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Şcoala Doctorală de Studii Inginereşti

THE STUDY OF THE ELECTRICAL PROPERTIES OF CERAMIC MATERIALS $NaTaO_3$ -TYPE WITH PEROVSKITIC STRUCTURE

PhD thesis - Summary
to obtain the title of PhD at
Polytechnic University of Timisoara
in the PhD field **Materials Engineering**

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The synthesis of perovskitic ABO3 compounds is an area of great interest at present, due to the particular properties of these materials, which makes them applicable in various fields (electronics, telecommunications, optics, energy, medicine, biology, etc.). The synthesis of these materials with particle sizes ranging from 1-100 nm has attracted the interest of researchers, especially in the last decade when research began to find new ceramic materials with electrical or thermoelectric properties. Among the more popular perovskitic materials are lead-based $PbZrO_3$ and $PbTiO_3$ (PZT) piezoelectric behaviors, using piezoelectric sensors and transducers [1]. In order to prevent and limit the use of lead-based systems on the market, studies have been conducted to obtain lead-free alternatives compatible with the latest environmental directives. In this way, compounds based on niobium and tantalum oxides, such as alkali tantalates and niobates, are considered to be the most promising compounds in the list of ceramic materials functional for future technologies [2]. Among these compounds, sodium tantalate ($NaTaO_3$) is a perovskite oxide which is a feasible alternative to lead compounds [3].An important feature of perovskites and similar structures is that these compounds are suitable for the doping process because their structure is very stable in terms of changes in tetrahedral A positions.

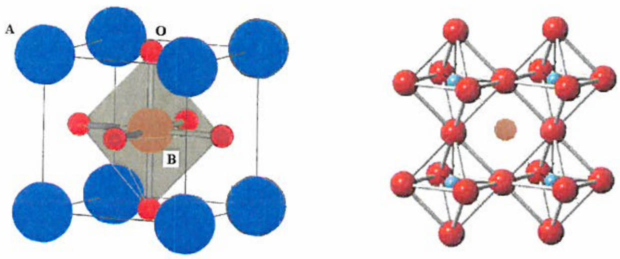
The main goal of the doctoral thesis is to carry out research and studies on obtaining perovskitik ceramic materials of sodium tantalate ($NaTaO_3$) in the form of powder, not doped or doped with Al or Cu metal ions, and their characterization in terms of properties electrical applications for use in applications. In order to accomplish the proposed goal we have considered several objectives: a) obtaining of sodium tantalate ($NaTaO_3$) samples in the form of powder, undoped and doped with metal ions, using different synthesis methods; b) morpho-structural, optical characterization and study of the electrical properties of the obtained NaTaO3 samples; c) Design and realization of an experimental installation allowing both the determination of the static electrical conductivity and the dynamic electrical conductivity of the samples based on the complex impedance measurements in the frequency range (20 Hz - 2 MHz) and at different temperatures between (30 - 200) ° C; d) Experimental and theoretical investigations on the electrical conduction mechanism in NaTaO3 ceramic materials not doped or doped with metal ions; e) determining the R and C parameters of the equivalent circuit resulting from the complex impedance measurements and the Nyquist diagrams; f) the effect of metal ions on the static and dynamic electrical conductivity of the samples prepared by the same method; g) the effect of the method of obtaining doped samples with the same type of metal ions on their electrical performance.

All these objectives have been met and the realized studies have been the subject of articles published in ISI or BDI journals as well as results presented at international conferences, thus leading to a series of original results and contributions presented in chapters 4, 5 and 6 of the PhD thesis.

The doctoral thesis is structured on six chapters, preceded by the introduction and followed by conclusions, references and annexes.

Chapter 1 with the title *Compounds with perovskitic structure*, presenting a study from literature showing the main features of perovskitik materials in general and the characteristics of sodium tantalate ($NaTaO_3$) in particular, while specifying their applications and uses in various fields.

