothesis of the basic structures. Moreover, an analysis of the IR vibrational modes "predicted by group theory on the basis of the structures compatible with the obtained results" was carried out to assign the symmetry of the main vibrational modes.

The UV-vis spectra of the specimens were obtained by means of UV-visible spectrophotometer Perkin Elmer Lambda 35 (USA) integrated with a sphere. A Spectralon® blank was used as reference. The reflectance data were transformed to absorbance data applying the Kubelka-Munk (K-M) method as follows:

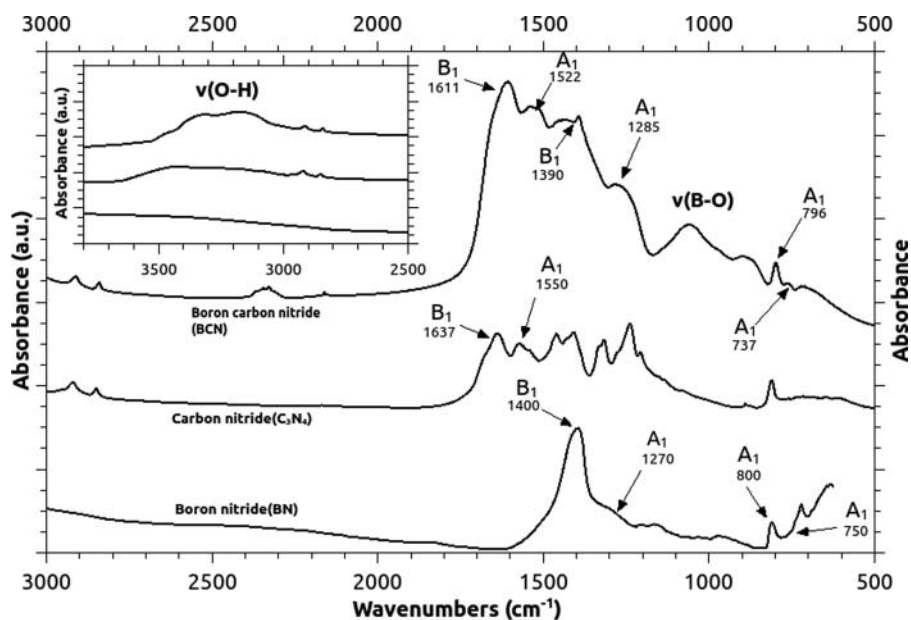
$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

where  $R$  is the reflectance and  $F(R)$  is the K-M function. The K-M function was plotted as a function of the energy ( $E = hc/\lambda$ ) and the band-gap value was calculated through the inflection point of this curve. The abscissa of this point is directly associated with the band-gap value (17).

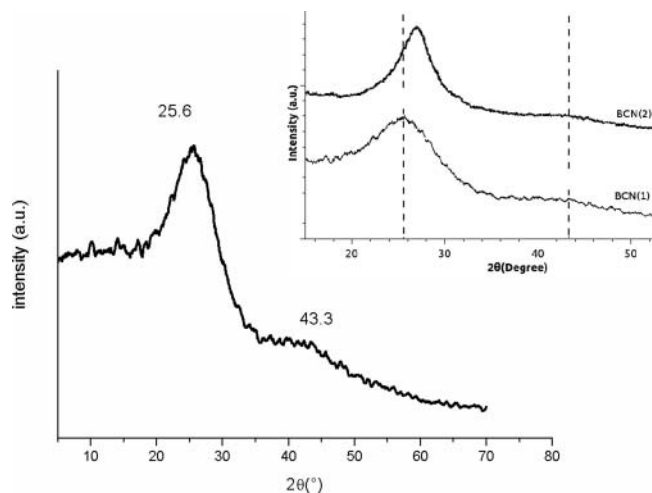
An X-ray photoelectron spectrometer (XPS), Thermo Scientific, K-Alpha Spectrometer was used to analyze the sample with monochromated small-spot XPS 30 mm and Ion Gun-Energy range at 100–4000 eV.

## Results and discussion

Figure 1 displays the FT-IR spectra of BCN,  $g\text{-C}_3\text{N}_4$  and boron nitride h-BN. The IR spectrum of  $g\text{-C}_3\text{N}_4$  corresponds to that already described by Dante et al. (3). Moreover, the boron nitride spectrum was obtained from NIST database (18). The peak of BCNO at 1611  $\text{cm}^{-1}$  may correspond with the asymmetric ring stretching similar to that of  $g\text{-C}_3\text{N}_4$  at 1637  $\text{cm}^{-1}$ .



**Figure 1.** FT-IR spectra comparison among BCNO,  $g\text{-C}_3\text{N}_4$  and h-BN. Capital letters with sub-indexes (e.g.,  $A_1$ ) stay for the  $C_{2v}$  point group representations of the vibrational modes.

