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RESEARCH ARTICLE

$CO_XSI_YTE_Z$ NANOCOMPOSITE MANUFACTURE BY SOLUTION COMBUSTION PROCESS ASSISTED BY MICRO-WAVE

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Abstract

A possible formation of the nanocomposite based on silicon, cobalt and tellurium was produced by the combustion synthesis process in solution (SCS) assisted by microwave in two stages, combustion using a conventional microwave oven and purification by means of calcination at 650 ºC in a muffle furnace. The new material was developed in different oxidant-fuel relationships where it observed the effects on the evolution of the phase and morphology of the powders, the structural, morphological and thermal properties were investigated by the X-ray diffraction technique (XRD), energy dispersive X-ray spectroscopy (EDX) coupled to the scanning electron microscope (SEM) and TGA and DTG curves. Through the analysis it is possible to suggest the development of a new stable material in single phase, being isostructural to the $Co_8Te_{12}O_{32}$ (ICDD-50702) of nanometric dimensions with interesting potentials due to the properties of the constituent elements.

Introduction:-

There is a growing interest in materials that have magnetic, optical and electronic properties, enhanced due to their development at the nanoscale, and can be applied in several technological areas such as nanoelectronics, nanomagnetic, nanocatalysis, nanoexplosives, pharmaceutical, among others [1]. Nanocomposites comprise a dimensional order class of nanomaterials, they can be formed by two or more atoms adding and improving the physical-chemical properties of the constituent elements [2], [3]. Several studies carried out through applications of nanocomposites based on cobalt, silicon or tellurium have shown promise because of the excellent properties acquired or improved due to the joining of these elements, however a structure constituted from the three elements $Co_xSi_yTe_z$ is still unknown, presenting short report in scientific literature or crystallographic database [4] - [6].

Within this line of reasoning, we emphasize the importance of the development of a nanocomposite made up of the elements cobalt, silicon and tellurium, in order to raise and understand the behavior of the physicochemical characteristics of this structure, suggesting possible applications, especially those that require magneto-photovoltaic properties. For the present study, the synthesis and structural characterization of a possible nanocomposites based on $Co_xSi_yTe_z$was carried out using the oxide-reduction protocol using solution combustion synthesis (SCS) with microwave heating [7], [8].

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Experimental Procedures:
Materials and Equipment:
This research used as base material in the nanocomposite synthesis process the reagents SiO_2 (<40, >63 μm, Vetec), $Co(NO_3)_2.6H_2O$ (98%, Sigma-Aldrich), Te (99,8%, Sigma-Aldrich) and urea (CH_4N_2O, 99%, Dinâmica), all analytical grade. Microwave oven was used electrolux MEV41 31 liters with microwave frequency 2450 MHz and a muffle furnace model JUNG 2895 with internal volume of 2 liters, maximum temperature of 1700 °C with temperature programming and heating time ramp. For characterization, a Bruker D8 Advance diffractometer with Bragg-Bretano geometry with radiation source was used Kα1 of Cu (1,54056Å). Scanning Electron Microscope (MEV), Jeol, JSM – 6610, equipped with EDS, Thermo scientific NSS Spectral Imaging. TG-DTA of brand Shimadzu in an atmospheric environment varying the temperature from 25 to 800 ºC with heating rate of 10°C/min.

Method:-

The synthesis methods for developing nanostructured materials are numerous and well established, using processes in solution, solid-solid, solid-gas, however each has its own merits and demerits in relation to the other. Most processes involving relatively toxic reagents, complicated synthetic routes and low scalability tend to be unviable and have low efficiency. On the other hand, an efficient synthesis will be useful when characteristics such as: energy savings, time and costs, adoption of environmentally friendly precursors, little residual production and a synthesis-properties relationship are beneficial for society [9].

The process of synthesis by combustion in solution (SCS) is based on the thermodynamic concepts applied in the area of explosives and propellants, it starts with the formulations of the stoichiometric composition of the elements generating a redox mixture, this mixture is put under an external source of heating generating an exothermic reaction, which becomes self-sustaining in a certain period of time, resulting in a porous powder. Some parameters influence the reaction and can be modified, such as the type of fuel, fuel-oxidant ratio, use of excess oxidant, ignition temperature, amount of water contained in the precursor mixture and other types of external sources [10], [11].

