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Studying the Structural Changes of $NiSb_2O_4$ by Temperature Using Sol-Gel Method

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Abstract
The research aims to prepare $NiSb_2O_4$ system and study its structure and characteristics by Sol-Gel method in aqueous solutions and using CH_3COOH acid as an organic stabilizer. The mixture was drained for three hours to get rid of water, and grind it to powder and sintered it at various temperatures for two hours. The structural changes were compared to Differential Thermal Analysis (DTA) schemes. This showed that the temperature of dewatering is 125.67°C and the temperature of dewatering of removal the other organic is 326.18°C.The X-rays results showed that the dual system is formed at 700°C and the crystals are growed clearly by increasing temperatures with sharp peak till 1100°C. The system starts to disintegrate to the initial oxides. Therefore, the composite at low temperatures and high thermal and mechanical specifications was attended. It was noted that the installer accelerated the formation at 700°C and the growth of crystals becomes more quickly.
Keywords: Sol- Gel , $NiSb_2O_4$, X-ray .

1- Introduction

The dual systems of common oxides compounds have been a topic of considerable interest in inorganic chemistry Scientific's and research groups in recent years. A number of these compounds have been synthesized by different methods, such as co-deposition method, solid-state, hydrothermal method and the (Sol - Gel) method, which had been followed in this research.

Some of the studied antimonite was the magnesium antimony, this study examined extensively the magnetic properties of magnesium antimony [1], The white crystals of the zinc antimonite was used in electrical insulation and in the field of electronics [2], in addition to its important applications in the field of optical catalysis [3], In this research the preparation of dual systems of NiO- Sb_2O_3 by using the method of the Sol-Gel was carried out. The Sol-Gel method is conceder one of the most important method in the industrial. The development of this method was achieved in 1960 mainly due to the need to find new synthesis techniques and less dust compared with the ceramic method [4].

Oxides composition of the nickel antimonite prepared by the Sol- Gel

1- Antimony tri oxide (Sb_2O_3): is a white powder, exist in two distinct crystals cubic (Senarmontite) and rhombic (Valentinite) [7] as shown in Figure (1)

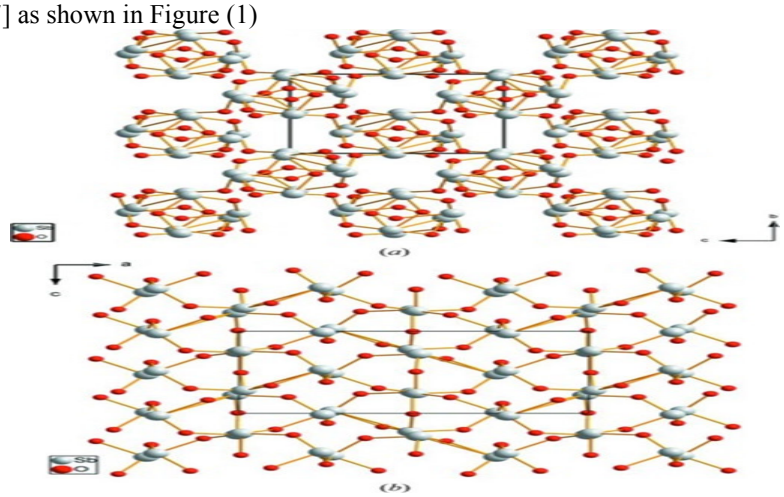

Figure 1: The crystals structure of antimony tri oxide where (a) cubic (b) rhombic

The transition temperature from the crystalline form to another is about 557°C, During the hydrolysis of antimony tri chloride at room temperature is formed Valentinite, whereas during the alkali treatment turns into a Senarmontite gradually. Its prepared by the hydrolysis of antimony tri chloride, and is used in many fields such as electro conductivity, activating catalysts, optical materials and functional fillings and [8], Its usually formed during the melting of antimony tri oxide Sb_2O_3 with polymer alkali meta antimonite (III) composition of $M^{1+}SbO_2$, and also consists of Antimonite $M^{2+}(SbO_2)_2$ where (M = Ni, Co, Fe, Mn, Zn, Mg) which is consists of strings of MO_6octethedral intertwined with SbO_3strings of pyramids.

