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CHEMICAL AND STRUCTURAL CHARACTERIZATION OF $ZN_{2-X}CO_XSIO_4$ (X=0.5) SOLID SOLUTIONS TYPE SYNTHESIZED BY TWO UNCONVENTIONAL METHODS (SOL-GEL METHOD AND PECHINI METHOD)

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Abstract: *$Zn_{2-x}Co_xSiO_4$ (x=0.5) nano-particles were successfully synthesized at a low temperature of 900°C both by Pechini method and sol-gel method with starting materials of $Zn(CH_3COO)_2 \cdot 2H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$ and $Si(OCH_2CH_3)_4$. The structural characterization of the precursors and derived synthesized oxide powders is done by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal analysis (TG-DTG) and electron microscopy (SEM, EDX and TEM) studies. The effect of heat-treating temperature on the crystallinity of the $Zn_{2-x}Co_xSiO_4$ (x=0.5) was investigated. Combined the XRD data and the strong FTIR peaks as signed to Zn-O and Si-O vibration indicate the formation of $Zn_{2-x}Co_xSiO_4$ (x=0.5) phase at a temperature of 900°C. Also the nano-crystals size distribution for sol-gel process was studied and the main diameter of nanoparticles was about 15nm.*

Keywords: *sol-gel · Pechini · $Zn_{2-x}Co_xSiO_4$ · nano-crystals*

Introduction

The green colored oxides of CoO-ZnO system, with low cobalt content, have demonstrated to be comparable in their physical and chemical properties with Cr (III) green pigments. [1]

Therefore, the Co-ZnO oxides are of interest as new ecological friendly colored pigments because they can be used as substitutes of chromium oxides. [1]

On the other hand, in recent years, oxide solid solutions of Co-doped ZnO have been of great interest for device applications, as in optoelectronics and term electronics, due to their electronic and magnetic properties. [1]

Cobalt-doped zinc orthosilicate ($Zn_{2-x}Co_xSiO_4$) – a solid solution of Zn_2SiO_4andCo_2SiO_4 – has a particular importance in inorganic pigments industry.

Co_2SiO_4 is at the bottom of obtaining a heat resistant pink-purple pigment. [2-5]

Size and dimensionality are now regarded as particularly important factors influencing the chemical and physical properties of the materials. [6]

Many low temperature methods have been proposed to replace the current solid-state reactions. [7]

In recent years, many new preparation approaches have been proposed, including spray pyrolysis route, sol-gel method, chemical vapor synthesis and hydrothermal method. [8]

Other studies from the literature have also reported information about non-standard methods for the synthesis of inorganic pigments: sol-gel method, Pechini method and co-precipitation method. [9-15]

Sol-gel is an alternative synthesis of these compounds and is generally preferred because it has many advantages such as: purity and advanced homogeneity of the synthesized compounds, much lower temperature heat

treatment and the possibility of modifying the properties of the synthesized compounds by varying parameters synthesis.

The sol-gel method and its modifications have been widely used for inorganic/ceramic, catalytic materials and also organic-inorganic hybrid structures. [16-19]

Sol-gel method is effective to improve the crystallization and control the morphology of synthesized material.

A process related to the sol-gel route is the Pechini method or liquid mix process. [20]

An important consequence of the molecular-scale mixing is a drastic reduction of thermal treatment temperature.

Among the methods, the hydrotermal synthesis has great advantage, such as better distribution of metal ions, controllable morphology and lower cost. [8]

However, the as-formed inorganic phosphors of these processes still require post-calcination at temperatures of 900°C or more to increase the crystallinity of the inorganic phosphors. [7]

Thus, the environmental burden of producing industrial phosphors could be greatly reduced if a single-step method was available that occurred rapidly at low temperatures. [7]

This paper aimed synthesis by two unconventional methods (sol-gel method and Pechini method) heat-treated in a conventional oven of $Zn_{2-x}Co_xSiO_4$ (x=0.5) solid solutions type and chemical and structural characterization of the synthesized compounds. [21]

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The $Zn_{2-x}Co_xSiO_4$ (x=0.5) nanopowders have been investigated by thermal analysis (TG-DTG), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and electron microscopy (SEM, EDX and TEM) studies.

Experimental

The $Zn_{2-x}Co_xSiO_4$ (x=0.5) was synthesized using two unconventional methods (sol-gel method and Pechini method). The starting materials were $Zn(CH_3COO)_2 \cdot 2H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$ and $Si(OCH_2CH_3)_4$. Reagents were all analytical pure regents in the experiments.

Sol-gel method

In the first step of the synthesis was necessary to obtain the SiO_2 soil which was made by acid hydrolysis of TEOS at room temperature. This step involved magnetic stirring for one hour of a mixture with the following molar ratio: H_2O : $Si(OCH_2CH_3)_4$: CH_3CH_2OH : HCl(6N) = 1 : 1 : 0.5 : 0.0013

Separate were prepared solutions with necessary stoichiometric quantities of $Zn(CH_3COO)_2 \cdot 2H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$ for the synthesis of $Zn_{2-x}Co_xSiO_4$ solid solution (x=0.5) and using a 25% NH_3 solution the two metals co-precipitation was carried out as hydroxides.

The two soils obtained were then brought into the same reaction vessel and mixed using magnetic stirring at room temperature for one hour.

Obtained co-precipitate was allowed to mature for seven days, then filtered and rinsed with distilled water. After filtration, obtained product was dried in an oven at 110°C and then heat-treated at 800°C, 900°C, 1000°C and 1100°C with a bearing heat treatment for two hours.