A perovskite structure can be defined as an elemental cubic cell having the chemical formula ABO3, wherein the cations A represent a monovalent or bivalent metal of the alkali metal, alkaline earth or even lanthanide metals and occupy the positions at the corners of the cube, the cations B represent a tetravalent or pentavalent metal and occupies the central position of the cube. Oxygen anions O, are placed in the middle of the cube faces (Figure 1.1 a). Also, the perovskite structure can be considered as consisting of a series of octahedrons BO_6 arranged in a simple cubic model (Figure 1.1b). These octahedrons are linked together by the oxygen atoms that are in common with the A atoms occupying the octahedral spaces. For such perovskites the lattice constant is about 4 Å.



a) b)

Fig.1.1. Perovskit structures ABO_3 (a) elemental cell; (b) octahedral series BO_6

A description of the perovskit $NaTaO_3$ with the cubic structure of the spatial group Pm3m was made for the first time by Ismailzade [4].

The most important parameters related to perovskite structures, and which are used to modify the chemical composition, are band width (electron hopping) and occupancy of the band (or doping level). These parameters control the kinetic energy of the conduction electrons, which determines both the phenomena resulting from the metal - insulator contact and the ferromagnetic - antiferromagnetic relation in the perovskites, ie the type of magnetic interactions [4]. In the final part of the chapter, there are presented general aspects related to the electrical, electrochemical, optical and thermoelectric properties of sodium tantalate.

The experimental determinations on the temperature dependence of electrical conductivity, $\sigma = f(T)$, show an exponential type dependence [5], following an Arrhenius type law, thus allowing the determination of the conductivity activation energy. The dielectric properties of the NTO type compounds have been little studied, determining the frequency and temperature dependence of the real (ε') and imaginary (ε'') components of complex dielectric permitivity in low frequency range [6]. It is noted that both components decrease with increasing frequency.

Based on the complex impedance measurements the conductivity σ_{AC} of the investigated samples, which theoretically can be expressed by Jonscher's universal law, can be determined [7]. In electrochemical impedance spectroscopy, the measurement of system impedance values according to frequency results in the recording of an impedance spectrum. The graphical representation of impedance spectra is either in the form of Nyquist diagrams or as Bode diagrams [8].

For the development of thermoelectric devices in order to convert the lost thermal energy into electrical energy, the $NaTaO_3$-based ceramic composite compounds. have been successfully used lately for power generation applications or as Peltier freezing, in a higher temperature range (750-1300 K) [9, 10].

Chapter 2 is a documented study of methods for obtaining perovskitic ABO_3 type compounds (conventional or ceramic methods and unconventional methods), while briefly describing the chemical methods of preparing ABO_3 powdered compounds.

Numerous methods have been proposed for the synthesis of nanocrystalline powders [6], the choice of the method of preparing the powders depending on the raw materials available, the preset properties required for different applications and the technical means available. Methods for obtaining perovskilic nanocrystalline materials can be divided into two categories: a) ceramic or conventional methods; b) unconventional methods.

In the first category, the production of oxide materials of the type ABO_3 in the form of nanoparticles is accomplished by solid phase reactions at relatively high temperatures, from metal oxides precursors or by the thermal decomposition in oxides of carbonates, nitrates, oxalates, sulphates, etc. [11]. The advantage of this method is to obtain well-crystallized materials, and the disadvantage is that the process involves a series of operations to be performed before the heat treatment such as grinding and mixing (homogenization), processes which can lead to impurification and loss of materials. In the second category, unconventional methods, the production of perovskitic ABO3 oxide nanomaterials can be made wet, at relatively low temperatures, thus removing the disadvantages specific to the ceramic method. The advantage of wet processes is to obtain a homogeneous molecular distribution, to provide better control over the reaction conditions, a close, almost uniform dimensional distribution, to obtain particles with fine granulation and a specific surface area controlled according to the proposed application range. The most commonly used methods are: hydrothermal method, solvotermal method, sol-gel method, chemical co-precipitation, microemulsion method, etc.

Yiguo Su et al., Shows in the paper [12] that the nanoparticles of powdered $NaTaO_3$ samples can be prepared by the *simple hydrothermal method*. For this purpose, the following materials and quantities were used: 0.442 g Ta_2O_5, 9.0 g sodium hydroxide and 22.5 ml deionized water, which were thoroughly mixed by magnetic stirring. The mixture thus obtained was added to a 30 ml teflon-lined autoclave which was closed and held at 200 °C for 24h. After cooling to room temperature in air, the mixture was filtered and washed with distilled water, then air-dried at 60 °C for 12 hours. The $NaTaO_3$ product thus obtained is in the form of a white crystalline powder of high purity, as determined by X-ray diffraction (XRD) analysis.

