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RESEARCH PAPER

Study of Plasma Parameters, Optical, and Structural Characteristics of Nanoparticles for MnO_2/CdO Combination by Laser Ablation Technique

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ABSTRACT

In this paper, the plasma parameters were studied using LIBS technology for lines of the emission spectrum of MnO_2/CdO compounds mixture (50%MnO_2 and 50%CdO) due to their exposure to high energy laser pulses (Nd-YAG laser),1064 nm, 1Hz. A temperature of electrons was calculated using the Boltzmann plot method in Local Thermal Equilibrium (LTE). The results showed the highest temperature (0.2017 eV) at laser energy of 350 mJ for the spectrum lines of the MnI element, as well as density of electron, Debye length and the number of particles into Debye sphere of the spectrum resulting from different laser energies at a constant frequency, is one hertz for each measures. Also, structural FE-SEM, XRD were measured at this values to define nanoparticles type was created, nearly particle size is 64.37nm for FE-SEM measurements and crystal particle size is 26.1 for maximum peak in XRD image by using Scherer equation in measure.

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INTRODUCTION

A spectroscopic techniques was used Laser Induced Breakdown Spectroscopy (LIBS) is based on the detection and analysis of atomic emission lines, which results in the sample being instantly ionized when the energy of photons from the laser is absorbed [1].

LIBS technology uses a high-power laser pulse to determine the elemental composition of the sample and the relative concentrations of the components of the target. Then, vaporize a small amount of the target material. The generated plasma contains the excited atoms and ions present in the target and sometimes contains molecules formed by reconnecting those atoms when the plasma decays. Atoms, ions, and molecules lose their energy by spontaneous emission of optical wavelength photons, so the spectroscopic analysis of plasma light will lead to the identification of the elements in the target material because the spectral lines within the emission spectrum are a unique spectral signature of the components [2].

Atomic components emit a characteristic light and can be seen using optical fibers and analyzed with a spectrometer. Optical emission spectrometry (OES) has recently attracted much interest as a technique for LIBS-based imaging. Because the energy from of the laser pulse heat up, removes, disintegrates, and ionizes the sample material, plasma is created. [3,4].

THEORETICAL PART

A spectrometer and detector are used to examine and analyze the plasma column.

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Quantitative and qualitative information, such as the starting composition, can be determined from the resulting plasma spectrum. The length, forms, and fluctuations of emission lines provide information about plasma temperature and electron density.

The ratio approach is one of the most used procedures for OES, and the Boltzmann plot method is one of the best techniques for measuring electron temperature at local thermodynamic equilibrium (LTE) [5].

The temperature of plasma is calculated from spectral lines dependent on the atomic emission spectroscopy theory, the following equation [6] gives the relative intensity of the spectral lines:

$$\ln\left(\frac{I_{ki}\lambda_{ki}}{g_k A_{ki}}\right) = -\frac{E_k}{k_B T_e} + C \quad (1)$$

where I_{ki} is the intensity of light emitted from the upper (k) to lower I levels, nm is the wavelength, g_k is the statistical weight of the upper level ($g_k = 2J_k+1$), A_{ki} is the Einstein transition probability of spontaneous emission, Ek /kB is the normalized energy of the upper electronic level, KB is the Boltzmann constant, and C is given by the relation:

$$C = \ln\left(hcN_k/4\pi Q(T)\right) \quad (2)$$

The partition function is Q (T).

$$\text{Slope} = -\frac{1}{k_B T_e} \quad (3)$$

The Stark effect is significant in the case of the laser induced plasma by the electric field generated, which is mostly caused by the collision of electrons, with minor contributions from the ion collisions.. Also, the density of electrons in the case of local thermal equilibrium can be calculated through the following relationship [7].

$$n_e(cm^{-3}) \geq 1.6 \times 10^{12} T_e^{1/2} \left(\Delta E_{ij}\right)^3 \quad (4)$$

n_e: Electrons density.

E_{ij} : the excitation energy in (eV) is the spontaneous transfer of radiation from the i plane to the j plane.