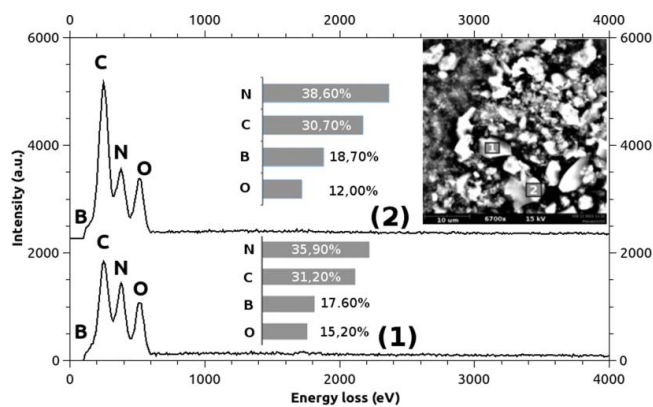


**Figure 2.** Main figure: XRD pattern of our BCNO material, In the insert, BCN1 XRD pattern from urea and boric acid synthesized in this research, and BCN2 XRD pattern from sodium borohydride and guanidine hydrochloride for a direct comparison [6].

The band at  $1522\text{ cm}^{-1}$  could match with a symmetric ring breathing at  $1522\text{ cm}^{-1}$  as in  $g\text{-C}_3\text{N}_4$ . At  $1285\text{ cm}^{-1}$  there is another symmetric stretching. The deformation peaks at  $796$  and  $737\text{ cm}^{-1}$  of BCN are analogous to those present in h-BN.

The band corresponding to hydroxyl groups in BCNO is weak as inserted in Fig. 1, but stronger than those of both carbon nitride and h-BN. The O-H stretching bands  $\nu(\text{OH})$  are located between  $3500$  and  $3000\text{ cm}^{-1}$ , while the B-O (of B-OH) stretching bands  $\nu(\text{BO})$  are located around  $1000\text{ cm}^{-1}$ . There is a certain discrepancy among the several IR spectra reported in other research reports, sometimes the spectra lack of the characteristic bands of  $\text{C}=\text{N}$  stretching around  $1600\text{ cm}^{-1}$ , but this may be due to the great variety of products under the same name of boron carbon nitride BCN (or BCNO). The ratio among these elements can vary considerably, including oxygen ratio that is the fourth element present in this class of materials (6, 19).

The X-ray diffraction pattern is shown in Figure 2. The peaks at  $25.6^\circ$  and  $43.3^\circ$  (BCN1) approximately correspond to the data of the research report by Lei et al. (6) starting from a



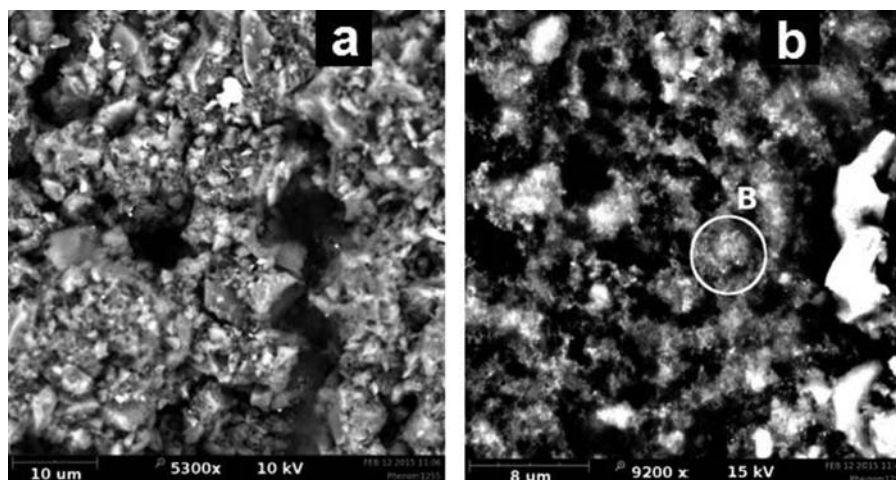
**Figure 4.** EDS analysis with elemental analysis in areas 1 and 2.

different mixture of reagents (urea, guanidine hydrochloride, and sodium borohydride) and attributed to a BCN material (BCN 2). The considerably broad peak at  $25.6^\circ$  can be attributed to the 002 plane reflection with an interplanar distance of  $3.49\text{ \AA}$ , higher but similar to those of h-BN ( $3.33\text{ \AA}$ ) and graphite ( $3.34\text{ \AA}$ ). The peak at  $43.3^\circ$  ( $2.09\text{ \AA}$ ) may correspond to an in-plane reflection.

An idea of both the morphology and particle size distribution is given by the SEM images shown in Figure 3. In the left-hand corner of Figure 3(b), it is easy to distinguish an area of diffused nanoparticles. On the other hand, a very irregular particle size distribution can be observed due to the process including milling in a agate mortar.