Microwaveassisted solution combustion synthesis is one of these possible variations and is an efficient method for obtaining inorganic nanopowders with various elements. Its principle explores an exothermic chemical reaction, generally rapid, between the salts of the metals of interest and a suitable organic fuel, using an external source of heating by microwaves with frequencies around 2450 MHz having as main characteristics the homogenization of the heating starting from the center to the ends of the solution and a short period of time for self-sustained combustion according to the stoichiometric composition of the reagents [12].

To obtain the nanocomposite based on $Co_xSi_yTe_z$ used the technique SCS microwave assisted, where the precursor mixture in urea was diluted in 10 ml of distilled water and homogenized with the aid of a magnetic stirrer, the solution was placed in a microwave oven programmed at maximum power with a burning time of 180 seconds in an atmospheric environment. The resulting powders were de-agglomerated, sieved then the purification process was carried out, in this step the samples were calcined at 650 ºC in a muffle furnace with the parameters of heating rate 10 ºC/min and burning time of 30 minutes in atmospheric environment. In Figure 1 we represent, by means of illustrations, the steps performed in the whole process used to obtain the nanocomposite.

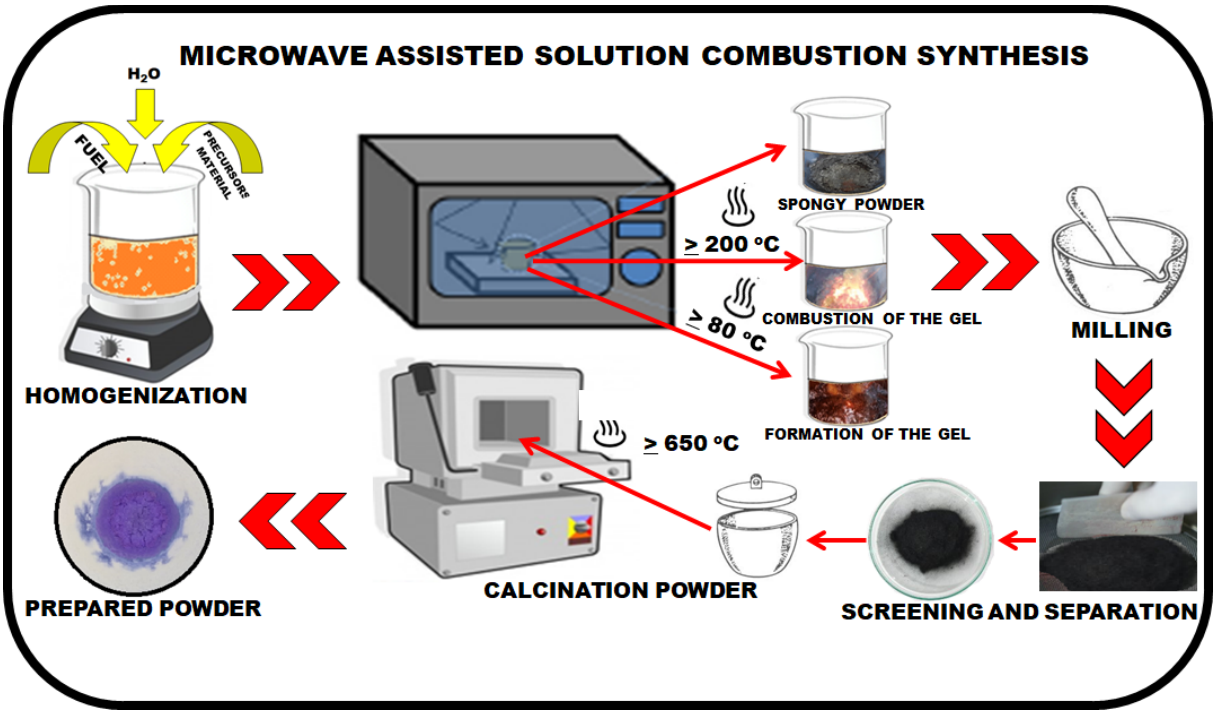


Figure 1:- Illustration of the steps carried out in the solution-assisted combustion synthesis (SCS) route and subsequent calcination process to obtain the nanocomposite based on $Co_xSi_yTe_z$.