The plasma frequency is set so that any perturbation of the plasma's semi-neutral equilibrium produces electric fields; this frequency, which is exclusively dependent on plasma density, is one of the most critical plasma parameters. The plasma frequency is frequently very high due to the small size of m, as estimated by the following equation [8]:

$$\omega_p = \left(e^2 \times n_e/\varepsilon_0 \times me\right)^{1/2} \quad (5)$$

ε_0 is vacuum permittivity, e is electron charge, n_e is density of electrons, m_e is mass of electron

The Debye length (λ_D) is a fundamental property of plasma behavior, describing the distance between a particular particle and another charged particle in the plasma medium that has a reverse charge. The Debye length is directly proportional to the square root of the electron temperature, as in the following equation [9]:

$$\lambda_D = \left(\varepsilon_0 k_B T_e/e^2 \times n_e\right)^{1/2} \quad (6)$$

The Debye length λ_D must be very small when

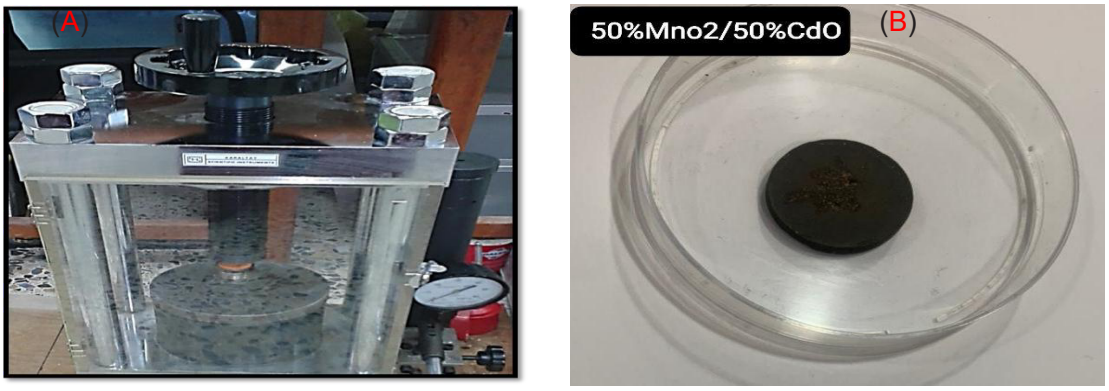

Fig. 1. (A) The pressure system used to compress research samples. (B) A picture of the sample prepared for the mixtures with equal weight ratios in this work after the pressing process

comparing this first condition for the existence of plasma with system dimensions d <<<L) [10] , λ_D Debye length in unit (cm), L dimension of the system (cm), Te electron temperature (eV), e is Electron charge (C). Also, the number of particles in Debye sphere is given by [10]:

$$N_D = \frac{4}{3\pi n_e} \lambda_D{}^3 \quad (7)$$

The major goal of this study is to employ a spectral emission of light to examine the properties of the plasma by using spectral lines of elements released from pure atoms around the plasma (CdO, MnO_2 at equal weight ratios of mixing).

MATERIALS AND METHODS

A sensitive scale was used to weigh 100% of the pure manganese oxide and 100% of the pure cadmium oxide. Then the samples were mixed with different weight percentages, as (50%) of the manganese oxide was mixed with (50%) of the Cadmium oxide was mixed well using a pottery mortar, and in the same way the rest of the mixtures were prepared (65% of manganese oxide with 35% of cadmium oxide).

Sample Compression

The powder was pressed from pure manganese oxide and cadmium oxide, which were mixed into tablets using a hydraulic press made in China, applying pressure (4 tons) for 10 minutes. This piston consists of a small mold in which the material to be pressed is placed to prevent the user from cracking the mold, the piston is surrounded by a thick glass blocker. The hydraulic oil in the piston increases the pressure that can be read when moving the pressure escalation lever using the counter. Steel molds are used according to the dimensions of the required sample, if the thickness of the disc for the pure substance and mixtures is up to (4 mm) with a diameter of (3 cm), this leads to the use of both surfaces of the pressed discs in the sedimentation process. Fig. 1 shows a picture of the hydraulic piston.After pressing, we expose the discs to laser pulses to measure the emission spectrum produced using pulsed laser fragmentation (LIBS).

