Effect of alloying on the structure and electric properties of ZnFe$_2$O$_4$/ZnMn$_2$O$_4$ heterostructure nanocomposites

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ABSTRACT
The heterostructure nanocomposite (1-x)ZnFe$_2$O$_4$/xZnMn$_2$O$_4$ (x = 0, 0.5, 0.8, 1) samples were prepared using the sol–gel method. The structural parameters and the percentages of the phases formed were determined utilizing the Rietveld method. Beside the two phases formed ZnFe$_2$O$_4$ (ZFO) and ZnMn$_2$O$_4$ (ZMO), a minor phase ZnO (3%) was observed in the sample x = 0.5. Analysis revealed phase percentages for composite samples different from intended (x) values due to the exchange of cations between the phases formed. The effect of composition ratio (x), as well as the frequency and temperature on the dielectric constant, dielectric loss, impedance spectroscopy and complex electric modulus and ac conductivity, was examined. The degree of correlation in each sample was also determined. Different conductivity mechanisms are found for different samples and frequency ranges. The 0.2ZFO-0.8ZMO sample disclosed higher conductivity and higher dispersion relative to other samples. The effect of temperature on the Cole–Cole plots was also studied.

1. Introduction
Forming semiconductor composites is a promising strategy to introduce new features as compared with individual semiconductor materials [1–3]. For example, the conducting and magnetic features of manganese ferrite/ magnetite core–shell structures indicate their suitability for many applications, like magnetic data storage, sensors, catalysis, and electromagnetic resonance wave absorption [4]. The photoelectrochemical hydrogen production was enhanced by creating the novel ternary composite Ag$_2$CrO$_4$/GO/MnFe$_2$O$_4$ [5]. Zinc ferrite ZnFe$_2$O$_4$ (ZFO) is a promising n-type spinel semiconductor material with a bandgap $\approx$ 1.9 eV [6]. Zinc manganite, ZnMn$_2$O$_4$ (ZMO) has a spinel structure and is getting attention because of its possible use in batteries and supercapacitors [7,8]. In addition, ZnO has distinct physical features such as wide direct bandgap (3.3 eV) and high excitation binding energy (60 meV) [9]. Unfortunately, fast charge recombination in ZFO regularly limits its practical uses, but by combining it with other semiconductor materials, this problem could be reduced [10]. The properties of ferrite materials can be tuned as they doped with a suitable element or alloying with other compounds. For instance, the elastic moduli...
of ZFO became high as it doped Ni, Mn, Ce [11]. The modification in the magnetic properties of ZFO formed by sol–gel-method was obtained as it doped with Co, Cu, Dy [12]. α-Fe2O3/ZFO/ZnO ternary hybrid nanodiscs were nominated as a promising candidate for photocatalytic applications due to their high photocatalytic efficiency [13]. Furthermore, by varying the composition ratio of the ZFO/LiFeO2 nanocomposites, the electromagnetic characteristics showed minimum reflection loss and the microwave absorption frequency bandwidth could be attuned [14]. As ZFO coated FeSiCr using a plasma arc discharging method, strong microwave absorption ability was detected [15]. CuO/ZFO microspheres have become a talented material for differentiating BTX gases [16]. ZFO/ZnO nanosheets assembled into microspheres have become a promising candidate in trimethylamine sensing [17]. When ZFO was combined with SnFe2O4, organic pollutant toxicity was rapidly eliminated [18]. The ZFO/SnO2 composite demonstrated effective photocatalytic activity for dye degradation [19]. The incorporation of Cu-ferrite with MnO2, nominated this composite to be used in electromagnetic shielding applications [20]. Regarding the preparation procedure, there are many methods, among of them the sol–gel procedure which has many advantages over the other methods such as a low-cost and effective way to form nano ferrite at a low temperature [21,22]. The main aim of the present work is to get the advantages of both materials, ZFO and ZMO, by alloying them in different proportions and to study the effect of these different proportions on the structure and dielectric characteristics of the developed composites. For this purpose, ZFO@ZMO nanocomposites were formed using the sol–gel method with different ratios. The structure characteristics, different elements analysis and dielectric performance of the prepared materials were examined using X-ray diffraction, X-ray photoelectron spectroscopy and impedance spectroscopy techniques.