Still in the synthesis process, it changed the parameter quantity of combustible, considering that it plays a crucial role in the properties of the final material. Thus, in the present research the synthesis of possible nanocomposites based on $Co_xSi_yTe_z$ the molar ratio of the combustible to the oxidant was adjusted, in stoichiometric proportions, saturated at 25% and poor -25% starting from the balanced equation that is represented in Table 01, also describing the identification of the samples, variations in the combustible/oxidant ratio and the steps in the preparation.

Table 1:- Nanocomposite manufacturing summary $Co_xSi_yTe_z$.

$Co_xSi_yTe_z$; x=1, y=2, z=1 **$2Co(NO_3)_2*6H_2O + SiO_2 + Te + 7(NH_2)2CO = Co_2SiTe + 9N_2 + 7CO + 26H_2O$**		
Identification	**Fuel/oxidant ratio**	**Synthesis Medium**
SCS 01-1	Stoichiometric	Microwave oven
SCS 01-2		Microwave oven/Calcination 650 ºC in Mufla
SCS 02-1	Saturation in 25% of urea	Microwave oven
SCS 02-2		Microwave oven/Calcination 650 ºC in Mufla
SCS 03-1	Deficiency in 25% of urea	Microwave oven
SCS 03-2		Microwave oven/Calcination 650 ºC in Mufla

Results and Discussions:-

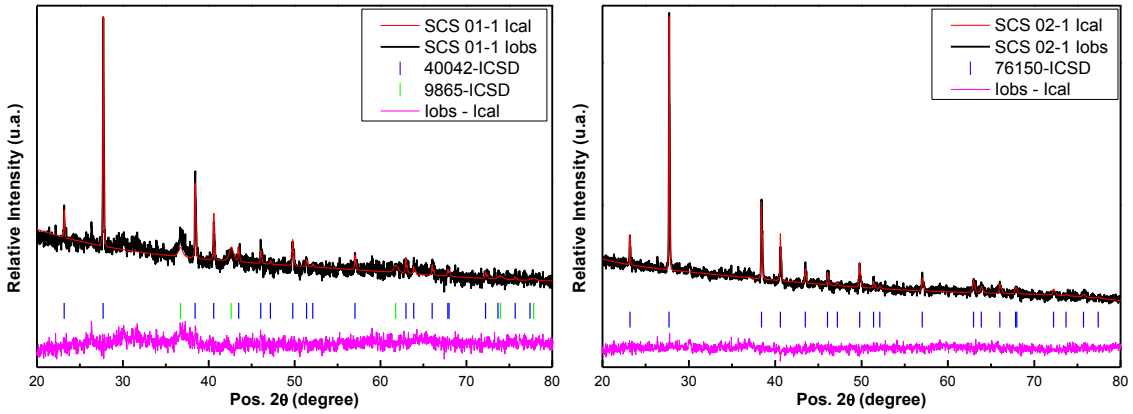
Structural analysis of the synthesized nanocomposites was performed by X-ray diffraction (XRD) and to identify the phases of the samples, the comparison of the experimental diffraction pattern with the ICDD database (International Center for Diffraction Data) was used. Using the Rietveld refinement method, he analyzed the crystallographic parameters using the program DBWSTools2.3[13], [14]. Morphological studies and X-ray dispersive energy analysis (EDX) were performed with the aid of a Scanning Electron Microscope (SEM) and the thermal behavior was studied by analyzing the TGA and DTA curves.

Figure 2 shows the experimental diffraction patterns, calculated, identification of the phases present, as well as the residual parameter of the synthesized samples refinement procedure. The results presented suggest that a single phase crystalline structures material was developed, with the exception of the SCS 01-1 sample, two phases were identified, the analyzes were performed with isostructural diffraction patterns, due to the lack of a pattern corresponding to the study compound. From these data, he verified a common structure of molecular formula $Co_8Te_{12}O_3$ (ICDD-50702) in the samples that were synthesized and calcined, regardless of the different fuel-oxidizing compositions used. From the identification of a crystallographic pattern, the Rietveld refinement process was carried out through the DBWSTools2.3 program, where information was collected, such as: structural parameters, spatial group, sizes of crystallite averages, quantification of the phases as well as the parameters of refinements all described in Table 02.

