Synthesis and characterization of Barium Titanium Oxides ($BaTiO_3$) Single perovskite Annealed by Different Temperatures

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Abstract

In this paper, the conventional solid state interaction method was used to prepare $BaTiO_3$ single perovskite samples, which were heated to a different annealing temperatures from 0 to 800 into 1200 degrees. The optical properties of the samples were investigated, using Fourier transformation infrared (FT-IR) and Ultraviolet visible (UV-Vis) spectroscopies. Whilst, UV-visible results were exhibited and explicit data of UV-visible which was used to evaluate the absorption, transmission, reflection, extension and energy band gaps. It's found that the effect of the annealing of samples' temperature on the extinction coefficient (k) decreased while the temperature was increasing. In addition, the reflection was directly proportional to the temperature. In this case, the materials turned closely into which is called a mirror. The increasing of energy band gap (Eg) is related to increasing in an annealing temperature. This transition was indirected and thereupon, "the phenomenon" uses especially, for the industrial devices, to convert materials from insulator to semiconductors. Furthermore, the chemical bonds within atoms were investigated and verified by FTIR data in this paper.

***Keyword**: Single Perovskite, Optical Properties, Annealing Temperature, Extinction Coefficient and Energy Band Gap*

Introduction

Single Perovskites are materials having the same kind of crystal composition as the barium titanium oxide, with a commonality formula of ABO_3. Inside this structure, an A-site ion, on the corners of the lattice, is customarily an alkaline or scare earth component. B-site ions, on the centrist of the lattice, could be 3D to 5D moving metals. The mineral perovskite was founded and denominated by Gustav Rose in 1839 from samples acquired in the Ural Mountains**[1, 2]**. Perovskite is named after the Russian mineralogist, Count Lev Aleksevich von Perovskite who was eyestrain Russian secretary of the interior in 1842**[3, 4]** . The terminology perovskite was inherently booked for the mineral ($BaTiO_3$). Goldschmidt (1926) of the University of Oslo led to the utilize of the term perovskite as a characterization of a stratum of composites subscribing the same general stoichiometry and associating

established in ($BaTiO_3$) provided the first synthetic perovskites. The technological development and the more requests of the futures society in material science domain; lays or persists required for developed material with enhanced characteristic**[5, 6]**. The perovskite structure consistency is lowered to tetragonal, orthorhombic, or trigonal in the majority of perovskites. Hereupon has evinced its congeniality for industrial implementation (100). The perovskite composition is discriminated by octahedral harmonized polyhedrons (formed by oxygen anions located at the corners of the octahedra) around the B cations, while the B-cations are placed at the centers. The octahedral polyhedrons are joined by their corners, constituting a three dimensional framework of octahedral chains. In the cavities of this, the A-cations are situated (with twelve ion coordinately)**[7]**.

Barium Titanium ($BaTiO_3$) has been a consequential material in the manufacture of electronic devices for a number of years due to its unique properties of high dielectric constant, high Ferroelectricity, and Piezoelectricity. $BaTiO_3$-based ceramics are a wide range of potential implementations in Ferroelectric Random Access Memory (FRAM), photoelectric humidity sensors, solid oxide fuel cells superconductors, ferrimagnets, high capacitance capacitors, pyroelectric detectors, and magneto resistors**[8]**. Tetragonal $BaTiO_3$ ceramics are hugely used in multi-layer ceramic capacitors (MLCC)**[9]**. Thermistors, and piezoelectric sensors, Conventional methods were used to prepare $BaTiO_3$. Ceramics are solid-state reaction operations which use TiO_2 and $BaCO_3$ as the raw materials at an elevated temperature of more than 1200 $^{\circ}$C. The large size and low purity of the $BaTiO_3$ ceramics which was obtained by the solid-state reaction have limited their applications in Nano technological fields. The miniaturization of electronic components and nanotechnology makes it necessary to synthesize nanometer-scale $BaTiO_3$ materials, including nanowires and nanoparticles with scientific appeal and technical urgency**[10]**. Device miniaturization and high dielectric constant can be achieved by controlling their microstructures and compositions, which are strongly dependent on the phase, uniformity, surface area, and size of the $BaTiO_3$ materials. For the applications in MLCC, $BaTiO_3$ powders are usually used as dielectric fillers and blended with a polymer to fabricate composite film with a compact and flexible surface. In order to manufacture a reliable $BaTiO_3$-based MLCC, high-quality $BaTiO_3$ powders with high purity, high crystallinity, high dispensability, and uniform small size are the precondition. The $BaTiO_3$ fillers with a narrow particle-size distribution and suitable phases are in favor of obtaining a compact composite film with a lower content of pores, and the dense and homogeneous $BaTiO_3$ phase in polymer matrix can lead to higher dielectric properties of the composite films**[11, 12]**.