2. Materials and methods

Nanocomposite \( (1-x) \text{ZnFe}_2\text{O}_4/x\text{ZnMn}_2\text{O}_4 \) \((x = 0, 0.5, 0.8, 1)\) samples were prepared by dissolving and heating at 85°C (60 min), 0.5 M solutions from each of the starting materials (iron nitrate, zinc acetate, manganese acetate) in 20 ml distilled water and 10 ml ethylene glycol using a magnet stirrer. To obtain the powder samples, the formed precursors were heated in an electric oven (400°C, 90 min), Figure 1. X-ray diffraction data (XRD) was measured employing the Panalytical X’Pert X-Ray Diffractometer (Cu-Kα). The morphology of the nano samples was investigated employing a high-resolution transmission electron microscope (JEOL JEM-2100, 200 keV). X-ray photoelectron spectroscopy (XPS) spectra were measured using a Thermo Scientific XPS (Model: KALPHA surface analysis). To measure the dielectric characteristics of the different samples, pellets from samples were produced from the powder under compression of \(9 \times 10^8\)Pa. The complex impedance using a low-frequency lock-in amplifier (LIA, SR510) was applied for the dielectric measurements.

The complex impedance, \(Z^*\), dielectric constant, \(\varepsilon^*\), electric modulus, \(M^*\), and electrical conduction (\(\sigma_{\text{total}}\)) were calculated employing the next formula [23]:

\[
Z^* = Z' - jZ'' = \frac{1}{j2\pi f \varepsilon^* C_0} = \frac{\varepsilon'' - j\varepsilon'}{2\pi f C_0[(\varepsilon')^2 + (\varepsilon'')^2]} \quad (1)
\]

\[
\varepsilon^* = \frac{1}{j\omega C_0 Z^*} \quad (2)
\]

\[
\varepsilon' = \frac{Z''}{\omega C_0 (Z'^2 + Z''^2)} \quad \text{and} \quad \varepsilon'' = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)} \quad (3)
\]

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad (4)
\]

\[
M^* = M' + jM'' \quad (5)
\]

Figure 1. Preparation schema for ZnFe2O4/ZnMn2O4 nanocomposite samples.
\[ M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - j\varepsilon''} = \frac{\varepsilon'}{(\varepsilon')^2 + (\varepsilon'')^2} + j\frac{\varepsilon''}{(\varepsilon')^2 + (\varepsilon'')^2} \]  
\[
\sigma_{\text{total}}(\omega) = \sigma_{dc} + \sum_i B_i(T)\omega^{n(T)}
\]

where \((Z' \text{ and } Z'')\), \((\varepsilon' \text{ and } \varepsilon'')\), \((M' \text{ and } M'')\) are the real and imaginary parts of impedance, dielectric constant, electric modulus, respectively. \(\tan\delta\), \(C_0\), \(f\), \(\sigma_{dc}\), \(\omega\) and \(B(T)\) are the dielectric loss, empty capacitance, frequency, dc conductivity, angular frequency and constant, respectively. \(n(T)\) is the frequency exponent, \(n\) value may be 0 < \(n\) < 1 for the short-range translational hopping motion and/or 1 < \(n\) < 2 for localized or reorientation hopping motion [24].

