

## Crystal-Chemical Study of $M^{II}Sn(OH)_6$ where ( $M^{II}=Zn, Fe, Cu, Ca$ )

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(Received 7 / 7 / 2011. Accepted 23 / 1 / 2012)

### □ ABSTRACT □

The compounds  $M^{II}Sn(OH)_6$  where ( $M^{II}= Zn, Fe, Cu, Ca$ ) have been synthesized at room temperature. The X-ray powder diffraction method, Infrared spectroscopy and DTA techniques were used to characterized the products. The cell parameters, volume of lattice, experimental and theoretical densities of the compounds were identified.  $FeSn(OH)_6$  was instable because of the particular oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  in air with particular substitution of  $OH^-$  by  $O^{2-}$ , that fact present the formula  $Fe^{III}SnO(OH)_5$ . Hydroxystannate of mixed bivalent- metals were obtained. The results demonstrate the formation of solid solutions for both ions Zn, Cu by replacement in different ratios. The DTA curve demonstrates two endothermic effects and one exothermic effect for all products.

**Keywords:** XRD, Differential thermal analysis, crystal and chemical properties, stannate.

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## الدراسة الكيميائية البلورية للمركبات $M^{\text{II}}\text{Sn}(\text{OH})_6$ حيث $M^{\text{II}} = \text{Zn, Fe, Cu, Ca}$

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(تاريخ الإيداع 7 / 7 / 2011. قُبِلَ للنشر في 23 / 1 / 2012)

### □ ملخص □

تم اصطناع المركبات  $M^{\text{II}}\text{Sn}(\text{OH})_6$  حيث  $M^{\text{II}} = \text{Zn, Fe, Cu, Ca}$  بدرجة الحرارة العادية. استخدمت طريقة انعراج الأشعة السينية ومطيافية الأشعة تحت الحمراء وتقنية التحليل الحراري التفاضلي لدراسة خواص المركبات الناتجة. تم تحديد أبعاد الشبكة البلورية وحجم الخلية الأساسية والكثافة التجريبية والنظرية لكل مركب ناتج. لقد كان المركب  $\text{FeSn}(\text{OH})_6$  غير ثابت بسبب الأكسدة الجزئية للحديد  $\text{Fe}^{2+}$  إلى  $\text{Fe}^{3+}$  في الهواء رافقه استبدال جزئي للشوارد  $\text{OH}^-$  بالشوارد  $\text{O}^{2-}$  وهذا ما أدى لوضع الصيغة الجديدة للمركب بعد الأكسدة وهي  $\text{Fe}^{3+}\text{SnO}(\text{OH})_5$ . كما تم الحصول على هيدروكسي ستانات المعادن المختلطة لمعدني ثنائي التكافؤ  $\text{Cu, Zn}$ . بينت النتائج أنه يتشكل محاليل صلبة لهيدروكسوستانات هذين المعدنين بنسب مختلفة بطريقة الاستبدال. يبين منحنى DTA لكافة المركبات وجود قمتين يعبر كل منهما عن فعل ماص للحرارة وقمة واحدة تعبر عن فعل ناشر للحرارة.

**الكلمات المفتاحية:** انعراج الأشعة السينية، التحليل الحراري التفاضلي، الخواص الكيميائية والبلورية، التصديرات (الستانات).

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## Introduction:

Tin occurs in nature as a hydroxystannate and has different bivalence metals. They have the general formula  $M^{II}Sn(OH)_6$ . The plane of determination this kind of minerals request a high care and profficiency. Studying these compounds in the side of composition, structure and properties is very rarely and not enough[1, 2, 3]. While most studies have focused on zinc hydroxystannate and stannate, the preparation of other metal hydroxystannates has rarely been concerned and explored[4, 5, 6,7]. In recent years, the preparation of metal stannates and hydroxystannates has drawn increasing interest owing to their excellent properties and promising applications in many fields[8,9,10,11]. Inorganic tin compounds, particularly zinc hydroxystannate and zinc stannate have attracted considerable interest, because of their nontoxicity and improved fire and smoke-suppressant properties in a wide range of polymers[12,13, 14, 9]. The difficulty of preparation in our research is connected with the high dispersion and many variant of phases and elements. These facts lead to difficulty in the separation of phases in the natural minerals[15,16]. Some characteristics of iron hexahydroxystannate were investigated by (Grabb, Hanneford1986)[17], the natural magnesium hexahydroxystannate was determined by (Faust, Scheller1971)[18]. On the other hand the manganese hexahydroxystannate was studied by(Moor, Smith1976)[19]. The preparation and physical characterization of some transition-metal hydroxides were reported in [11], but all of these works are still deficient for some applications of these materials[8]. For our research The ions  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Zn^{2+}$  and  $Ca^{2+}$  were chosen as a bivalent- metals due to the closeness in the ionic radius between first three elements, but the  $Ca^{2+}$  ion was used for the comparison purposes. So we have  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Zn^{2+} = 0.80 - 0.83(\text{\AA})$ , but  $Ca^{2+} = 1.04(\text{\AA})$ .

