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Synthesis and Characterization of (MoO_3 / $NiAl_2O_4$) Nanocomposites and Studying Their Structural, Electrical and Magnetic Properties

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Abstract

(MoO_3 / $NiAl_2O_4$) composite was prepared by ceramic method and calcined at (450℃, 550℃ and 650℃). The effects of the annealing temperature on the structural, magnetic and electrical properties of the samples were studied by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), vibrating sample magnetometry (VSM) and LCR-meter. XRD tests proved that the grain size values of phases are ranged between (55.34 and 58.68nm), as it is shown that a temperature of (550℃) leads to the disappearance of (MoO_3) phase and the emergence of new ($NiMoO_4$) phase and this shows that the degree of heating increased the granular size.

The results of the FESEM of *(MoO_3 / $NiAl_2O_4$)* showed that the particle size values increased with the appearance of new phases. VSM tests proved that when increasing the amount of nickel and reduce the amount of alumina in nanocomposites, there is an increase in magnetic saturation (Ms) and this increase is irregular and leads to an increase in crystals size. The results of dielectric tests showed the emergence of the highest peak of the real and imaginary dielectric constant, at the lowest frequency which decreases with increasing frequency at low frequencies.

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Keywords: XRD, FESEM, Magnetic properties, Electrical properties.

تحضير وتشخيص متراكبات MoO3 /NiAl2O4 النانوية و دراسة خصائصها التركيبة و الكهربائية والمغناطيسية

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الخلاصة

تم تحضير المتراكب MoO3 / NiAl2O4 بتأثير درجات الحرارة المختلفة و المكلسنة عند 450°C، 550°C و 650°C بالطريقة السيراميكية. وتم تشخيصها من خلال دراسة الخواص التركيبية والكهربائية والمغناطيسية. وقد تبين من نتائج حيود الاشعة السينية للمتراكب MoO3 / NiAl2O4 المحضر ان قيم الحجم الحبيبي للمتراكب محصورة بين (55.34nm و 58.68nm)، اذ ان يبين عند درجة الحرارة 550℃ يؤدي الى اختفاء الطورMoO3 وظهور الطور NiMoO4 وهذا يعود الى انه كلما ازدادت درجة الحرارة ازداد الحجم الحُبيبي. وتبين من نتائج فحوصات المجهر الالكتروني الماسح الباعث للمجال FESEM للمتراكب MoO3 / NiAl2O4 ان قيم الحجم الحبيبي تزداد بظهور الاطوار الجديدة، وتبين من نتائج فحوصات VSM عند زيادة كمية النيكل وتقليل كمية الالومينا في المركبات النانوية نلاحظ زيادة مغنطة التشبع المغناطيسي Ms وتكون هذه الزيادة غير منتظمة وهذا يؤدي الى زيادة حجم البلورات، ان جميع المساحيق لها حلقة هسترة خطية تقريبا والتي تسلك سلوك البارامغناطيسية لجميع المركبات النانوية، وكذلك تبين من نتائج فحوصات الخصائص العزلية ظهور اعلى قمة لثابت العزل الحقيقي والخيالي عند اوطأ تردد فهو يتناقص مع زيادة التردد عند الترددات الواطئة اما في التوصيلية المتناوبة عند الترددات العالية تزداد التوصيلة بزيادة تردد مجال الكهربائي المسلط.

الكلمات المفتاحية: XRD، FESEM، الخواص المغناطيسية، الخواص الكهربائية.

Introduction

Oxide spinels have been investigated in the solid-state sciences due to their usefulness as pigments, refractory, catalysts and electronic ceramics [1]. Interest in the synthesis of spinels like $NiAl_2O_4$ has increased due to its excellent strength and good wettability with metals at high

temperature, the $NiAl_2O_4$ can be used as a good ceramic skeleton for infiltration of metals at high temperature [2].

Oxide is used in nanowires, nanofibers, plastics, and textiles in specific applications of alloys and oxidation catalysts, cracking catalysts, hydrogenation catalysts and pigments also besides to use in the production of ceramics and glass and as raw materials in the industry of molybdenum metals [3]. Several preparation methods have been studied to obtain crystalline MoO_3 / $NiAl_2O_4$ spinels with small particle sizes, such as sol-gel synthesis [4 and 5], sonochemical method [6], microwave heating [7], polymer solution route [2] and solid-state reaction [8].

The aim of the present work is the synthesis of $NiAl_2O_4$-MoO_3 composites by a ceramic method and studying the effect of temperature on their structural, electrical, and magnetic properties.