3. Results and discussion

3.1. Structure investigations

Structural analysis of the heterostructure system \((1-x)\) ZnFe\(_2\)O\(_4\)-xZnMn\(_2\)O\(_4\) \((x = 0.0, 0.5, 0.8, 1.0)\) is performed by applying the Rietveld method implanted in the MAUD program [25,26]. The percentages of the phases developed, the cell parameters (Å), and the average crystallite size (nm) for the heterostructure nanocomposites are listed in Table 1. Analysis manifested pure single cubic phase (Fd-3m) for the pure sample (ZFO) \((x = 0.0)\), and pure ZnMn\(_2\)O\(_4\) (ZMO) for the sample \(x = 1.0\) with tetragonal structure (S.G. I 4\_1/m d), Figure 2(a-d). Beside the two phases formed (ZFO) and (ZMO), a minor phase ZnO (3%) observed in the sample \(x = 0.5\). As shown in Table 1, all samples exhibited a nanometer size and the size increased with the parameter (x). For the heterostructure samples with \(x = 0.5\) or 0.8, both phases ZMO and ZFO are formed. The obtained percentages for the developed phase are not equal to the intended values of the alloying parameter (x), which requires the exchange of cations between the phases ZMO and ZFO. Moreover, the cation exchange causes a redistribution of cations between the tetrahedral and octahedral sites of ZMO and ZFO. Furthermore, the change in lattice parameters of both ZMO and ZFO with the parameter (x), Table 1, is a good confirmation of cation exchange among the two phases. The changes in cell parameters are ascribed to the difference in the cations radii of Mn and Fe which is dependent on the residence site. The TEM images taken for sample \(x = 1.0\) are depicted in Figure 2(e, f) with different magnifications. It could be seen that the particle size is in the nano scale around 20 nm with a narrow size distribution and homogeneous particle morphology. The average particle size is the same as the crystallite size obtained from Rietveld analysis, Table 1, suggesting most particles are comprising single crystallite. The lattice microstrain increased for the nanocomposite samples as shown in Table 1, which may be attributed to the defects produced by the grain boundaries of the different phases present in nanocomposites.

To further investigating the elemental composition and the chemical binding states of the prepared materials, X-ray photoelectron spectroscopy (XPS) analysis is carried out, Figure 3, for the sample 0.5ZFO-0.5ZMO. Via decomposition of the XPS peaks, it can be noticed from Figure 3(a) that the Mn 2p spectrum consists of two peaks at binding energies 641.7 and 653.3 eV corresponding to the spin–orbit coupling at the 2p\(_1/2\) and 2p\(_3/2\) states of Mn\(^{3+}\). No satellite peak at around ~647 eV is observed which indicate that no Mn\(^{2+}\) ions is present. Moreover, the Mn 3s spectrum, Figure 3(b), is decomposed into two peaks with energy separation of 5.6 eV confirming the manganese is present as Mn\(^{3+}\) only [27]. The Zn 2p spectra, Figure 3(c), disclosed two sub-peaks at 1021.2 and 1044.3 eV, attributed to Zn\(^{2+}\) 2p\(_1/2\) and 2p\(_3/2\) states, respectively [3]. The Fe 2p spectrum consists of two groups of sub-peaks resulting from spin–orbit coupling at the 2p\(_1/2\) and 2p\(_3/2\) states. The fitting peaks at 710.4 and 724.2 eV in Figure 3(d) are ascribed to Fe\(^{3+}\) at octahedral sites, while the peaks at 712 and 727.2 eV are ascribed to Fe\(^{3+}\) at tetrahedral sites [28]. The peaks at (715.5, 719.2) eV and 732.5 eV are satellite peaks for Fe 2p\(_3/2\) and F 2p\(_1/2\) respectively confirming the state of Fe in the sample is Fe\(^{3+}\) [29]. Comparing the area of the fitted peaks, or even comparing the intensity-scale of the different cations spectra in Figure 3, one can find that the molar ratio of the cations Zn, Mn and Fe are very near to that used during preparation.

3.2. Dielectric properties

The change in the dielectric constant \((\varepsilon')\) at room temperature with frequency for the \((1-x)\)ZFO-xZMO samples is revealed in Figure 4(a,b). One can notice that all samples displayed a high value for dielectric constant at

