

The Fundamentals and Challenges of Oxide Materials

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Edited by

Mihail Lungu and Catalin Nicolae Marin

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CHAPTER 1

METHODS OF SYNTHESIS OF OXIDES

ANTOANETTA LUNGU, PAULINA VLAZAN,
PAULA SFIRLOAGA, MARIA POIENAR

1.1. Introduction

This chapter covers the methods of synthesis of the spinel, perovskite, and crednerite-type oxides. Metal oxides are one of the best studied categories of materials, as they present a wide range of structures and properties. The method used to obtain spinelic oxides (MnFe_2O_4) under conditions of maximum purity and optimum efficiency is determined by the fact that the structure and properties of mixed oxide systems depend primarily on the method. As such, five categories of methods are presented. These are chemical co-precipitation, direct calcination, and the hydrothermal method (including the classical hydrothermal method, and the ultrasound and microwave-assisted hydrothermal methods). Some of these methods, along with others (direct reaction in sealed silica tubes or ultrasound assisted co-precipitation, for example, in the case of crednerite CuMnO_2 materials) have been used to obtain crednerite materials and will be described in the present book. To obtain perovskite materials, the sol-gel and ultrasonic methods with an immersed sonotrode in a reaction medium were used, followed by heat treatment at low temperature.

The synthesis of nanomaterials with specific electrical and magnetic properties is a field of great interest today. This is due to the particular properties of these materials, being significantly different to those of the bulk material and giving them wide applicability in various fields (including electronics, telecommunications, optics, aerospace, energy, medicine, and biology, etc.). The larger the specific surface area of a nanostructural material, the smaller the particle size. For this reason, the synthesis of nanostructural materials, with particle sizes in the nanometer range (1-100 nm), has attracted the interest of researchers, as evidenced by the multitude of scientific articles published in this field. One of the major

current directions of research in this field is the elaboration of new synthesis methods that allow, through accessible technologies, the synthesis of nanomaterials as fine as possible and with controlled morphologies.

In recent years, numerous studies in the field of magnetizable nanosystems, magnetic nanoparticles, and nano-magnetodielectric composites have been undertaken, responding to the current fundamental direction in the development of the nanosciences. The properties of nanocomposites are determined according to their chemical nature, shape, size, the matrix in which the particles are dispersed, and the interaction between the nanoparticles and the matrix.

Metal oxides are one of the best studied categories of materials, as they have a very wide range of structures and properties [1]. The preparation of polycrystalline materials to obtain materials with optimal properties for a desired application can be difficult due to a number of factors that must be taken into account to ensure their reproducibility. When obtaining metal oxide nanoparticles with specific properties by chemical methods, the most important factors to be considered concern their structural properties—crystalline or amorphous structure; size, shape, and morphology of the surface—and chemical properties—composition of the material, interface, and surface.

Metal oxides, having either a spinel, perovskite, or rednrite crystal structure, have been the topic of extensive studies and technological applications due to their useful and varied functional properties (catalytic, optical, electrical, magnetic, etc.), in combination with their chemical, thermal, and mechanical stabilities [2].

The numerous properties displayed by metal oxides, depending on both the structure and nature of the M^1 and M^2 metals, makes this class of materials suitable for applications in an extremely wide variety of fields including medicine, catalysis, oxygen obtaining devices, and electronic and magnetic devices, etc.

In this chapter we present a number of procedures for obtaining metal oxide samples by various methods.

1.2. General Methods for Obtaining Metal Oxides

Numerous methods have been proposed for the synthesis of metal oxides, this diversity being attributed to the difficulties of obtaining particles of specific sizes and with physico-chemical characteristics as close as possible to ideal [3]. Such particle characteristics include:

1. Small-size.
2. Narrow width.
3. Ease of dispersibility.
4. High chemical purity.
5. Homogeneous composition.

The choice of method for preparing metal oxides depends on:

- the raw materials used;
- the preparation scale (laboratory, micro-production, series);
- and the available technical means.