Experimental work

Materials used

Analytical grade chemicals, aluminum chloride hexahydrate $AlCl_3.6H_2O$, ammonia solution, (36%), sodium hydroxide, (NaOH), nickel chloride hexahydrate ($NiCl_2.6H_2O$), citric acid ($C_6H_8O_7$), ammonium heptamolybdate $(NH_4)_6$ $Mo_7)_{24}.4H_2O$ were used without further purification processes.

Instruments used in characterization

The X-ray diffraction system which used in this research is in the Ibn Al-Haytham College of Education, University of Baghdad and the type of XRD is (6000- XRD) manufactured in Japan by (Shimadzu). The field emission scanning electron microscope (FESEM) which is used in this study is (MIRA3, Mode lTE-SCAN) and in a research laboratory in Iran. An (LCR-8105G) devise of Thai origin and produced by (GWINSTEK) is used to measure and study the electrical properties which is in the central laboratory - College of Science - University of Diyala.The

magnetic properties were measured by magnetization of oscillating model A (VSM- LBKFB model) in Iran and produced by (Meghnatis Daghigh Kavir).

Procedure for preparation

The composite (MoO_3 / $NiAl_2O_4$) was prepared by a ceramic way and at different temperatures in which molybdenum oxide powder 0.15g and nickel alumina powder 0.85g, were mixed and then grinded by a hand mill and converted into a homogeneous powder and then sieved using a sieve size of 75µm. In order to homogenize the dry mixture completely, the powder is taken and placed in a container of alumina intended to withstand at high temperatures and sintered in the oven at temperatures (450℃, 550℃, 650℃) for 3 hours and then left inside the oven to cool. The benefit of the sintering process is that it helps to get rid of unwanted phases and secondary phases which formed to get the required pure phase.

Results and discussion

XRD studies of prepared composite

X-ray diffraction patterns of calcined composites are shown in figure 1. The sample calcined at 450℃ showed three phases, $NiAl_2O_4$, NiO and MoO_3. The peaks positions appearing at 2θ = 12.7°, 23.3°, 25.4°, 27.2°, 33.7°, 38.8°, 49.2° and 55.1° can be readily indexed as (020), (110), (040), (021), (111), (060), (002), and (112) crystal planes of the phase (MoO_3) respectively. The peaks positions appearing at 2θ = 37.2°, 43.2°, 62.9°, 75.4° and 79.4° can be readily indexed as (111), (200), (220), (311), (222) crystal planes of the phase (NiO) respectively; and those peaks positions appearing at 2θ = 19.1°, 31.4°,19.0°, 31.3°, 45.7°, 55.8°, 59.6°, 65.5° and 77.7° can be readily indexed as (111), (220), (400), (422), (511), (440), (533) crystal planes of the phase ($NiAl_2O_4$) respectively as well, which is in accordance with that of the standard patterns (ICDD, No. 005-0508), (ICDD, No. 010-1049) and (ICDD, No. 010-0339) respectively.

The results also showed an increase in the peaks intensity which may be due to the non-interference of $NiAl_2O_4$ in the crystalline planes within the MoO_3 lattice since there is no interference between these elements at this temperature [9]. When the calcination temperature increased, the peaks of the phase MoO_3 were reduced until they disappeared at temperature of (550℃) to show the composites phase ($NiMoO_4$), which leads to a decrease in the granular size, this is consistent with the results obtained by (Widiyadi) [9]. Note that the phase MoO_3 disappeared when the calcination temperature increased to 550℃ and 650℃ showing three phases, $NiAl_2O_4$, NiO and $NiMoO_4$.

The peaks positions appearing at 2θ = 23.4°, 25.3°, 32.5° and 47.3° can be readily indexed as ($\bar{4}02$), ($\bar{2}20$), ($\bar{1}12$), (110) crystal planes of the phase ($NiMoO_4$) respectively, which is in accordance with that of the standard pattern (ICDD, No. 033-0948). Note that the intensity of the peaks increases with increasing temperature and that the increase in the peaks may be due to the entry of (MoO_3) in the crystalline planes within the NiO lattice or vice versa, causing the dispersion of the X- ray within the crystal planes, since the incoming materials are not of the same phase, this compensation may be partially inappropriate, which leads to an increase in the intensity of the peaks and thus leads to an increase in the particle size. This is consistent with the results obtained by (Wang) [10].