An alternative to the solid phase reaction method used to obtain $NaTaO_3$ nanoparticles is the sol-gel method [13]. Reagents used in the sol-gel method [74] were CH_3COONa (Nihon Shiyaku), $TaCl_5$ (Alfa Aesar) and citric acid ($C_6H_8O_7 \cdot H_2O$: Riedel-deHaën). The solutions of CH_3COONa (0.9M), $TaCl_5$ (0.8M) and citric acid (4.6M) were mixed to form a colloidal solution of $NaTaO_3$. Molar ratio, Na/Ta/citric acid was 1/1/5. The solution was stirred continuously at 90 °C until the soil became a gel. The gel was then calcined at 350 °C for 1 hour and 500 °C for 3 hours to result in $NaTaO_3$ particles. This perovskite material of the $NaTaO_3$ type derived from sol-gel synthesis exhibits remarkably greater photocatalytic activity in water than the $NaTaO_3$ material synthesized by the solid state reaction method. At the same time, $NaTaO_3$ obtained by sol-gel and solid state, have different crystalline structures: monoclinic P2/m and orthorhombic Pcmn, respectively.

Among the nonconventional methods described in the paper for the production of

ABO3 ceramic compounds, they mention: hydrothermal method, ultrasonic method, sol-gel method and chemical co-precipitation method.

Chapter 3 summarizes the structural and morphological analysis methods that can be applied to $NaTaO_3$ samples and the techniques for determining their electrical properties. Among the many methods of characterization (morphological, structural, elemental, phase, electrical, dielectric) are presented those methods that were used in the elaboration of the paper. The structural and morphological analysis of perovskit materials was performed by X-ray diffraction (XRD) and electron microscopy (SEM / EDAX). X-ray diffraction is a non-destructive technique that allows accurate information about the chemical composition and crystalline structure of the materials. X-ray diffraction analysis was performed with a Bruker AXS D8 Advance X-ray diffractometer fitted with an X-ray tube with Cu anode found in the "Solid-Crystallographic Solid-State Assay Laboratory (LDCCS)" at the Faculty of Physics, University West of Timisoara. Scanning Electronic Microscopy (SEM / EDAX) allows the determination of component particle morphology, dimensional measurements on component particles, and qualitative X-ray microanalysis (identification of elements present in the sample). The SEM / EDAX analysis was performed at the National Institute for Research and Development for Electrochemistry and Condensed Matter, using the Quanta 200 electronic scanning device. The infrared spectroscopy (FT-IR) of the investigated samples is based on the principle of electromagnetic radiation absorption by different materials in the IR range and is used to identify and determine the structure of compounds identifying substances based on characteristic spectral prints. FT-IR spectra were performed using a Shimadzu Prestige-21 spectrometer in the 400-4000 cm^{-1} range at the Polytechnic University of Timisoara. Samples were measured as pills in KBr.

Investigation of electrical properties of perovskititic materials of the $NaTaO_3$ type was done by static and dynamic electrical resistivity measurements respectively complex impedance. For this purpose, we designed and realized an experimental laboratory installation (Figure 3.1), which allows determination of electrical resistance and electrical conductivity, as well as their temperature dependence in the range (30-200) ^{0}C. At the same time, by connecting the system to an Agilent RLC-meter (E4980A), we could determine the frequency dependence of the complex impedance in the low frequency range (20 Hz - 2MHz) and at different temperatures.