Pechini method

In the first step of the synthesis, the SiO_2 soil was prepared by a sol-gel method using TEOS as a precursor of silicon. $Si(OCH_2CH_3)_4$ is first hydrolyzed for one hour using magnetic stirring.

Stoichiometric amounts of $Zn(CH_3COO)_2 \cdot 2H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ necessary on forming of non-stoichiometric $Zn_{2-x}Co_xSiO_4$ (x=0.5) chemical compound is dissolved in distilled water and then mixed with a aqueous solution of citric acid and ethylene glycol with a molar ratio: $C_6H_8O_7$: $C_2H_6O_2$ = 3 : 1

At the end of this stage, mix in the resulting mixture over SiO_2 soil and continue the magnetic stirring for one hour, maintaining a constant temperature of 80°C.

The obtained precipitate is filtered, rinsed with distilled water and dried in an oven at110°C to obtain the xerogel.

Xerogel was then heat-treated in an oven on the following temperatures: 800°C, 900°C, 1000°C and 1100°C, maintaining temperature at the landing two hours on each time and for all the compounds. [22]

The molar ratio of oxides in solid solution $Zn_{2-x}Co_xSiO_4$ (x=0.5) was assessed by flame atomic absorption measurements using anatomic absorption spectrometer Shimadzu AA 6200.

To determine the zinc and nickel in the synthesized compound, a known amount of the sample was brought into solution by means of a HACH Digesdahl device using aqua regia (HNO_3: HCl=3: 1). [23]

After bringing into solution, there were determined zinc and nickel concentrations by atomic absorption spectrometry at 213.9 nm wavelength for zinc and 240.7 nm wave length for cobalt.

Forming and characterization of $Zn_{2-x}Co_xSiO_4$ (x=0.5) solid solution synthesized by the sol-gel and Pechini method respectively, was evaluated by differential thermal analysis using a DTG Shimadzu derivatograph-TA-514H, by X-ray diffraction using a SHIMADZU diffractometer with radiation Cu Kα, by FTIR spectrometer using a BRUKER VECTOR 22 Fourier transform and by electron microscopy using an electronic microscope PHILIPS CM 120 STEM. [24-33]

Results and discussion

Measurements of atomic absorption showed similar concentrations of zinc and cobalt from the theoretical ones, which allow the evaluation of the molar ratio ZnO: CoO = 3: 1

Table 1 presents the results of atomic absorption determinations:

Table 1. Theoretical and practical percentage composition of Zn and Co in $Zn_{2-x}Co_xSiO_4$ (x=0.5) compound

Compound	Synthesis method	% Zn		% Co	
		theoretical	practical	theoretical	practical
$Co_{0.5}Zn_{1.5}SiO_4$	Sol-gel	44.65	37.23	13.42	10.95
$Co_{0.5}Zn_{1.5}SiO_4$	Pechini	44.65	42.24	13.42	12.63

Complex thermal analysis performed on solid sample, thermally untreated bring important information about the formation of $Zn_{2-x}Co_xSiO_4$ (x=0.5).

Figure 1 presents TG-ATD curves recorded in 20-1000°C temperature range, for $Zn_{2-x}Co_xSiO_4$ (x=0.5) synthesized by the sol-gel method.

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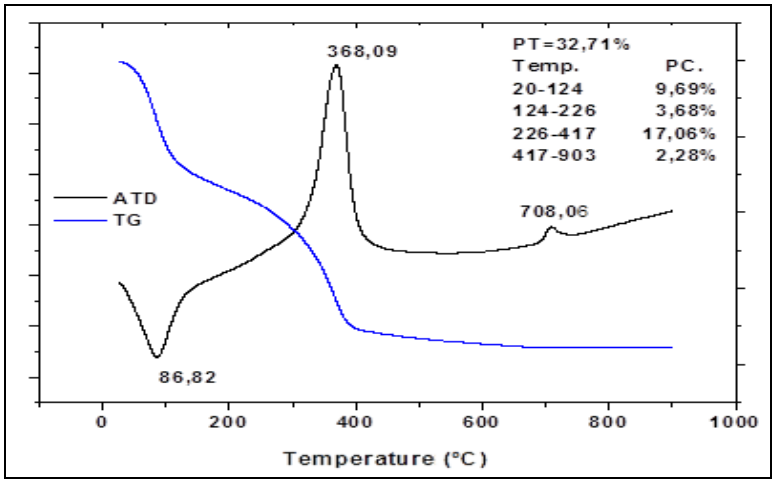

Figure 1: Complex thermal analysis of $Zn_{2-x}Co_xSiO_4$ (x=0.5) powder synthesized by sol-gel method

Figure 1 presents an exothermic effect arising from the temperature of 368.09°C and 708.06°C, with end of thermal effect appears at 86.82°C attributed to the dehydration process.
Total mass loss recorded in the range 20-903°C in the TG curve is 32.71% and occurs in four stages:

- First weight loss of 9.69% occurs in the range 20-124°C and can be attributed to the loss of water adsorbed compound;
- In the range 124-226°C, the weight loss is only 3.68%;
- In the range 226-417°C appears the most important mass loss of 17.06% (which represents approximately 52%), corresponding to the reforming of the synthesized compound;
- In the range 417-903°C, the weight loss is only 4.30%, which presents that the synthesized solid solution was formed since the 708.06°C.