In this study, the single perovskite samples were synthesized using solid-state interaction methods at room temperature, and at a different temperatures annealing (800 and 1200 ^{O}C) for 24 hours.

Experiment

The single provskite oxides samples were synthesized by solid state interaction methods at room temperature, and at a different temperature annealing (800 and 1200 ^{O}C) for 24 hours. They were
prepared by mixing stoichiometric amounts of (B aCO_3 and TiO_2), the ratio of all amounts were calculated from the following equation

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2\uparrow$$

Traditionally, barium titanate is prepared by a solid-state reaction that involves ball milling of $BaCO_3$ and TiO_2. The mixture has to be calcined at high temperature. In some reports the needed calcination temperature was as high as 800 ^{o}C to 1200 ^{o}C **[13]**, and in some other work it was at room temperature. Barium titanate powders prepared by a solid-state reaction are highly agglomerated, with a large particle size and high impurity contents due to their inherent problems such as high reaction temperature, heterogeneous solid

phase reaction, which result in poor electrical properties of the sintered ceramics. To eliminate these problems, many wet chemical synthesis routes are developed to generate high purity, homogeneous, reactive ultrafine barium titanate powders at low temperatures. Then, using UV Visible spectrometer to study the optical properties of the samples, and FTIR to measure the vibrational frequencies bonds in the molecule single perovskite oxide**[14, 15]**.

Results and Discussion

After preparing the samples by solid state interaction methods at room temperature, and at a different temperature annealing (800 and 1200 ^{O}C) for 24 hours; UV Visible spectrometer was used to study the optical properties, and Fourier Transform Infrared spectroscopy (FTIR) for describing the vibrational modes.

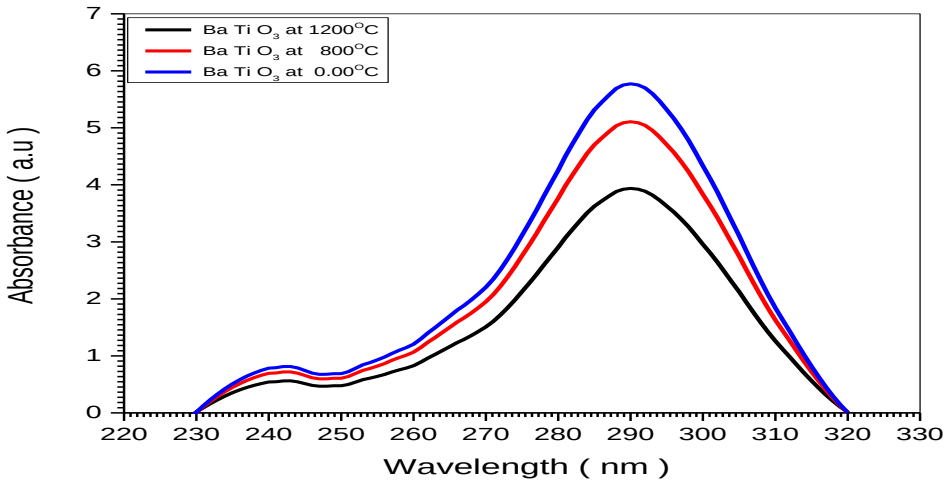

Figure (1) Optical absorbance spectra of $BaTiO_3$ samples at different annealed temperature.

From figure (1), the absorbance is clear for the three samples, and the curve behavior is matched and coincided with the Barium Titanium Oxide that was heated with different temperatures, and wherein the samples of ($BaTiO_3$) was studied using UV-VS min 1240 spectrophotometer. Also, Fig (1) shows the rapid increase of the absorption at wavelengths 290nm and whereupon the corresponding photon energy is 4.28 eV. The absorption is proportional reversing with an annealed temperature**[16, 17]**.

