Nano-sized Ceramic Powders with n-type Semiconducting Properties Obtaining and analysis

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Ceramic matrix composites represent a class of high valuable materials especially for high tech applications but also, in their powder form the ceramics are more often used as agents to change the properties of polymer matrix. As it is well known, the quality of a composite resides in the nature and quality of the interphase matrix-immersed phase or matrix-immersed phases. In the case of nano-sized agents, the most important aspect is related to the high value of specific area which determines the transport phenomena and the loading transfer between matrix and modifying agents. On the other hand, the small dimensions of particles are very important regarding the mechanical response of material. If the fact that each particle acts as a structural defect, the larger dimension of the particles implies larger damage on the mechanical properties, despite the particles effects on other important properties - electric, thermal or chemical properties. As complex oxides are showing special properties - for instance they are semiconductors - their use in polymer matrix should be focused on obtaining energy producing or energy storage materials which should be cheaper than the traditional ones. The present study is about obtaining and characterizing nanosized ceramic powders for further use as modifying agents into polymers. The method used is the citratedgels method but tests were also performed using oxalic acid instead of citric acid, being known that both acids can lead to gel mixtures. The obtained results – especially regarding the particles dimensions – are encouraging the development of studies with other precursors for further designed applications with epoxy resins.

Keywords: nano-sized ceramics, SEM analysis, Raman analysis

Some ceramic compounds are known to have special properties, useful in different domains, as for example: are less expensive, easy to synthesize and have relatively high dielectric constants as compared to polymers and good electrochemical coupling coefficients [1, 2]. Beside these properties, there are also several drawbacks (ex.: high stiffness and brittleness) that can limit the utilization of these kind of materials [3]. On the other hand, some polymers may possess the exact properties that are lacking in the ceramic materials. This is why, designing ceramic doped polymers could lead to obtaining materials possessing properties inherited from both constituent substances.

Thin films of polymeric composites could also be obtained, one condition being that the doping ceramic powder to be constituted from nano-sized particles. A small particle size distribution of the ceramic material will increase the surface area in contact with the polymer, being well known that surface area of materials increases significantly when their size reduces from bulk to nano dimensions [4]. Thus, a better polymer-ceramic interaction could be realized while making possible the formation of transparent thin films.

Based on the abovementioned facts, the purpose of the research presented in this article was to obtain a ceramic powder with nano-sized constituent particles, and semiconductor properties. For this, a complex compound was planned to be synthesized, different ways being taken into consideration in order to identify an easy obtaining process. All four approached processes included the solgel method, using instead different acids and mixing steps. The constituent chemical elements were chosen to be cobalt, cadmium, tantalum and manganese 1M fraction of each. The complexity of the designed ceramic powder is explained by the need of a large number of electrons situated on a high energy band, a characteristic that could make the final composite material sensitive to the electromagnetic radiations, thanks to a desired low band gap such that as much of the available energy from the Sun would be harvested [5-8]. The obtained materials were then analyzed by using SEM, Raman, XRF techniques and a set-up to determine the conductivity type of the powders.

Experimental part

Materials and methods

The materials utilized to obtain the ceramic powders included chemical compounds delivered by a specialized supplier and also some readily available ones. All these, the obtaining methods and the analysis techniques of the obtained powders are further on presented in the following subsections of this study.

The chemical compounds (CoCl₂; CdN₂O₆ · 4H₂O; TaCl₃ and MnSO₄ · H₂O) containing the elements needed to be part of the final ceramic powders and the oxalic acid (C₂H₂O₄) were acquisitioned from Sigma Aldrich while the ethanol 96% (C₂H₆O) and the citric acid (C₆H₈O₇) were procured from other vendors. The amount of each utilized chemical compound, temperatures and time intervals of obtaining processes are presented in table 1.