The EDS scanning zones are displayed in Figure 4. Two areas were selected and their corresponding results are shown in Figure 4. The analysis showed the presence of oxygen, boron, carbon and nitrogen on both targets.

The UV-vis spectrum of BCNO is shown in Figure 5, while the behavior under an UV lamp of BCN suspended in acetonitrile exhibiting fluorescence is displayed in the insert and compared with the pure solvent. The onset of UV absorption was around  $340\text{ nm}$ . The energy gap ( $E_g$ ) was  $3.22\text{ eV}$ . This value is considerably lower than that computed and measured for h-BN between  $5$  and  $6\text{ eV}$  (14,15). The suspension was very stable in the polar solvent acetonitrile, probably due to the hydroxyl



**Figure 3.** SEM image of the particles of the same specimen: (a) material as is with particle agglomeration, and (b) material deposited from methanol suspension on carbon paper with clouds of nanoparticles, circle B emphasizes a cloud of nanoparticles.



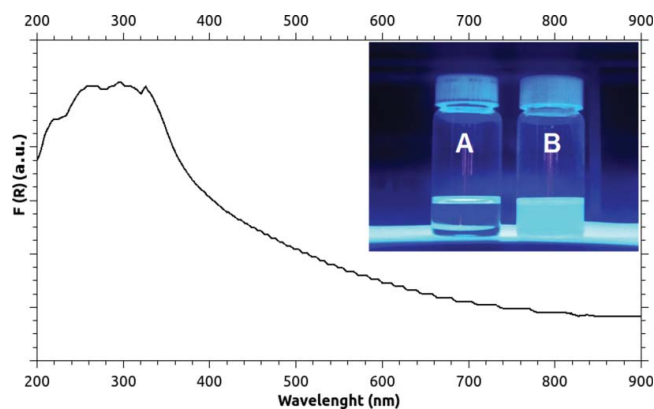


Figure 5. UV-vis spectrum of BCNO. In the insert: pure acetonitrile (flask A), suspension of BCNO in acetonitrile (flask B).

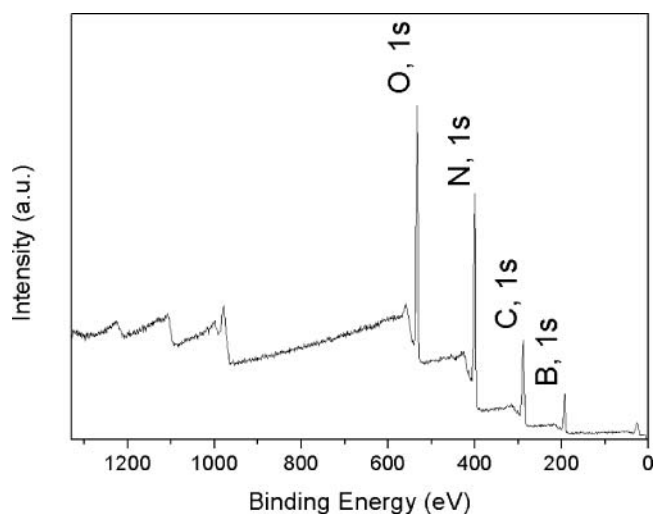


Figure 6. XPS full scan.

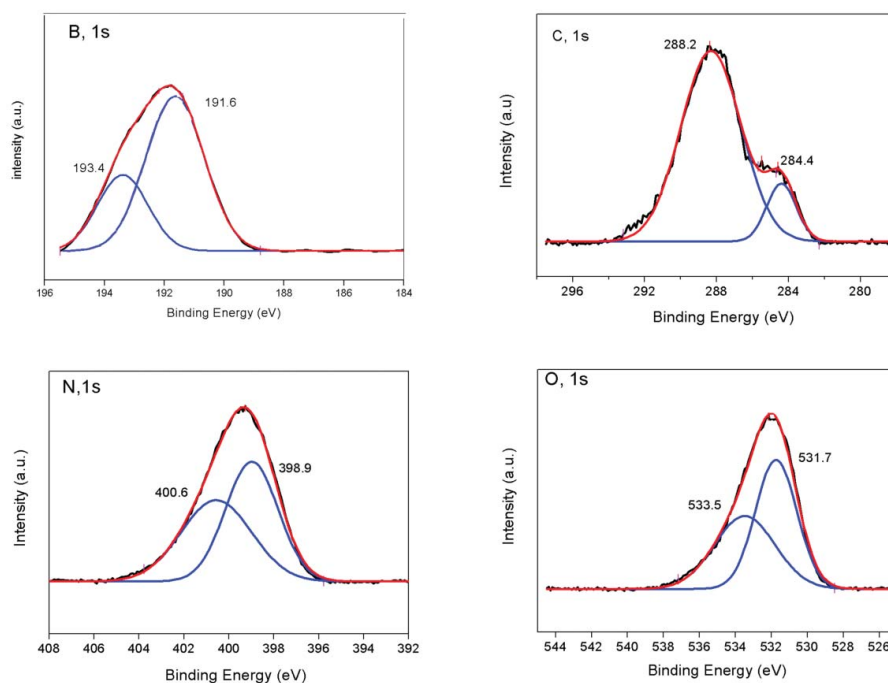


Figure 7. XPS deconvolution peaks of C 1s, N 1s, B 1s, and O 1s.