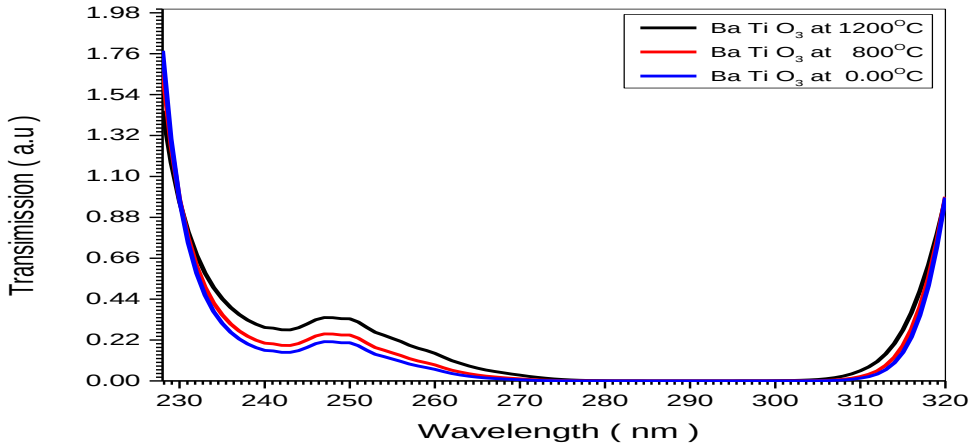

Figure (2) Relation between transimission and wavelengths of (BaTi O $_3$) samples

Figure (2) shows the relation between transmission and wavelengths, and the decrease of the transmission at wavelengths (228-320 nm) was noticed and seen, rapidly. The annealed temperature of the ($BaTiO_3$) samples, which effected the transmission value increased with the increase of an annealed temperature**[7, 18]**.

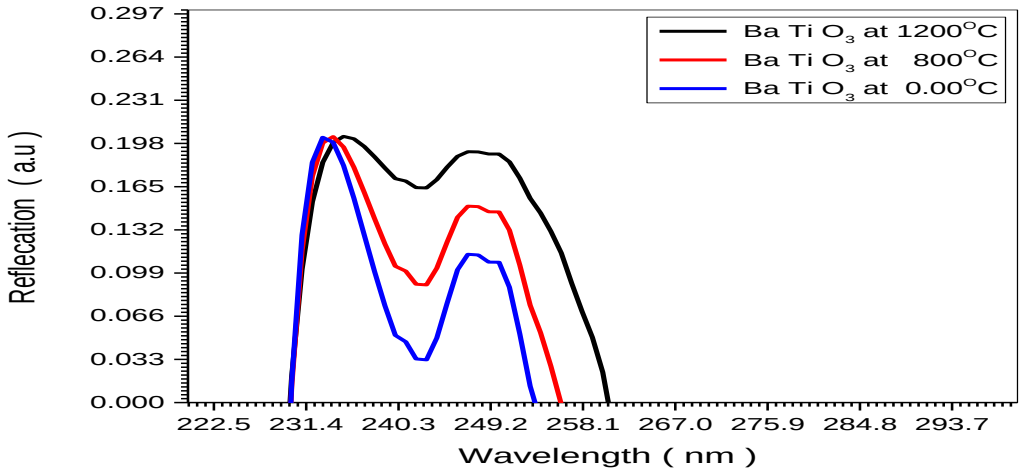

Figure (3) Relation between reflection and wavelengths of ($BaTiO_3$) samples.

The optical reflectance (R) spectra in the (229.6–260.25 nm) wavelength range for the Barium Titanium Oxide was heated at room temperature, and at different temperature annealing (800-1200 ^{O}C) samples are depicted in Fig (3). The maximum reflection was being observed in (233.05 to 250.23nm) range of all samples, in this range, too the samples should be mirrored, and then it decreases beyond the 250.23 nm and before 230 nm. From this result, it was found that the reflection is proportional to the temperature**[16, 19]**.