## Aim of research:

The main aim of our work is to identificate the structural effects during the isomorphic substitution of these bivalent- ions. Assume that the ionic radius of  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Zn^{2+}$  are approximately similar, the isomorphic replacement must be occurs during the preparation.

We try to determinate the above mentioned compounds because of the amount of analogous natural mineral obtaining by different references was very little.

## Chemicals methods of research:

### 1-Chemicals:

High purity  $SnCl_4 \cdot 5H_2O$ , KOH and KCl from Aldrich,  $CaCl_2 \cdot 2H_2O$ ,  $FeCl_2 \cdot 4H_2O$  and  $ZnCl_2$ ,  $CuCl_2$  from Merck were used as starting materials, ethanol, distilled water. All chemicals used were of analytical grade and used as received from their source.

### 2-Experimental section:

$CaSn(OH)_6$ ,  $ZnSn(OH)_6$ ,  $FeSn(OH)_6$ ,  $(Zn,Cu)Sn(OH)_6$  were obtained by (Struz, Contag) method of synthesis, which was reported earlier[20]: stoichiometric proportions of  $K_2Sn(OH)_6$  and  $M^{II}Cl_2$  ( $M^{II} = Zn, Fe, Ca$ ) were independently dissolved in water. Each solution was mixed under heating and large amount of water was added until clear solution were obtained. The resulting solutions were then added together and the mixture was heated at approximately 60 °C for 5 minutes, then the mixed solution was cooled until room temperature. After some time of cooling, sediment of bivalent-metal hexahydroxystannate was obtained. The solution was exposed to filtration, and washing with 1% KOH solution, then in the distilled water. The obtained materials were subsequently dried in air at 90 °C.

On the other hand, potassium hexahydroxystannate  $K_2Sn(OH)_6$  was used as a starting material in the second stage. It was obtained by precipitation  $Sn(OH)_4$  from the water solution of  $SnCl_4 \cdot 5H_2O$ , then the sediment was filtrated and washed with 1% KOH solution, the resulting compound was dissolved in 1M KOH solution under basic condition (pH= 13 – 14).

In the typical synthesis procedure of  $CuSn(OH)_6$ , it was taken 2 gr  $CuSO_4 \cdot 5H_2O$ , and dissolved in 200 ml distilled water with stirring. Then 10ml concentrated ammonia solution was added to the aforementioned  $CuSO_4$  solution under vigorous magnetic stirring. Blue precipitate soon appeared and then dissolved, and a dark blue solution was obtained. After that, 50 ml of 0.05M  $Na_2SnO_3$  solution was added dropwise to the dark blue solution over a period of 3 min, then the mixture was stirred of a 5 min at a room temperature. Finally, the precipitate was centrifuged and reused with distilled water several times until pH= 7 and washed with absolute ethanol then dried at 60 °C overnight for characterization. Using other starting materials, the same result was observed in reference[10].

### **3-Physical and Analytical Measurements:**

The formation of different phases was controlled by different techniques. IR spectra were recorded on a JASCO- Infrared spectrophotometer Fourier Transform FT/IR- spectrum-(400- 4000 $cm^{-1}$ ) using KBr Disks. X-Ray powder diffraction patterns were obtained by X-Ray powder Diffractometer Model PW-1840 from Philips using a Guinier dewollfa Camera with nickel filter and copper radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The compositions of the phases and thermal behavior were illustrated by differential thermal analysis DTA technology Model DTA -50 from SHIMADZU. The experimental density was measured by pycnometer.

### **Results and discussion:**

The XRD patterns for our products have been matched standard cards by using the strongest peaks (d, I): [ 3.90(100), 2.758(52), 1.592(29)] (Card No.20-1455) for  $ZnSn(OH)_6$ , [ 3.793(100), 2.77(57), 4.052(56)] (Joint commette on powder Diffraction Standards- File Card No. 20-0369) for  $CuSn(OH)_6$  and [ 4.060(100), 1.814(60), 1.657(40)] (Card No. 31-0653) for  $FeSn(OH)_6$ . More than, an x-ray diffraction scan was registrated in the range of  $2\theta$  (10 -90 $^{\circ}$ ). It is worth noting that the Zn,  $Fe^{2+}$  and Ca hydroxystannates were synthesized by solid state reaction and hydrothermal methods in addition to determination of physical properties and electrical conduction in the references [13, 14, 9].

As far as the synthesis of the  $FeSn(OH)_6$  compound has some obstacles related to the oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  in addition to the changing of the color from gray-blue to dark-gray. On the same time the obtained  $Fe^{3+}$  hexahydroxystannate using  $FeCl_3$  was not achieved, because the reaction produced amorphous precipitate.