Figure 2 presents schematic evolution of mass loss (TG curve appreciated) versus temperature for $Zn_{2-x}Co_xSiO_4$ (x=0.5) compound.

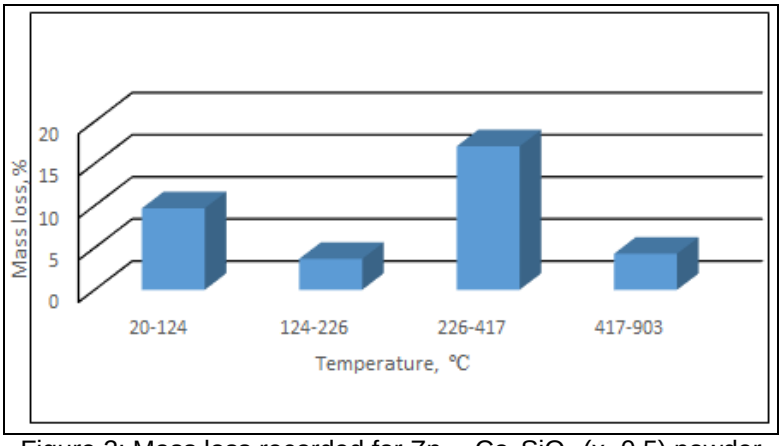

Figure 2: Mass loss recorded for $Zn_{2-x}Co_xSiO_4$ (x=0.5) powder

Formation of synthesized compound $Zn_{2-x}Co_xSiO_4$ (x=0.5) was investigated using X-ray diffraction with Cu Kα radiation.
Analyzing the XRD patterns, it can be seen that the maximum intensities obtained for the powder investigated belong to specific interference of the synthesized compounds, which confirm the formation of $Zn_{2-x}Co_xSiO_4$ (x=0.5) at low temperature (still to 708.06°C).
Figures 3 a) and b) presents diffractograms obtained on $Zn_{2-x}Co_xSiO_4$ (x=0.5) powder, synthesized by sol-gel method (a) or by Pechini method (b) heat-treated at 900°C.

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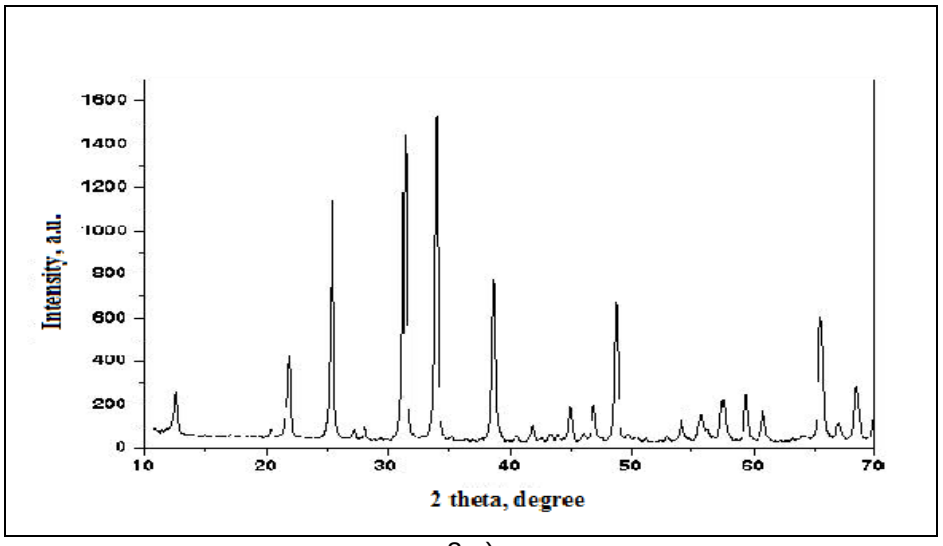
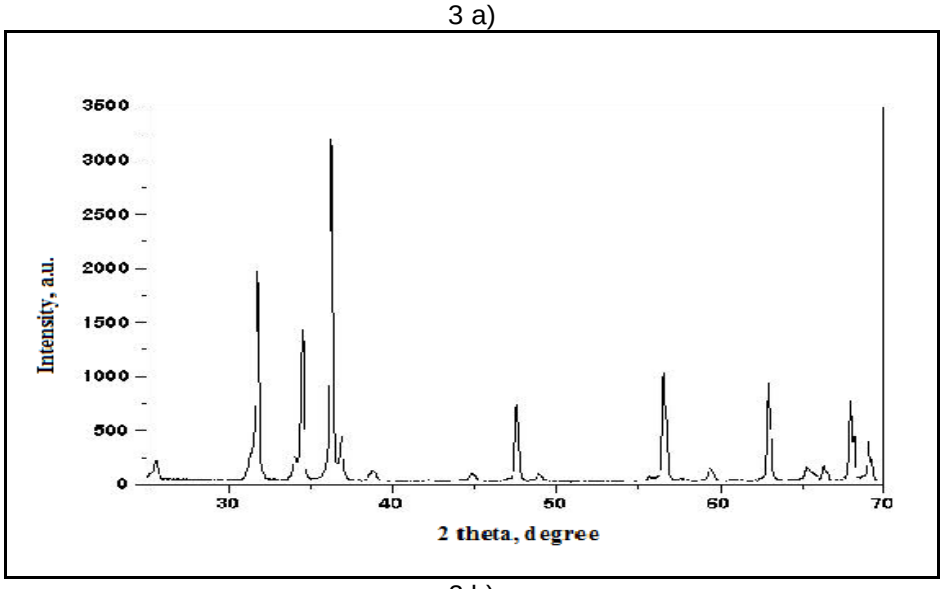