Two methods were used in the obtaining of the ceramic powders. The first one consisted in separate mixing of the ethanol, the citric acid / oxalic acid and the chemical compounds. Each chemical compound was placed in a

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Powder notation/quantity obtained [g]	Materials and their fraction used to obtain the powder	Stirring time/temperature	Quenching time/temperature	
CoCdTaMnO _{XI} /14	$\begin{array}{c} TaCl_{5} \left(1M\right) - 8.49 \ g \\ CoCl_{2} \left(1M\right) - 3.08 \ g \\ CdN_{2}O_{6} \cdot 4H_{2}O \left(1M\right) - 7.31 \ g \\ MnSO_{4} \cdot H_{2}O \left(1M\right) - 4.01 \ g \\ Ethanol \left(96\%\right) - 120 \ ml \\ Citric \ acid - 130 \ g \end{array}$	 each substance stirred in ethanol and 10 g of citric acid for 5 h at lab temperature; 250 rpm at 50 °C for 10 days. 	4 h/580 ℃	
CoCdTaMnOyl/12	$\begin{array}{c} TaCl_{5} \left(1M\right) - 8.49 \ g \\ CoCl_{2} \left(1M\right) - 3.08 \ g \\ CdN_{2}O_{6} \cdot 4H_{2}O \left(1M\right) - 7.31 \ g \\ MnSO_{4} \cdot H_{2}O \left(1M\right) - 4.01 \ g \\ Ethanol \left(96\%\right) - 210 \ ml \\ Oxalic \ acid - 40 \ g \end{array}$	 each substance stirred in ethanol and 10 g of oxalic acid for 15 min at lab temperature; 350 rpm at 80 °C for 24 h. 	4 h/580 ℃	Table 1MATERIALS ANDSTEPS USED TOOBTAIN THECERAMIC POWDERS
CoCdTaMnO _{x2} /14	$\begin{array}{l} TaCl_{5} \left(1M\right) - 8.49 \ g \\ CoCl_{2} \left(1M\right) - 3.08 \ g \\ CdN_{2}O_{6} \cdot 4H_{2}O \left(1M\right) - 7.31 \ g \\ MnSO_{4} \cdot H_{2}O \left(1M\right) - 4.01 \ g \\ Ethanol \left(96\%\right) - 100 \ ml \\ Citric \ acid - 40 \ g \end{array}$	- all substances stirred in ethanol and citric acid for 4 days at 300 rpm and 50 °C.	4 h/580 ℃	
CoCdTaMnOy2/12	$\begin{array}{l} TaCl_{5} \left(1M\right) - 8.49 \ g \\ CoCl_{2} \left(1M\right) - 3.08 \ g \\ CdN_{2}O_{6} \cdot 4H_{2}O \left(1M\right) - 7.31 \ g \\ MnSO_{4} \cdot H_{2}O \left(1M\right) - 4.01 \ g \\ Ethanol \left(96\%\right) - 100 \ ml \\ Oxalic \ acid - 40 \ g \end{array}$	- all substances stirred in ethanol and oxalic acid for 2 days at 300 rpm and 50 °C.	4 h/580 °C	

separate sealed glass recipient, in order to dissolve and for the chlorine to break its bonds with the elements from the respective chemicals. The second method consisted in mixing (using a SCILOGEX, MS-H280-Pro type mixer/ heater) the citric acid / oxalic acid in ethanol until dissolution, and then the already weighed chemicals were added to the mixture. In both cases, after all chemicals were placed in the same glass recipient, the next step consisted in mixing at 250-300 rpm and 50-80 °C from 1 to 10 days. The mixing was considered finished when a high viscosity gel was obtained. This gel was then placed in a ceramic crucible and quenched for 4 hours at 580 °C in a LMH 07/12 type furnace (produced by LAC). The powder obtained after quenching was milled using a mortar and a pestle, then different analyses followed.