Practical Steps for Operating the LIBS Technology

LIBS technology was designed to detect induced plasma emission spectra from compressed disks, it consists of a Nd-YAG laser and a passive specificity factor switch operating with a basic wavelength (1065nm) and a pulse duration (10ns) used to generate plasma, laser energies (150,250,350,450mJ) were used . By means of

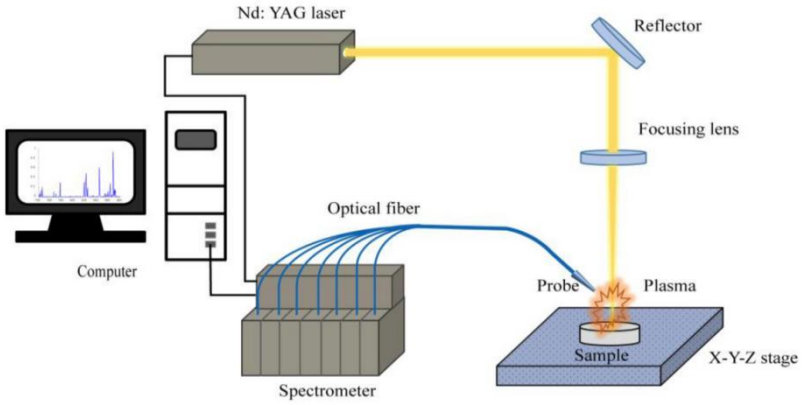

Fig. 2. A schematic diagram of a measurement experiment [11].

Table 1. Spectroscopic parameters of selected MnI emission spectral lines at laser energy=150 mJ

Intensity (a.u.)	λ(nm) Exp.	λ(nm) NIST	$g_i A_{ik}(s^{-1})$	E_i. E_k (cm^{-1})
103.051984	405.821	405.9388	1.4e+07	24788.05 - 49415.35
102.515563	446.25	446.108	1.7e+07	24802.25 - 47212.06
57.7475948	637.519	638.476	1.2E+06	30425.71 -46083.89

the fluorescent lens, the laser pulse was focused on the sample, the incoming diameter decreased from (5 mm) from the laser head to (0.027 mm) on the sample, with a focal length of (10 cm).

The target is placed in the sample holder, the sample was placed at the same distance from the focusing lens as the focal length of the lens (10) cm. The optical fiber was positioned and adjusted at an angle of 45 degrees with the laser axis, with a distance of (5 cm) from the sample.The luminescent lens, placed at the inlet of the optical fiber, collects and focuses the plasma emission into the aperture of the optical fiber, which has a diameter (NA = 0.22/200 µm , the plasma emission fibers are submitted to the slit inside the spectrum analyzer model (Spectra View 2100), with a silicon-charged device sensor (Si-CCD), which consists of a set of detectors to record spectral lines with (600 Lines/mm) notches, as It works to scatter the As shown in Fig. 2, light is detected and converted into digital signals according to the wavelength reflected by the mirrors.

Then the program (Visual Spectra 2.1) converts the digital signals, and detects the spectral lines of the materials inside the target. The spectrum was recorded at an accuracy of 0.8nm over a range of wavelengths (200-900) nm. Using the NIST database, all spectral data were verified.

RESULTS AND DISCUSSION

The plasma emission spectrum to MnO_2/CdO mixture is shown in Fig. 3. It was observed that the spectral lines of magnesium emission were obtained in emission spectra produced from a sample of the mixture using an Nd-YAG laser at different laser energies at an atmospheric pressure According to the research, they dominate the emission spectra, and the cadmium lines are weak. The resulting range featured several spectral lines, some of which were selected and applied to The Boltzmann plot method was used to calculate the plasma temperature. As an example of utilizing the Boltzmann equation to estimate plasma temperature was dependent the information in