The particle size was calculated using the equation Debai Spark $D = \frac{K\lambda}{\beta COS\theta}$. As shown in figure 1 the X-ray diffraction patterns of the composite (MoO_3 / $NiAl_2O_4$), and table 1 shows information values at the direction (200) of the composite (MoO_3 / $NiAl_2O_4$).

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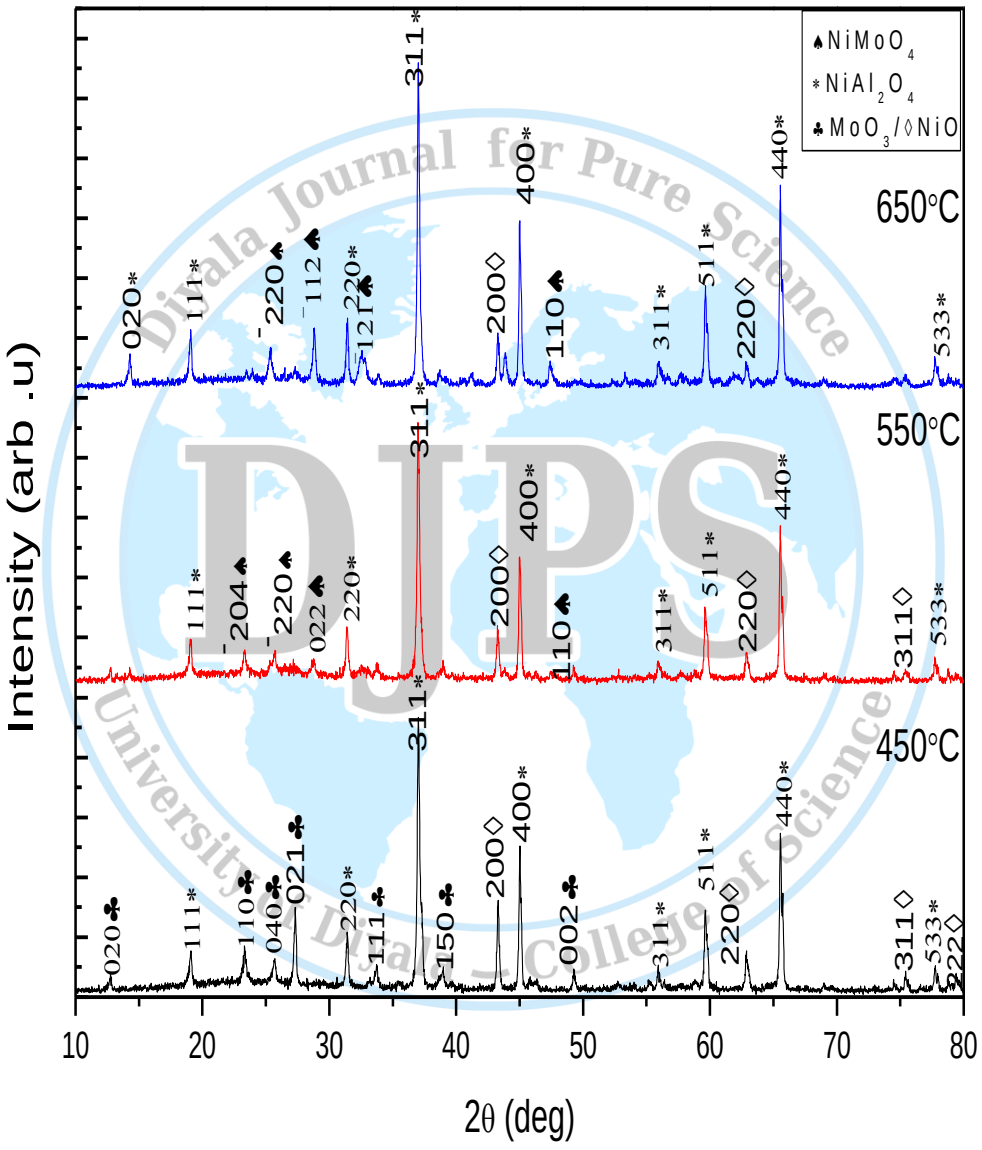

Figure 1: X-ray diffraction patterns of (MoO_3 /$NiAl_2O_4$) composite.

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Table 1. Synthetic information values at direction (200) for composite (MoO_3 / $NiAl_2O_4$).