For this reason the synthesis of  $Fe^{II}Sn(OH)_6$  was repeated using the directed cover to protect the obtained compound from the oxidation. For this aim it was used a thin cover from varnishe (Lacquer), after that the X-ray powder diffraction pattern present a pronounced clear diffractogram with strongest peaks[3.89(100), 2.75(70), 1.74(40)], (Database Code 0009240)

This result allow to identificate cell parameters of the compounds.  $Fe^{II}Sn(OH)_6$  has been indexed on a cubic unit cell according to  $\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$  with the following

dimension  $a = 7,759 \pm 0.003 \text{ \AA}$ , the cell volume is  $471,529 \text{ \AA}^3$  and it contain 4 molecules of hydroxystannate. In comparison with [9] the parameter  $a$  has some deviation related with synthesis method. When the varnish cover was removed, the sample rapidly becomes dark-gray. This is related with the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  which accompanied by a decrease in the cell parameters to  $a = 7,627 \pm 0.002 \text{ \AA}$ . the decrease of the cell parameters is clear and caused by the decreasing of the ionic radius for iron ion from  $r_{\text{Fe}^{2+}} = 0.80 \text{ \AA}$  to  $r_{\text{Fe}^{3+}} = 0.64 \text{ \AA}$ . See table.2.

The products  $\text{M(II)Sn(OH)}_6$  ( $\text{M} = \text{Zn}^{2+}, \text{Fe}^{2+}, \text{Ca}^{2+}$ ) and  $\text{Fe(III)SnO(OH)}_5$  are isostructural, they all have cubic type of lattice, so we can confirm the isomorphous substitution in these cations. The relationship between lattice parameter  $a$  for obtained cubic compounds and ionic radius of metals shows the value of  $a = 7,63 \text{ \AA}$  is in agreement with ionic radius of  $\text{Fe}^{3+}$  ( $r_{\text{Fe}^{3+}} = 0,67 \text{ \AA}$ ).

Generally the X-ray powder diffraction method demonstrated moderation some peaks of the diffractogram while some other peaks became stronger in  $\text{Fe}^{3+}\text{SnO(OH)}_5$ . This fact explains some changes in the size of crystal lattice of  $\text{Fe}^{\text{II}}\text{Sn(OH)}_6$  after the oxidation of iron. The X-ray powder patterns of the synthesized compounds are shown in Figs. (1- 6).

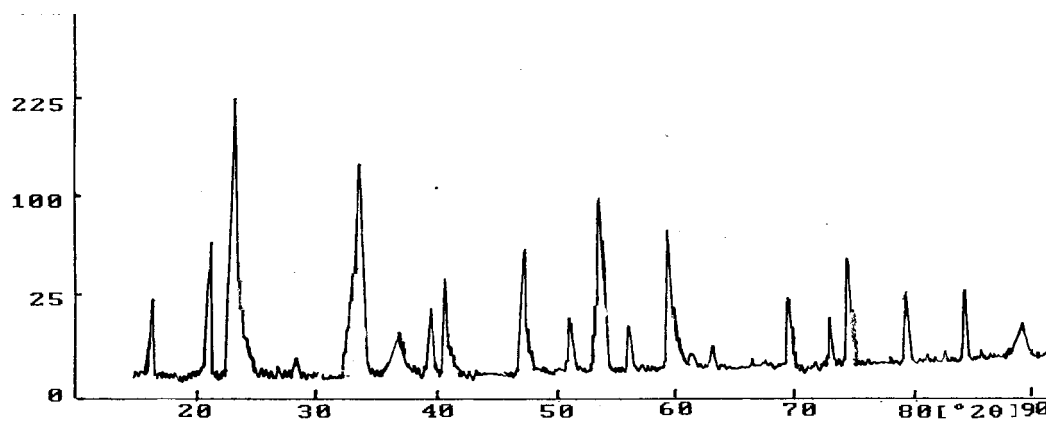


Fig.1. X—ray powder diffraction pattern for  $\text{FeSn(OH)}_6$

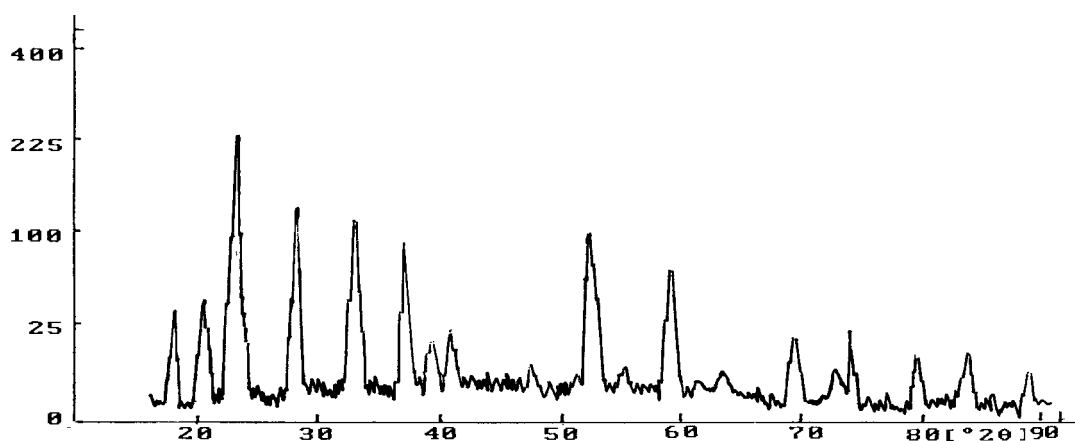


Fig.2. X—ray powder diffraction pattern for  $\text{FeSnO(OH)}_5$ .