| Table 1. The cell parameters (Å), average crystallite size is (nm), and the phase percentages for the heterostructure \((1-x)\)ZnFe\(_2\)O\(_4\)-xZnMn\(_2\)O\(_4\) samples for different values of (x). |
|---|---|---|---|---|---|---|---|
| x  | Size (nm) | Strain x10\(^{-4}\) | ZnFe\(_2\)O\(_4\) | ZnMn\(_2\)O\(_4\) | ZnO |
|---|---|---|---|---|---|---|---|
| 0.0 | 24.0 | 17 | 8.438(2) | 100 | — | — | — |
| 0.5 | 18.0 | 39 | 8.421 | 86.3 | 5.759(1) | 8.991(2) | 10.3 | 3.2477 | 5.2194 | 3.4 |
| 0.8 | 19.5 | 22 | 8.432 | 12 | 5.788 | 8.982 | 88 | — | — | — |
| 1.0 | 21.0 | 11 | — | — | 5.732 | 9.189 | 100 | — | — | — |
lower frequencies, which decreased as the frequency increased reaching a constant value at higher frequencies for all samples except ZFO sample. This feature is a typical behavior of ferrites that follows Koop's model [30]. In this model, samples may be divided into two parts: the highly conducting grains separated by the non-conducting grain boundaries [30]. At low frequencies, the electrons and holes, resulting from the different iron (Fe$^{2+}$, Fe$^{3+}$) and manganese ions (Mn$^{2+}$, Mn$^{3+}$) in the matrix, accumulate at the grain boundaries owing to their non-conducting characteristics, which yield high polarization values, causing a large dielectric constant. As the frequency raised, the frequency of hopping electrons and holes could not follow the frequency of the applied field, therefore the dielectric constant decreased. As the ZMO content raised in the (1-x) ZFO-xZMO matrix, the dielectric constant increased. According to the XRD analysis, samples with x = 0.5 and 0.8 have multi-phases, and therefore have several grain boundaries which help to accumulate more charges and therefore increase the dielectric constant. Furthermore, according to XRD analysis, Table 1, the crystallite size increased while microstrain decreased as the amount of ZMO increased in the matrix from x = 0.5.
Figure 3. XPS analysis for the 0.5ZnFe$_2$O$_4$–0.5ZnMn$_2$O$_4$ nanocomposite.

to 0.8. The increasing in the grain size and reduction in the microstrain caused an increase in the dielectric constant value [31]. Where sample with larger grain size has more ions and therefore the polarization and dielectric constant increased [31,32]. Similar observation was detected in nano MnFe$_2$O$_4$ sample [31]. On the other hand, the behavior of the dielectric constant in the case of ZFO sample may caused by the existence of more than one type of polarization in the sample [33].

The influence of temperature on the behavior of the dielectric constant ($\epsilon$') versus the applied frequencies is shown in Figure 5 for all samples. As noticed from the graph, the dielectric constant for ZFO slightly changed while the dielectric constant of the ZMO sample decreased with increased temperature. In contrast, the dielectric constant of the composite samples ($x$ = 0.5, 0.8) first increased then decreased with increasing the temperature. These changes are better shown in Figure 6 for temperature dependence of real dielectric constant ($\epsilon_r$) at different frequencies. Furthermore, as the frequency raised, the maximum of the dielectric loss at a higher frequency is due to the strong relationship between the dielectric feature and the conduction of ferrite materials. Furthermore, the $\tan \delta$ values in all samples are higher than in the ZFO sample. The broad peak was observed in the ZFO sample (Figure 7), demonstrating a relaxation character of the sample which takes place when the frequency of the hopping electrons and holes nearly equivalent that of the applied frequency, above and after this frequency it cannot follow the applied field and hence $\tan \delta$ reduced beyond it [36]. Besides, the change in $\tan \delta$ with temperature can be connected with the thermal activation of charge carriers that takes place from changes in drift mobility [37].

Figure 8 displays the ac conductivity ($\sigma_{ac}$) vs the frequency for all samples at various temperatures. It is noticed from the figure that the ac conductivity can be divided into several regions depending on the composition of each sample. In all cases, the ac conductivity increased with frequency but at a different rate. According to Koop's theory [30], ferrite consists of grains (good conductor) and grain boundaries (poor conductor). At low frequency, the grain boundary has a dominant influence and consequently, the hopping of electrons and holes between iron and manganese ions with different oxidation states happened and ac conductivity rose. As the frequency increased, high-conductive grains contributed to the conductivity process besides the hopping process, therefore the ac conductivity increased. Figure 9 revealed the ac conductivity at room temperature for all samples as a function of frequency. As revealed from the figure, the value of $\sigma_{ac}$ was increased as ZFO alloyed with ZMO reached its highest value in the 0.2ZFO-0.8ZMO sample. This increase may be owing to
Figure 4. (a, b) Real dielectric constant ($\epsilon$) and (c, d) dielectric loss (tan $\delta$) at 30°C for (1-x)ZnFe$_2$O$_4$-xZnMn$_2$O$_4$ samples.