Sample Calcined at	450̊ C	550̊ C	650̊ C
Hk l	200	200	200
θ2(deg)	43.2677	43.3170	43.2812
dhkl (Å)	2.08938	2.08712	2.08876
FWHM (deg)	0.15380	0.17450	0.16160
Lattice constant (a)Å	4.178	4.174	4.177
D (nm)	58.6830	51.1683	55.24582
Cell volume V Cell (Å 3)	72.969	72.733	72.904

FESEM investigation of prepared composite

The compositions were studied for all prepared ceramics samples (FESEM) was used to examine the morphology and to evaluate the average grain size to verify it where (Image-J, version 1.47) was used. The images shown for all overlays were magnified by (50.0 KX) and (20.0 KX) with scale of 200 nm and 1 μm.

Figure 2 shows FESEM images of the composite (MoO_3 / $NiAl_2O_4$) prepared at different temperatures, (FESEM) images of sample calcined at a temperature of (450°C) show that particles includes mushroom-like forms nanoparticles having irregularly shaped on their surface and this is consistent with the results obtained by (Chithambararaj) [11], while FESEM images of the compounds at temperatures (550℃ and 650℃) show that a group of particles of these compounds is homogeneous because of the phase ($NiMoO_4$) nanoparticles is obtained and the appearance of some particles in the form of mushroom-like and some are in the form of hexagonal rods.

The structures are interconnected and form irregularly shaped particles, which is consistent with the results of (Umapathy) [12]. The average grain size of all prepared compounds was calculated using Image-J software, version 1.47, and the image with magnification (50.0 KX) of the sample. The results are listed in table 2.

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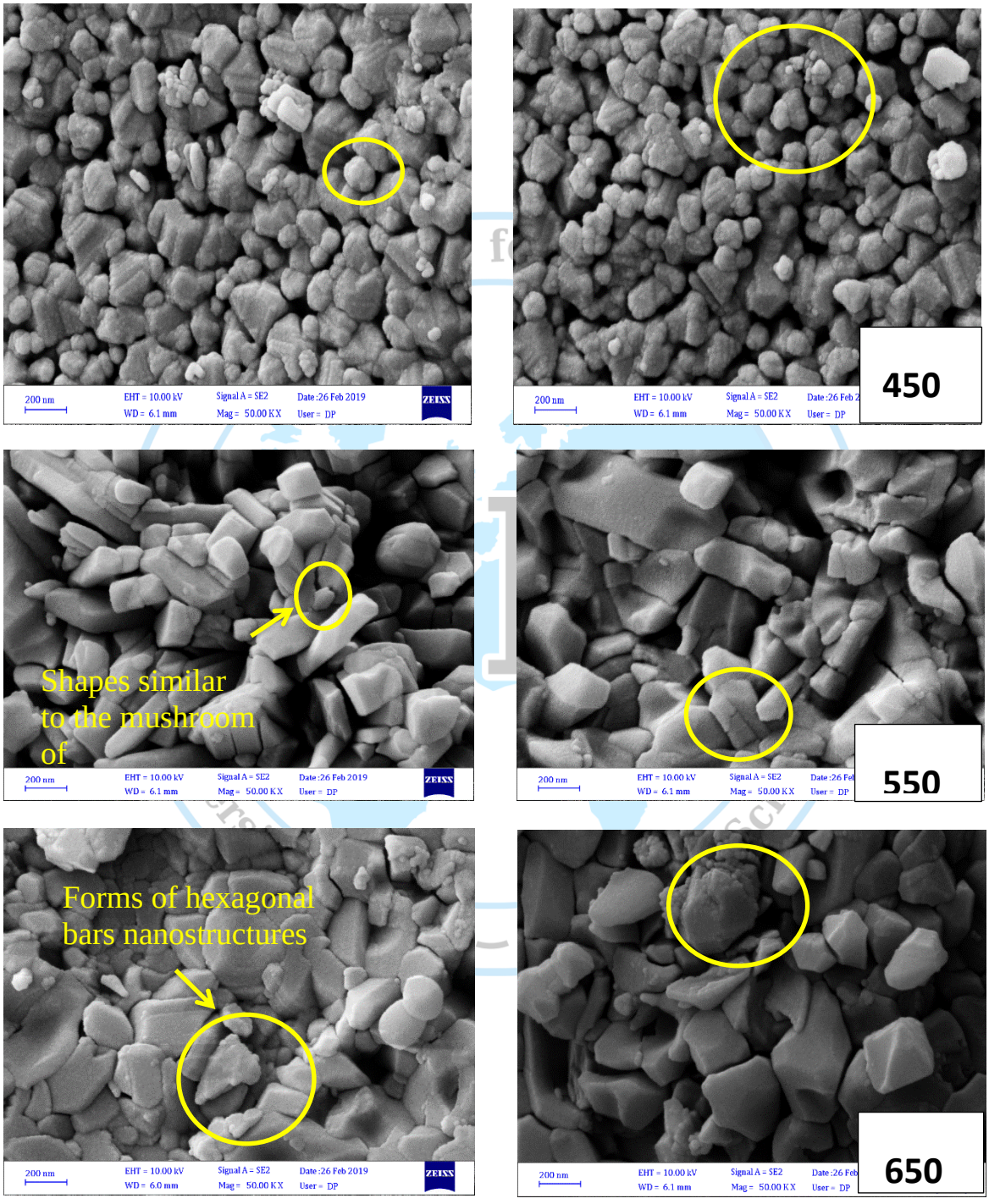