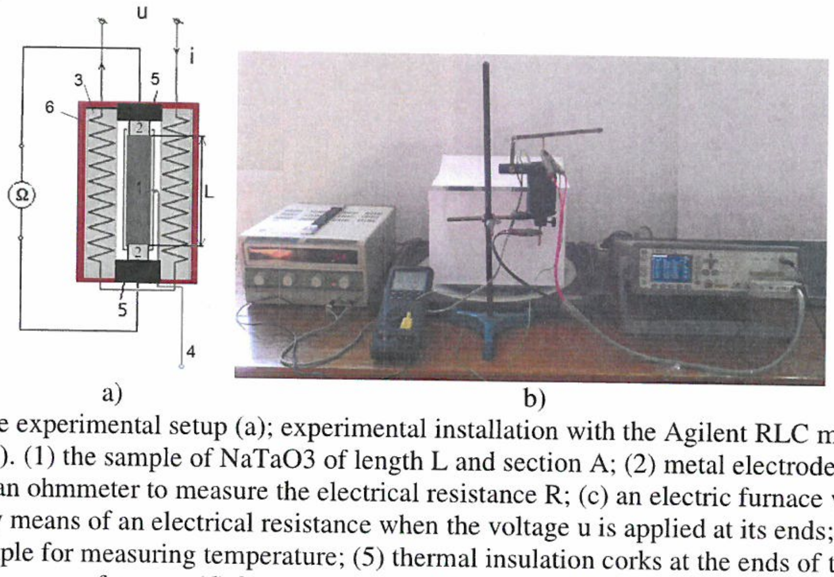


Fig. 3.1. The experimental setup (a); experimental installation with the Agilent RLC meter (E4980A). (1) the sample of NaTaO3 of length L and section A; (2) metal electrodes connected to an ohmmeter to measure the electrical resistance R; (c) an electric furnace which is heated by means of an electrical resistance when the voltage u is applied at its ends; (4) thermocouple for measuring temperature; (5) thermal insulation corks at the ends of the furnace; (6) furnace thermal insulating enclosure

In **Chapter IV** of the doctoral thesis, entitled "*Preparation and structural and morphological characterization of perovskite $NaTaO_3$ samples*", their own contributions were presented in the preparation of $NaTaO_3$ samples and the morphological and structural characterization of the obtained samples. Eleven samples of sodium tantalate non doped or doped with Al or Cu metal ions were synthesized by three different methods: the hydrothermal method, the ultrasonication method with sonotrode immersion in the reaction medium, and the sol-gel method using different precursors.

All samples were structurally and morphologically analyzed by X-ray diffraction (XRD) and scanning electronic microscopy (SEM/EDAX), UV-VIS spectroscopy and infrared spectroscopy (FT-IR). X-ray diffraction analysis shows that the sol-gel method is the most appropriate method for the synthesis of single crystalline phase $NaTaO_3$ samples. The X-ray diffraction spectrum of SG-Al and SG-Cu samples (obtained by the sol-gel method) allowed the determination of network parameters and showed that the samples belong to the spatial group Pcmn (space group number 62) belonging to the orthorhombic crystallographic family , with average particle sizes between 36 nm and 39 nm. Based on the ultrasonication method with sonotrode immersed in the reaction medium first reported by us, two samples of $NaTaO_3$ doped with aluminum ions (US-Al sample) and copper ion doped $NaTaO_3$ were synthesized (US- Cu), the results being published recently in the paper [14].

The IR absorption spectra of the samples show that in the presence of Cu or Al dopant ions in the $NaTaO_3$ structure, irrespective of the synthesis method (ultrasound or sol-gel), the main absorption band (Na-O) disappears, accompanied by the appearance a strong absorption band attributable to the excitement of stretching of Ta-O and Cu-O and Ta-O and Al-O groups, with a much greater share of Al-doping.

Some of these researches were communicated as preliminary results at international conferences [15].

Chapter 5 entitled "*Experimental studies on the electrical properties of non-doped perovskitic $NaTaO_3$ samples*" comprises experimental studies and own contributions to determine the electrical properties of non-doped perovskite samples of $NaTaO_3$. In this way, three results were presented as follows: 1) the study of electrical properties of tantalum and sodium oxide composite materials [16]; 2) the study of electrical properties of NaTaO3 samples by the impedance spectroscopy method [17]; 3) proposing a theoretical model for the determination of complex dielectric components of perovskite materials of the $NaTaO_3$ type using complex impedance measurements.