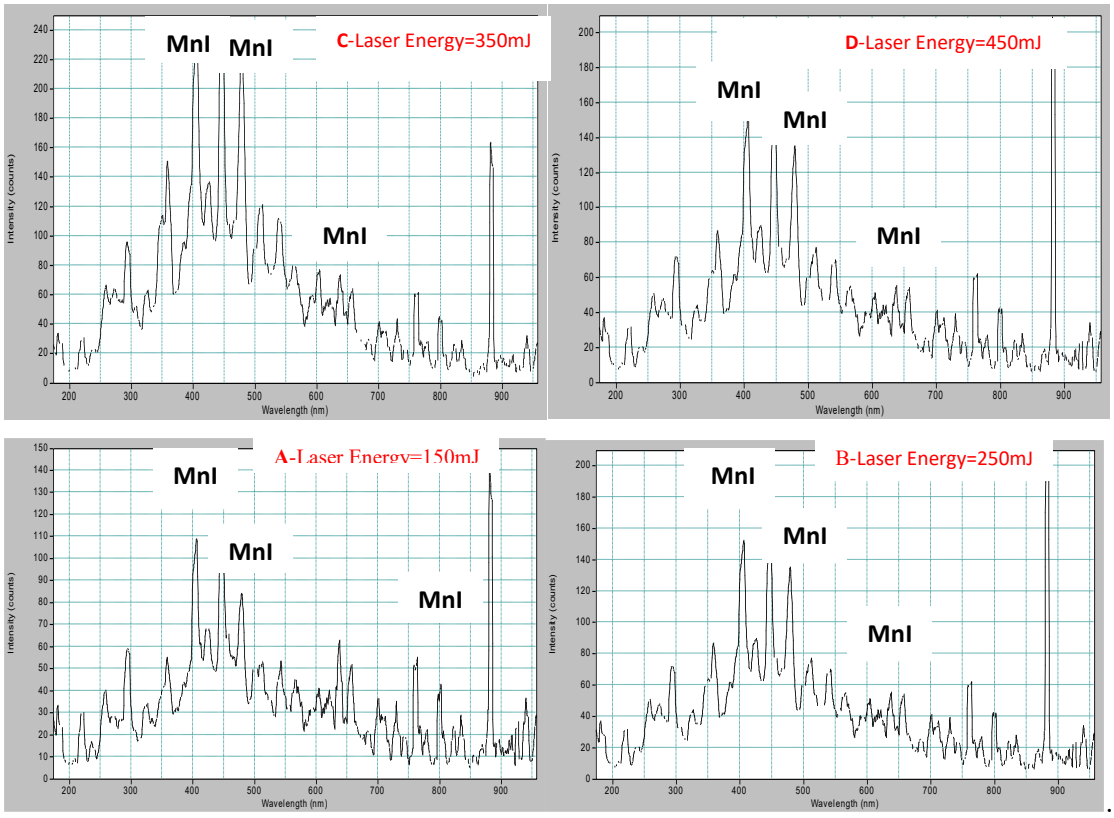

Fig. 3. Emission spectrum of a mixture of compounds at a Pulse frequency of 1 Hz and pulsed laser energies of A-E=150 mJ ,B-E=250mJ, C-E=350mJ, D- E=450mJ

Table 1.

The results obtained from the emission spectrum of MnO_2/CdO mixture with equal weight ratios at 1 Hz laser pulse frequency showed some scientific conclusions in Fig. 3

The emission spectrum of the element MnI was obtained with three values selected with high intensities are presented in Fig. 4. They compared with the NIST database and by applying the Boltzmann plot method used in this study, the plasma parameters such as electron temperature, plasma frequency, electron density, Debye length and the number of particles in the Debye sphere were calculated according to Table 2.

The effect of changing the laser pulse energy on the nature of the plasma formed on the surface was studied, as the best laser energy was used at 350 mJ according to the given results in Table 2.