groups of BCNO, as shown by IR spectrum in the region between 3500 and 3100  $\text{cm}^{-1}$ .

To better interpret the IR bands of BCNO, two possible ring arrangements were considered:  $\text{BC}_2\text{N}_3$  and  $\text{B}_2\text{CN}_3$  (that are the most common repeating basic units of the planar structure similar to that of graphite). The  $\text{BC}_2\text{N}_3$  ring is closer to the atomic percentages found by EDS, which were for zone 1 of Figure 4 (a): 42.38% (N), 36.83% (C) and 20.77% (B) (similar to those of zone 2 of Figure 4 (b)). These values are quite similar to those computed for the ring  $\text{BC}_2\text{N}_3$ , which are N (50%), C (33.3%) and B (16.67%).

Moreover, both rings correspond to the  $C_{2v}$  point group. In Figure 1, each peak was assigned to the vibrational mode of  $C_{2v}$  such as  $A_1$  (symmetric stretching),  $B_1$  (asymmetric stretching) of the corresponding hypothetical rings  $\text{B}_2\text{CN}_3$  and  $\text{BC}_2\text{N}_3$  (both rings without direct bonds among the N atoms) on the basis of their similitude to either boron nitride BN or polymeric carbon nitride  $\text{C}_3\text{N}_4$ , respectively. According to the aforementioned similitudes and symmetry considerations the  $\text{BC}_2\text{N}_3$  ring modes  $A_1$  and  $B_1$  were assigned to peaks at 1611 and 1522  $\text{cm}^{-1}$ , respectively; while the  $\text{B}_2\text{CN}_3$  ones were assigned 1390 and 1285  $\text{cm}^{-1}$ , respectively (see Figure 1). However, the bending modes between 800 and 700  $\text{cm}^{-1}$  were difficult to distinguish between the two rings.

Ultimately, both the two proposed structures generate vibrational modes compatible with the IR spectrum so that both are the basic units to build the material layer similar to graphite layers.

The XPS full scan is shown in Figure 6, and the clear presence of the peaks of B 1s, C 1s, N 1s, and O 1s can be noticed. The deconvolution of these peaks is shown in Fig. 7.

The C1s peak exhibits two components, one at 288.2 and the other at 284.4 eV attributable to C-N and C-C bonds, respectively. N1s exhibited two main components: 400.6 and 398.9

assigned to C-N and B-N bonds, respectively. Regarding O1s, two components were found centered at 533.5 and 531.7 eV, which may correspond to C-O-C bonds in the plane rings, and to B-O bonds probably of B-OH terminal groups (6). From the peak area analysis the following ratio was found among the four elements:  $B_{0.6}C_{0.8}N_{1.3}O_{1.0}$  confirming that more properly the material is a boron carbon nitride oxide (16), with a high content of carbon and oxygen. Although, the most oxygen belonged to terminal OH, also was considerably present in the main layered structure as bridge between carbon atoms C-O-C. This composition normalized with respect to N led to the general formula  $B_{0.46}C_{0.61}N_1$ , which is quite reasonably similar to that of the most probable ring supposed by IR and EDS analysis  $B_{0.33}C_{0.66}N_1(BC_2N_3)$ . Therefore, the prevalent ring type seems to be  $BC_2N_3$ . Moreover, the high content of carbon explains why the IR modes relative to CN vibrations are so intense.

## Conclusions

A solid state reaction between urea and boric acid carried out at 600°C led to a boron carbon nitride oxide (BCNO) material with an interlayer distance of 3.49 Å, slightly higher than that of graphite 3.35 Å. IR showed bands similar to those of boron nitride and carbon nitride, as well as a considerable presence of hydroxyl groups linked to terminal boron atoms. XPS confirmed a structure with a high content of carbon and oxygen with the atomic ratios  $B_{0.6}C_{0.8}N_{1.3}O_{1.0}$ . The optical band gap was estimated to be 3.22 eV typical of a wide band-gap semiconductor but lower than that of h-BN. The particle size was very dispersed from micro to nanosize. Due to the hydroxyl groups the material was able to be dispersed in polar solvents and exhibited fluorescence under a UV lamp.

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