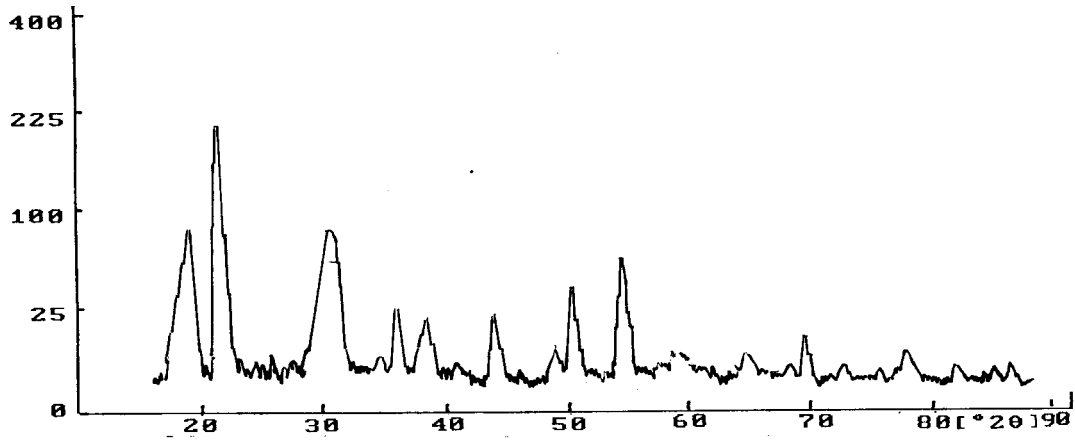


Fig.3 . X—ray powder diffraction pattern for  $CaSn(OH)_6$

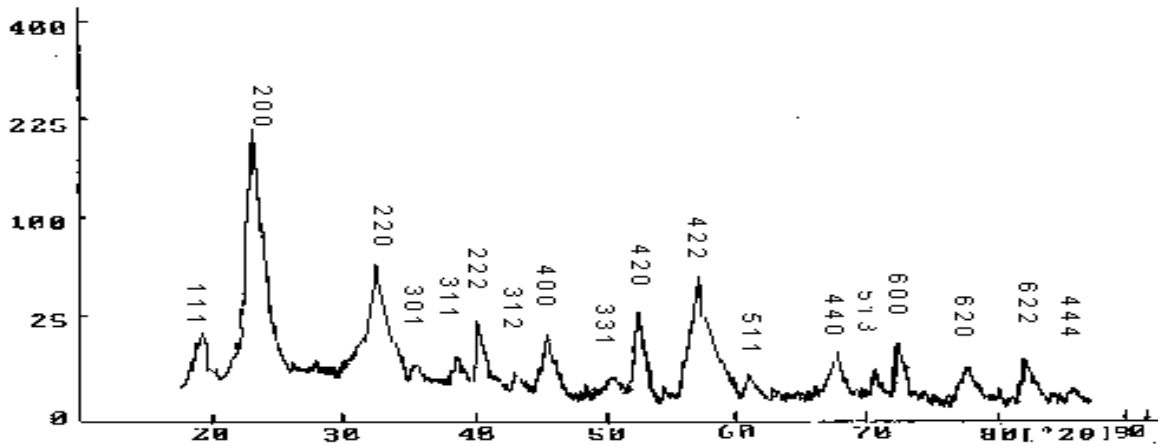


Fig.4. X—ray powder diffraction pattern for  $ZnSn(OH)_6$

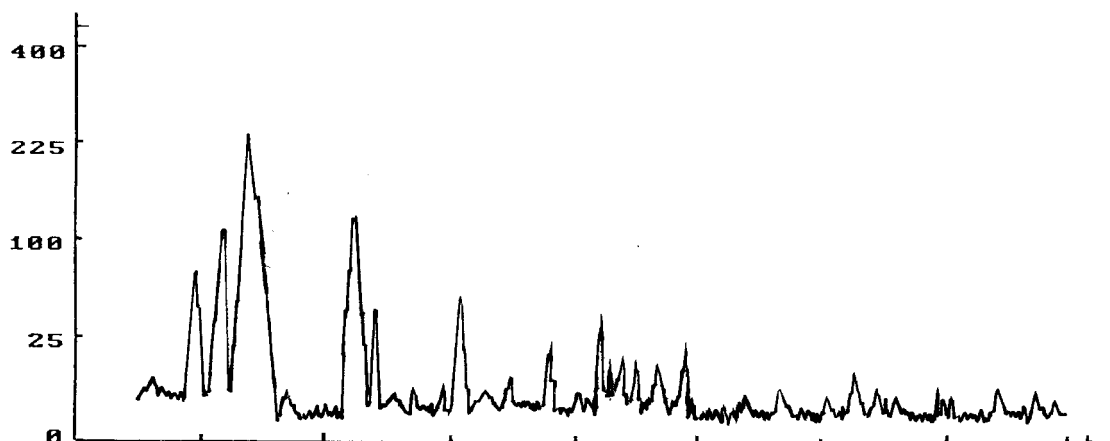


Fig.5. . X—ray powder diffraction pattern for  $CuSn(OH)_6$

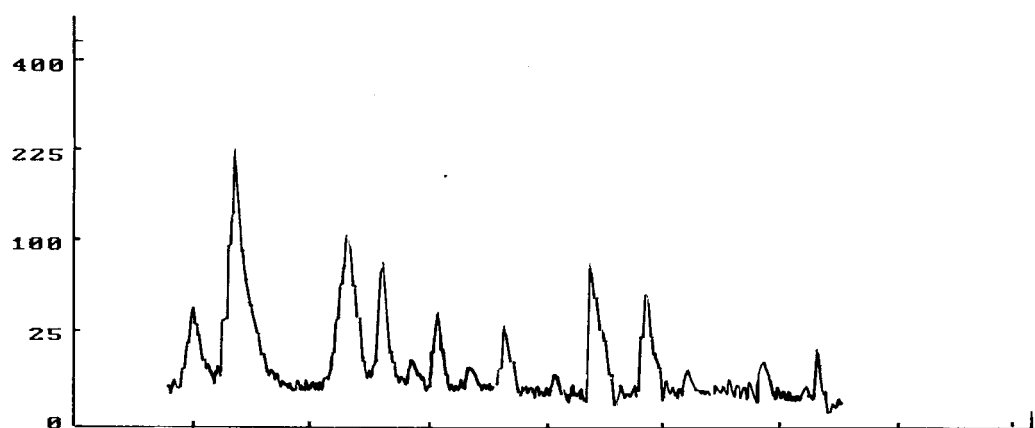
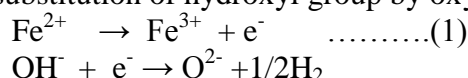


Fig.6. . X—ray powder diffraction pattern for (Zn,Cu)Sn(OH)<sub>6</sub>

On the other hand increasing the charge from Fe<sup>2+</sup> → Fe<sup>3+</sup> needs negative charge, compensation the electric charge of compound needs one negative charge (-1), this will be at the expense of substitution of hydroxyl group by oxygen as the following equation:



Opening the Fe<sup>II</sup>Sn(OH)<sub>6</sub> sample , all iron(II) oxidized to iron(III) at the time not exceed 7 minutes , this transformation demonstrate, Fe<sup>II</sup>Sn(OH)<sub>6</sub> occurs in just inert or reducing atmosphere . Owing to their ability of being rapidly oxidized, Fe(II) salts are often used as redusing agents, therefor we must looking for other formula for the above mentioned compound.

Using the infra-red spectrum indicated that, during the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> at the same time decreasing the peaks concerned to OH<sup>-</sup> groups was observe in the range of 3100 – 3300 cm<sup>-1</sup> and 1190 cm<sup>-1</sup>. This fact leads to some distraction in the crystal structure and