Figure 2: FESEM images of the compounds (MoO_3 / $NiAl_2O_4$) prepared and coated with different temperatures

Table 2: Grain size values for (MoO_3 / $NiAl_2O_4$) prepared and calcined at different temperatures

Sample Calcined at	450℃	550℃	650℃
(Average Grain Size) nm	103.856	78.645	**91.645**

Magnetic properties of prepared composite

One of the most important magnetic properties of any magnetic material is the relationship between the magnetic flux density (B) and the strength of the projected magnetic field (H) which is called the hysteresis loop (B-H Loop). The hysteresis loop is defined as the energy scale lost per unit volume per single magnetization cycle.

The magnetic properties of the nanoparticles (MoO_3 / $NiAl_2O_4$) at room temperature were determined by magnetization of oscillating models (VSM) with the applied magnetic field ranging from (+15000 to -15000) and symbolized by (Oe).

The values of magnetization saturation (Ms) as shown in figure 3 are obtained for the composite ($NiAl_2O_4$ / MoO_3) and calcined with different temperatures (450°C, 550°C, 650°C). VSM tests were performed at room temperature and the results of the examination of all three powders showed a linear hysteresis loop and exhibit the behavior of paramagnetic materials for all nanocomposites because the relaxation time is equal to the time required for polarization [13]. That is, when a magnetic field is applied, the single moment is toward the applied magnetic field. If the magnetic field is gone, these momentums will be changed in random directions with a result equal to zero, as shown in table 3. This is consistent with the results of (Nasiri) [13].

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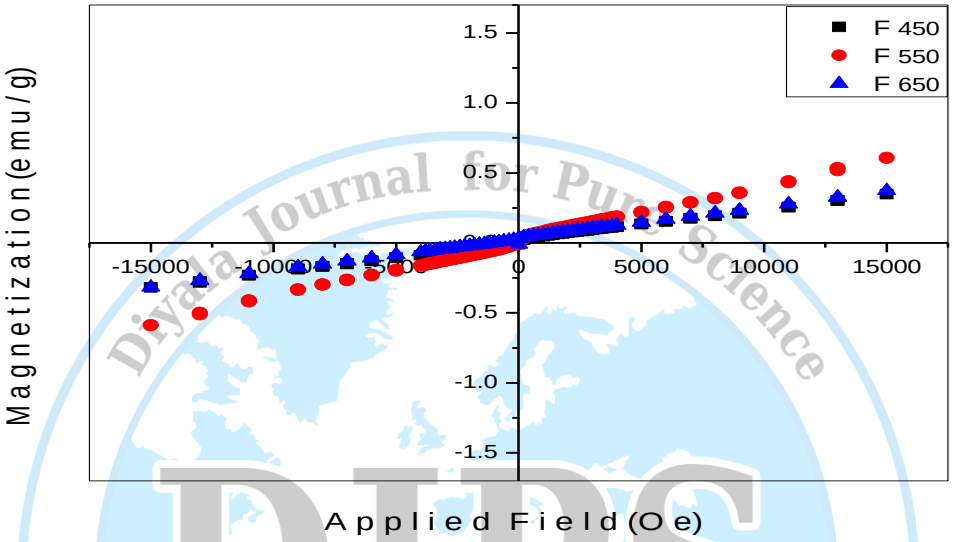

Figure 3: Nearly linear magnetic hysteresis loop (M-H) for composites (MoO_3 / $NiAl_2O_4$) prepared and calcined at different temperatures

Table 3: Values of saturation magnetization Ms (emu / g) and magnetic field applied for the composites (MoO_3 / $NiAl_2O_4$) calcined at different temperatures

