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Studies on Preparation, Characterization and Humidity Sensing of Mg- Substituted YPO_4

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YPO_4 and $Mg_2P_2O_7$ mixed ceramic semiconductor samples were prepared and investigated to be used as humidity sensors. The samples were characterized using XRD. Surface area, SEM, and electrical conductivity under the effect of humidity at room temperature were measured and discussed. X-ray patterns showed the formation of YPO_4 in tetragonal phase and $Mg_2P_2O_7$ in monoclinic form. Adding $Mg_2P_2O_7$ improves the surface area of YPO_4 which affected the electric conductivity. The humidity sensing of the pure and mixture samples was studied by dependences of the electrical conductivity on the mixture content and the sensitivity was also calculated. The results indicated that the electrical conductivity increased as relative humidity increased up to 76% due to the protonic conductivity which specified the action of water content on the phosphate molecules. After 76% relative humidity (RH), the value the electrical conductivity and sensitivity started to decrease due to the blocking of the phosphates molecules under high humidity value.

Keywords: Yttrium phosphate, Sensing, Preparation and Characterization.

Inspite of using a huge amounts of phosphate materials in many applications such as fertilizers, detergents, ion exchangers, special glasses, corrosion inhibitions [(1-4)], special phosphates find their applications in advanced industrials such as super protonic conductance, sensors and UV shielding materials.

Due to the high thermal stability and high resistance of rare earth phosphates towards the oxidizing agents, many researches were devoted to prepare these materials to be suitable for new applications [(5-7)] . In the present work a trial to prepare and characterize the Mg- substituted YPO_4 to be suitable for humidity sensors was done.

In the field of the humidity sensing, a wide variety of techniques are available to measure the humidity. The common humidity sensors are the solid state materials such as aluminum oxide, polymer film, silicon oxide and ceramic

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sensors. In general, ceramic humidity sensors have advantages for their chemical and thermal stabilities, thus many metal oxides such as $MgFe_2O_3$, $ZnCr_2O_4$, $LiZrVO_4$, Al_2O_3-TIO_2-SmO_2, hydroxyapatite, $Al(PO_4)$ and $Zr(HPO_4)_2$, have been used as suitable humidity sensing materials. These sensors are more acceptable because the relative humidity is measured against electrical conductivity. These types of humidity sensors enhance the manufacturing of sensors devise [8-10] .

Several metal phosphates were investigated as humidity sensing materials, and some of them including $Ti(HPO_4)$ H_2O had good humidity sensing where the electrical resistance of these materials was lowered at relative humidity range of 11% to 94 % [11] .

As we continue our policy for preparation and application of the metal phosphates [12-15] . This work aimed to prepare and characterize YPO_4 and its substituted samples with Mg_2 P_2O_7 to be used as new humidity sensors based on the dependence of the electric conductivity on the relative humidity.

Experimental

Preparation

YPO_4, (YP), was prepared via the solid state reaction route by mixing stoichiometric molar amounts of Y_2O_3 and (NH_4) H_2PO_4, and then fired at 1200°C for 8hr (sample 1). Magnesium pyrophosphate, $Mg_2P_2O_7$, (MgP), was prepared by reacting 1:1 molar ratio $MgCl_2$ with $(NH_4)H_2PO_4$ solution, drying the precipitate then calcined at 850°C for 3hr (sample 2) [16] . Three mixtures of YP and MgP were prepared in different weight percentages, 25% MgP (sample 3), 50% MgP (sample 4) and 75% MgP (Sample 5).

Characterization

The crystal structure of YPO_4 and $Mg_2P_2O_7$ were investigated by using X-ray diffraction (XRD), Brukur D8 advanced diffractometer (Germany) with Cu Kα radiation. The surface area of the prepared samples was measured by using quantachrome instrument, Quantachrome Nova automated gas sorption system version 1.12. The micrographs of YPO_4 and $Mg_2P_2O_7$ and their mixtures were taken by scanning electron microscope (SEM: Jeol-Jax- 840A, Japan) with electronic probe micro analyzer.

Humidity sensing study

To study the effect of the relative humidity(RH), on the electrical properties of the prepared samples, weighed discs of the dried samples were exposed to atmospheres of different relative humidity values (20, 35, 76, 92,100%) [17] . For the preservation of disc humidity, the following procedure was followed: saturated solutions of $MgCl_2$, NaCl and KNO_3, in equilibrium with some of their respective crystals, were kept each in desiccators at 25°C. The relative humidity values were determined by a suitable hydrometer and the obtained values were in consistent agreement with the reported values. The samples were exposed to the specified humidity for 4 weeks. This period was quite sufficient for the samples to attain equilibrium with their respective atmospheres where the weight of the

sample came to constancy during the last two weeks. The conductivity was measured directly after the equilibrium had been attained by using LCR Hioki instrument (Japan) at 50 KHz and 4 volts.

