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# EFFECT OF TEMPERATURE ON THE STRUCTURAL AND OPTICAL PROPERTIES OF $WO_3$ NANOPARTICLES PREPARED BY SOLVO THERMAL METHOD

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The tungsten oxide ($WO_3$) nanoparticles were prepared by simple solvo thermal cum chemical method. By using tungsten chloride in a cyclohexanol as a solvent. The nanoparticles are synthesized at different temperatures such as room temperature, 100°C, 200°C, 300°C, and 400°C respectively. The formation of $WO_3$ nanoparticles were confirmed by powder x-ray diffraction technique. Functional groups present in the nanoparticles for various modes of vibrations were confirmed by Fourier transform infrared spectroscopy analysis and Raman spectroscopy analysis. Ultraviolet – Visible NIR spectral analysis were used to find its optical transparency. The surface properties of the nanoparticles were investigated by Scanning Electron Microscope images. The micro structures of the nanoparticles were studied by the EDX spectrometry. The results show that the temperature used to synthesize nano particle is a key factor to get definite $WO_3$ nanoparticles.

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*Keywords:* X-ray diffraction, Tungsten oxide, Nano particles, Chemical synthesis

## 1. Introduction

In the last several decades, many transition metal oxides have been exploited in many challenging fields of information science, nano and micro-electronics, computer science, energy, transportation, safety engineering, military technologies, optoelectronic, electro chromic devices etc[1].Among them tungsten oxide ($WO_3$) is one of the most interesting materials exhibiting a wide variety of novel properties for advanced technological applications. It exhibits structural transformations and sub-stoichiometric phase transitions, which attracted the attention of researchers over the past few years to explore their potential scientific and technological applications in the fields of display systems and microelectronics [2, 3].

The semiconductor materials such as $WO_3$, $TiO_2$ and $V_2O_3$ are having band gap around 3eV and good chemical stability in aqueous solutions. These materials possess specific characteristics to use as photo electrodes in energy harvesting devices [4, 5, 6, 7]. It exhibits electro chromic properties which make it suitable for variable reflection mirrors, dazzle free mirrors in automobiles, variable sun protection system usually called 'smart window' (variable transmittance) and surfaces with tunable emittance of thermal control in satellites. It has been recognized as a significant chromic material that can be colored through electro, photo, laser and thermo chromism process [8]. Compared with other wide band gap semiconductors $WO_3$ can be used as an efficient photo-anode for water splitting under visible light elimination or gas detection.

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Moreover $WO_3$ nanoparticles are also interesting electro chemical materials due to their nano crystalline nature which affords an open and porous structure. The tungsten oxide ($WO_3$) nanoparticles can be prepared by various methods including chemical deposition [9, 10], sputtering [11], gas condensation [12], evaporation [13], sol-gel method [14] and laser deposition [15]. Kumar et al [16] already studied the effect of pH on the thermo chromic and photo chromic properties of the$WO_3$ nanoparticles. In this paper we investigated the effect of synthesized temperature on the structural properties of $WO_3$ nanoparticles.

## 2. Experimental

Tungsten chloride (Sigma Aldrich 99.99%) and Cyclohexanol were used as a precursor. 20 mg of Tungsten chloride was slowly dissolved in 5 ml of cyclohexanol to obtain a uniform solution with the help of magnetic stirrer. The solution initially shows yellow in color after 30 minutes stirring, color of the solution gets change into white color then the white color was changed into sky blue color after 45 minutes stirring. The solution was continuously stirred until to get dark blue color. The dark blue color indicates the formation of $WO_3$ nanoparticles. Then the solution was centrifuged and washed with distilled water until to reach neutral pH of the solution. During this period the nanoparticles settled in the bottom of centrifugal tube. After the centrifuge, the solution was subjected to slow evaporation to remove the excess solvent present in the solution at room temperature. After the evaporation of solvent the $WO_3$ nanoparticles were collected and transformed to a 125 ml Teflon-lined stainless steel autoclave at different temperature such as 100°C,200°C,300°C and 400°C for 5 hours respectively. X-ray diffraction method using CuKα radiation has been used to study the structure of the synthesized nanoparticles. This study was carried out by employing a Brukker Axs D8 Advance X-ray differactometer with CuKα (λ=1.5406) radiation using a tube voltage and current of 40kv and 30mA respectively. The sample was scanned from 15°-80°in 2θ with step size of 0.5° 2θ and scan speed of 0.5°2θ per second. Surface morphology of the synthesized nanoparticles was studied using scanning electron microscopy (SEM; Philips XL40), and the atomic compositions of the nanoparticles was measured by energy dispersive X-ray analyses (EDXA; Inca, oxford instruments) operated at 120 kV. The FTIR spectrum was recorded using pelletation method in the range 400 to 4000 $cm^{-1}$using a Shimandzu FTIR spectrometer. The functional group present in the $WO_3$ nanoparticles was confirmed by Raman Spectroscopy RA400, Mettler Toledo. The UV-Vis-NIR spectrum of the synthesized nanoparticles was recorded in the range 200-800nm using a Cary 5000(1.09 versions) with a scanning rate of 600nm/min.