The resulted materials were studied from the morphological point of view by using the scanning electron microscopy methodology. The samples were placed on a sample holder using a carbon tape, to decrease the sample mobility. To increase the conductivity, the samples were coated with a 2 nm thick layer of gold using a SPI-Sputter Coater with Etch Mode (West Chester, Pennsylvania, USA) for 40 s, with a current of 18 mA. The apparatus used for morphology tests was a Scanning Electron Microscope (SEM) Quanta 200 FEI, operating at 15 kV and with an electron beam current of 110 μ A using a second electron detector. The samples were analyzed using magnifications between 50 and 50,000X, the most representative images being presented later in this paper.

Raman scattering was used to determine vibrational properties of the samples. A StellarNet Inc type LASER and spectrometer (795 nm) were used, and for acquisition and interpretation of the results a StellarNet Inc software and a BIO-RAD software/data base were utilized. The milled samples were analyzed by being exposed directly to the LASER radiation, without utilization of any type of vials.

Elemental composition of samples was determined by using an INNOV-X type (α A-4000 series) X-ray fluorescence spectrometer with an X-ray tube with

acceleration tension of 40 kV, a Si-PiN<280 eV diode detector (thermoelectrically cooled), with 5.95 eV/K- α line. After quenching, relevant quantities of samples were placed in small plastic bags and three different sets of values were acquisitioned for each sample, before each reading the sample being thoroughly mixed. The final values represent the average of the three readings.

The rectification method was used for this type of analysis. This method involves determining the sign of the majority carrier based on the polarity of a rectified AC signal at the point of contact with the semiconductor material. Figure 1 illustrates this setup. When the four-point collinear probe comes in contact with the sample, a metalsemiconductor *diode* is created at the interface between each probe and the sample. An AC current is sourced between the first two probes and a DC voltmeter is used to sense the polarity of the voltage between probes 2 and 3. The metal-semiconductor Schottky diode at probe 2 will be either forward- or reversed-biased, depending on the polarity of the current, as well as the conductivity type. As a result, the voltmeter will read a positive voltage for ptype material and a negative voltage for n-type material [9].



Fig. 1. Circuit for determining conductivity type using the rectification mode [9]

Results and discussions

Using the analyzing techniques described above, several important characteristics of the obtained materials were investigated. The most important feature was considered to be the size of the constituent particles, which was determined by using the scanning electron microscopy method. Other analyses were also carried out, aiming the characterization of the materials from the chemical composition point of view (using the Raman scattering and X-ray spectrometry) and to determine the possibility that the powders would be of semiconductor types and if so, which kind (using a set-up described above). The last characterization method is of great importance in the event of utilization these powders as additives in obtaining energy producing or energy storage materials.

Results of SEM analysis

The main purpose of this work was to obtain nano-sized ceramic powders. Thus, the analysis of the obtained materials was of great importance. Each material was studied at different magnifications mentioned above and further on, only the ones at the highest resolution are presented (fig. 2).

The images in figure 2 clearly depict easily friable materials, numerous small particles being also readily visible. Since the exact dimensions of constituent particles of the studied materials are hard to notice using only the scale (situated in the down right corner of the picture) provided automatically by the SEM software, for each



Fig. 2. SEM images of the four obtained materials, captured at 50,000X

ceramic powder several measurements have been provided separately. All these separate measurements were made to emphasize the sizes of the smallest constituents of the ceramic materials. The lowest value presented in these images is 23.3 nm and the highest is 138.2 nm. Taking into account the friability observed during the grinding (and also visible from the SEM images) and the measurements of individual particles, we can conclude that the obtained powders are constituted from particles of nano-metric sizes.

Results of Raman scattering analysis

This type of analysis was necessary in order to observe any similitudes between the chemical composition of the obtained materials, since the purpose of using different obtaining methods was to identify the easiest one and not to produce different types of chemical compounds.

Figure 3 depicts the spectra obtained for all four materials using the Raman scattering analysis. Placing the results of all studied materials in the same graph makes it easy to observe the similar trends of all resulted curves. These results represent strong evidence, that all powders have roughly the same chemical composition and in accordance, they should also have similar behaviors when used as additives in obtaining polymeric materials.