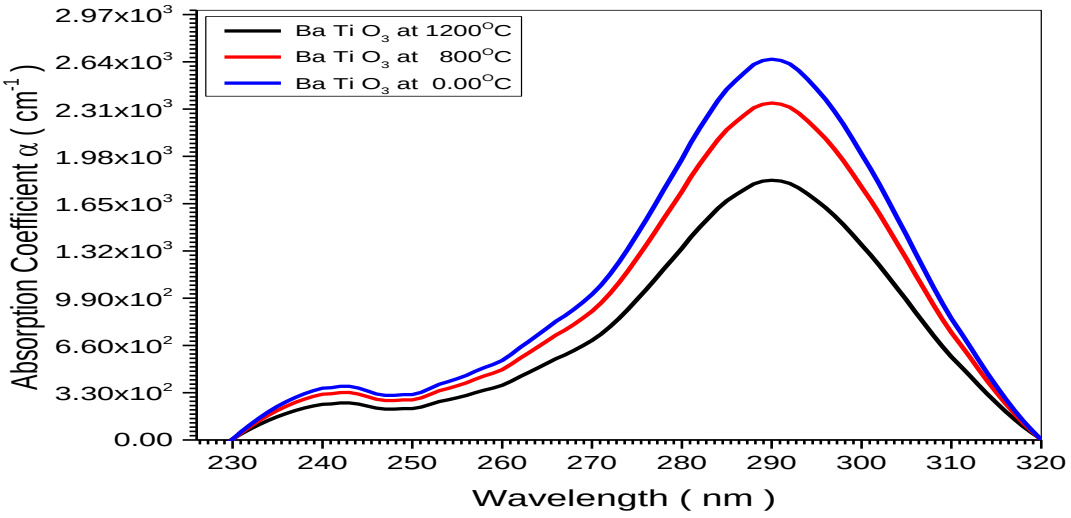

Figure (4) Relation between absorption coefficient and wavelengths of $BaTiO_3$ samples.

The absorption coefficient (α) of the three prepared samples of $BaTiO_3$ in a different annealed temperature was found from the following relation $\alpha = \frac{2.303xA}{t}$, where (A) is the absorbance and (t) is the optical length in the samples. In fig (4), the plot of (α) with wavelength (λ) of the samples was shown for the BariumTitanum Oxide at dirfferant annealed temperature ($BaTi\ O_3$). The absorption coefficent was obtained for the sample at (room temperature) and where, α = $2672x10^3$ cm^{-1} at UV region (290 nm), but for

(800 ^{O}C) sample, α = 2357x10^{3} cm^{-1}, and for (1200 ^{O}C) sample, whereas the value of α = 1821x 10^{3} at the same wavelength. This means that the transition might be corresponding to a direct electronic transition and the properties of this state are highly important since they are responsible for electrical conduction. The absorption coefficient decreased while increasing the anealing temperature**[6, 18]**.

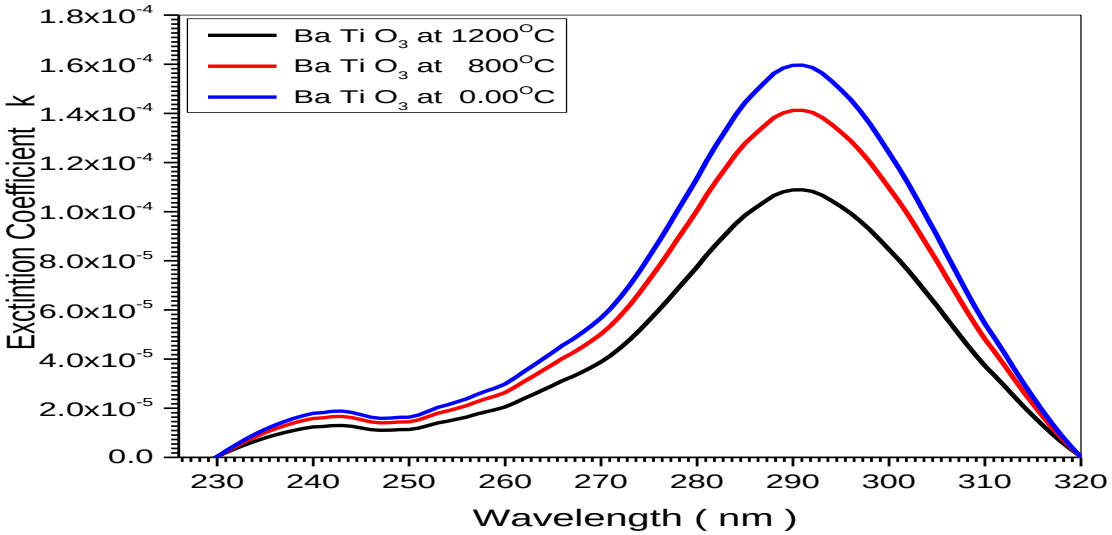

Figure (5) Relation between exctintion coefficient and wavelengths of (BaTi O_3) samples