Results and Discussion

X- ray measurements

Typical XRD patterns of $Mg_2P_2O_7$ and YPO_4 are given in Fig 1. The x-ray patterns emphasized the formation of YPO_4 and $Mg_2P_2O_7$. For $Mg_2P_2O_7$, a monoclinic phase (PDF 72-0019) was formed. For YPO_4, a tetragonal phase (PDF 84-0335) was produced. In general rare earth orthophosphates are known to exist as two types of crystal structures, one is monoclinic monazite type that accommodates the larger rare – earth elements (La-Gd) and the other is tetragonal xentotime- type that incorporates the smaller rare earth elements (Sc,Y,Tb,-Lu) [18]. All the rare earth orthophosphates that have been reported as protonic conductors have the monazite- type structure. However, considering a structural similarity between the monazite and xenotime- type structures, protonic conduction can be expected also in xenotime- type. In all cases the mechanism of conductivity for phosphates compounds is protonic in agreement with the literatures [19].

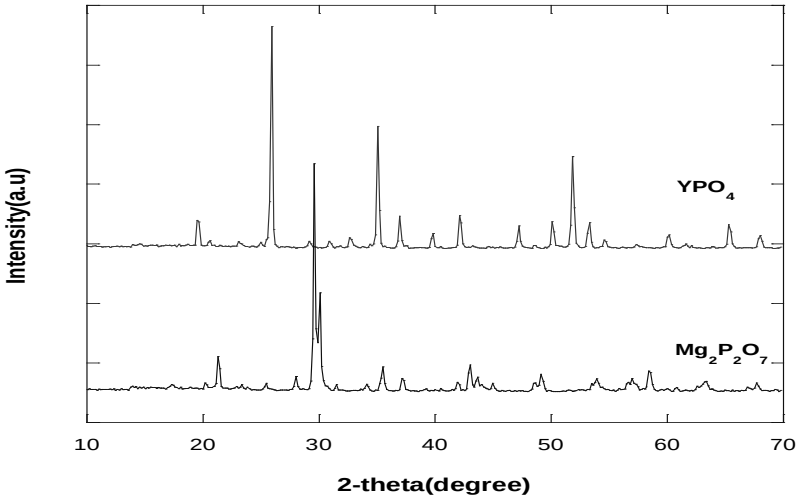

Fig. 1. XRD patterns of YPO_4 and $Mg_2P_2O_7$.

Surface area measurements

The surface area of both YPO_4 and $Mg_2P_2O_7$ was performed by using Quantachrome Inst. The measured surface area of YPO_4 was 20.0 m^2/g and 41.6 m^2/g for $Mg_2P_2O_7$. From the values of the surface area, it may be concluded that the substitution of YPO_4 by $Mg_2P_2O_7$ improves the surface area which by turn affects the protonic conductivity.

Scanning electron microscope

The surface morphology of pure YPO_4 (a) and $Mg_2P_2O_7$ (b) and their different mixtures (c-f) were analyzed by SEM as shown in Fig. 2. The observation indicated that the pure YPO_4 has compact surface but the pure $Mg_2P_2O_7$ posses layer structure. The effect of $Mg_2P_2O_7$ incorporation into YPO_4 changes the compact surface into irregular winding structure induced porous structure. These structures enhanced the gas diffusion and reaction within YPO_4 blended $Mg_2P_2O_7$. Whereas Fig. 2(e) displays the photomicrographs of loose structure in larger magnification where the loose structure containing multipores which could be observed [20,21] .