2- Nickel Oxide NiO : it is a green powder with regular hexagonal prism structure as shown in Figure (2)

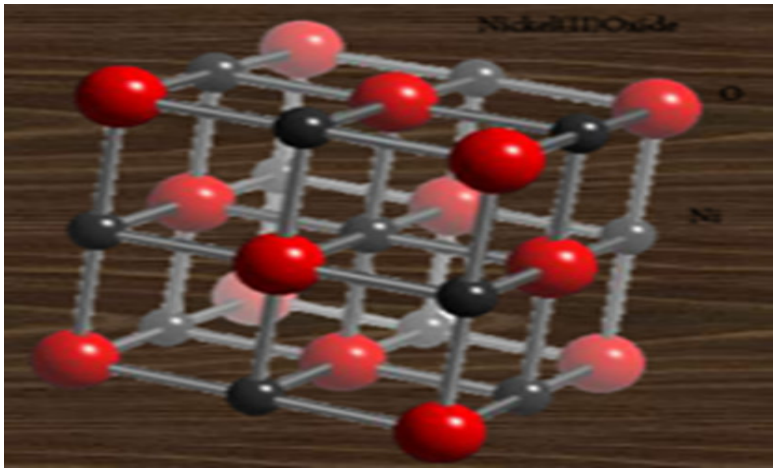

Figure 2: The crystals structure of Nickel Oxide

Nickel oxide is a consider one if of insulators type, due to it's the electronic structure and chemical bonds , is also considered very important oxides because played as a special catalyst and has important electronic and magnetic properties.

It is used in a large range of applications including sensitive devices, negative electrode in battery, the thin film and the fuel cells electrodes.

2- Materials and equipments:

- Samples dryer: Memmert brand
- Incinerator type Carbolit, temperature up to1100°C.
- X-Ray powder diffraction, Philips-PW-1840 model
- Differential Thermal Analysis (DTA),Chimadzu
- Anhydrous Antimony tri Chloride ple $SbCl_3$ (Medex 99.5%)
- Nickel Chloride $NiCl_2.6H_2O$ (BDH 97%)
- Sodium hydroxide (Medex 99.5%)
- Acetic acid (Riedel-de 99.5%)
- Distilled water for washing and extension

This material has a high purity in order to obtain accurate results on the one hand and to avoid the occurrence of unwanted secondary reactions during work on the other hand.

3- Experimental

Samples were prepared from stereochemistry ratios determined by the following equation:

$$2SbCl_3 + NiCl_2.6H_2O + 8NaOH \rightarrow NiSb_2O_4 + 8NaCl + 10H_2O$$

A solution of nickel chloride (1M), solution of antimony tri chloride (2M) and solution of sodium hydroxide (8M) where prepared, with molar ratio of Ni/Sb is 1/2. The solutions of nickel chlorides and antimony tri chlorides was added to the solution of Sodium hydroxide gradually with constant stirring by magnetic stirrer, after the completion of the addition stirring continued for two hours in order to ensure the mixing is complete. The precipitate then faltered and washed several times with distilled water ,and was tested with a solution of silver nitrate to insured it is free of chlorine ions completely. A (6 gram) of the precipitation was taken to carry a stabilizer experiment and the rest of compound kept the in distilled water. The experiment of acetic acid as stabilizer was carried out to determine the best acetic acid concentration. The (6gram) divided evenly over the four equal size test tubes and put in each of the four 10ml of distilled water and numbered these tubes from 1 to 4 , then was added to:

Tube 1 1 ml of 0.25M acetic acid
Tube 2 1 ml of 0.50M acetic acid
Tube 3 1 ml of 0.75M acetic acid
Tube 4 1ml of 1.00 M acetic acid

The four tubes left then for 72 hours, after shaking evenly, it was found that solution in the tube 1 is the most homogeneous and stable, meaning that the most appropriate concentration for the installer (acetic acid) is: 0.25M.

4- Results and Discussion:

Samples are analyzed by X-ray powder diffraction and differential thermal analysis and the results were as

follows:

4-1-Studying x-ray diffraction diagrams (XRD):

4-1-1 at (500°C):

The prepared crystals were studied by X-ray spectroscopy at (500°C); and the figure (4-b) was obtained.

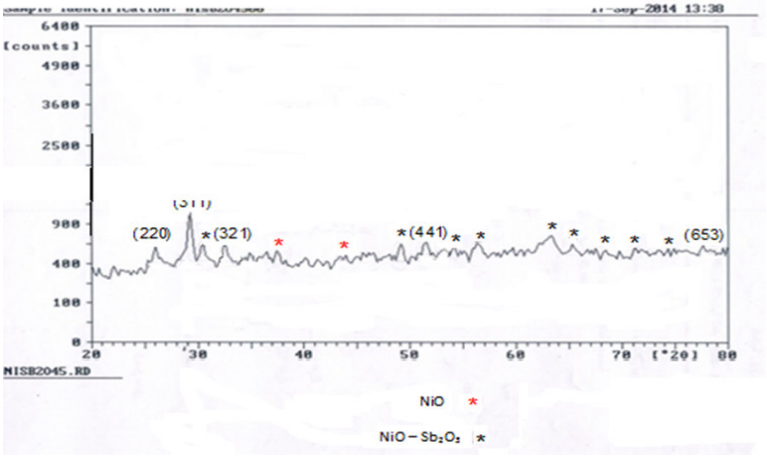

Figure (4-b): The scheme of X-ray diffraction for a sample of nickel antimonite with molar ratio Ni:Sb = 0.5 , undergone a calcination at 500°C for two hours in the presence of stabilizer