With regard to the first research obtained in the PhD thesis, the aim was to study the influence of the preparation method on the electrical conductivity for two samples of powdered Ta-Na oxides (samples A and B obtained by the hydrothermal method) compared to a Perovskitic NaTaO3 sample (sample C obtained by the sol-gel method). The temperature dependence of the samples was measured using the experimental laboratory installation (Figure 3.1). Based on the electrical resistivity measurements, the samples had a behavior typical of a semiconductor, so that the thermal activation energy Ea of the analyzed samples could be determined, obtaining the following values: $E_{a\ (sample\ A)} = 0.47$ eV, $E_{a\ (sample\ B)} = 0.45$ eV and $E_{a\ (sample\ C)} = 0.82$ eV. In the investigated temperature range (30 - 200) °C, the electrical conduction mechanism in the samples was analyzed based on Mott's variable range hopping model VRH (variable range hopping model) [18] and the parameters (T_0), the density of the localized states at Fermi level $N(E_F)$, the hopping distance R and the hopping energy W. The results showed that the Mott parameters of samples A and B have approximately the same values but are very different of that of sample C. This difference can be correlated with sample composition, i.e., samples A and B are mixtures of $NaTaO_3$ and sodium oxides and tantalum (Na-Ta), while sample C is pure $NaTaO_3$. These results were published in the journal ISI, *Acta Physica Polonica A* in 2016, or communicated to international confederations [16].

The second study presented in this chapter relates to the study of the electrical properties of $NaTaO_3$ samples using the complex impedance method. It was applied to four samples of $NaTaO_3$ prepared by two methods: the hydrothermal method and the sol-gel method respectively. The aim of the study was to investigate the dielectric and resistive characteristics of the samples, while pursuing the effect of the synthesis method and the composition of the samples on these characteristics. In this respect, the real Z' and imaginary Z" components of the complex impedance of the samples in relation to the frequency *f* of the field were determined in the frequency band (20 Hz - 2 MHz) and at room temperature. The results were correlated with the morpho-structural characteristics and the method of obtaining the investigated samples and with the equivalent electric circuit corresponding to the experimentally obtained impedance spectrum. On the basis of the equivalent circuit, the resistive (R) and capacitive (C) parameters related to the particle contributions and the particle separation limit respectively were evaluated, the results obtained being published in [17].

The last study presented in this chapter consisted in proposing a theoretical model for determining complex components of dielectric permeability of powder $NaTaO_3$ samples using complex impedance measurements. Based on the developed theoretical model, the following relations were established for determining the relative complex dielectric components:

$$\varepsilon_r' = \frac{1}{\omega\varepsilon_0}\cdot\frac{Z''}{|Z^*|^2}\cdot\frac{d}{A}$$
$$\varepsilon_r'' = \frac{1}{\omega\varepsilon_0}\cdot\frac{Z'}{|Z^*|^2}\cdot\frac{d}{A} \qquad (5.1)$$

The relationship (5.1) shows that the two components ($\varepsilon_r'(\omega)$ and $\varepsilon_r''(\omega)$) can be determined if both the geometry of the sample (length *d* and cross section *A*) and the real Z'(ω) and imaginary Z"(ω) of complex impedance of the sample.

These results were published in papers [16, 17], or presented at international conferences: [19, 20].

Chapter 6 entitled "*Experimental studies on the electrical properties of metalic ions doped perovskitic NaTaO₃ samples*", presents the experimental studies and their own contributions regarding the determination of the electrical properties of perovskititic NaTaO3 samples doped with Al or Cu metal ions. Thus, a first study relates to the influence of Cu ionization doping of an ultrasonic $NaTaO_3$ sample (US-Cu sample) on the structure and mechanisms of electrical conduction in this sample. Based of complex impedance measurements, in the frequency range 20 Hz to 2 MHz and at temperatures in the range (303-393) K, the conductivity spectrum (Figure 6.1) has two parts: a low frequency plate corresponds to static conductivity (dc-conductivity) and a high-frequency dispersion region corresponding to ac-conductivity, in accordance with Jonscher's universal law [7].

Static conductivity results show that in the low temperature range of 30 °C to 70 °C it increases with temperature rise but at temperatures above 80 °C the static conductivity σ_{dc} decreases with temperature rise. Behavior of static conductivity σ_{dc} was explained based on Mott's variable-hopping VRH (variable-range hopping) model. Based on this model, thermal activation energy for the conduction E_{cond} of the sample was determined, the results showing a linear increase with the temperature increase, between 175 meV and 215 meV [14].