zxtinction coefficient (K) was calculated using the relation $k = \frac{\alpha\lambda}{4\pi}$. The variation of the (K) values as (λ) function were shown in fig. (5) for Barium Titanum Oxide ($BaTiO_3$) samples when was heated with different anlealing temperature and it's observed that the spectrum shape of (K) is similar to the shape of (α). The Extinction coefficient (K) value was obtained at (290 nm) whereas, the wavelength was dependent on the samples preperation methods (solid state reaction). The value of (K) at 290 nm for ($BaTiO_3$) sample at (room temperature) equal 1.603x10^{-4} while for the other samples of ($BaTiO_3$) were handling for (1200 ^{O}C) anealing temperature equal 1.09 x10^{-4} at the same wavelength (290nm). The effect of annealing temperature on the samples was that the extinction coefficient (k) decreased while the annealing temperature was increasing.

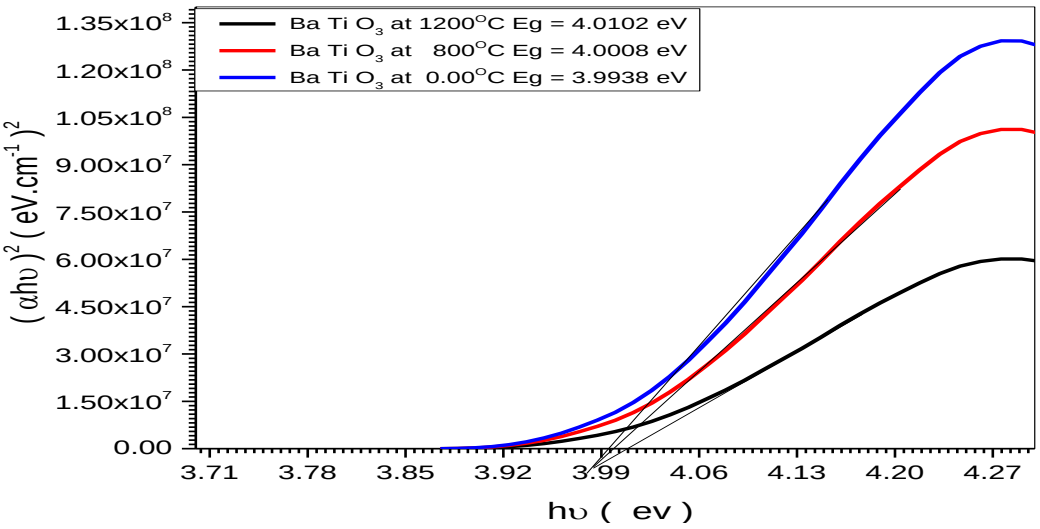

Figure (6) Optical energy band gaups of (BaTi O_3) samples

The optical energy gap (E_g) was calculated by the relation $(\alpha h\upsilon)^2 = C(h\upsilon - E_g)$, where (C) is constant. By plotting $(\alpha h\upsilon)^2$ vs photon energy ($h\upsilon$) as shown in fig (4) for the BariumTitanum Oxide which was heated at different temperatures. As of extrapolating, the straight thin portion of the curve to intercept the energy axis, the value of the energy gap was calculated. In fig (6), the value of (E_g) of (room temperature) sample was obtained (3.99389938 eV) while for the other samples (800 ^{O}C) are equal to (4.0008 eV), and for (1200 ^{O}C)the value of (Eg) was found to be (4.00102eV). The increase of (Eg) is related to the increase in annealing temperature. The transition is indirect and this is used for the industrial devices en route for converting materials from insulator to semiconductors**[2, 20]**.