fraction replacement of OH<sup>-</sup> group to O<sup>2-</sup> due to the expression (1). The variation in IR spectrum was accompanied with gradual change of the color as time goes on. The stable spectrum was obtained after 10 minutes. The strong changes of the spectrum were indicated between 5 – 7 minutes that is in agreement with decreasing the peaks of OH<sup>-</sup> in the range of ( 550 – 570 cm<sup>-1</sup>). According to these facts, and the obtained data it can be concluded that, the formula of iron hexahydroxystannate can be given as Fe<sup>3+</sup>SnO(OH)<sub>5</sub>, The thermal effects and IR- spectroscopy are listed in table.1.

**Table1: The thermal effects and IR- spectroscopy**

M Properties	Zn	Fe2+	Fe3+	(Cu,Zn)	Cu	Ca
T <sub>1</sub> (Endo)	66	80	85	94	70	80
T <sub>2</sub> (Endo)	291	270	285	280	285	275
T <sub>3</sub> (Exo)	700	812	730	750	695	740
VibrationOH (IR)	3200(vs) 3140(vs)	3150(vs)	3150(m)	3400(s) 3200(s)	3400 3100	3150 3100
Vibration OH(IR)	1180(vs) 1100(w)	1205(vs) 1100(w)	1190(m)	1180(s) 970(m)	1190	1185
Sn –O –Sn (IR)	850(w)	850(vw)	850(vw)	850(w)	850	850
O – Sn- O (IR)	785(m)	810(m)	800(w)	785(m)	785	780
Sn – O –X (IR)	650(m)	690(vw)	670(m)	660(m)	660	670
Sn – O (IR)	545(vs) 450(m)	570(vs)	585(vs)	545(vs) 375(m)	585	570

(w)weak, (vw) very weak, (m) middle, (s)strong, (vs) very strong The mentioned above exploration of  $Fe^{3+}SnO(OH)_6$  leads to the following:

1-  $Fe^{II}Sn(OH)_6$  crystallized just in the solution as a bivalent iron salt.