With the refinement data it was possible to extract the values in 2θ of the width at half the height of the most intense peak (FWHM) and obtain the average value of the crystallite diameter according to the equation proposed by the Scherrer method ($Dm = 0.9\lambda/B\cos\theta$) where Dm is the size of the crystallite in nanometers (nm), λ is the wavelength of the X-rays in nm, B is the width of the half height of the most intense reflection (FWHM) and must be in radians and θ corresponds to the Bragg angle [15]. The values obtained are in the range of 47.6 to 124 nm, suggesting a smaller diameter value for SCS 02-2 calcined sample and in the rich combustible-oxidant ratio.

Table 2:- Information from data collected from the Rietveld refinement of the diffraction patterns of the synthesized samples such as: nomenclatures, molecular formula, percentage and the ICDD codes of the phases found, width at half height of the most intense peak (FWHM), average diameter (nm) of nanoparticles using the Debye-Scherrer equation and the adjustment indexes of the Rwp and Rp refinement.

Nº	Fórmula molecular	% Fases	Cod ICDD	FWMH 2θ	Diâmetro nm	R_{wp}	Rp
SCS 01-1	Te_3	5.,2	40042	0.0828	98.8	3.31	2.60
	Co_4O_4	48.8	9865				
SCS 01-2	$Co_8Te_{12}O_{32}$	100	50702	0.1349	60.6	5.74	4.33
SCS 02-1	Te_3	100	76150	0.0660	124	2.93	2.33
SCS 02-2	$Co_8Te_{12}O_{32}$	100	50702	0,1718	47,6	5,50	4,29
SCS 03-1	Te_3	100	40041	0,0869	94,2	3,36	2,62
SCS 03-2	$Co_8Te_{12}O_{32}$	100	50702	0,1501	54,5	4,85	3,74