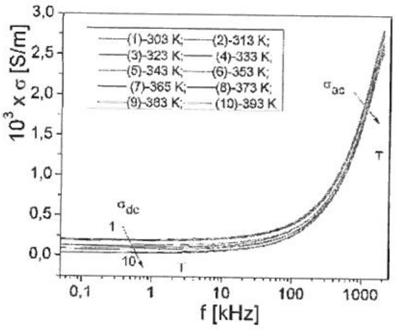


Fig. 6.1. The frequency dependence of the electrical conductivity σ

The obtained results for the electrical conductivity in the alternative field were explained on the basis of the *correlated barrier hopping* (CBH) model [21], in which the conduction phenomenon from the Cu ion-doped NaTaO3 sample is due to a hopping process of the charge carriers from the material, between the state neighbors. Using this model the energy of the band gap W_m of the investigated sample was determined. The results obtained for W_m show that the doping of $NaTaO_3$ sodium tantalate with Cu metallic ions results in lowering the band gap energy of the sample having a minimum at 0.48 eV at 70 °C and then increasing. The minimum energy value of the W_m for the investigated sample correlates very well with the static conductivity σ_{DC}, which has a maximum at 70 °C. The results were published in ISI, *J. Mater. Sci: Mater. Electron*, in 2016.

Another study presented in this chapter relates to the influence of the preparation method on the electrical performance of two samples of $NaTaO_3$ doped with Al ions but obtained by two different methods: sol-gel method (SG-Al sample) and ultrasonication method -Al), study based on complex impedance measurements. The static conductivity of the SG-Al sample is greater than about 6.5 times that of the US-Al sample, which could be an increase in electrical performance for NaTaO3 synthesized by the sol-gel method in the ratio with samples obtained by the ultrasonic method and doped with Al metallic ions. The results obtained for the alternating electric conductivity σ_{ac} of the two samples allowed the determination of the energy of the forbidden band W_m and of the minimum lenght of R_{min} using the theoretical model CBH. These results show that doping of $NaTaO_3$ ceramic material with Al metallic ions leads to a lower energy bandwidth of less than *1 eV* for both doped samples irrespective of the method of preparation used, less than for uncoated material, which can cause an increase in electrical conductivity and electrical performance of $NaTaO_3$ samples doped with Al metallic ions.

The last study presented in this chapter deals with the effect of dopant on the electrically conductive mechanisms of two samples of $NaTaO_3$ doped with Al or Cu ions and prepared by the same sol-gel method. The results show that the energy of activation due to conduction, Econd is higher for the SG-Cu sample compared to the SG-Al sample, behavior explained on Mott's variable-hop hop variable-range hopping model. At the same time, the obtained result can also be correlated with the fact that in the investigated samples the phenomenon of conduction in the alternative field is due to a process of hopping of the charge carriers from the material, between the neighbor states, according to the CBH model, which in case of NaTaO3 sample doped with Cu ions (SG-Cu) is only present at high temperatures above 70 ° C.

Some of the results obtained in this chapter have been **published** in the paper [14] or communicated at international conferences [22].

The doctoral dissertation ends with the chapter titled "*General Conclusions and*

Original Contributions", in which the author presents the main conclusions and contributions, followed by the bibliographical references and their annexes.

In the paper are included the researches we made at "Politehnica" University of Timişoara during the period 2013-2017, as well as some results regarding the obtaining and characterization of the samples, obtained at the National Institute of Research and Development for Electrochemistry and Condensed Matter (INCEMC) Timisoara, or those concerning the electrical characterization of perovskititic materials, obtained at the West University of Timisoara. Among the main results obtained from the study, the following can be mentioned:

1. preparation of 11 samples of sodium tantalate ($NaTaO_3$), non-doped or doped with Cu or Al metal ions, using three different synthesis methods and different precursors: hydrothermal method, ultrasonic sonotrode immersion method in the reaction medium; and the sol-gel method. All the samples obtained were analyzed morphologically and structurally by X-ray diffraction analysis, SEM, X-ray dispersion spectroscopy (EDAX), UV-VIS spectroscopy and infrared spectroscopy (FT-IR). Based on these analyzes, the parameters of the crystalline lattice were determined, the majority of the diffraction RX analysis confirmed by the FT-IR analysis and the average dimensions of the crystallites, all the results of the structural and morphological analyzes being synthesized in the chapter 4.

2. X-ray diffraction analysis shows that the sol-gel method is the most appropriate method for the synthesis of pure crystalline perovskite pure $NaTaO_3$ samples. The X-ray diffraction spectrum of the SG-Al and SG-Cu samples allowed the lattice parameters to be determined and shows that the samples belong to the spatial group Pcmn (space group number 62) belonging to the orthorhombic crystallographic family.