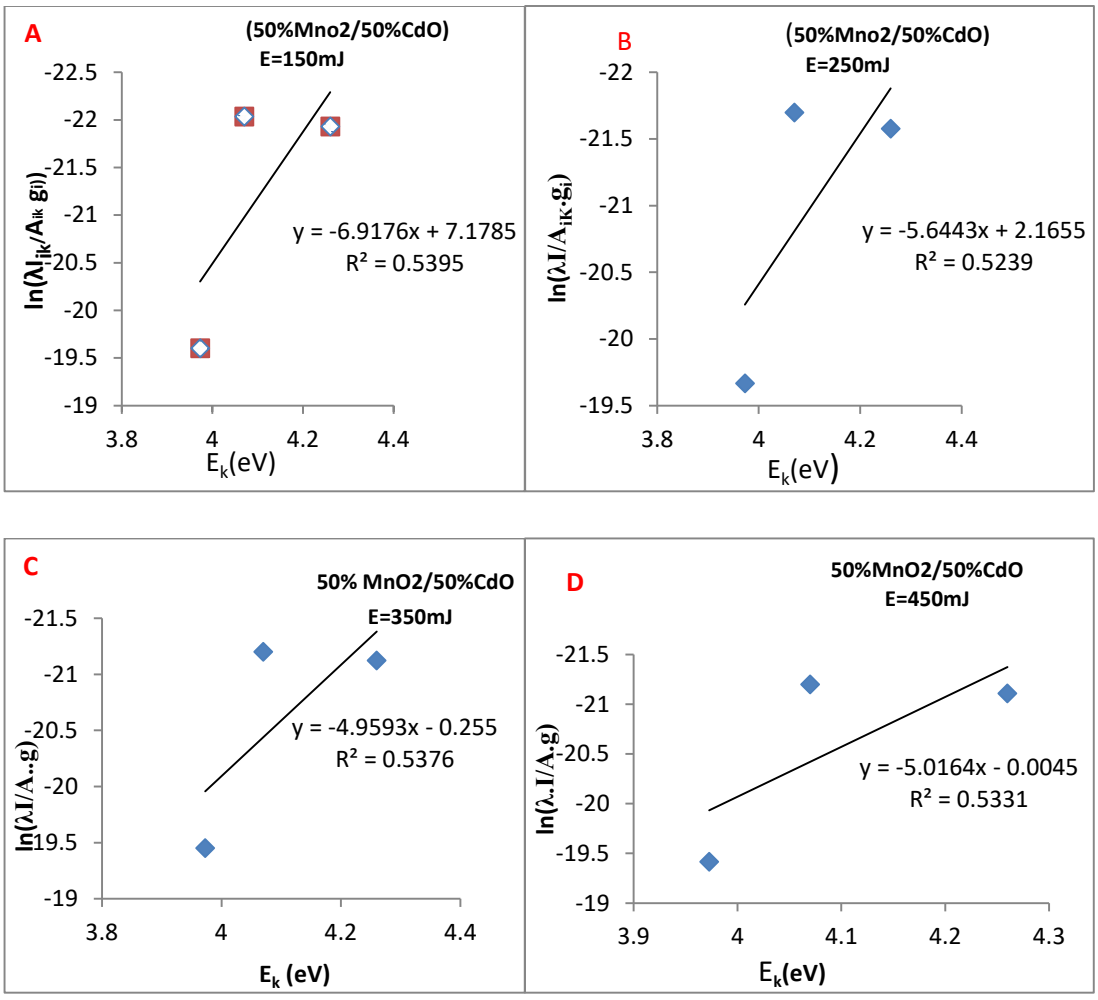

Fig. 4. Boltzmann plot for MnI spectrium lines at different of laser energy A-E=150mJ, B-E=250mJ, C-E=350mJ, D- E=450mJ.

Table 2. Plasma Parameters Measurements as a function for change of laser energy at pulse frequency is 1Hz.

Element type	Laser energy(mJ)	T_e(eV)	n_e(cm^{-3})	λ_D(cm)	N_D	ω_P(Hz)
MnI	150	0.144656	2.52E+15	5.64E-05	1.88E+03	2.36E+08
MnI	250	0.177246	2.79E+15	5.93E-05	2.44E+03	2.97E+09
MnI	350	0.201728	2.97E+15	6.13E-05	2.86E+03	3.07E+09
MnI	450	0.199432	2.95E+15	6.11E-05	2.82E+03	3.06E+09

The Structural properties of Thin Film
FE-SEM Measurements

Fig. 5 shows a scanning electron microscope image of a mixture of manganese oxide and cadmium oxide by weight (50%:50%) for each compound in the distilled water solvent. It is noted that the particles are spherical in most of them, and some particles fuse with each other to form larger particles In size, the reason is due to the phenomenon of coalescence that occurs between the particles caused by the aggregation nucleation process and the conditions for the formation of nanoparticles, and the extent of the spacing between the particles is due to the low concentration of cadmium oxide particles, which increases with the increase in the number of pulses of rays The laser is falling on the target. The measurements of FE-SEM is shown in Fig. 5, hence the low values is 64.37 nm

X-ray diffraction tests (XRD)

Models of manganese oxide and cadmium oxide films were examined for the weight ratio 50%: 50% for the elements manganese oxide and cadmium oxide using the X-ray system to determine the crystal structure, and the X-ray scattering energy system was used to find out the molecular weight ratios of the compounds·