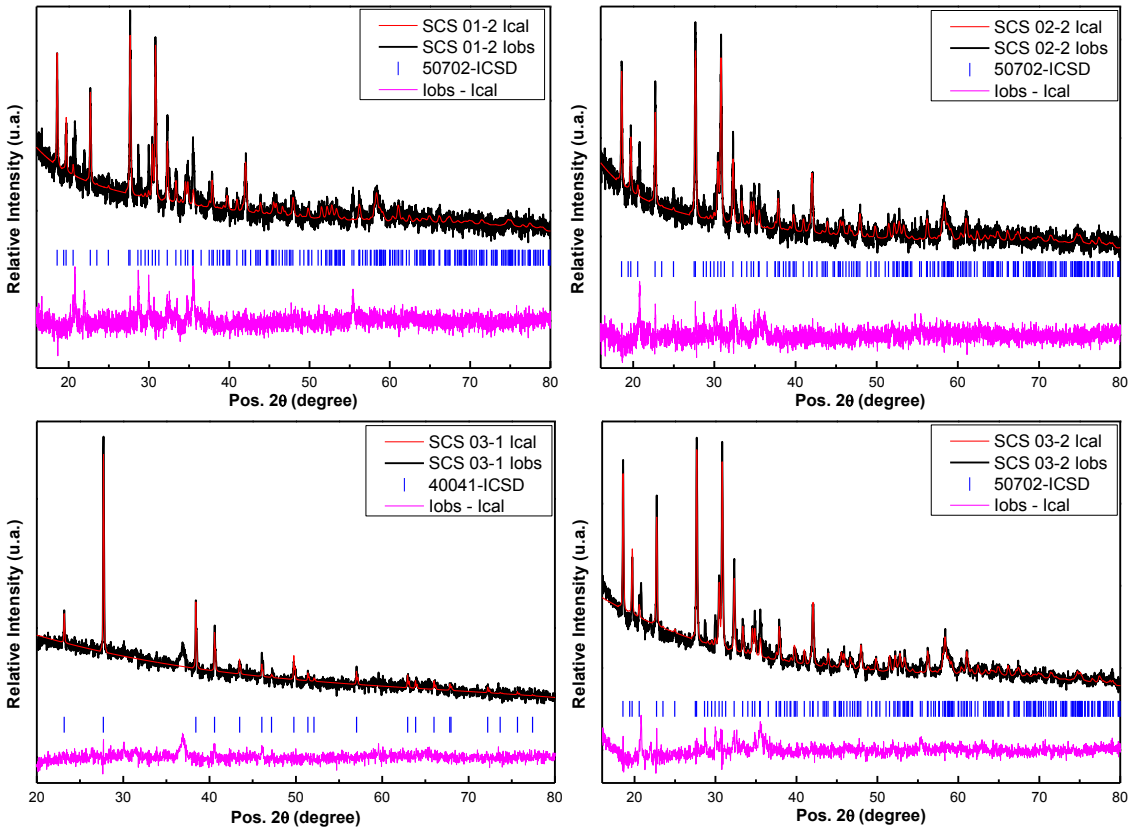


Figure 2:- XRD pattern of the samples developed in the stoichiometric, rich and poor fuel variations, each graph shows sample identification, observed intensity (Iobs), calculated intensity (Ical), ICSD code of the phases and the differences between intensities (Iobs)-Ical).

The thermal analysis of the samples is shown in Figure 3 by means of the TGA (mass% vs temperature ºC) and DTG (1st derivative) curves, through the graphs we can observe three characteristic regions, two regions of mass reduction in the range of 80 to 130 °C associated with dehydration, another in the range of 150 to 250 °C due to the loss of gaseous compounds by the sample and a third region in the range of 380 to 500 °C where we observed an increase in mass that may be characteristic of the oxidation process corroborating with the EDS and DRX data, after this range, a stability is observed which we can relate to the transition process from multiple phases to single phase. Regarding the different oxidant-fuel configurations in the synthesis process, it is possible to differentiate a slight change in the intensity of transitions above 400 ºC of the analyzed samples.

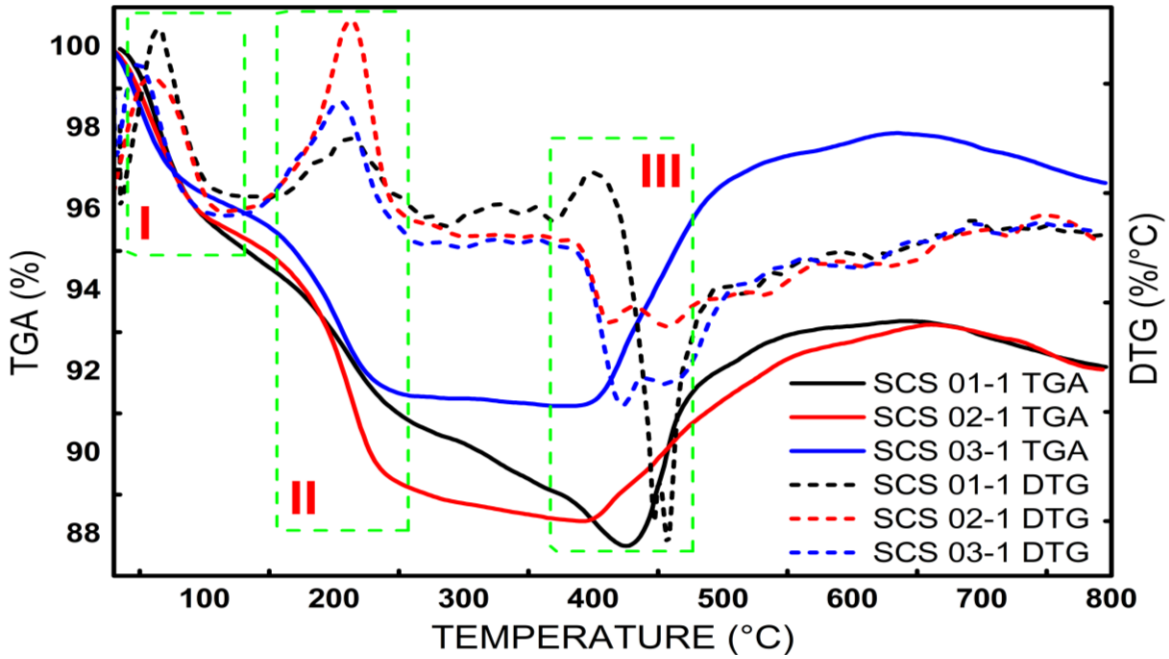


Figure 3:-Thermogravimetric (solid lines) and derived thermogravimetric curves (sectioned lines) to evaluate the thermal decomposition of the SCS 01-1, SCS 02-1 and SCS 03-1 samples synthesized in different proportions of the combustible/oxidant ratio.