## 3. Results and Discussion

### 3.1 Powder X-ray diffraction analysis.

X-ray diffraction pattern has been used to investigate the phase of the synthesized $WO_3$ nanoparticles. The X-ray diffraction pattern of $WO_3$ nanoparticles prepared at different temperatures is shown in Figure. 1.

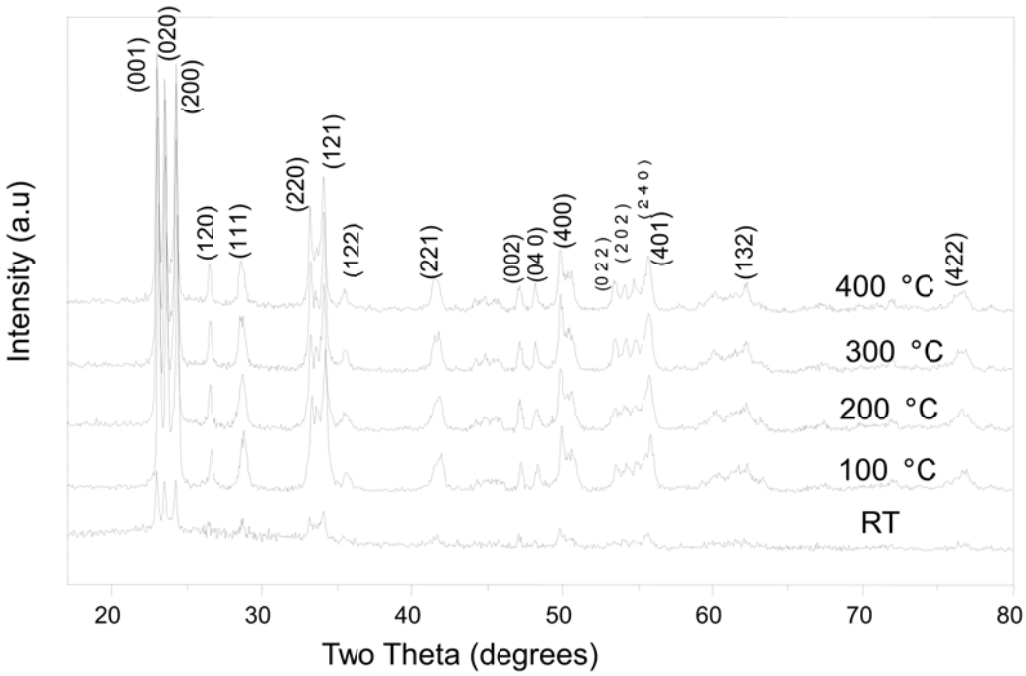


*Fig. 1. X-ray diffraction pattern of $WO_3$ as prepared, 100°C, 200°C, 300°C and 400°C annealed samples.*

From this XRD, it reveals that the crystal structure and prepared orientation of the crystallites that make up a definite micro structure. In this XRD pattern $WO_3$ nanoparticles obtained for different temperatures, such as room temperature,100°C,200°C,300°C and 400°C respectively. The characteristics peaks of (001), (020), (200), (120), (111), (220), (121), (221), (040), (240), (132), (422) observed at 2ɵ value 23.00, 23.50, 24.23, 26.49, 28.68, 34.00, 41.56, 48.19, 50.43, 55.71, 62.11, 76.28 respectively. The main peak of (001) and (200) corresponds to the 2θ value of 23.00 and 24.23 respectively and are prominent for temperature T = 400˚ C. In this XRD patterns matched with monoclinic $WO_3$ nanoparticles (JCPDS No. 05-0392). [16, 17]. The gradual emergence of different peaks as one goes from temperature T= 400˚C. This observation reveals that in the process of nano structure formation, definite planes of the growth are affected by the varying temperatures. From the XRD pattern the lattice parameter values are calculated by analytical method and are given in table 1.