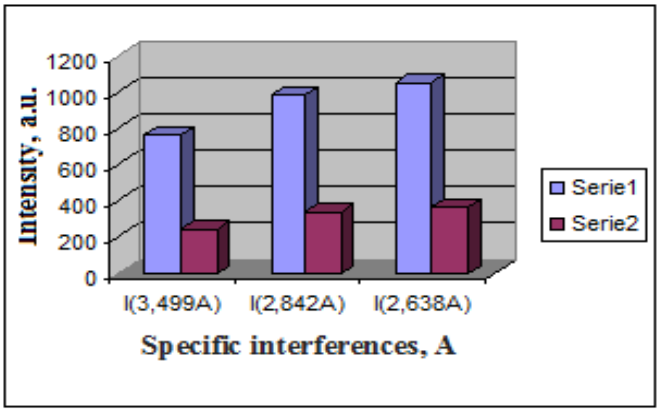
3 a)



3 b)

Figure 3: Obtained diffractograms for $Zn_{2-x}Co_xSiO_4$ (x=0.5) heat-treated at 900°C for two hours synthesized by: a) the sol-gel method; b) the Pechini method

Figure 4 a) and b) presents the evolution of the intensity of the two $Zn_{2-x}Co_xSiO_4$(x=0.5) specific interference, synthesized by sol-gel method (a) and Pechini method (b) by different heat treatment temperatures (900°C–Serie1 and 1000°C–Serie2).



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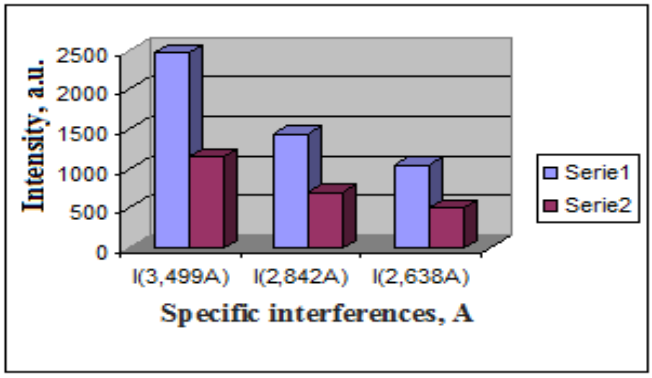
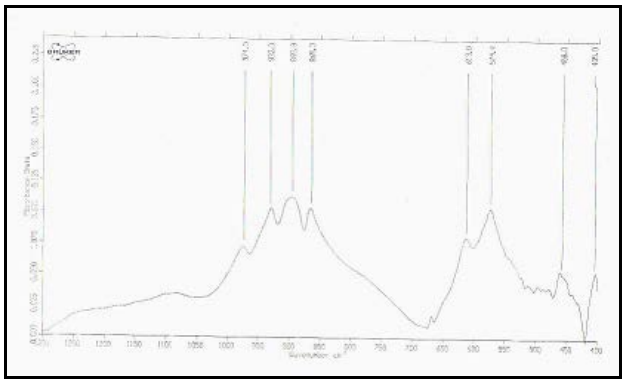
4 a)



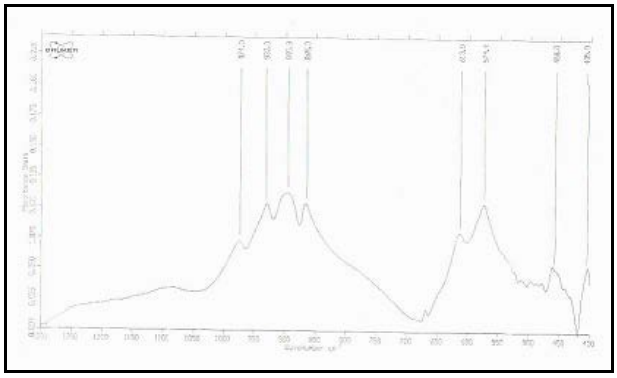
4 b)

Figure 4: The evolution of the intensity of the two $Zn_{2-x}Co_xSiO_4$(x=0.5) specific interference, synthesized by sol-gel method (a) and Pechini method (b) with different heat treatment temperatures(900°C–Serie1 and 1000°C–Serie2)

The information presented in Figure 4 allows the choice of the optimum temperature for the formation of $Zn_{2-x}Co_xSiO_4$ (x=0.5). Thus, specific interference of the two synthesized compound was identified a specific intensity peak at 900ºC.
At this temperature, the $Zn_{2-x}Co_xSiO_4$(x=0.5) compound synthesized in the laboratory was formed as mono-mineral single phase, well-defined crystalline structure. Increasing the heat treatment temperature at 1000°C leads to a decrease in the intensity of specific interference of $Zn_{2-x}Co_xSiO_4$ (x=0.5) compound.
In order to obtain more information about the compound synthesized, were performed spectroscopic analyzes FT-IR using Bruker Vector 22 with Fourier transform.
Figure 5 presents FTIR spectra for samples synthesized by the sol-gel method (a) and Pechini method (b), thermo set at 900°C.



5 a)



5 b)

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Figure 5: FTIR spectra for samples synthesized by the sol-gel method (a) and Pechini method (b), thermo set at 900°C.