Numerous methods for the synthesis of metal oxides have been suggested. The main methods for obtaining nanocrystalline materials include [4]:

- a. Conventional methods (ceramic methods). These consist of obtaining oxide materials in the form of nanoparticles by solid phase reactions at relatively high temperatures from metal oxide precursors, or by thermal decomposition into oxides of carbonates, nitrates, oxalates, and sulphates [5]. The advantage of this method is that we obtain well-crystallized materials. The disadvantage is that the realization of this process involves a series of operations that must be performed before heat treatment that can lead to impurity and loss of material, such as through grinding and mixing [6].
- b. Unconventional methods leading to wet oxide nanomaterials, at relatively low temperatures, thus eliminating the specific disadvantages of the ceramic method. The advantage of such wet processes is that we can obtain a homogeneous molecular distribution, ensuring better control of the reaction conditions, with a close dimensional distribution that is almost uniform. In this way, fine-grained particles and a specific and controlled surface can be obtained, depending on the proposed field of application. The degree of crystallization can also be controlled. The most commonly used unconventional methods are: chemical precipitation; the hydrothermal method; the solvothermal method; the sol-gel method; the combustion method; and the microemulsion method [7].

The use of synthetic methods for obtaining metal oxides under conditions of maximum purity and optimum efficiency is justified by the fact that the

structure and properties of mixed oxide systems depend mainly on the method used for their synthesis.

In this chapter we present several methods for obtaining metal oxides that have been used by our research team. These methods have been used to obtain manganese ferrite, perovskite, and crednerite-type oxides.

1.3. Synthesis of Manganese Ferrites by Various Processes

This section presents five methods used to obtain manganese ferrite: the classical chemical co-precipitation method; the ultrasonic-assisted co-precipitation method; the direct calcination method; the classical hydrothermal method; and the hydrothermal method with the use of dopants (fig. 1-1).

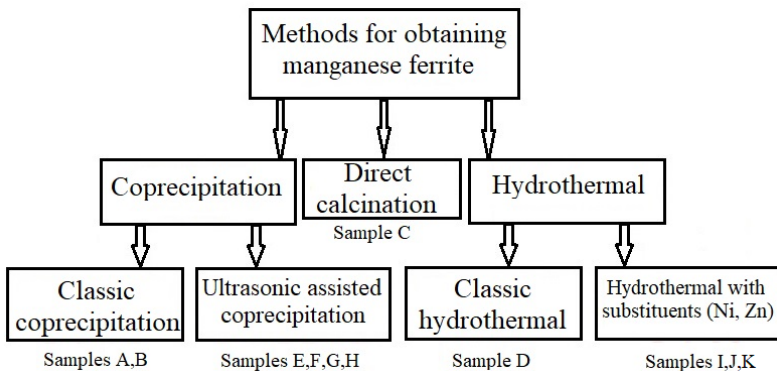


Fig. 1-1. Unconventional synthesis methods for manganese ferrite.

Next, we describe the working technology used for sample preparation, making a comparison with the methods used by other authors for the synthesis of samples of the same type. Images of powdered manganese ferrite samples, obtained by the methods listed above, are shown in fig. 1-2.