Sample	Ms (emu/g) 450℃	Ms (emu/g) 550℃	Ms (emu/g) 650℃	Applied Field (Oe)
MoO_3 / $NiAl_2O_4$	0.3324	0.6076	0.3586	**15000**

Electrical properties of prepared composite

The electrical properties such as dielectric constant, tangent loss, and electrical conductivity were studied using the LCR meter, for all samples. The alternating electrical properties were measured as a function of the frequency of the alternating electric field at room temperature and within the frequency range (50 Hz-1MHz), The real dielectric constant was calculated using equation $\varepsilon'_r = \frac{Cd}{\varepsilon_\circ A}$ for the sample within the frequencies (50 Hz-1MH). The behavior of the compounds of the reactants was determined by figure 4 according to formula $((MoO_3)_X$ / $(NiAl_2O_4)_{(1-x)})$ and at different temperatures, its note that increasing the frequency value of the

projected electric field is accompanied by a decrease in the value of the dielectric constant but at high frequencies the value of the dielectric constant is almost constant.

This indicates that the dipole moment follows the electric field at low frequencies and this results from all types of polarization it is consistent with the results of (Ahmad) [14]. At high frequencies, there is no change in the direction of the ions as well as the absence of interaction of the exchange of electrons between the ions, that is the value of the dielectric constant remains constant at high frequencies and this result is consistent with the results obtained by (Ahmad) [14]. The change in the behavior of the dielectric constant at low frequencies of all samples is attributed to the appearance of the highest peak at the lowest frequency, which results from the polarization of the vacuum charge and ion polarization and it is consistent with the results of (Ahmad) [14].

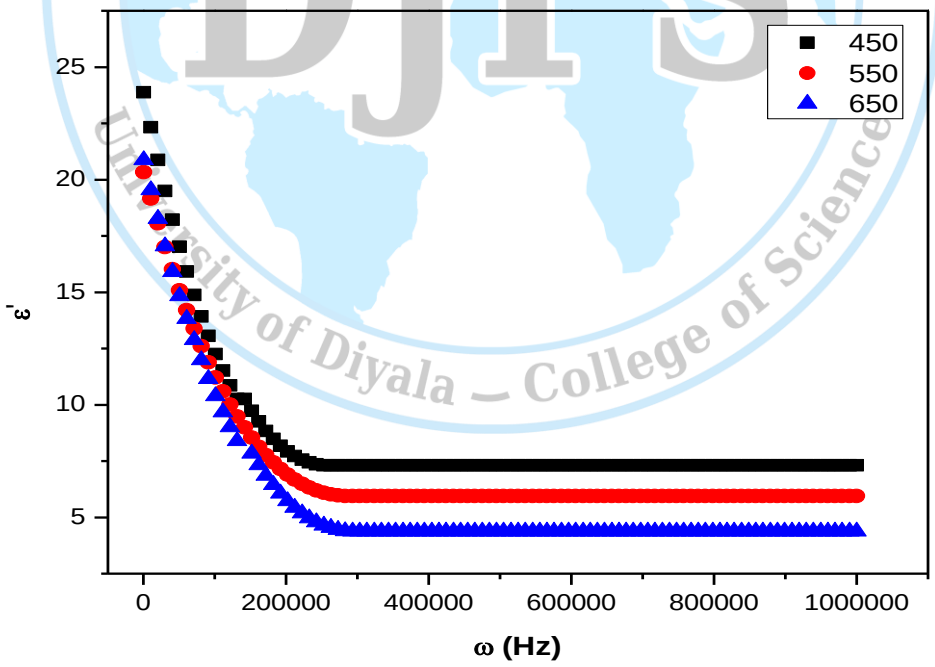

Figure 4: The real dielectric constant (ε') for of the composites (MoO_3 / $NiAl_2O_4$) prepared and calcined at different temperatures as a function of frequency (Hz)

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The imaginary dielectric constant was calculated using equation $\varepsilon_r'' = \frac{d}{w\varepsilon_\circ AR}$ within the frequency range (50 Hz-1MHz) and at room temperature. A similar behavior was observed in figure 5 according to the formula $((MoO_3)_X$ / $(NiAl_2O_4)_{1-X})$ and at different temperatures (450℃, 550℃, 650℃), as the imaginary dielectric constant at low frequencies behaves the same has of real dielectric constant and thus be higher the value of the dielectric constant at the lowest frequency is greatly increased and then later becomes less dependent on it, which is consistent with the results of (Ahmad) [14].