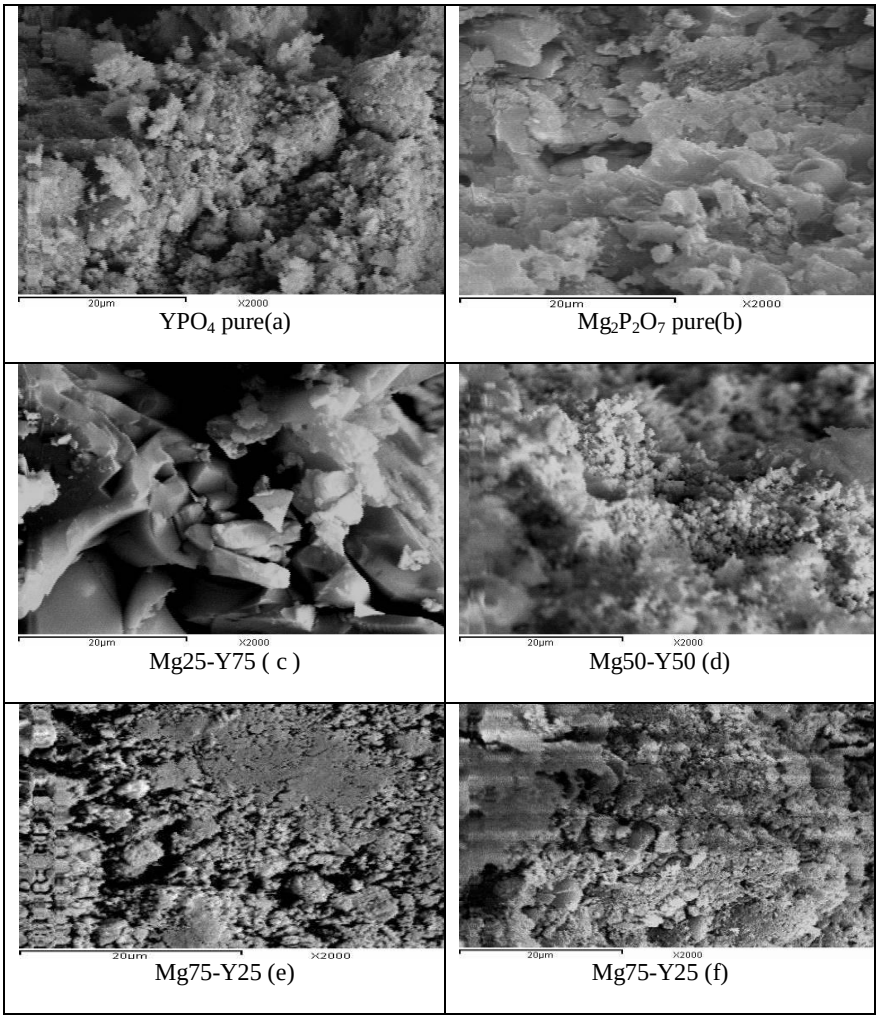

Fig. 2. SEM images of pure YPO_4, $Mg_2P_2O_7$ and their mixtures.

Humidity sensing

To study the ability of using both the YPO_4 and $Mg_2P_2O_7$ as humidity sensors, the dependence of the electrical conductivity on the relative humidity (RH) was studied.

In the previous researches, it was found that the electrical conductivity of rare earth phosphates exhibited protonic conduction in moisturized atmosphere by substituting the alkaline earth metals for rare earth elements [22]. Figure 3 shows that, the conductivity of YPO_4 increased as the relative humidity (RH) increased. By substitution of YPO_4 with $Mg_2P_2O_7$, it is observed that the conductivity increased by increasing $Mg_2P_2O_7$ percentage. All the prepared samples showed high conductivity values at RH equal to 76%, so this value of RH was selected to study the effect of adding $Mg_2P_2O_7$ to YPO_4 and also to study the best sample which can be used as humidity sensor. After this value the electrical conductivity started to decrease by increasing the percentage of $Mg_2P_2O_7$. This may result from the aggregation between the phosphate groups [23] in presence of humidity (Fig. 4). The sensitivity of the samples increases with water content forming a maximum value at about 76% then start to decrease as represented in Fig. 5.

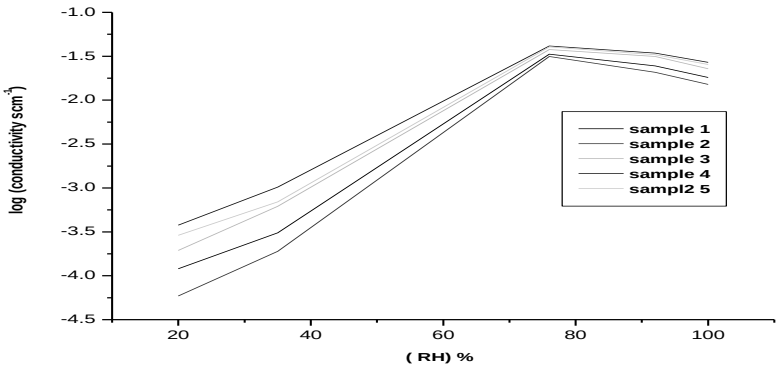

Fig. 3. Relation between electrical conductivity and relative humidity of YPO_4, $Mg_2P_2O_7$ and their mixtures at room temperature.