3. In the presence of Cu or Al doping ions in the NaTaO3 structure, irrespective of the synthesis method (ultrasonic or sol-gel), the IR absorption spectra of these samples show that there is a significant reduction in the weight of the main absorption band (Na-O) to disappearance, accompanied by the appearance of a strong absorption band attributable to excitement of stretching of the Ta-O and Cu-O (or Al-O) groups with a much greater share in the case of doping with Al, a result first observed by us for the investigated evidence that will be studied in future research.

4. In order to determine the electrical conductivity of the samples and to highlight the electrical relaxation processes, complex impedance measurements were performed in a frequency range between 20 Hz and 2 MHz and at different temperatures between 30 °C and 200 °C. For this purpose, an experimental installation was realized that can be connected to an Agilent 4090-A type RLC meter (see chapter 3).

5. Performing a study on temperature dependence of electrical resistivity at different temperatures *T*, from the range (30 - 200) °C, for two samples of composites of Na-Ta oxides, synthesized by hydrothermal method at different reaction temperatures, time 12 hours (160 °C for sample A and 200 °C for sample B). A third sample, consisting of pure $NaTaO_3$, which was prepared by the sol-gel method (denoted sample C) was chosen as the reference sample. On the basis of the electrical resistivity measurements, the thermal activation energy of the samples E_a was determined, obtaining a value of 0.47 eV for sample A, 0.45 eV for sample B (consisting of a mixture of Na-Ta oxides including $NaTaO_3$) and 0.82 eV for sample C (sample containing only perovskit phase $NaTaO_3$) thus confirming the typical semiconductor behavior for all samples.

6. In the investigated temperature range, the static conduction mechanism in all samples was well explained using the variable range hopping model Mott (VRH). Based on this model, the following model parameters could be calculated: the characteristic temperature coefficient T_0, the density of the states located at Fermi $N(E_F)$, the hopping distance *R* and the hopping energy *W*. The Mott parameters of samples A and B are approximately the same values, but are very different from those of sample C. This difference can be correlated with the sample composition, namely, samples A and B are mixtures of $NaTaO_3$ and sodium oxides and tantalum (Na-Ta), while sample C is $NaTaO_3$ pure.

7. Based on the complex impedance measurements, $Z(f) = Z'(f) - iZ''(f)$ in the frequency range 20 Hz - 2 MHz at room temperature the frequency dependence of the real Z' and imaginary Z'' components of the investigated samples obtained either by the hydrothermal method at the same reaction temperature of 600 °C but with different sintering times (6 hours for sample S1 and 12 hours for sample S3) and 800 °C respectively 12 hour sintering (sample S2) or the sol-gel method (SG sample). The imaginary component Z '' of samples S1 and S3 exhibits two corresponding peaks in two relaxation processes, which means that the capacitive and resistive properties of the samples determined by the relaxation processes correspond to particles and particle separation limits, respectively. This is correlated with the fact that the crystalline structure of these samples has two phases ($NaTaO_3$ and Ta_2O_5). The imaginary component Z'' of samples S2 and SG has only one maximum corresponding to a relaxation process, which means that the capacitive and resistive properties of the samples correspond only to the particles. This behavior of the samples can be correlated with the fact that the crystalline structure of these samples has a single phase ($NaTaO_3$) with perovskite structure.

8. The $NaTaO_3$ powder sample doped with Cu metal ions synthesized by the sonotrode ultrasonication method immersed in the reaction medium was analyzed electrically using complex impedance measurements in the frequency range of 20 Hz- 2 MHz and at temperatures in the range (303-393) K. The imaginary component Z'' exhibits a maximum at a frequency f_{max} for all investigated temperatures, indicating the existence of an electrical relaxation process due to the presence of charge carriers in the investigated sample, thus allowing for the corresponding relaxation times. By increasing the temperature between 30 °C and 70 °C, the relaxation time decreases with temperature, following an Arhenius law, while at high temperatures between (80-120) °C, the relaxation time increases rapidly with increasing temperature. In the temperature range between 30 °C and 70 °C, the thermal activation energy due to the relaxation process was evaluated, obtaining the value of 0.20 eV.