Figure 5. The frequency dependence of the real dielectric constant ($\epsilon$) at different temperatures for (1-x)ZnFe$_2$O$_4$-xZnMn$_2$O$_4$ samples.
Figure 6. Temperature dependence of real dielectric constant ($\epsilon'$) at different frequencies for (1-x)ZnFe$_2$O$_4$-xZnMn$_2$O$_4$ samples.

Figure 7. The dielectric loss (tan$\delta$) at different temperatures for (1-x)ZnFe$_2$O$_4$-xZnMn$_2$O$_4$ samples.
Figure 8. (a-d) ac conductivity plots at different temperatures and (e-h) the temperature variation of the universal exponent (n) for (1-x)ZnFe$_2$O$_4$-xZnMn$_2$O$_4$ samples.
the presence of different Fe and Mn ions in the matrix with different contents.

The degree of correlation in each sample can be explored using the parameter $n$ in the Equation (6) by getting the slope of the linear relation between $\ln \sigma_{\text{ac}}$ versus $\ln \omega$, Figure 8(a-d). The temperature dependence of extracted $n$ values for each sample is represented in Figure 8(e-h). The different conductivity mechanisms in each sample can be described by: (i) the small polaron (SP) mechanism, as $n$ value raised with temperature, (ii) overlapping large polaron tunneling (OLPT) as $n$ values reduced with the temperature until a minimum value, then it raised again, (iii) correlated barrier hopping (CBH) mechanism, where $n$ is decreased with temperature and (iv) quantum mechanical tunneling (QMT) model, where $n$ is constant with temperature, respectively. The $n$ values for the ZFO sample in the low and high-frequency ranges follow the OLPT model [38]. In the intermediate frequency range, the sample exhibited the QMT and SP mechanisms [38]. In the ZMO sample, at a low-frequency range, the system has SP and CBH mechanisms. At a higher frequency range, the QMT mechanism is dominant. For nanocomposite with $x = 0.5$, at low frequency, the system exhibited a CBH mechanism. In the intermediate frequency range at higher temperatures, the system follows the SP and QMT mechanisms. At a higher frequency range, the system follows OLPT and CBH mechanisms. Finally, sample with $x = 0.8$, the system follows (OLPT), (SP, OLPT) and (CBH) in the low, intermediate and high-frequency ranges, respectively. The changing in the conductivity mechanisms with temperature and frequency in the different samples may result from the present of different phases, different ions and also the changing in the grain size in each sample, Table 1.

In dielectric materials, the influence of grain and grain boundaries can be investigated using impedance spectroscopy [39]. Figures 10 and 11 show how the real ($Z'$) and imaginary ($Z''$) parts of impedance change with frequency and temperature. As revealed from the figure, the real part of impedance spectroscopy has a high value at low frequency and it reduced with raising of the frequency until it attendance a constant value. The low value of impedance at a higher frequency may be owing to the space charge polarization which eventually gave rise to the high conductance. The amount of ZMO in the nanocomposite affected the value of $Z'$. As ZFO alloying with ZMO reached its lower value in the 0.2ZFO-0.8ZnMO sample, the $Z'$ values decreased; thus, it has a higher conductivity when compared to parent samples and other composite samples.

As a result of the Debye phenomenon, the relaxation processes are highly dominated as $Z''$ plotted as a function of frequency. All samples exhibited a highest value at a specific frequency except the ZFO sample. The position of the maximum value was varied as the temperature changed. The broadening in the peaks established the temperature dependence of the electrical relaxation phenomena in the material [40]. The charge carriers in these samples may contribute to the intrinsic conductivity in addition to the several dipolar relaxation mechanisms. In the case of the ZFO sample, the high value of $Z''$ at low frequencies may be due to space–charge relaxation caused by the association of charge carriers and oxygen vacancies trapped at the electrode interface.