2- The formation of  $Fe^{II}Sn(OH)_6$  in the air is unstable and the oxidation from  $Fe^{2+}$  to  $Fe^{3+}$  does not lead to distortion in crystal structure, but some constriction in the crystal lattice and particular replacement of  $OH^-$  by  $O^{2-}$  were observed . Then the right formula must be expressed as  $Fe^{3+}SnO(OH)_5$ .

Differential thermal analysis measurements were performed up to  $1000^{\circ}C$  at a heating rate of  $30^{\circ}/min$  under Argon flowing. The DTA curve obtained during heating of  $ZnSn(OH)_6$  presents three main thermal effects : the first one illustrated a pronounced endothermic peak at approximately  $66(60 - 90^{\circ}C$  for other compounds), that can be attributed with elimination the physical absorbed water. The second thermal effect at nearly  $291(280 - 290^{\circ}C$  for other compounds)is also endothermic peak , it is related with removal  $OH^-$  groups and formation amorphous phase. The last third effect occurs at approximately  $700^{\circ}C$  ( $700-800^{\circ}C$  for other compounds)represent exothermic effect , that can be offer distruction of crystallization of  $SnO_2$ . We confirm the reference data [9] about the decomposition of  $ZnSn(OH)_6$  and  $CaSn(OH)_6$  above  $600^{\circ}C$ . The other compounds demonstrate the same form of DTA. When the isomorphic substitution of cations  $Zn \rightarrow Fe \rightarrow Cu \rightarrow Ca$  occurs , the maximum of dehydroxylization temperature of hydroxystannate corresponding the amorphous phase was slightly changed, fig.7.

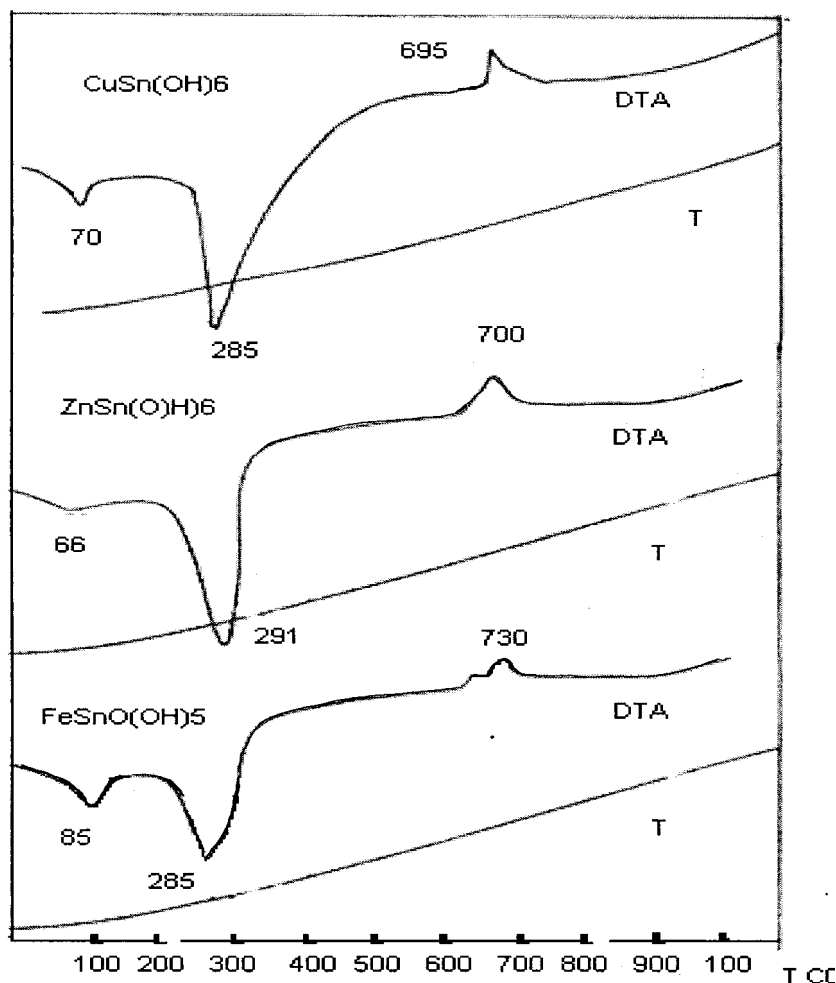


Fig.7: DTA curve for  $ZnSn(OH)_6$  .



### Hydroxystannate of mixed bivalent- metals:

The compound (Zn, Cu)Sn(OH)<sub>6</sub> was prepared by the same previous method of synthesis, taking stoichiometric amounts of ZnCl<sub>2</sub>:CuCl<sub>2</sub> = 1:1. X-ray powder diffraction pattern for some hydroxystannate of mixed bivalent- metals showed a little displacement of peaks (d) and intensity (I). This replacement related with the resemblance in the atomic dispersion of atoms and different in the cubic lattice parameters 7,716 – 7,746 Å and this fact was a result of ionic radius changes. The diagram  $a = f(r)$  represents a linear characteristic for the parameter  $a$  as a function of ionic radius. See fig.8.