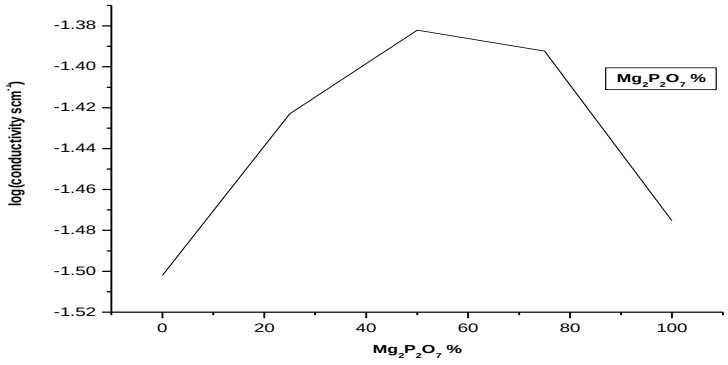

Fig. 4. Relation between electrical conductivity and $Mg_2P_2O_7$ percentage at room temperature at 76% RH.

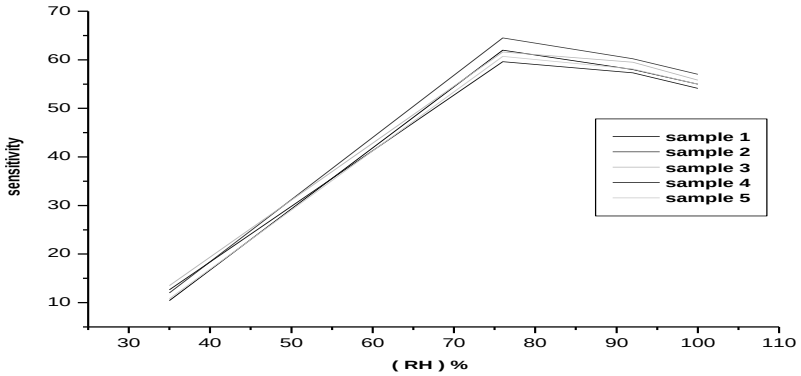

Fig. 5. Relation between sensitivity and relative humidity at room temperature.

The increase of both electrical conductivity and sensitivity with humidity may be due to the increase of the number of protons responsible for conduction which introduced from the water vapor and also the substitution of the rare earth phosphates by divalent metal pyrophosphate in the moisturized condition dissolved the protons into the phosphates forming hydrogen phosphate groups (HPO_4) as pointed out by Amezawa[22]. The decrease in the electrical conductivity and sensitivity at higher relative humidity after 76% may be due to the blocking of the phosphate molecules [23].

Conclusion

From this study, it may be concluded that YPO_4 and $Mg_2P_2O_7$ were formed in hexagonal and tetragonal phases, respectively. The mixing of $Mg_2P_2O_7$ with YPO_4 improves the surface area which has high effect on the electrical conductivity. From the dependence of the electrical conductivity on the relative humidity it may be concluded that these phosphate materials can be used as humidity sensing material. Also, by comparison of the low material price of $Mg_2P_2O_7$ to YPO_4 high price, it can be seen that the substitution of Y by Mg decreases the production cost of the sensor material.

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دراسات تحضير وتوصيف وخاصية المحسات المائية لمادة فوسفات الاريتريوم المطعم بالماغنيسيوم

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تم تحضير كل من فوسفات الاريتريوم البسيطة وفوسفات الماغنيسيوم الكثيفة وتوصيفها لاستخدامها كمحسات مائية . تم توصيف العينات الناتجة باستخدام طيف حيود الأشعة السينية وقياس المساحة السطحية ودراسة تغير التوصيل الكهربائى اعتمادا على نسبة الرطوبة عند درجة حرارة الغرفة . دلت الأشعة السينية على تكوين فوسفات الاريتريوم البسيطة فى صورة ثلاثية فيما تكون فوسفات الماغنيسيوم فى طور احادية الميل. دلت الدراسة على ان اضافة فوسفات الماغنيسيوم تحسن من خواص السطح وكذلك الخواص الكهربائية لفوسفات الاريتريوم .

دلت نتائج الدراسة على زيادة التوصيل الكهربائى بزيادة نسبة الرطوبة حتى 67% نتيجة لميكانيكية التوصيل البرتونى ،عند زيادة نسبة الرطوبة عند 67% تبدأ خاصية التوصيل الكهربائى والحساسية فى الانخفاض نتيجة تكون تكتلات كبيرة من المواد الفوسفاتية .