In figure 5 a) there is an absorption band at 974 cm^{-1} due to vibration of free silanol type groups on the surface of the solid.

At 458 cm^{-1} absorption band appears associated vibration δ Si-O, and at 932 cm^{-1} band is assigned to present a bond v Si-O. At 613 cm^{-1} absorption band appears attributable to bond v Zn-O.

In figure 5 b) the absorption band appears at 1102.3 cm^{-1} due to vibration asymmetric bonds Si-O-Si.

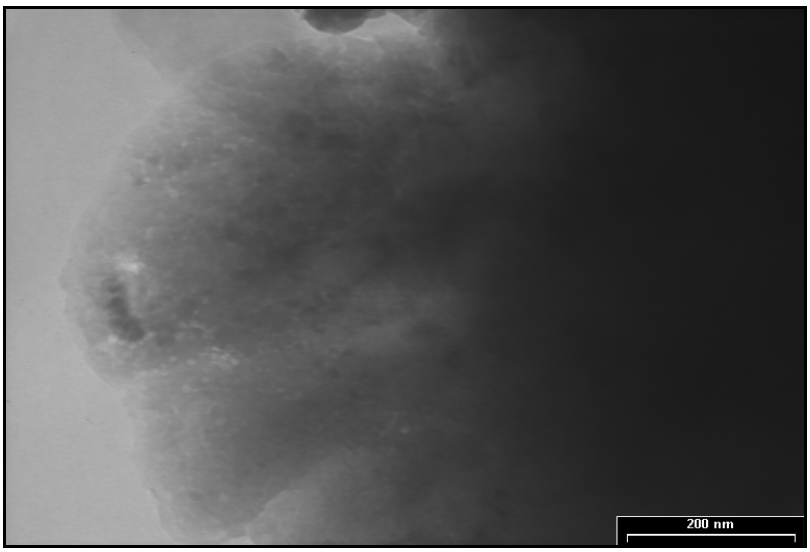
At 447.8 cm^{-1} absorption band appears associated vibration δ Si-O and 891.4 cm^{-1} band assigned to the connection is present v Si-O.

At 576.2 cm^{-1} absorption band appears attributable to bond v Zn-O.

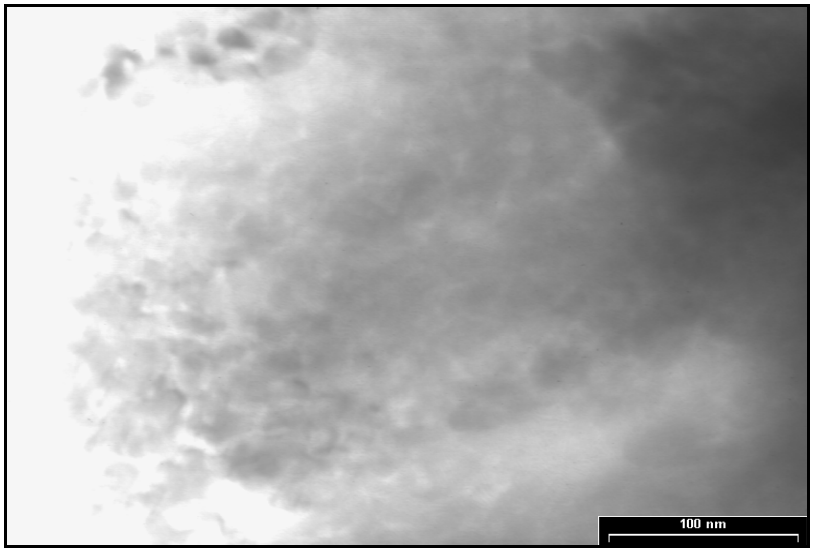
These results are similar to standard values of catalogs spectra, demonstrating that $Zn_{2-x}Co_xSiO_4$ (x=0.5) powder was formed. [13]

Particles morphology obtained by synthesis of $Zn_{2-x}Co_xSiO_4$ (x=0.5) by sol-gel method and Pechini method was assessed by electron microscopy measurements.

In figure 6 is shown TEM image of the compound $Zn_{2-x}Co_xSiO_4$ (x=0.5), synthesized by sol-gel method at 900°C obtained by electron microscopy measurements on 200 nm (a) and 100 nm (b):



6 a)



6 b)

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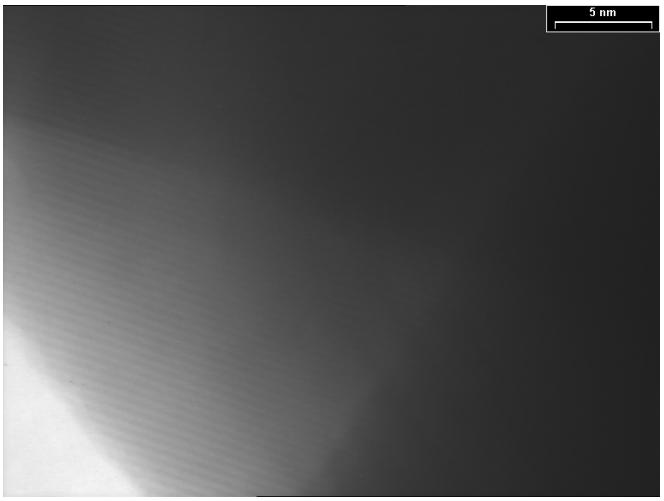
Figure 6: TEM image of the compound $Zn_{2-x}Co_xSiO_4$ (x=0.5), synthesized by sol-gel method heat-treated at 900°C obtained by electron microscopy measurements at: a) 200 nm and b) 100 nm