The points concerning to ( Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup> Zn<sup>2+</sup>, Cu<sup>2+</sup>-Zn<sup>2+</sup>, Ca<sup>2+</sup>) are located on the same line and declare obtaining mixed metals phases. The lattice parameters ( $a$ ) and ( $V$ ) all increase monotonically with increasing average ionic radius Cu<sup>2+</sup>(0.72), Fe<sup>2+</sup>(0.74) Zn<sup>2+</sup>(0.76). The extremely small volume  $V_c$  (444.19 Å<sup>3</sup>) for Fe<sup>3+</sup>SnO(OH)<sub>5</sub> in comparison with other products indicates a smaller ionic radius of Fe<sup>3+</sup> in FeSnO(OH)<sub>5</sub>. The simple equation  $\rho_T = \frac{M.Z}{V.N}$  have been used for the calculation of theoretical density of the compounds (M: molecular weight, V: volume of crystal cell, Z: number of molecules in one unit cell, N: Avogadro's constant). Experimental density  $\rho_E$  have been determined by pyknometer method .

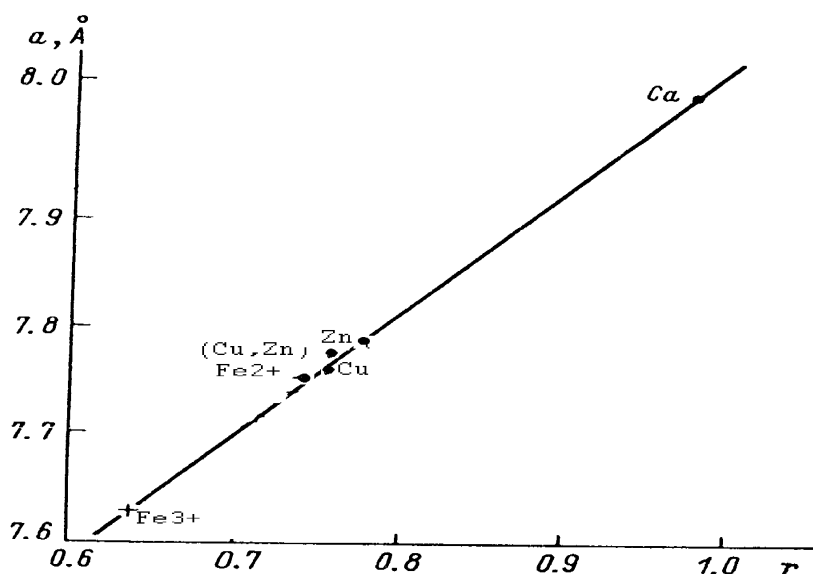
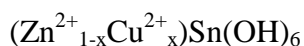


Fig. 8: The relationship between ionic radius  $r(\text{Å}^0)$  of metal and lattice parameter  $a(\text{Å}^0)$ .

Table.2: Crystal properties of bivalence-metal hydroxostannates

Compound	parameters(Å)	Z	$V_c(\text{Å})^3$	$\rho_T \text{ gr/cm}^3$	$\rho_E \text{ gr/cm}^3$
CaSn(OH) <sub>6</sub>	$a= 8.1432$	4	539.99	3.23	3.21
ZnSn(OH) <sub>6</sub>	$a= 7.794$	4	473.458	4.023	4.011
FeSn(OH) <sub>6</sub>	$a=7.7834$	4	471.529	3.910	3.893
Fe <sup>3+</sup> SnO(OH) <sub>5</sub>	$a =7.6300$	4	444.19	4.11	4.13
(Zn,Cu)Sn(OH) <sub>6</sub>	$a=7.735$	4	462.790	4.040	4.030
CuSn(OH) <sub>6</sub>	$a=7.580$ $c= 8.0956$	4	465.144	4.05	4.052

IR- spectrums for synthetic hydroxystannates  $CaSn(OH)_6$ ,  $ZnSn(OH)_6$ ,  $Fe^{2+}Sn(OH)_6$ ,  $CuSn(OH)_6$  are similar. The difference connected with the relative location of absorption peaks which depends on difference of chemical composition, at the same time the structural type was saved as a cubic unit cell . The IR- spectra of the compounds show strong bands at  $(3100- 3400\text{ cm}^{-1})$  assigned to the stretching vibrations of OH. In all products the IR spectra show weak bands  $850\text{cm}^{-1}$  assigned to stretching vibration of Sn – O – Sn . IR-spectrums of mixed Zn, Cu hydroxystannates are in agreement with the spectrum of  $ZnSn(OH)_6$  and  $CuSn(OH)_6$  separately and her is isomorphic substitution  $Zn^{2+} \rightarrow Cu^{2+}$  was observed . Depending on the amount of  $Zn^{2+}$  and  $Cu^{2+}$  in the compound we can express the general formula as:



Data of IR – spectrum and X-ray diffraction show the same crystal structure of Zn, Ca and Fe hydroxostannates. These results reveal the formation of solid solutions containing ionic substitution in isomorphic form with the same type of structure.Fig.9.