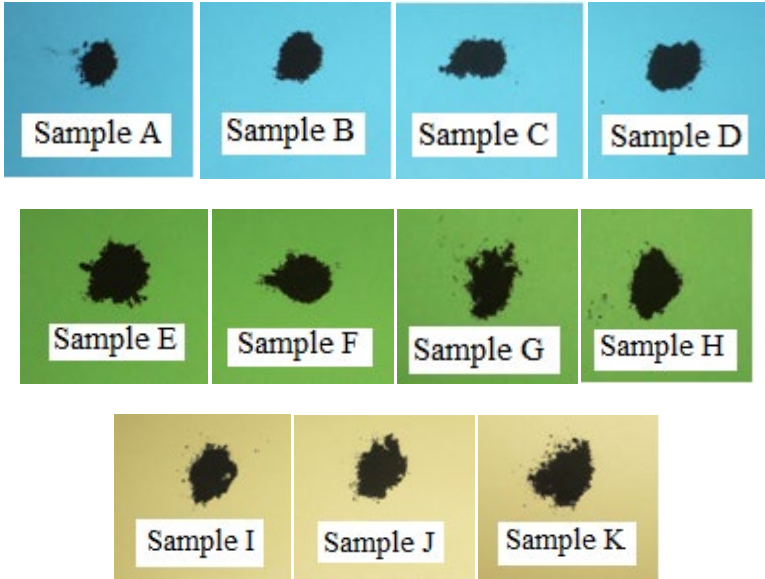


Fig.1-2. Images of manganese ferrite samples obtained.

1.3.1. The classical co-precipitation method

For the synthesis of MnFe_2O_4 by the method of co-precipitation, Amighian et al. [8] used an aqueous solution of reactants ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$) and NaOH as a precipitating agent.

In contrast to these authors, who used sulfides as reactants (iron and manganese sulfide), the method proposed here for the preparation by co-precipitation of ferrite powders of MnFe_2O_4 (samples A and B) was performed using $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ și $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as reactants. The procedure was as follows: one sample was obtained by simple co-precipitation and calcination at 200°C and the other by simple co-precipitation and calcination at 900°C . The samples were synthesized in powder form.

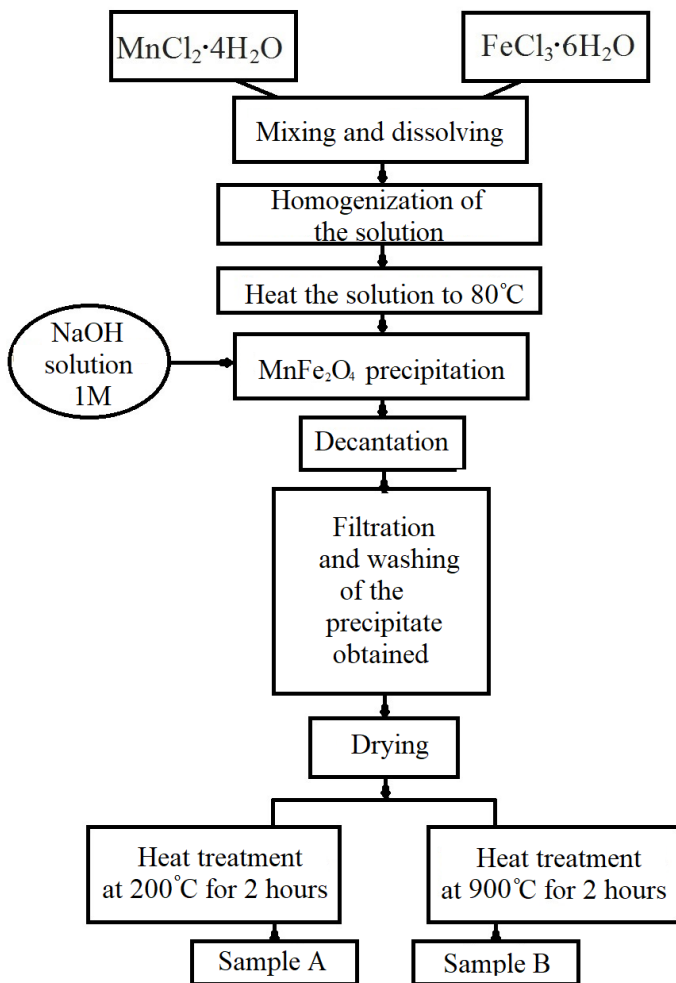


Fig. 1-3. Technology for obtaining manganese ferrite by the method of chemical co-precipitation.