In figure 7 are shown TEM images of the compound $Zn_{2-x}Co_xSiO_4$ (x=0.5), synthesized by Pechini method heat-treated at 900°C as measured by electron microscope obtained at 10 nm (a) and 5 nm (b):

7 a)



7 b)

Figure 7: TEM images of the compound $Zn_{2-x}Co_xSiO_4$ (x=0.5), synthesized by Pechini method at heat-treated at 900°C as measured by electron microscope obtained at: a) 10nm and b) 5nm

In figure 8 are shown HRTEM images of the compound $Zn_{2-x}Co_xSiO_4$ (x=0.5), synthesized by the sol-gel heat-treated at 900°C obtained by measurements of high-resolution electron microscopy at 10 nm:

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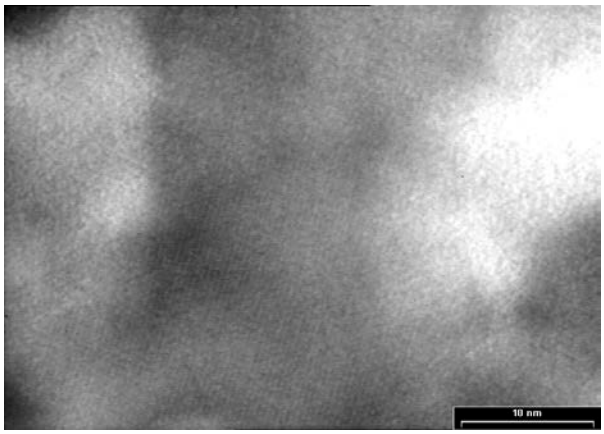

Figure 8 HRTEM images of the compound $Zn_{2-x}Co_xSiO_4$(x=0.5), synthesized by the sol-gel method obtained heat-treated at 900°C as measured by high-resolution electron microscopy at 10 nm

Figure 9 presents HRTEM image of the compound $Zn_{2-x}Co_xSiO_4$ (x=0.5), synthesized by Pechini method at 900°C as measured by electron microscopy obtained high resolution at 5 nm:

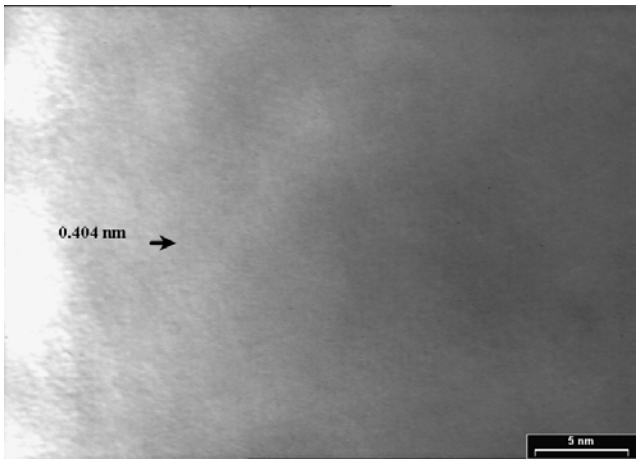

Figure 9: HRTEM image of the compound $Zn_{2-x}Co_xSiO_4$(x=0.5), synthesized by Pechini method at 900°C as measured by electron microscopy obtained high resolution at 5 nm

Figure 10 presents the images obtained by electron diffraction $Zn_{2-x}Co_xSiO_4$ (x=0.5) compound synthesized by the sol-gel method (a) or by the Pechini method (b) at 900°C:

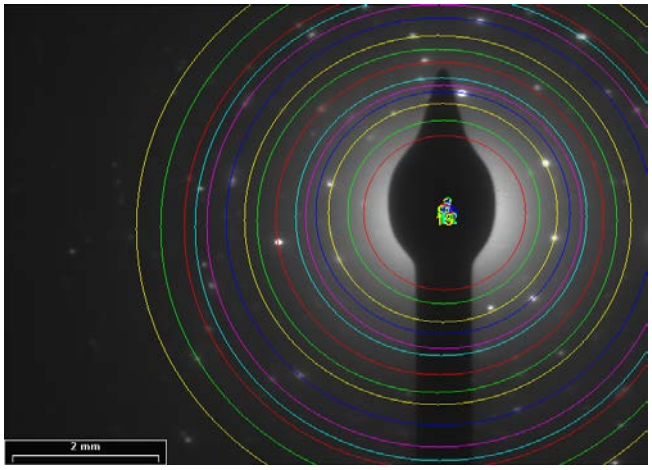

Figure 10: The electron diffraction pattern of the compound $Zn_{2-x}Co_xSiO_4$ (x=0.5) heat treated at 900°C, synthesized by sol-gel method