Results of XRF analysis

The chemical composition of the powders was complemented by the elemental composition analysis. This investigation was realized by using the X-ray spectrometry method. One of the drawbacks of the apparatus used in this procedure is that, when a particular element exceeds 10% in the composition of the studied material, the utilized software only presents this situation by indicating a greater than 10% notification, instead of a more precise value.

Nevertheless, the results in table 2 emphasizes that the obtained ceramic powders contain more than 10% of each desired element, while the other elements present in the composition could be considered as contaminants (infiltrated during the obtaining procedures) or even reading errors of the analyzing apparatus. Either way, these results prove that the elemental composition of the powders is close to the desired one, even though the quantity of oxygen was impossible to determine since, for this technique, this element has an atomic mass too low for its identification.



Fig. 3. Raman spectra obtained for the studied ceramine powders

Sample	Element [ppm]										
	Mn	Co	Ni	Ta	Hg	As	Se	Zr	Cd	Sb	Fe
CoCdTaMnO _{X1}	>10%	>10%	3062	>10%	6158	1533	4984	12	>10%	20092	594
CoCdTaMnOyl	>10%	>10%	3164	>10%	6366	1611	5189	35	>10%	21728	1288
CoCdTaMnO _{x2}	>10%	>10%	3601	>10%	6314	1501	5070	0	>10%	22303	0
CoCdTaMnOy2	>10%	>10%	3327	>10%	6116	1592	5058	0	>10%	22037	682

Table 2ELEMENTAL COMPOSITIONOF CERAMIC POWDERS,OBTAINED BY USING THEX-RAY SPECTROMETRYTECHNIQUE



Fig. 4. The sigmoid curves obtained during determination of the conductivity type for all four studied powders

Results regarding the determination of conductivity type for the ceramic powders

This type of determination revealed the nature of the studied materials from the conductivity point of view. Using currents with values starting from -100 mA and finishing at 100 mA, the conductivity type for all four analyzed materials were revealed to be that of n-type semiconductors. This statement is based on the results presented in figure 4 where the trends of the curves are, for all studied materials, towards the negative voltage, regardless the sign of the applied current.

Including these materials in the n-type semiconductor category is mostly due to the presence of more free electrons that may flow [10], which in turn is a consequence of the way that the constituent elements were arranged during the materials' formation. The utilization of these materials are further on intended for polymeric thin films obtaining (also with n-type semiconductors properties), and future studies will aim to also produce p-type semiconductors (polymeric thin films doped with ceramic powders), the final purpose being the obtaining of thin photo-voltaic cells.

Conclusions

In the pursuit of obtaining materials for electricity generation technologies, suitable additives should be first identified. The aim of the research presented in this article was to obtain a complex mixture ceramic material with nano-sized constituent particles. This first feature of the obtained materials was proved by SEM analysis, being a necessary condition in further producing thin films with special properties. Although, different methodologies were used in synthesizing the ceramic powders, the final chemical composition was desired as being similar between the obtained materials. This goal was also achieved, and proved by Raman scattering and X-ray spectrometry analyses. The chemical composition and particles dimensions being that similar between the four obtained powders, the only criteria to determine the preferred ceramic material to be used in future researches is the time necessary to be obtained. Between all four, the fastest produced ceramic powder was CoCdTaMnO_y, the one obtained using ethanol and oxalic acid mixed with the desired chemical substances at 350 rpm at 80 °C, for 24 h, then calcined at 580 °C for 4 h.

The final aim of this work was to identify the conductivity type of the ceramic powders. This was realized by using double function a set-up, namely inducing negative and positive currents within the samples and detecting the sign of the voltage in the studied materials. The results revealed that all four powders are n-type semiconductors, their utilization being thus suitable for obtaining thin films materials with n-type semiconducting properties.

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