The measurement was carried out on the prepared mixture sample after being scattered by a pulsed laser and using the Scherrer equation and matching it with the results close to it that

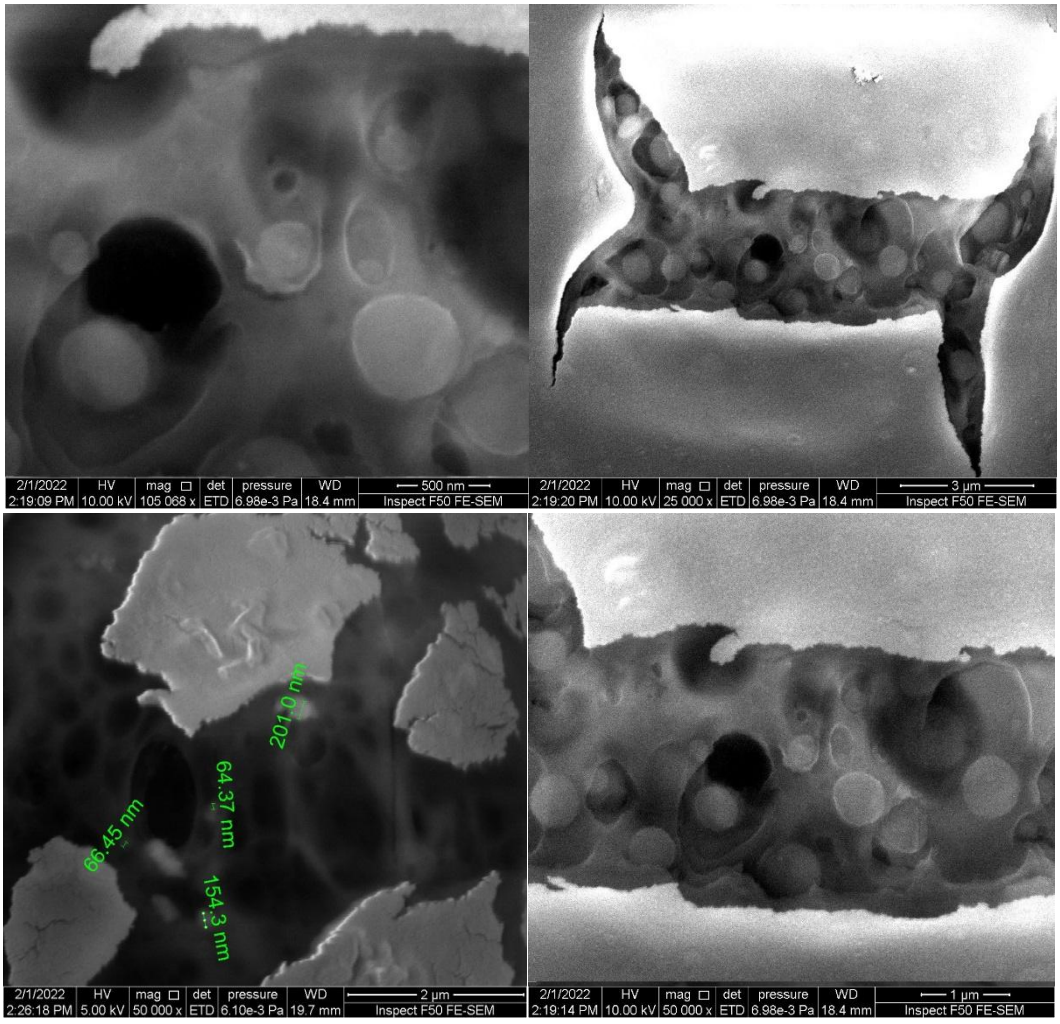

Fig. 5. FE-SEM images for MnO2/ CdO compound mixture.