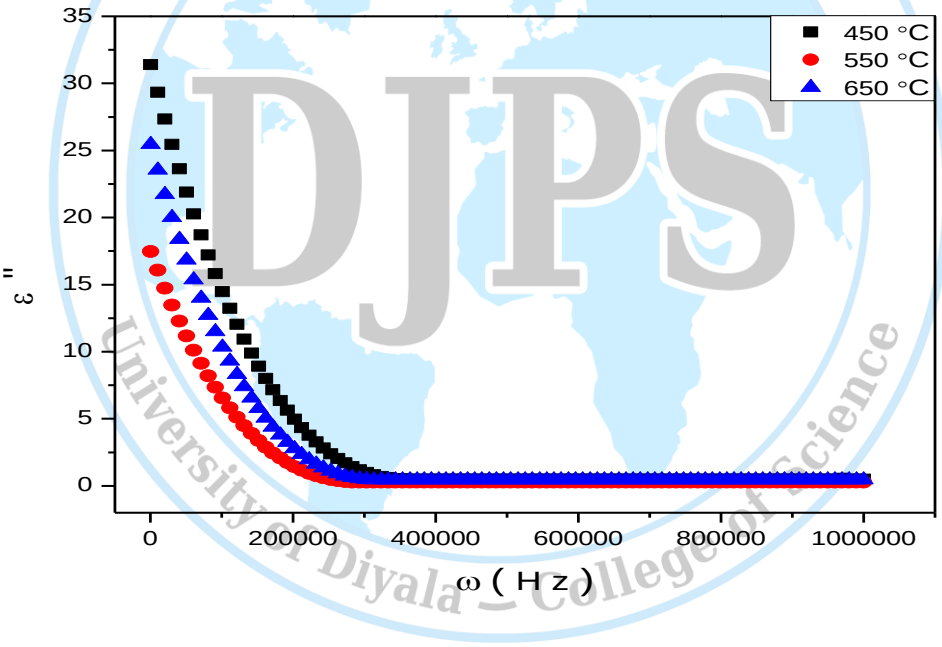

Figure 5: The imaginary dielectric constant (ε") for of the composites (MoO_3 / $NiAl_2O_4$) prepared and calcined at different temperatures as a function of frequency (Hz)

The alternating conductivity ($\sigma_{A.C}$) was calculated in the frequency range (50 Hz-1MHz) at room temperature. The same behavior of the composites of the reactants was detected in Figure (6) according to the formula $((MoO_3)_X$ / $(NiAl_2O_4)_{1-X})$ and at different temperatures (450℃, 550℃, 650℃), it was found that there is a change in the alternating electrical conductivity with

the frequency of the composites with nanocrystalline sizes, The alternating electrical conductivity increases with increasing frequency value, which is consistent with the results obtained by Atta-Allah [15].

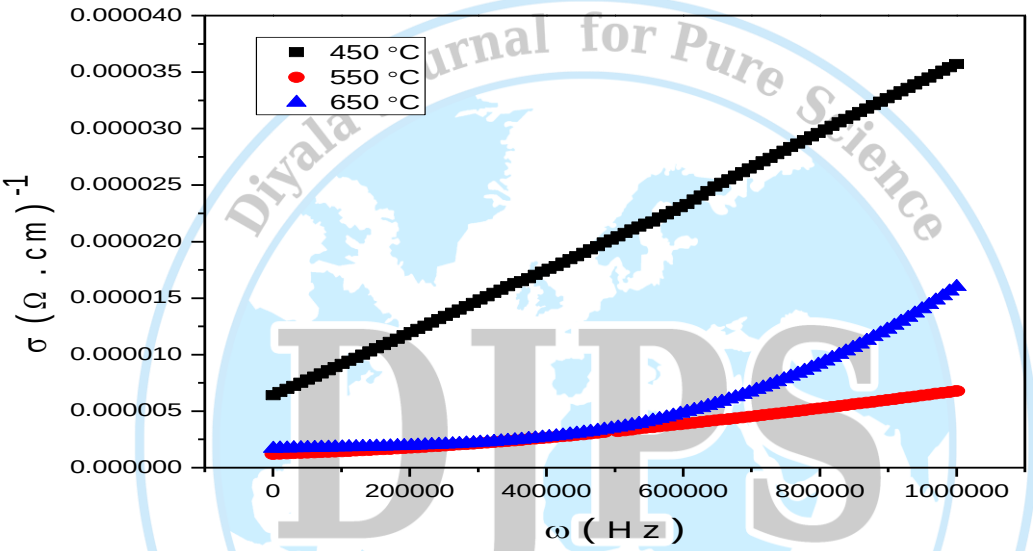

Figure 6: A.C conductivity ($\sigma_{A.C}$) for of the composites (MoO_3 / $NiAl_2O_4$) prepared and calcined at different temperatures as a function of frequency (Hz).