The reagents used to obtain the manganese ferrite powder were mixed in the stoichiometric ratio Mn: Fe = 1: 2 and dissolved in distilled water. The reactants were 0.945 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, and 2.733 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to which 16 ml of 2 M NaOH solution was added until the mixture reached pH = 11. Precipitation of the ferrite was performed by mixing

with a Heidolph-type magnetic stirrer equipped with a heating plate for 2 hours at a temperature of 80-90 °C. After decanting, filtering, and washing of the precipitate with ethyl alcohol to remove chlorides and neutralize the solution to pH = 7, the samples were dried in an oven at 80 °C. One sample was then heat treated at 200 °C and the other at a temperature of 900 °C. A diagram of the process for obtaining manganese ferrite by the co-precipitation method is shown in fig. 1-3 [9, 10].

The obtained powder was characterized by X-ray diffraction using the PANalytical X'Pert PRO MRD diffractometer to identify the existing phases and highlight the degree of crystallization. The morphology and structure of the surfaces were studied using a scanning electron microscope (SEM-EDX).

1.3.2. The ultrasonically-assisted co-precipitation method

The principle of this method is the same as for the classical hydrothermal method, but the stirring of the reactant mixture is done with the help of ultrasound, the autoclavation time being 100 minutes. The use of ultrasound as a means of obtaining manganese ferrite nanocrystals has the advantage that crystallization is favoured by the ultrasonic field and takes place at lower temperatures and pressures than in the case of the classical hydrothermal method.

The crystallization rate increases due to the increased number of nucleation centres produced by ultrasonic agitation. The phenomenon of controlled cavitation in the reaction medium minimizes the growth of crystals and the formation of conglomerates so that the obtained particles have a narrow dimensional distribution.

To obtain manganese ferrite, the corresponding metal salts were used as precursors: 2.02 g $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, 1.0749 g $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, and 1 M NaOH solution as the precipitating reagent. All reagents were purchased from Merck and were of confirmed analytical purity. The metal salts were dissolved in distilled water and then the 1 M NaOH solution was added with continuous stirring up to a pH value of 11, with the corresponding metal hydroxides co-precipitating.

To obtain the final product, the suspension obtained was subjected to ultrasound for 20 minutes at 80 °C using a high-intensity ultrasonic processor Sonics VCX-750 Vibra-Cell equipped with a probe that was immersed in the reaction mixture. The working frequency used was 20 kHz, the net power was 750 kW, the amplitude was 80 %, and the on/off pulses were set at 30: 10 (30 seconds running and 10 seconds at rest).

The pulsation cycle was programmed so as not to require additional cooling of the suspension. Due to the replacement of the conventional heating system by an ultrasonic field heating system with an immersed sonotrode, the synthesis time was considerably reduced.

The precipitate obtained was separated by decantation, followed by filtration and washing several times with distilled water to give a neutral pH. Finally, it was washed 2-3 times with ethanol and the washed precipitate was dried in an oven at 80 °C for 2 hours. From this first sample, three other samples were collected that were subjected to heat treatment at 400 °C, 700 °C, and 1,000 °C [11, 12]. The workflow for the process of obtaining manganese ferrite is presented in fig. 1-4.