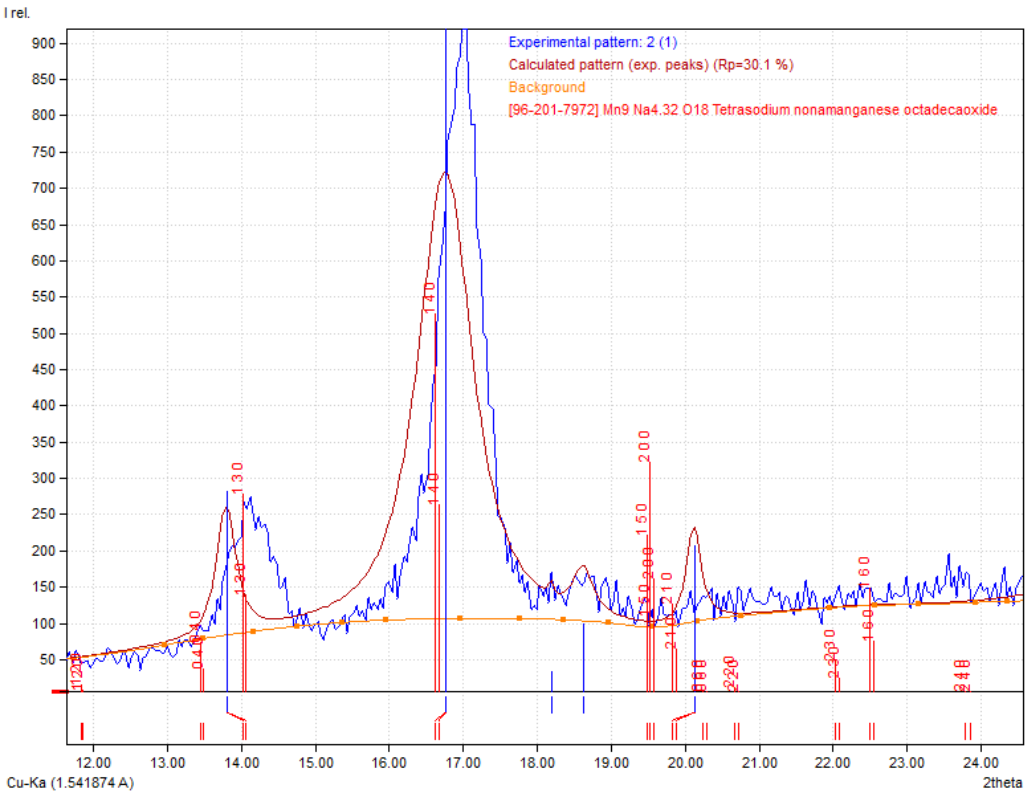

Fig. 6. Represents of XRD Peaks for MnO_2/CdO mixture.

the highest peak was at Θ = 16.82, and Miller's coefficients for it and using and applying the mentioned equation after converting the angle units to the diagonal units was obtained Crystal size of about 26.1 nm.

The manganese oxide / cadmium oxide nano film is mostly polycrystalline with crystalline peaks, especially at the corners (8.49, 15.88) with crystallization size of (26.1), (91.3)} nm respectively and it is compatible with the identification card as in Fig. 6), it was noticed the appearance of some small peaks, which indicate the emergence of crystallization. Also, indicates the emergence of some peaks to indicate the existence of a synergistic bond between manganese oxide atoms and cadmium oxide atoms. Fig. 6 indicates that there is a clear crystallization with two peaks to indicate an increase in crystallization due to the increase in the synergistic bonds between manganese oxide and cadmium oxide, despite the oxidation of cadmium oxide atoms. The researchers concluded it as shown in the figures) with the presence of weight values related to manganese oxides when preparing aqueous solutions of manganese oxide and cadmium oxide. That is, the preparation conditions have a significant impact on the structural and morphological properties as well as the optical properties. As for the values of the granular sizes, as their values range between (26.1-91.3 nm) to indicate that nanosolutions can be manufactured using the laser scraping method with different values that depend on the laser energy and the components of the composition and determine the crystal sizes from the process of separating nanoparticles using the centrifugal system, while the value of the separation distance Between the crystalline levels, it was (4.061)A° for the film of the prepared sample.

CONCLUSION

The results showed that the spectrum of manganese element is dominant in this mixture through spectral emission compared with the element cadmium, where the percentage of its appearance was weak, and this indicates the formation of manganese nanoparticles at a high rate compared to other elements to increase the ionization ratio of manganese atoms. The

study showed that the proportion of the mixture is the first effect of manganese elements in the formation of the plasma responsible for the production of nanoparticles at the values of the applied energies, through which the produced energies of the highest intensity will depend in create of thin films.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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