Table 3:- Reaction heat obtained from the results of the thermograms of the samples from the nanocomposite SCS 01-1, SCS 02-1 and SCS 03-1.

Sample	**(ΔH_{P1}) (J)**	**(ΔH_{P2})(J)**	**(ΔH_{P3})(J)**	**(ΔH_{P4})(J)**	**(ΔH_{P5})(J)**	**(ΔH_{P6})(J)**
SCS 01-1	2.9	1.26	0.8	-18.7	0.3	4.3
SCS 02-1	6.0	-9.4	7.5	1.5	-9.1	4.7
SCS 03-1	4.9	-107.4	150.7	1.15	-38.6	4.1

Table 03 presents the quantitative data of the reaction heat (endothermic and exothermic) obtained through the area limited by the baseline of each peak of the curves in Figure 3. The theory of differential thermal analysis states that the area of the DTA curve bounded by the baseline is directly proportional to the material's heat of transformation [16,17]. Thus, according to the specialized literature, the area in each region of the DTA curve is numerically equal to endothermic or exothermic enthalpy. Such that $A=m/k\Delta H$, where m is the lost mass of the sample and k is the thermal conductivity of the material. Therefore, in Table 03, only the value of the area is presented without considering the variation in mass of the sample (the data will be considered in a next work). Negative values refer to the region where the physical-chemical process was endothermic and the positive sign to the region where the process was exothermic. The morphological study and the EDX spectra are presented in Figures 4 to 6, where in the micrographs under analysis it is possible to visualize irregular polycrystalline aggregates with rod-shaped, particulate and laminated dimensions as we vary the fuel-oxidant ratio in the process synthesis. The EDX spectra reveal some traces of gold and carbon contamination due to the metallization process, however they reveal the presence of the elements (Co, Si, Te) in all samples, we also verify the presence of the oxygen element that can correlate to the synthesis process in an atmospheric environment.

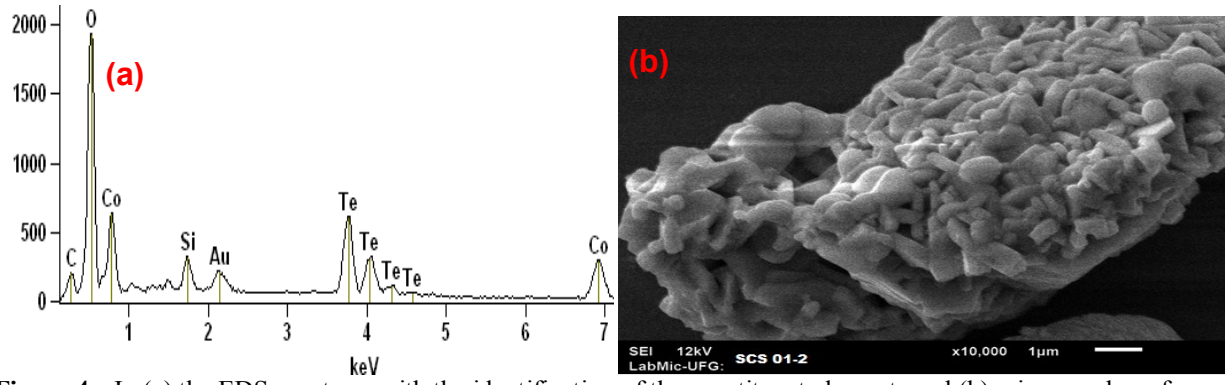


Figure 4:- In (a) the EDS spectrum with the identification of the constituent elements and (b) micrograph performed by the SEM technique of the SCS 01-2 sample in the stoichiometric combustible-oxidant ratio.