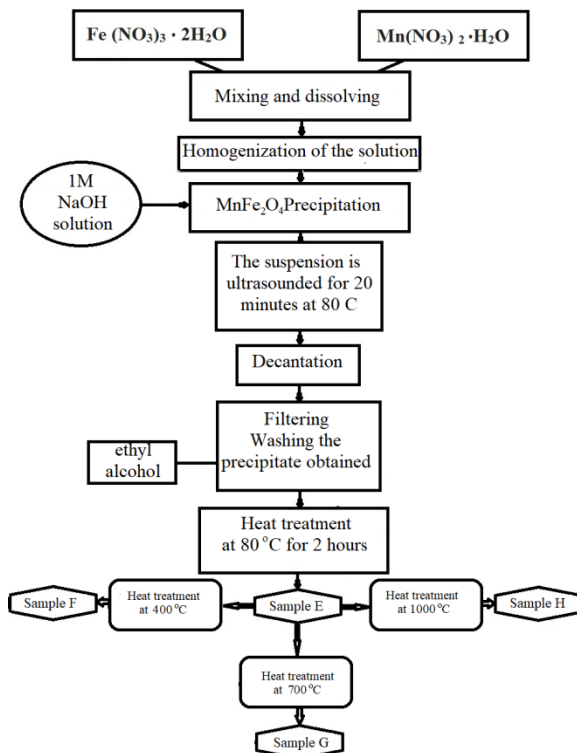


Fig. 1-4. Obtaining ferrite powders of MnFe_2O_4 by the ultrasonic method with a sonotrode immersed in the reaction medium.

1.3.3. The direct calcination method

A sample was obtained using $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as precursors, using the same amount of each reactant as in section 1.2.1. Thus, a mixture of 0.945 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ with 2.733g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was obtained by grinding and the addition of 0.61 g urea, followed by washing with ethanol. The ethanol was evaporated by heating and the resultant mixture was burnt at 700 °C for 4 hours. The workflow for the process of obtaining manganese ferrite by direct calcination is presented in fig. 1-5 [13].

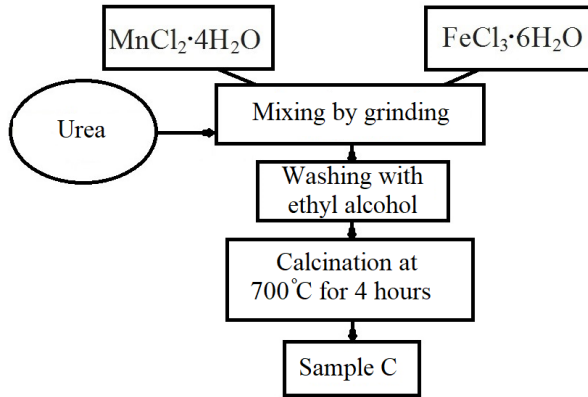


Fig. 1-5. Obtaining manganese ferrite by the direct calcination method.

1.3.4. Synthesis of manganese ferrites by the hydrothermal method

The hydrothermal process is one of the most successful methods for growing crystals of different materials [49]. This method has a number of advantages, including obtaining a pure product with high crystalline homogeneity and control over the shape and size of the particles.

1.3.4.1. The classical hydrothermal method

A sample was obtained by the hydrothermal method. As with the other samples, the same precursors were used with the same amounts: 0.945 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved together with 2.733 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in distilled water and 12 ml of 2 M NaOH was added to precipitate the

manganese ferrite with a pH of 11. The mixture was introduced into a Morey-type autoclave at a temperature of less than 250 °C and a pressure of 80 bar [14, 15]. The resulting product was subjected to filtration, washing, and drying. A diagram of the workflow for obtaining manganese ferrite by the hydrothermal method is presented in fig. 1-6.