Conclusion

MoO_3/$NiAl_2O_4$ was prepared by ceramic method and through the tests carried out, one can conclude the following:

1-XRD Pattern for the prepared composites (MoO_3 / $NiAl_2O_4$) have found that the phases formed through the preparation process with different temperatures effects (450℃, 550℃, 650℃), are (NiO / $NiAl_2O_4$ / MoO_3, $NiMoO_4$ / $NiAl_2O_4$ / MoO_3, $NiMoO_4$ / $NiAl_2O_4$ / MoO_3) respectively. It was found that the grain size of these phases are ranged between (55.34 and 58.68nm), as it is shown that a temperature of (550℃) leads to the disappearance of (MoO_3)

phase and the emergence of new ($NiMoO_4$) phase and this shows that the degree of heating increased the granular size.

2 - FESEM tests proved that the compounds (MoO_3 / $NiAl_2O_4$) have formed nanostructures in different forms namely, hexagonal structures, structures similar to mushroom, and that the values of granular size increase with the emergence of phases.

3- VSM tests for the (MoO_3 / $NiAl_2O_4$) calcined at different temperatures (650℃, 550℃, 450℃) showed that when the nickel quantity increased and the amount of alumina in nanocomposites was increased, the magnetization saturation was increased. This leads to an increase in the size of the crystals, as well as showing that all three powders have an almost linear hysteresis loop that exhibits the paramagnetic behavior of all nanocomposites.

4- Dielectric tests proved that the composites (MoO_3 / $NiAl_2O_4$) calcined at different temperatures (650℃, 550℃, 450℃) showed of the highest peak of the real and imaginary dielectric constant at the lowest frequency which decreases with increasing frequency at low frequencies range. At high frequencies, the dielectric constant is not frequency dependent, indicating that the dipole moment follows the electric field at low frequencies. In alternating conductivity at high frequencies, the conductivity increases with the frequency of the electric field projected due to the electrical conduction mechanism through the bouncing of the charge carriers, i.e. the charges jump up and down within the known jumping cases.

References

1. L. Gama, M. A. Ribeiro, B. S. Barros, R. H. A. Kiminami, I. T. Weber, A. C. F. M. Costa, Journal of Alloys and Compounds, 483 (1-2), 453-455 (2009).
2. J.W. Kim, P.W. Shin, Lee M. J. Lee, S. J. Lee, Journal of Ceramic Processing Research, 7, 117 (2006).
3. A. Ganguly, R. George, Bulletin of Materials Science, 30, 183-185 (2007).

4. C. O. Arean, M. P. Mentruit, A. J. Lopez, J. B. Parra, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 180 (3), 253 (2001).

5. F. Meyer, R. Hempelmann, S. Mathur, M. Veith, Journal of Materials Chemistry, 9, 1755 (1999).

6. P. Jeevanandam, Yu. Koltypin, A. Gedaanken, Materials Science and Engineering B, 90 (1-2), 125 (2002).

7. M. Mohammadpour Amini, L. Torkian, Materials Letters, 57 (3), 639 (2002).

8. A. Yamakawa, M. Hashiba, Y. Nurishi, Journal of materials science, 24 (4), 1491-1495 (1989).

9. A. Widiyadi, G. A. Guspiani, J. Riady, R. Andreanto, S. D. Chaiunnisa, W. Widayat, E3S Web of Conferences, 31, 03011 (2018).

10. Y. Wang, G. Xiong, X. Liu, X. Yu, L. Liu, J. Wang, Z. Feng, C. Li, The Journal of Physical Chemistry C, 112 (44), 17265-17271 (2008).

11. A. Chithambararaj, A. C. Bose, Journal of Alloys and Compounds, 509 (31), 8105-8110 (2011).

12. V. Umapathy, P. Neeraja, A. Manikandan, P. Ramu, Transactions of Nonferrous Metals Society of China ,27 (8), 1785-1793 (2017).

13. H. Nasiri, J. V. Khaki, N. Shahtahmassebi, Materials & Design, 109, 476-484 (2016).

14. I. Ahmad, World Applied Sciences Journal, 22 (6), 796-801 (2013).

15. S. S. Atta-Allah, M.K. Fayek, Journal of Physics and Chemistry of Solids, 61 (9), 1529–1534 (2000).