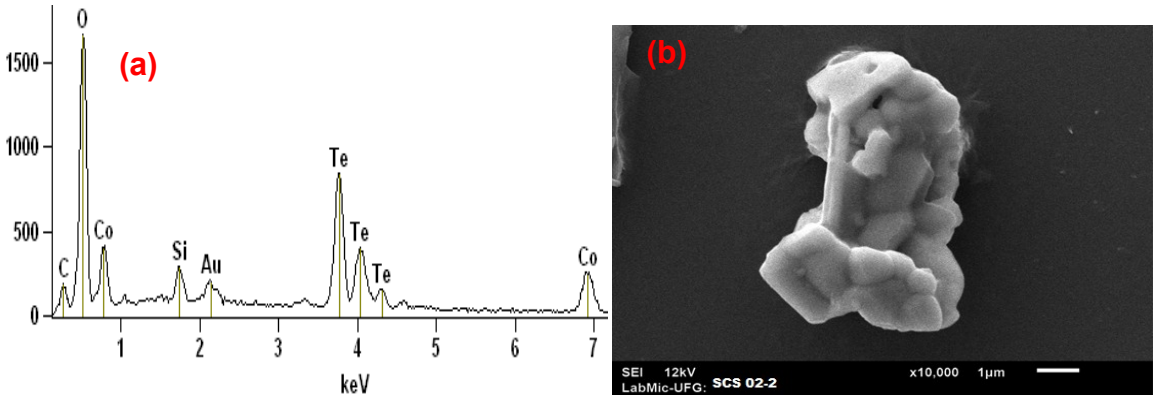


Figure 5:- In (a) the EDS spectrum with the identification of the constituent elements and (b) micrograph performed by the SEM technique of the SCS 02-2 sample in the saturated oxidant-fuel ratio.

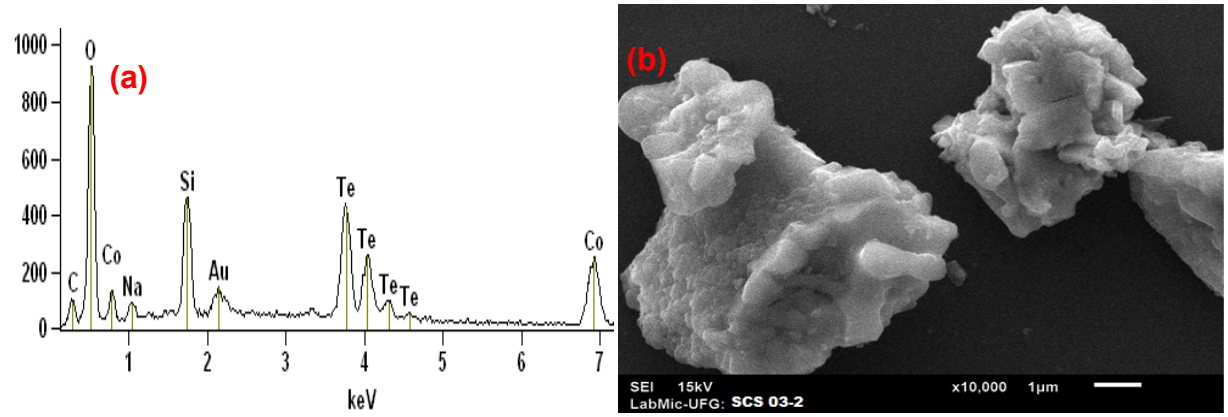


Figure 6:- In (a) the EDS spectrum with the identification of the constituent elements and (b) micrograph performed by the SEM technique of the SCS 03-2 sample in the proportion deficient in oxidant-fuel.

Conclusions:-

In the present study we present the results of the process of synthesis and structural, thermal and morphological characterization of a possible new nanocomposite from the elements cobalt, silicon and tellurium by the method of combustion in solution (SCS) assisted by microwave.The results showed that it was possible to form a crystalline nanostructure with different shapes, where the EDS data indicate the presence of the elements (Co, Si, Te, O) in the samples, the X-ray diffraction measurements showed multiple phase structures and unique according to the different configurations of the synthesis process, through the collected data and applying mathematical models, the survey of the crystallographic parameters and the average diameter of the nanostructures was carried out, through this information and suggestive a new nanostructure with isostructural characteristics to the structure $Co_8Te_{12}O_{32}$

(ICDD-50702) with average crystallite diameter at 47.6 nm. The thermogravimetric characteristics were performed only on samples without the calcination process to observe the thermal behavior, which indicates an increase in mass at temperatures between 500 and 600ºC observed in oxidation processes, with endothermic and exothermic enthalpies verified through EDS and EDX.