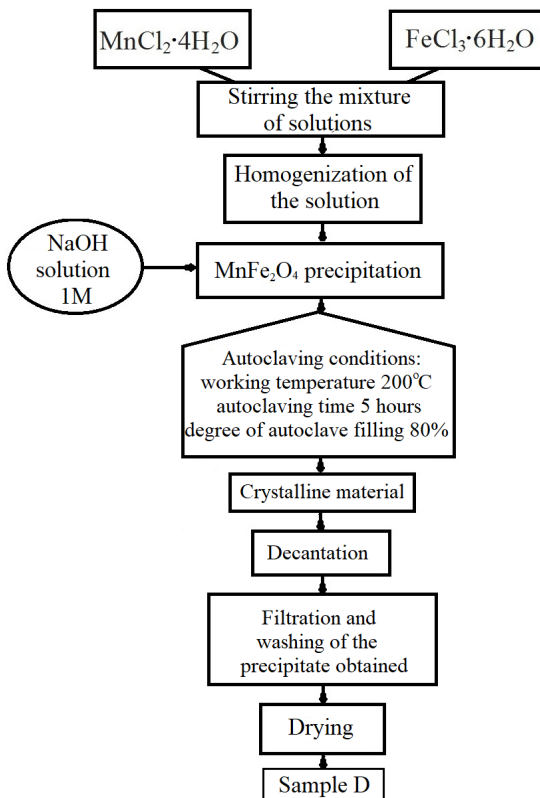


Fig. 1-6. Obtaining manganese ferrite by the simple hydrothermal method

1.3.4.2. The hydrothermal method with Ni and Zn substituents

Hydrothermal manganese ferrite powders and Ni and Zn substituted manganese ferrite powders were obtained. The first samples were obtained by the hydrothermal method using the following reactants: 1.7895 g $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, and 4.8372 g $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$. The metal salts were

dissolved in distilled water and then 1 M NaOH solution was added to give a pH of 11. The mixture was placed in a Morey-type autoclave at 220 °C for 12 hours. The resulting product was filtered, washed, and dried to obtain ferrite powders of MnFe_2O_4 [16].

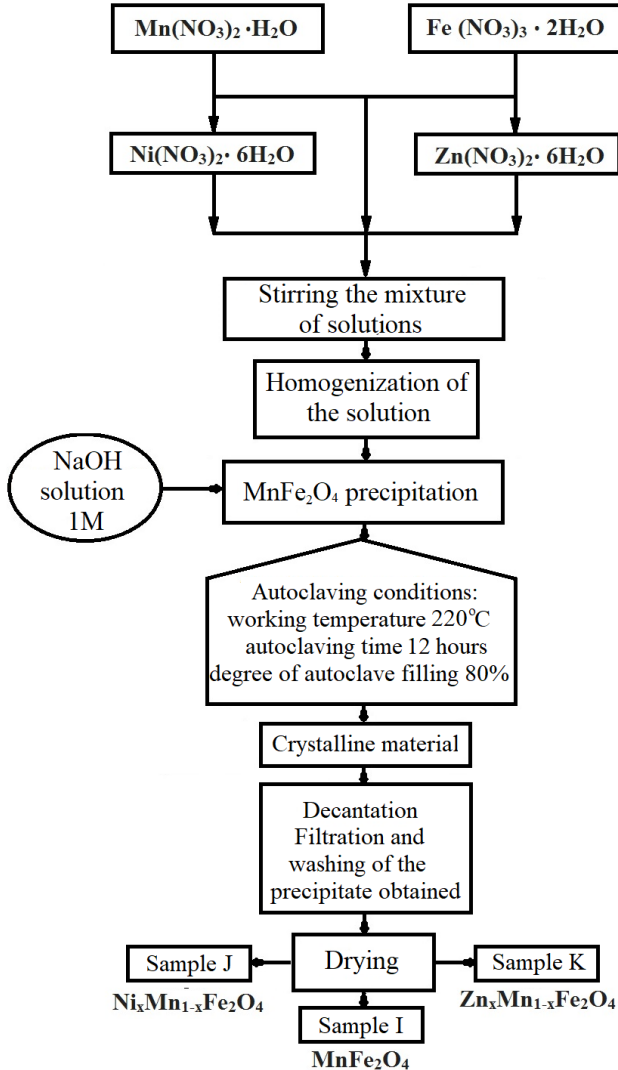


Fig. 1-7. Diagram for obtaining ferrite samples with Ni and Zn substituents.

An Ni-substituted manganese ferrite sample was synthesized from a mixture of three reactants: 1.2554 g $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 4.8372 g $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, and 0.5754g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4 %) solution with a concentration of 0.002 M. The reactants were dissolved in distilled water and then 1 M NaOH solution was added to give a pH value of 14. The mixture was placed in a Morey autoclave at 220 °C for 12 hours. After filtration, washing, and drying, $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ferrite powder was obtained [17].