*Determine lattice parameter values of $WO_3$ nanoparticles*

| Temperatures | Lattice parameters (A˚) |
|---|---|
| Room Temperature | a=6.987; b=6.156; c= 6.59 |
| 100˚C | a=7.023; b=7.304; c= 7.458 |
| 200˚C | a=7.125; b=7.369; c= 7.752 |
| 300˚C | a=7.220; b=7.462; c= 7.836 |
| 400˚C | a=7.312; b=7.621; c= 7.920 |

### 3.2 FTIR Analysis

Fourier Transform Infrared (FTIR) spectroscopy is a promising method for observing molecular vibrations. Figure 2 shows the FTIR spectra of $WO_3$ nanoparticles prepared at 100°C.

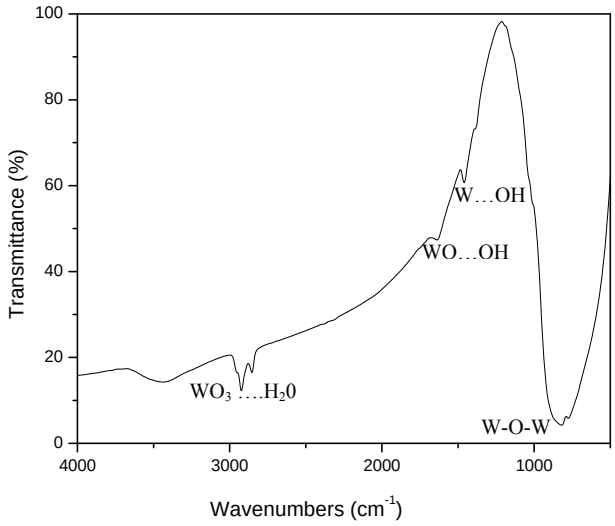


*Fig. 2. FTIR spectra of as prepared $WO_3$*

FTIR spectra give us the information with regard to different mode of vibrations of atoms or molecules with associated energies in the infra red regime. The stretching vibration of WO3 nanoparticles accrued at 963 $cm^{-1}$. In fact $WO_3$ nanoparticles consist of packed corner sharing $WO_6$ octahedral containing 4 atoms and 6 fundamental normal modes of vibrations. Intercalated water molecules (W-OH…..$H_2O$) are characterized by a prominent peak at 2900 $cm^{-1}$. The presence of these peaks indicates the formation of $WO_3$ nanoparticles. Different functional groups present in the synthesized material were assigned based on the correlation table given in the standard manners. The assigned vibration modes of different functional groups present in the material are given in table 2.

*FTIR assignments*

| S.No. | Group | Wave numbers ($cm^{-1}$) | Assignment |
|---|---|---|---|
| 1. | W-OH…$H_2O$ | 2900 | $\nu_{sym\ (OH)}$ |
| 2. | O-H | 1526 | νOH |
| 3. | W-OH | 1441 | δW- OH |
| 4. | W=O,W-O | 963 | ν W-O |
| 5. | W-O-W | 892 | ν ( W-O-W) |

### 3.3 Laser Raman spectral analysis

The Raman spectra of the synthesized $WO_3$ nanoparticles prepared at 100°C and 400°C is shown in Figure. 3.