Table (3) illustrated the results of the previous X-ray spectroscopy of the sample shown in Figure (4-b):

$NiO\text{-}Sb_2O_3$ (Ni:Sb=1:2) , (T = 500°C)					
Peak	Angel Θ2	Θ	I / I_o Intensity	d , A° Distance	hkl
1	29.000	14.500	100	3.041	311
2	25.700	12.850	39.55	3.460	220
3	32.400	16.200	37.26	2.672	321
4	51.000	25.500	32.55	1.782	441
5	77.580	38.79	18.66	1.230	653

From the previous table, it was noted that all the previous peaks related to trioxide antimony comparing to by reference cards for this oxide. The presence of small and new peaks , which did not appear in the previous diagram indicates to the beginning of the form of dual systems, and the crystal lattice constant is : a = 10.062 A°.

4-1-2 at (900°C):

The sintered crystals were studied at this temperature by X-ray spectroscopy, the diagram was obtained as the following (4-d):

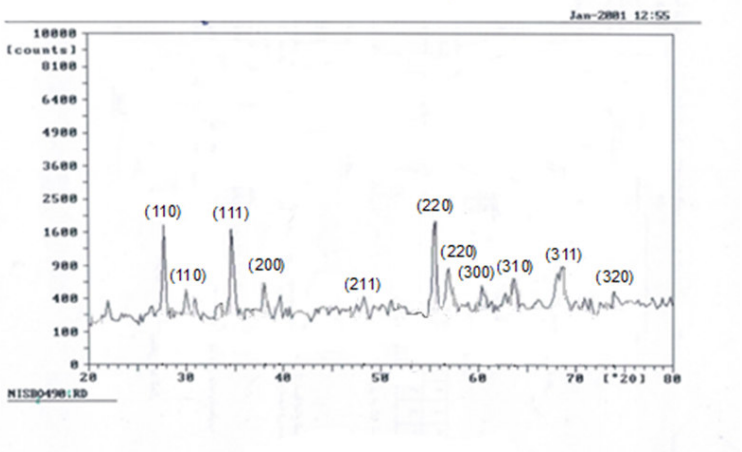

Figure (4-d): The scheme of X-ray diffraction for a sample of nickel antimonite with molar ratio Ni:Sb = 0.5 , undergone a calcination at 900°C for two hours in the presence of stabilizer

Table (5) illustrated the results of the previous X-ray spectroscopy of the sample shown in Figure (4-d):

$NiSb_2O_4$ (Ni:Sb= 0.5) , (T = 900°C)					
Peak	Angle Θ2	Θ	I / I_o Intensity	d , A° Distance	hkl
1	55.500	27.750	100	1.721	220
2	34.500	17.250	73.15	2.782	111
3	27.900	13.950	70.14	3.190	110
4	56.600	28.300	49.25	1.623	220

From the previous table, it was notate that at the 700°C and 900°C there are a great of match between them, the presence of all peaks that indicate the form of the new compound appeared, but becomes more clear and intense. This is evident through increased peak's density with narrowed margin indicating that the increase of burning temperature leads to an increase in the size of the crystal and improving the crystal process [11], [12]

4-1-3 at (1100°C):

The sintered crystals were studied at this temperature by X-ray spectroscopy, and the diagram was as following (4-e):

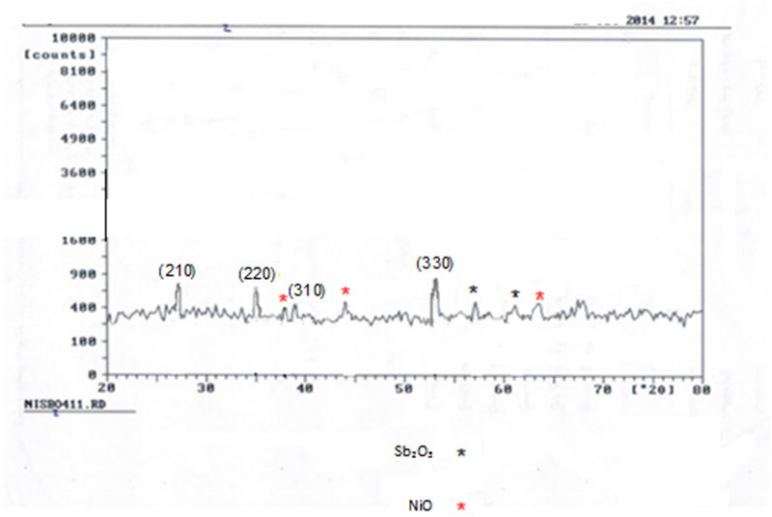

Figure (4-e): The scheme of X-ray diffraction for a sample of nickel antimonite with molar ratio Ni:Sb = 0.5 , undergone a calcination at 1100°C for two hours in the presence of stabilizer