A sample of manganese ferrite substituted with Zi was obtained using the following mixture of reactants as precursors: 1.2554 g $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 4.8372 g $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, and 0.5949 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4 %) solution with a concentration of 0.002 M. The mixture was made by dissolving in distilled water and adding 1 M NaOH solution to give a pH of 12. The mixture was placed in a Morey autoclave at a temperature of 220 °C for 12 hours. After filtration, washing, and drying, $\text{Zn}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ferrite powder was obtained. The workflow for obtaining these ferrite samples is presented in fig. 1-7.

1.4. Obtaining ABO_3 -type Compounds with a Perovskite Structure

Here, we present the following proposed methods of synthesis for obtaining NaTaO_3 samples: the hydrothermal method; the sol-gel method; and the ultrasound method.

The physical properties of perovskite-type oxides can be greatly modified by changing their crystalline and electronic structures. At the same time, the perovskite structure allows the substitution of metallic elements in the periodic table, either in the tetrahedral state A, or in the octahedral state B [18, 19]. This leads to a very large number of compounds with remarkable properties, including ferroelectric (BaTiO_3 , KNbO_3 , PZT), piezoelectric (PZT, (K, Na) NbO_3 -NN), and ferromagnetic (SrRuO_3), compounds with nonlinear optical (LiNbO_3 , LiTaO_3) and catalytic properties (NaTaO_3); compounds with ionic-electronic conductivity ((La, Sr) MnO_3); and compounds with high electronic mobility (SrTiO_3) [18, 20].

The synthesis of these materials, with particle sizes in the range of 1-100 nm, has attracted the interest of researchers, especially over the past decade when research began to focus on finding new ceramic materials with thermoelectric properties. Perovskite materials, such as SrTiO_3 [21, 22], NaCoO_3 [23], and CaCoO_3 [24], have been shown to have a high ZT merit factor. Continuing research in this direction, new perovskite materials have been identified and developed, such as sodium

tantalum (NaTaO_3), with thermoelectric properties, as well as good photocatalytic characteristics [25]. At the same time, the $\text{NaTaO}_3\text{-Fe}_2\text{O}_3$ composite material has a high Seebeck voltage of -300 mV at a high temperature gradient, $\Delta T = 650$ K, and with linear temperature dependence [26, 27, 28]. However, its electrical conductivity is low, so the power factor must be increased.

In this section, we present three methods of synthesis for obtaining NaTaO_3 samples: the hydrothermal method; the sol-gel method; and the ultrasonic method. All the NaTaO_3 samples obtained were undoped (pure) or doped with Cu or Al metal ions [29].

1.4.1. The hydrothermal method for the synthesis of powdered NaTaO_3 samples

The precursors used for the synthesis of NaTaO_3 ceramic materials by the hydrothermal method were: 0.500 g of tantalum powder with a purity of 99.9 %, 5 ml of hydrofluoric acid (HF), and 0.5 g of citric acid (as a chelating agent) in 75 ml H_2O and NaOH to adjust the pH to 6.5. The mixture was then introduced into a Morey-type autoclave with a capacity of 37.6 ml, occupying 80 % of the total volume of the autoclave. The autoclave solution was maintained at 160 °C for sample A and 200 °C for 12 hours for sample B.

After decantation and filtration, the resulting precipitate was washed with double-distilled water on filter paper and then dried in an air oven at 800 °C resulting in the two powder samples. In order to obtain new samples of sodium tantalite (NaTaO_3) by the hydrothermal method, the working method was modified from the one used to obtain the 2 initial samples. As precursors 0.500 g of tantalum powder with a purity of 99.9 % and 10 ml of fluoric acid (HF) were also used, with citric acid as a chelating agent. Precipitation was performed in an aqueous sodium hydroxide solution (2 M NaOH) at pH = 9 and the solution was stirred with a magnetic stirrer for 2 hours at 85 °C.