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References:-

1. C. C. Kock, Nanostructured Materials : Processing, Properties and Applications, 2º ed. Norwich, NY, U.S.A: William Andrew, 2006.
2. P. H. C. Camargo, K. G. Satyanarayana, e F. Wypych, "Nanocomposites: synthesis, structure, properties and new application opportunities", Mater. Res., vol. 12, nº 1, p. 1–39, mar. 2009, doi: 10.1590/S1516-14392009000100002.
3. S. K. Kumar e R. Krishnamoorti, "Nanocomposites: Structure, Phase Behavior, and Properties", Annu. Rev. Chem. Biomol. Eng., vol. 1, nº 1, p. 37–58, 2010, doi: 10.1146/annurev-chembioeng-073009-100856.
4. Ž. Kaminskienė, I. Prosyčevas, J. Stonkutė, e A. Guobienė, "Evaluation of Optical Properties of Ag, Cu, and Co Nanoparticles Synthesized in Organic Medium", Acta Phys. Pol. A, vol. 123, nº 1, p. 111, 2013, doi: 10.12693/APhysPolA.123.111.
5. L. Mangolini, "Synthesis, properties, and applications of silicon nanocrystals", J. Vac. Sci. Technol. B, Nanotechnol. Microelectron. Mater. Process. Meas. Phenom., vol. 31, nº 2, p. 020801, 2013, doi: 10.1116/1.4794789.
6. B. R. Dahal, R. P. Dulal, I. L. Pegg, e J. Philip, "Electrical transport and magnetic properties of cobalt telluride nanostructures", J. Vac. Sci. Technol. B, Nanotechnol. Microelectron. Mater. Process. Meas. Phenom., vol. 34, nº 5, p. 051801, 2016, doi: 10.1116/1.4959576.
7. Y. E. Gogotsi, Nanomaterials Handbook, nº 13. CRC Press, 2006.
8. D. Schaming e H. Remita, "Nanotechnology: from the ancient time to nowadays", Found. Chem., vol. 17, nº 3, p. 187–205, 2015, doi: 10.1007/s10698-015-9235-y.
9. F. Deganello e A. K. Tyagi, "Solution combustion synthesis, energy and environment: Best parameters for better materials", Prog. Cryst. Growth Charact. Mater., vol. 64, nº 2, p. 23–61, 2018, doi: 10.1016/j.pcrysgrow.2018.03.001.
10. J. C. Toniolo, "Influência da razão combustível-oxidante nas características de óxidos nanoestruturados sintetizados por combustão em solução", UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL, Porto Alegre, 2009.
11. P. A. M. Vitor, D. K. Topolski, A. N. C. Lima, S. R. Bragança, e C. P. Bergmann, "Preparação e caracterização de espinélio MgAl2O4 nanoestruturado através de síntese por combustão em solução", Ceramica, vol. 62, nº 363, p. 230–236, 2016, doi: 10.1590/0366-69132016623632019.
12. R. L. B. A. Medeiros, H. P. Macedo, A. A. S. Oliveira, M. A. F. Melo, e D. M. A. Melo, "Síntese de MgAl 2 O 4 por combustão assistida por micro-ondas : influência dos parâmetros de síntese na formação e na estrutura cristalina", vol. 62, p. 191–197, 2016.
13. L. Bleicher e J. M. Sasaki, "Introduçao à Difraçao de Raios-X em Cristais". Universidade Federal do Ceará, p. 1–20, 2000.
14. L. Bleicher, J. M. Sasaki, e C. O. Paiva Santos, "Development of a graphical interface for the Rietveld refinement program DBWS", J. Appl. Crystallogr., vol. 33, nº 4, p. 1189–1189, ago. 2000, doi: 10.1107/S0021889800005410.
15. A. Monshi, M. R. Foroughi, e M. R. Monshi, "Modified Scherrer Equation to Estimate More Accurately Nano-Crystallite Size Using XRD", World J. Nano Sci. Eng., vol. 02, nº 03, p. 154–160, 2012, doi: 10.4236/wjnse.2012.23020.
16. Brown M. E., Gallagher P. K., Handbook Thermal Analysis and Calorimetry, V.5 Elsevier 2008.
17. Santos J. G., The Thermodynamic Method of Vitrification of Copaíba Oil-Resin (CopaiferaLangsdorffii), International Journal of Science and Research (IJSR) ISSN: 2319-7064, p. 145-152.