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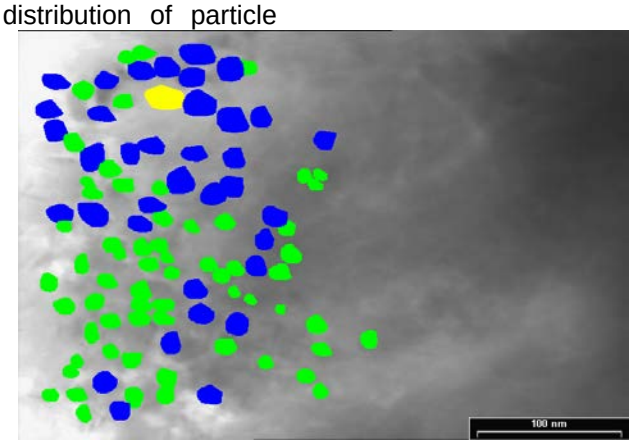
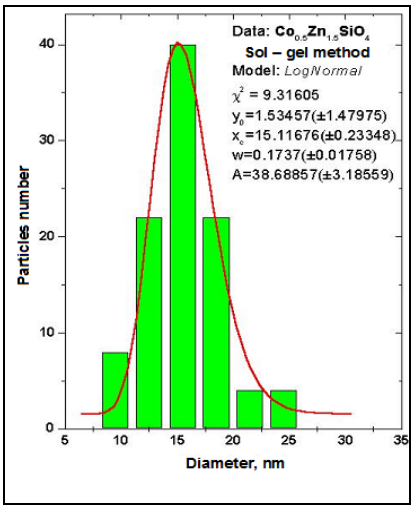
In order to estimate the number and size of the obtained particles, first is accomplished the counting step and then distribution of particle diameters is statistical represented on a logarithmic scale – Figure 11 a) and b).



11 a)



11 b)

Figure 11: a) Particles counting; b) The statistical distribution of particle diameters of $Zn_{2-x}Co_xSiO_4$ (x =0.5) compound, synthesized by sol-gel method heat-treated at 900°C

Looking at the graph from Figure 11, it can be seen that heat-treated at 900°C, the solid solution $Zn_{2-x}Co_xSiO_4$ (x=0.5) presents particles characterized by a diameter in the range of 9-25 nm, with an average diameter of 15nm.

CONCLUSION

Considering our own experimental results on the synthesis and characterization of solid solution $Zn_{2-x}Co_xSiO_4$ (x=0.5), the following conclusions can be drawn:

- $Zn_{2-x}Co_xSiO_4$ (x=0.5) solid solution was synthesized at low temperature from chemically pure reactive $Zn(CH_3COO)_2{\cdot}2H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$ and $Si(OCH_2CH_3)_4$, dosed in stoichiometric ratio using two unconventional methods of synthesis: sol-gel method and Pechini method;
- Atomic absorption determinations allow assessment molar ratio ZnO: CoO as 3: 1, which is conform with theoretical data;
- Derivatograph analysis certify the incomplete formation of $Zn_{2-x}Co_xSiO_4$ (x=0.5) solid solution from 368.09°C and complete formation at a temperature above 708.06°C;
- Diffractometer analysis revealed the formation of $Zn_{2-x}Co_xSiO_4$ (x=0.5) as full mono-mineral crystalline phase at 900°C, the temperature on which we recorded the highest values of intensity interference for the specific compound synthesized;

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- FTIR confirm the formation of $Zn_{2-x}Co_xSiO_4$ (x=0.5) by the existence of specific band for the bond Zn-O on 613 cm^{-1} and the specific band for the bond Si-O to 458 cm^{-1} or 932 cm^{-1};
- Electronic microscopy determinations revealed the presence of fine particles of $Zn_{2-x}Co_xSiO_4$ (x=0.5) synthesized by the sol-gel with a mean diameter of 15nm.