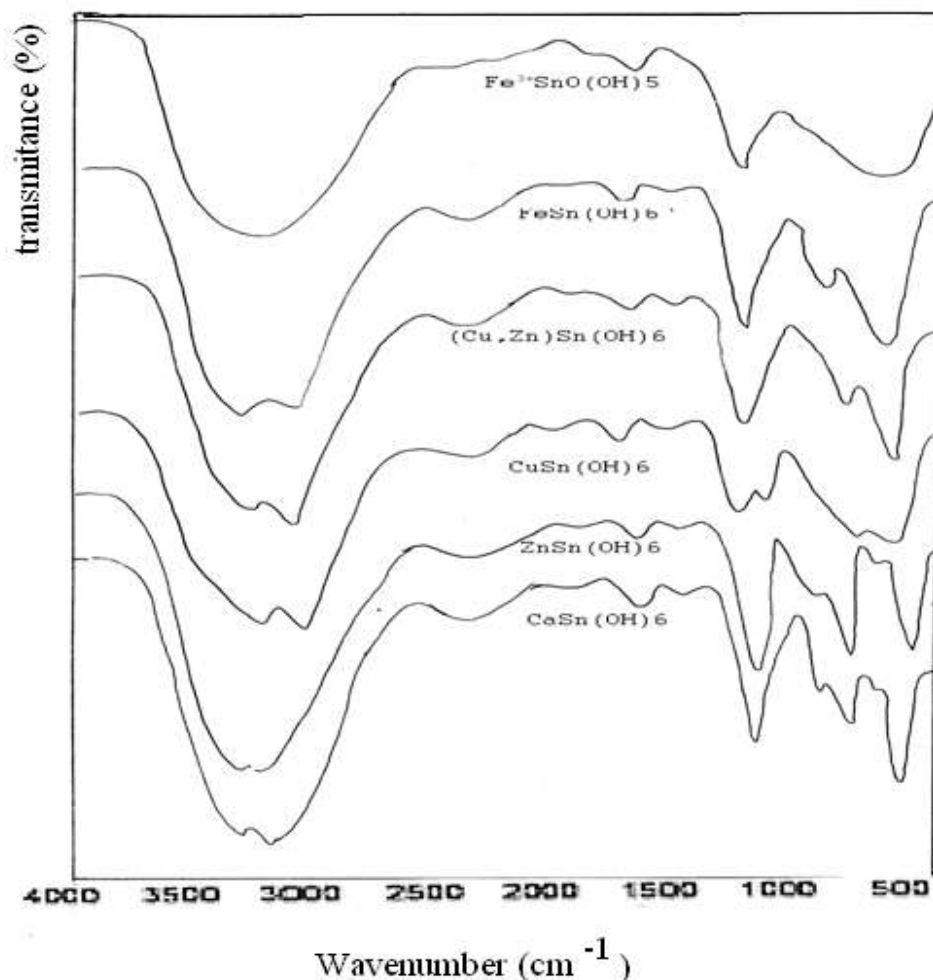


Fig.9: IR spectra for the  $M^{II}Sn(OH)_6$  where  $(M^{II} = Zn, Cu, Fe, Ca)$  ,  $Fe^{III}SnO(OH)_5$  and  $(Zn, Cu)Sn(OH)_6$

In case of  $\text{Cu}^{2+}$  it was indicated a little distortion connected with the Jahn-teller effect. Copper hydroxystannate has a tetragonal structure according to  $\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{b^2}$  with lattice constants  $a=7,5866\text{\AA}$ ,  $c=8,1030\text{\AA}$ .  $Z= 4$ ,  $V= 466,31 \text{\AA}$ . Also these values are in good agreement with what reported in [10].

### CONCLUSION:

The results of chemical and crystal study of artificial bivalent- metal hydroxystannates show the following points:

- 1-  $\text{M(II)Sn(OH)}_6$ , where  $(\text{M(II)}) = \text{Zn, Fe, Cu, Ca}$  and  $\text{Fe}^{3+}\text{SnO(OH)}_5$  products were successfully prepared by (Struz, Contag) method .
- 2- The DTA curves show two endothermic effects and one exothermic effect.
- 3- The compound  $\text{Fe(II)Sn(OH)}_6$  is unstable in air in which  $\text{Fe}^{2+}$  oxidized to  $\text{Fe}^{3+}$  with particular substitution of  $\text{OH}^-$  by  $\text{O}^{2-}$ . The illustrated facts affirm the formula  $\text{FeSnO(OH)}_5$ .
- 4- Hydroxostannate of mixed bivalent- metals were prepared in the same conditions as mentioned above in the experimental part. The result further demonstrates the formation of solid solutions for system (Zn- Cu) by replacement.

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