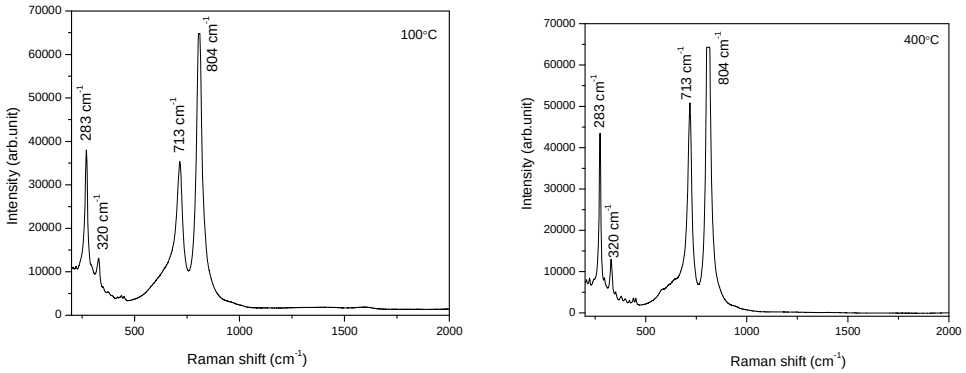


*Fig. 3. Raman spectra of $WO_3$ nanoparticles prepared at 100°C and 400°C*

Laser Raman spectroscopy is used to identified the functional groups present in the material. In this method have efficient than that of FTIR spectroscopy because some of the additional peaks also observed in laser raman spectroscopy than that of FTIR spectroscopy. Here the mode at 804 $cm^{-1}$ and 713 $cm^{-1}$ corresponds to the stretching vibrations of O-W-O, where as the modes at 320 $cm^{-1}$ and 283 $cm^{-1}$ corresponds to bending vibrations of W-O-W. These peaks are characteristics of $WO_3$ nanoparticles as well. No impurity peaks other than $WO_3$ nanoparticles were observed, which shows that purity of the as synthesized material.

### 3.4. UV-VIS-NIR Spectral Analysis

The optical absorption properties of the WO3 nanoparticles were studied by UV-visible spectroscopy and the results are presented in Fig. 4.

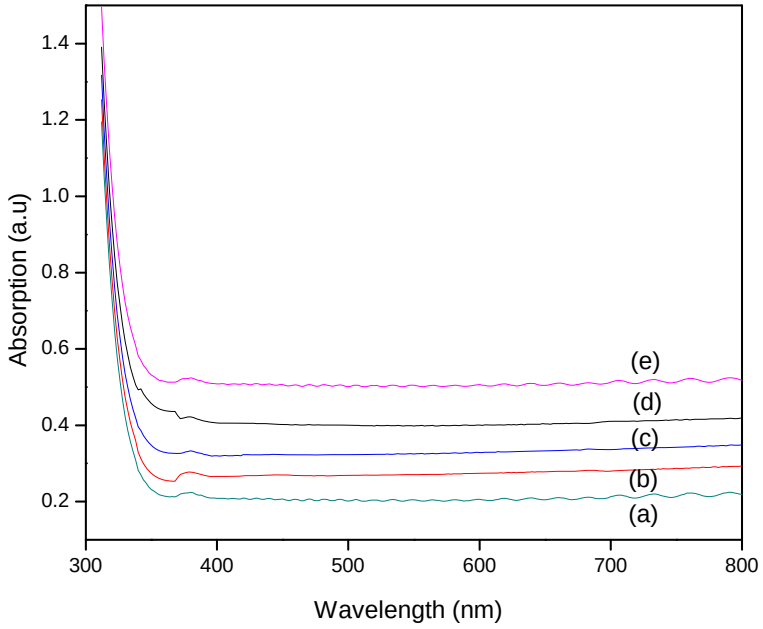


*Fig. 4. UV-VIS-NIR Spectral Analysis of $WO_3$ as prepared, 100°C, 200°C, 300°C and 400°C annealed samples*

The optical properties of WO3 nanoparticles in the visible region are dominated by the absorption threshold, which is defined by the band gap energy of the materials. The onset positions of light absorption for all particles were found to be almost similar because of very change in particle size of the materials with annealing temperature as was observed by XRD study of annealed particles. However, this small change of the crystallite size was reflected on the UV–visible spectral data in the region of 371–396 nm wavelengths with a red shift of absorption wavelength. The results in this study are in good agreement with previous researches.