BIBLIOGRAPHY

[1] Araceli E. Lavat, Claudia C. Wagner, Julia E. Tasca, Interaction of Co–ZnO pigments with ceramic frits: A combined study by XRD, FTIR and UV–visible, Ceramics International 34 (2008) 2147–2153
[2] Hideki Taguchi, Yasuo Takeda, Hiroyasu Shibahara, Synthesis of olivine-type $Co_{1.6}SiO_4$ at low temperature, Materials Letters 52(2002)
[3] Alexandra Navrotsky, Faivel S. Pintchovski, Syun-Iti Akimoto, Calorimetric study of the stability of high pressure phases in the systems CoO-SiO_2 and FeO-SiO_2 and calculation of phase diagrams in MO-SiO_2 systems, Physics of the Earth and Planetary Interiors 19 (1979)
[4] W. Lottermoser, R. Müller, H. Fuess, Antiferromagnetic in synthetic olivines, Journal of Magnetism and Magnetic Materials (1986) 54-57
[5] B.M. Wanklyn, The prediction of starting compositions for the flux growth of complex oxide crystals, Journal of Crystal Growth 37 (1977)
[6] Junxi Wan, Zhenghua Wang, Xiangying Chen, Li Mu, Weichao Yu, Yitai Qian, Controlled synthesis and relationship between luminescent properties and shape/crystal structure of $Zn_2SiO_4:Mn^{2+}$ phosphor, Journal of Luminescence 121 (2006) 32–38
[7] Masafumi Takesue, Kenji Shimoyama, Kazuaki Shibuki, Atsuko Suino, Yukiya Hakuta,Hiromichi Hayashi, Yasuo Ohishi, Richard Lee Smith Jr., Formation of zinc silicate in supercritical water followed with *in situ* synchrotron radiation X-ray diffraction, Journal of Supercritical Fluids 49 (2009) 351–355
[8] Yaqi Jiang, Jie Chen, Zhaoxiong Xie, Lansun Zheng, Syntheses and optical properties of α- and β-Zn_2SiO_4:Mn nanoparticles by solvothermal method in ethylene glycol-water system, Materials Chemistry and Physics 120 (2010) 313–318
[9] Ioan Lazau, Utilizarea metodei sol-gel in obtinerea unor pigmenti din clasa nesosilicatilor, Materiale de Constructii vol. XXVIII nr. 1(1998)
[10] Cornelia Pacurariu, Ioan Lazau, Alexandrina Sim, Radu Ioan Lazau, Studiu comparativ privind utilizarea metodei sol-gel si a altor metode in sinteza unor compusi oxidici, Rev. Chim. (Bucuresti) 54, nr. 6 (2003)
[11] S. Hazra, A. Ghosh, D. Chakravorty, Classical hopping in sol-gel cobalt silicate glass, Journal of Psysics: Condensed Matter 49(1996)
[12] Vlamirir E. Gaishun, Dmitri L. Kovalenco, Valeri S. Gurin, Sol-gel method preparation of thin films as source ob B and Sb as dopants for silicon electronic engineering, Journal of Sol-Gel Science and Technology, vol. 32, nr. 11(2004)
[13] R.F.S. Lenza, W.L. Vasconcelos, Preparation of silica by sol-gel method using formamide, Materials Research, vol. 4, nr. 3(2001)
[14] O.M. Kanunnikova, S.F. Lomayeva, A.E. Muravyev, AFM and XPS investigations of silica films manufactured by sol-gel method and ion sputerring, Materials reserach, vol. 18, nr. 5(2004)
[15] R. Reisfeld, Smart optical materials by sol-gel method, Journal of sol-gel science and technology, vol. 37, nr. 8(2004)
[16] S.N. Koc, F. Oksuzomer, E. Yasar, S. Akturk, M.A. Gurkaynak, Materials Research Bulletin 41 (2006) 2291-2297
[17] V. Ciupina, I. Carazeanu, G. Prodan, C. Guguta, MicrochimicaActa 147 (2004) 151–155
[18] I. Carazeanu Popovici, E. Chirila, V. Popescu, V. Ciupina, G. Prodan, Journal Materials Science 42 (2007) 3373–3377
[19] I. Carazeanu Popovici, V. Ciupina, G. Prodan, M.A. Girtu M, Journal of Optoelectronics and Advanced Materials 10 (2008) 2942–2946
[20] Pechini MP, US Patent 3.330.697 (1967)
[21] S. R. Lukić, D. M. Petrović, LJ. Đačanin, M. Marinović-Cincovića, Ž. Antića, R. Krsmanovića, M.D. Dramićanina, Gel combustion synthesis of transition metal ions doped Zn_2SiO_4 powder, Journal of Optoelectronics and Advanced Materials Vol. 10, No. 10 (2008) 2748-2752
[22] Takamitsu Yamanaka, Crystal structure of Ni_2SiO_4 and Fe_2SiO_4 as a function of temperature and heating duration, Physics and Chemistry of Minerals, vol. 13, nr. 4 (1986)
[23] E. Chirila, Chimie analitica. Aplicatii, Ovidius University Press (2002)
[24] V. Ettler, O. Legendre, F. Bodenan, J.C. Touray, Primary phases and natural weathering of old lead-zinc pyrometallurgical slag, The Canadian Mineralogist, vol. 39, nr. 3 (2004)
[25] C. Brotzeller, H. Jaitner, B. Hock, O. Neumann, R. Geick, W. Treutmann, S. Hosoya, K. Hato, Various

DOI: 10.21279/1454-864X-16-I1-064

exchange interactions and anisotropies in Fe_2SiO_4 and Journal of Magnetism and Magnetic Materials, 104-107(1992)
[26] W. Schmidt, C. Brotzeller, P. Schweiss, H. Tietze-Jaensch, R. Geick, W. Treutmann, Magnetic excitations in Co_2SiO_4, Journal of Magnetism and Magnetic Materials (1995) 140-144
[27] Xuefan Jiang, G.Y. Guo, First-principle studies of the electronic structure and magnetism in fayalites: M_2SiO_4 (M=Fe and Co), Journal of Magnetism and Magnetic Materials, 282(2004)
[28] P. Bindu, J.V. Kingston, M.N. Sudheendra Rao, Dianionic silicate derivates of transition metals: synthesis by a facile ion exchange route, characterization and thermolysis studies, Polyedron, 23(2004)
[29] Chung-Cherng Lin, Vibrational spectroscopic study of the system α-Co_2SiO_4 - αNi_2SiO_4, Journal of Solid State Chemistry, 157(2001)
[30] P.N. Lisboa-Folho, M.R.C. de Almeida, P.L. Gallo, E. Azevedo, C.A. Paskocimas, E. Longo, W.A. Ortiz, Magnetic phases of imperfectly crystalline Co_2SiO_4, Journal of Non-Crystalline Solids, 273(2000)
[31] E. Kondoh, R.A. Donaton, S. Jin, H. Bender, W. Vandervorst, K. Maex, Interaction between Co and SiO_2, Applied Surface Science, 136 (1998)
[32] A. Martucci, D. Busso, M. Guglielmi, L. Zbroniec, N. Koshizaki, M. Post, Optical gas sensing properties of silica film doped with cobalt oxide nanocrystals, Journal of Sol-Gel Science and Technology, vol. 32, nr. 1-3 (2004)
[33] P. Dutta, B.C. Dunn, E.M. Eyring, N. Shah, G.P. Huffman, A. Manivannan, M.S. Seehra, Characteristics of cobalt nanoneedles in 10% Co/Aerogel Fischer-Tropsch Catalysts, American Chemical Society 17 (2005)

DOI: 10.21279/1454-864X-16-I1-064