Table (6) illustrated the results of the previous X-ray spectroscopy of the sample shown in Figure (4-e):

$NiSb_2O_4$ (Ni:Sb= 0.5) , (T = 1100C°)					
Peak	Angle 2Θ	Θ	I/I_o Intensity	d , A° Distance	hkl
1	53.000	26.500	100	1.720	330
2	34.815	17.407	94.75	2.582	220
3	26.925	13.462	81.50	3.313	210
4	38.650	19.325	36.84	2.331	310

It was found that at 1100°C the dual systems compound $NiSb_2O_4$ began to disintegrate clearly, whereas most of the peaks of the compound disappeared and appeared new peaks of NiO and Sb_2O_3 oxides. The occurrence of intense peaks in 1100°C for Sb_2O_3 and NiO oxides refers to the growth of crystals, and it differed from what it was in 300°C. This is consistent with scientific references, which indicates that increasing the temperature leads to crystals growth of (increase peak's intensity)

4-1- Thermal behavior study by using (DTA):

The DTA spectra was carried out and spectrum is shown in (Figure 3)

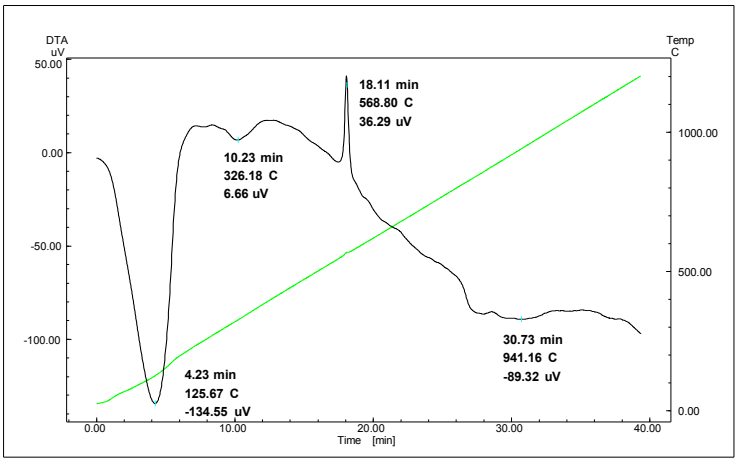

Figure 3: DATA spectrum of nickel antimonite sample with molar ratio Ni:Sb = 1: 2 in the presence of (CH_3COOH) as stabilizer

The DTA spectra for zinc antimonite sample showed several absorptions destined towed the bottom (endothermic) and absorptions destined to top (exothermic), at different temperatures. Table (1) explained these absorptions and its locations.

Table 1: The results analysis of DTA scheme

Compound	Peak(C°)	type	Explanations
$NiSb_2O_4$	125.67°C	Endo	Removing crystallized water molecules
)Ni:Sb=0.5(	326.18°C	endo	Evaporating of Organic stabilizer
With stabilizer	568.80°C	exo	Beginning of Nickel antimonite forming
	941.16°C	endo	Beginning of nickel antimonite disintegrate

References

1- FJELLVAGa. H. KJEKSHUSb. A., (1985), Crystal and Magnetic Structure of MnSb204, Acta Chemica Scandinavica, 39, 389-395.
2- Fairooz. N. Al-gubury. H., (2013), Photocatalytic degradation of n- Hexacosane Using coupled ZnO-Sb_2O_3 and tungsten lamp, Journal of Applicable Chemistry, 1, 22-32.
3- Mekap. A. Das. P. Choudhary. R., (2014), Dielectric and electrical properties of ZnSb2O4 ceramics, ADVANCED MATERIALS Letters, 3, 152-156.
4- Sol-Gel methods, 1-37.
5- Willmes. Deutsch V.H., (1662), Taschenbuch chemische Substanze, 8171.
6- Hu. Y. Zhang. H. Yang. H., (2007), Direct synthesis of Sb_2O_3 nanoparticles via hydrolysis-precipitation method, Journal of Alloys and Compounds, 428, 327–331.