### 3.5. SEM and EDAX analysis:

The scanning electron microscope images of the $WO_3$ nanoparticles prepared at different temperatures are shown in Figure.5. (a, b , c and d)

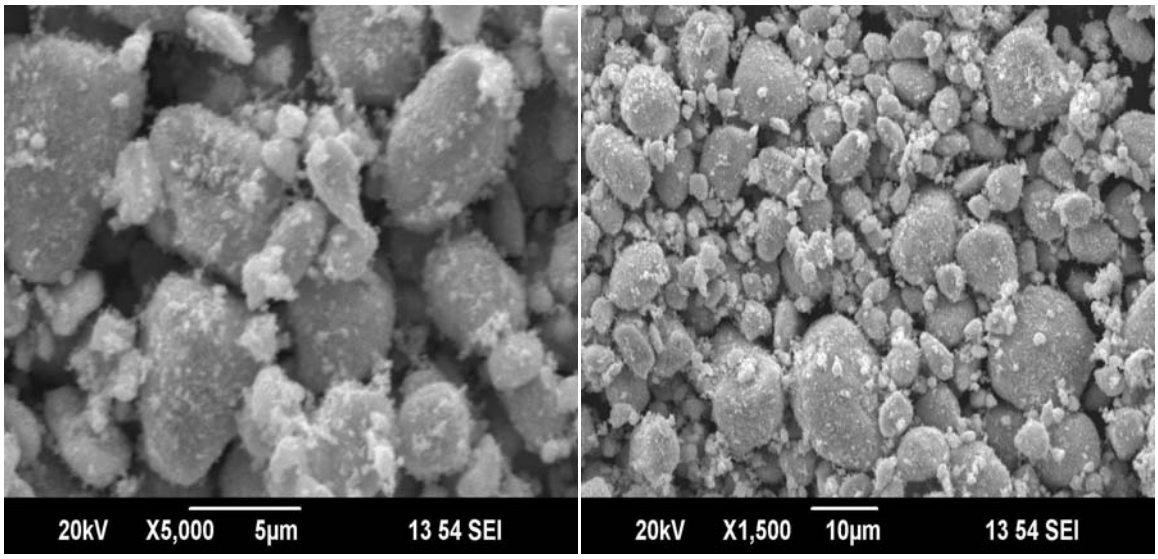


*Fig. (5.a) and (5.b) at 100˚C*

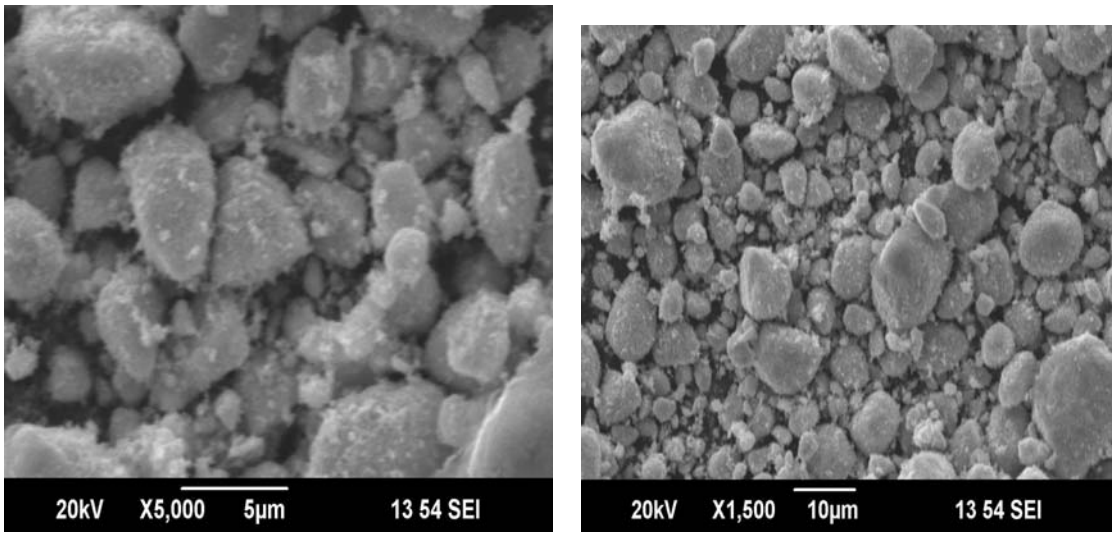


*Fig. (5.c) and (5.d) at 400˚C*

The surface morphology of the $WO_3$nanoparticles is put in the evidence from SEM images and to determine the particle size range, a number of SEM images were taken and examine in figure. (5.a), (5.b), (5.c) and (5.d). Fig (5.a) and (5.c) is a low magnification SEM image of the