Complex impedance spectroscopy is a powerful technique to understand the function of electrode/electrolyte interfaces, grain and grain boundaries, and the resistance of dielectric materials. The Cole–Cole graph of all samples is revealed in Figure 12 at various temperatures. As displayed from the graph, the impedance spectra revealed one semicircle arc at different temperatures. The centers of the arcs exist beneath the real axis, demonstrating a non-Debye-type character. The maxima and diameters of the different arcs vary depending on the composition of the sample and the investigated temperature. The decreasing or increasing in the semi-circle diameter confirmed the decline or improvement in the dc resistance, because of the raising or lowering in the mobility of the charge carriers. At room temperature, the sample with $x = 0.8$ in (1-x) ZFO-xZMO system has a lower diameter; therefore it displays a higher conductivity relative to other samples. According to Table 1, the crystallite size of sample with $x = 0.8$ is higher than that of sample with $x = 0.5$. Therefore, the impedance decreased due to the increasing in the grain size and reduction in the grain boundary [11,31,32,41–44]. The dielectric modulus is a very helpful parameter to clarify the relaxation characteristics of the ferrites [45]. Figure 13 depicts the variation of the real part of the modulus $M'$ with frequency at various temperatures. At a low frequency, the modulus has nearly zero value for all samples except the ZFO sample as a result of the existence of large capacitance. Furthermore, as the frequency increased, the value of $M'$ increased, which is due to the relaxation process [46,47]. All samples exhibited a continuous dispersion
Figure 10. The real impedance ($Z'$) at different temperatures as a function of frequency for (1-x)ZnFe$_2$O$_4$ - xZnMn$_2$O$_4$ samples.

Figure 11. The imaginary impedance ($Z''$) as a function of frequency at different temperatures for (1-x)ZnFe$_2$O$_4$ - xZnMn$_2$O$_4$ samples.
Figure 12. Impedance spectroscopy plots at different temperatures for (1-x)ZnFe$_2$O$_4$-xZnMn$_2$O$_4$ samples.

Figure 13. The real part of electrical modulus, $M'$ as a function of frequency at different temperatures for (1-x)ZnFe$_2$O$_4$-xZnMn$_2$O$_4$ samples.
caused by the induced electric field within the samples, which is responsible for the short-range mobility of charge carriers. A higher dispersion was observed in the 0.2ZFO-0.8ZMO sample. Figure 14 depicts the changing of the imaginary part of the electric modulus ($M''$) with frequency at different temperatures. At room temperature, all samples displayed one relaxation peak. As the temperature raised, the relaxation peak was split into peaks in the case of ZMO and 0.2ZFO-0.8ZMO samples. The positions of peaks were altered as the temperature raised, which indicated that the relaxation phenomenon has a temperature-dependent character in each sample. In nanocrystalline materials, the smaller size of grains caused an improvement in dipoles at grain boundaries. As the interaction between these dipoles at grain boundaries increased appreciably, the relaxation frequency decreased, causing a shift in the relaxation peak towards a low-frequency range at higher temperatures [48]. The peak revealed at a low frequency represented the grain boundary contribution, whereas the peak emerged at a higher frequency characterized the grain contribution.

4. Conclusions

XRD analysis manifested that samples with $x = 0.0$ (ZMO) and $x = 1.0$ (ZFO) exhibited a single cubic spinel phase (Fd-3 m) and a tetragonal spinel structure (S.G. I 41/a m d), respectively. Samples with $x = 0.5$, and 0.8, disclosed both phases, ZMO and ZFO with a minor ZnO phase in case of $x = 0.5$. The obtained percentages for the formed phases are not equal to the alloying parameter ($x$), necessitating a cation exchange among the ZMO and ZFO phases at the octahedral and tetrahedral sites of. TEM images displayed particle size in the nano range $\sim 20$ nm with narrow size distribution and homogeneous particle morphology. XPS analysis revealed that the molar ratio of the cations Zn, Mn and Fe are very near to that used during preparation. As the ZMO percentage raised in the ZFO/ZMO matrix, the dielectric constant increased. Samples with $x = 0.5$ and 0.8 exhibited a ferroelectric nature. The dielectric loss values in all samples are higher than in the ZFO sample. The ac conductivity was increased for the nanocomposites reaching its highest value for the $x = 0.8$ sample. The ZFO and ZMO samples exhibited (OLPT, QMT, SP) and (SP, CBH, QMT) mechanisms, respectively, based on the measured frequency range. Nanocomposite with $x = 0.5$ demonstrated (CBH), (SP, QMT) and (OLPT, CBH) mechanisms in the low, intermediate, and high-frequency ranges, respectively. The sample with $x = 0.8$ bayed (OLPT), (SP, OLPT) and (CBH) mechanisms in the low, intermediate, and high-frequency ranges, respectively.

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