Functional Group	Sample wavenumber (cm^{-1})	Type of Vibration causing IR absorption
Alkanes: CH_4 methane	2438 and 2840	H-C-H Asymmetric & Symmetric Stretch
Alkanes: CH_4 methane	1447	H-C-H Bend
Esters: CHO = O –CH_3 Methyle formate	1758	C=O Stretch
Ethers: Diethyl Ether(aka-Ethyl Ether)	1056	(C-O Stretch)
Carboxylic Acids CH= O – OH Formic Acid	3423 , 2840 and 2438	Hydrogen-bonded O-H Stretch [Note: This peak can obscure other peaks in this region
C – Br	689	Aliphatic bromo compounds, C - Br stretch
	858	third overtone C–H stretching
	419	combination S–S stretching

Table (1) FTIR Group of single perovskite samples $BaTiO_3$ at different annealing temperatures

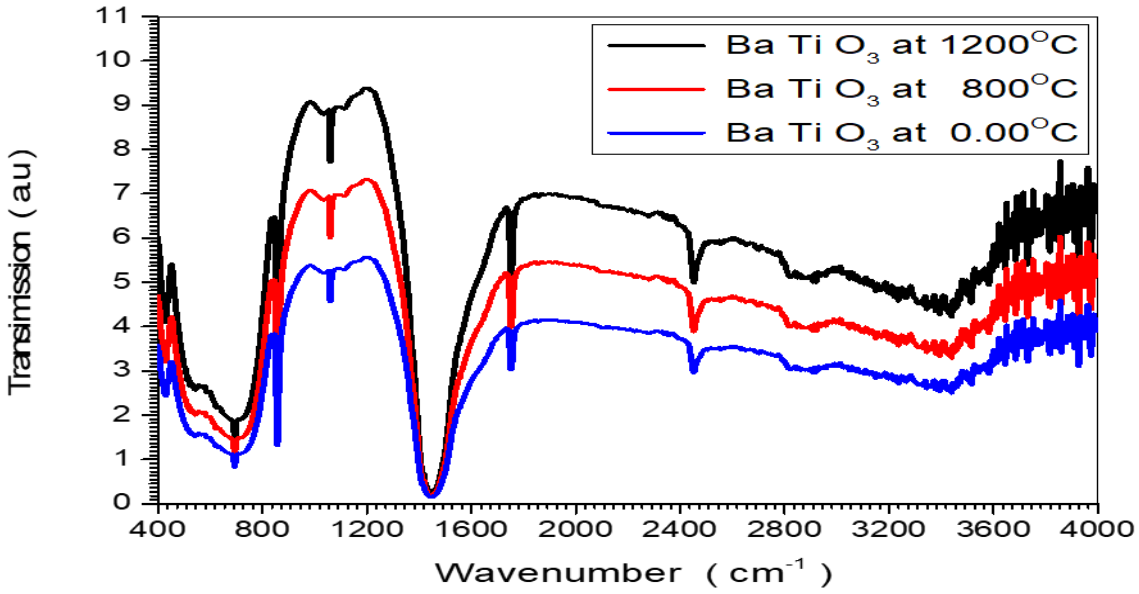

Figure (7) FTIR spectra of the as-prepared and annealed $BaTiO_3$ samples at different annealing temperatures.

In Fourier transformation infrared spectroscopy (FTIR) spectra were recorded in the solid phase of the Barium Titanium oxide samples. Which is used as a basic line (KBr) powder with the samples and the measurements were performed in the region between 3423-419 cm^{-1}. FTIR spectra of the samples are shown in Figure (7). The chemical structure and bonds of $BaTiO_3$ samples were verified. Several bonds due to combinations of H-C-H, C=O, C-O, O-H, C - Br and S–S entities appear in the 3423–419 cm^{-1} range**[21, 22]**. The obtained FTIR results were shown in table (1).

Conclusion

There were three samples of single perovskite oxides ($BaTiO_3$) synthesized, using a solid-state interaction at room temperature, and at different temperatures annealing (800 and 1200 ^{O}C) for 24 hours. From the optical results, it was clear obviously, that the energy band gap increased from 3.991 to 4.001 eV while increasing the annealing temperature, and absorption coefficient also increased while annealing temperature was increasing due to the increase of density. All the bands vibrational at the range (419 to 3423 cm^{-1}) due to combinations of H-C-H, C=O, C-O, O-H, C increasing- Br and S–S entities appear.

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