9. From the temperature dependence of static conductivity $\sigma_{dc}(T)$ and based on Mott's variable-range hopping model (VRH), the activation energy was determined due to the conduction processes in the investigated sample. The results show a linear increase in E_{cond} activation energy with a temperature increase of between 175 meV and 215 meV, the values obtained being similar to those obtained for the activating energy corresponding to the electrical relaxation (ΔE_{relax} = 0.20 eV). The mechanism of electrical conduction in the investigated sample can be explained by the hopping of the carriers between the localized states. Thus, in the low temperature range of 30 °C to 70 °C, the electrons are not free and the static conductivity increases with the temperature increase, but at temperatures above 80 °C the electrons are all free and consequently the static conductivity σ_{dc} decreases as the temperature rises.

10. The results obtained for the electrical conductivity in the alternative field σ_{AC} of the sample show that σ_{AC} suddenly increases at high field frequencies (f> 200 kHz) and depends on temperature. These results can be explained on the basis of the correlated barrier hopping (CBH), in which the conduction phenomenon of metal ion doped $NaTaO_3$ samples (Cu ions) is due to a leakage process of the load carriers, between the closest neighbors. Using this model, the energy of the forbidden band W_m of the investigated sample was determined. The results obtained for the W_m of the investigated sample, in the temperature range of 30 °C to 70 °C, show that the doping of $NaTaO_3$ sodium tantalate with Cu metallic ions leads to the lowering of the prohibited band of the Wm sample, which has a minimum value 0.48 eV at 70 °C, after which it starts to increase, which can lead to an increase in electrical conductivity, so the electrical performance of doped NaTaO3 samples with Cu metal ions.

11. The static electrical conductivity σ_{dc} of Al-doped $NaTaO_3$ samples remains approximately constant for both samples up to the frequency of 10 kHz. The σ_{dc} value for the sample of Al-metal-doped $NaTaO_3$ by sol-gel (SG-Al) is greater than about 6.5 times that of the ultrasonication (US-Al) represents an increase in electrical performance for $NaTaO_3$ samples synthesized by the sol-gel method in relation to samples obtained by the ultrasonication method and doped with Al metallic ions.

12. For two ceramic samples of $NaTaO_3$, obtained by the sol-gel method but doped with different metal ions, Al (S1 or SG-Al sample) or Cu ions (sample S2 or SG-Cu), a study on the effect of dopant on the electrical properties of the investigated samples using complex impedance measurements in the frequency range between 200 Hz and 2 MHz and at different temperatures in the 30-90 °C range. The results obtained for the electrical conductivity show that the conductivity spectrum for both samples at each temperature T is formed by both the static component σ_{dc} corresponding to the low frequencies and which remains approximately constant up to the frequency of 10 kHz and the AC component which increases fast with frequency and corresponds to high frequencies (f> 200 kHz).

13. The σ_{dc} component for both samples increases with temperature when the T temperature rises from 30 °C to 50 °C, indicating that the conduction process is thermally activated, then decreases with temperature rise from 50 °C to 90 °C, in agreement with Mott and Davis's VRH theory. In this way, the results show that the activation energy due to the conduction, Econd is higher in the case of Cu-Cu (SG-Cu) -complete sample compared with the sample of Al (SG-Al) doped. The results obtained for the electrical conductivity in the alternating field of the two samples can be correlated with the fact that in the investigated samples the conduction phenomenon is due to a hopping process of the charge carriers from the material between the closest neighbor states according to the model CBH (*correlated barrier hopping)*, which is only present at high temperatures above 70 ° C in the case of the S2-doped Cu ions. At the same time, the obtained result can also be correlated with the fact that the conduction energy E_{cond} for S2 doped S2 doped with Cu ions is greater than the E_{cond} conduction energy for the sample S1 doped with Al ions.

14. Using the correlated barrier hopping model (CBH), the energy of the band gap W_m, of the two investigated samples was determined. From the results obtained, it is observed that the addition of Al or Cu metal ions in the structure of the perovskitic compound $NaTaO_3$ leads to a decrease in the energy of the band gap energy to temperatures (40-50) °C, after which W_m starts to increase with the increase of the temperature, tending to 0.9 eV values (for sample S1 doped with Al ions) and 0.75 eV respectively (for sample S2 doped with Cu ions), approaching the value of the energy of the value band gap energy of undoped $NaTaO_3$, which is between (1-3) eV.

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