$WO_3$nanoparticles. Fig (5.b) and (5.d) shows a large number of individual nano particles lying a top one another with a size range of 200-400 nm along long axis and 300-500 nm in short axis. A spherical shape $WO_3$nanoparticles were obtained by solvo thermal cum chemical method. These spherical particles are rough surfaces as indicated in fig (5.a), (5.b), (5.c) and (5.d). The average particle sizes of the synthesized WO3nanoparticles have the same particle size with different temperatures.

Energy dispersive x-ray analysis (EDAX) pattern of the $WO_3$ nanoparticles prepared at 100°C is shown in Figure.6. The origin of copper is from the copper coating on the particle. The EDAX spectrum reveals the representative peaks of oxygen and tungsten with copper peak from the formvar carbon-coated grit in figure (6). All the carbon had been removed during the sintering process [18]. The tungsten element is found in small which is consistent with the concentration of XRD patterns and SEM micrographs.

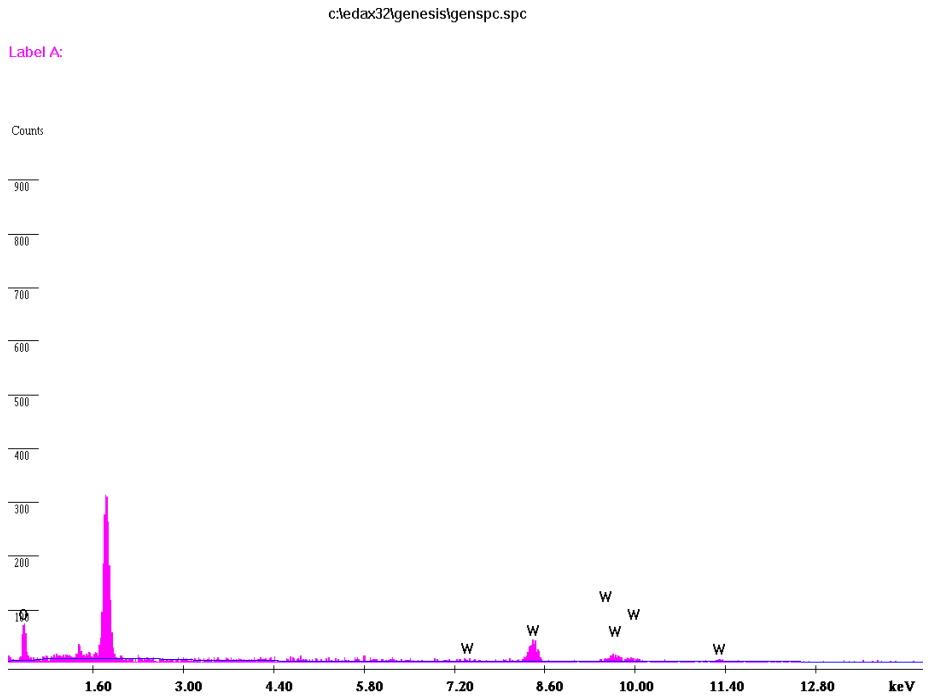


*Fig. (6). Energy dispersive x-ray analysis (EDX) pattern of the $WO_3$ nanoparticles prepared at 100°C.*

## 4. Conclusion

$WO_3$ nanoparticles were synthesized with different temperatures by using solvo thermal cum chemical method and its structural, optical and surface properties were studied. We have synthesized $WO_3$ nanoparticles with different temperatures and obtained spherical shape $WO_3$ nanoparticles. From the XRD analysis we confirmed the formation of $WO_3$ nanoparticles. The functional groups present in the synthesized materials was confirmed by FTIR and laser raman spectroscopy. SEM and EDAX reveals that the surface morphology of the synthesized material and composition of $WO_3$ nanoparticles. The optical absorption of the synthesized $WO_3$ nanoparticles was studied by UV-VIS-NIR spectroscopy. The significant about this research is that the heat treatment has to be controlled the crystallites of $WO_3$ nanoparticles.

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