The solution obtained was then introduced into the Morey type autoclave and synthesis of the autoclave mixture was done by heat treatment at two temperatures for 6 and 8 hours, respectively, obtaining the following 4 samples: sample S1, 600 °C for 6 h; sample S2, 800 °C for 6 h; sample S3, 600 °C for 12 h; and sample S4, 800 °C for 12 h. For each sample, after decantation and filtration, the resulting precipitate was washed with distilled water on filter paper and then dried in an air oven at 800 °C, giving 4 samples of powdered sodium tantalite [30, 31].

1.4.2. Synthesis of NaTaO₃ samples in the form of undoped/doped powders with Al or Cu ions by the ultrasonic method

The precursors used for the synthesis of NaTaO₃ ceramic materials, doped or undoped with Cu or Al ions, by the ultrasonic method with a sonotrode immersed in the reaction medium were: tantalum ethoxide (Ta(OC₂H₅)₅), sodium hydroxide (NaOH), and copper nitrate (Cu(NO₃)₂) or aluminium nitrate (Al(NO₃)₃), representing about 0.04 %, all of analytical quality, along with bidistilled water and ethyl alcohol.

The detailed procedure for synthesis is as follows: 1 ml of tantalum ethoxide was added to 50 ml of bidistilled water, stirred continuously by a magnetic stirrer, and with the addition of 0.017 g of copper nitrate or 0.0375 g of aluminum nitrate. Precipitation was performed in an aqueous sodium hydroxide solution (2 M NaOH) up to pH = 13. The obtained suspension was subjected to an ultrasonic process for 15 minutes, with the help of the mobile processor and the sonotrode Sonics Vibra Cell immersed in the reaction medium. Its working parameters were: amplitude 80 %; and pulsation: 10 seconds On/5 seconds Off. The obtained precipitate was filtered and washed with bidistilled water to give a neutral pH and then it was heat treated at a temperature of 600 °C for 6 hours [31]. In this way, by an efficient and simple method using ultrasonic vibrations in the reaction medium, as first reported by us in [32], we obtained the following samples: NaTaO₃ doped with aluminium ions (noted US-Al sample) and NaTaO₃ doped with copper ions (noted US-Cu sample).

1.4.3. Synthesis of samples of NaTaO₃ in the form of undoped/doped powder with Al or Cu ions by the sol-gel method

For the synthesis of sodium tantalite (NaTaO₃) samples by the sol-gel method, purely analytical chemicals were used (Aldrich 99.98 %). The initial materials used were 1 ml of tantalum ethoxide and a solution (1: 1) of ethyl alcohol and distilled water at room temperature. Precipitation was performed in an aqueous sodium hydroxide solution (1 M NaOH) at pH = 7, with continuous stirring using a magnetic stirrer. The resultant mixture was a white suspension that was heated for a further 2 hours at 90 °C.

A gel was obtained that had been dried in an oven at 110 °C for 4 hours. For crystallization, the precipitate was heat treated for 6 hours at 600 °C, with a heating rate of 5 °C. A sample was obtained by the sol-gel

method of pure NaTaO_3 in powder form, denoted the SG sample. For the synthesis of sodium tantalate (NaTaO_3) doped with Al or Cu metal ions, the same precursors and the same reaction conditions were used, but 0.04 g of copper nitrate with the formula $\text{Cu}(\text{NO}_3)_2$ were added to the suspension with continuous stirring, or aluminum nitrate with the formula $\text{Al}(\text{NO}_3)_3$. The resulting suspension was heated for 2 hours at 90°C and the gel-like product was then dried in an oven at 110°C for 4 hours. Finally, for crystallization, the NaTaO_3 samples, doped with Al ions or Cu ions, were subjected to heat treatment for 6 hours at a temperature of 600°C , with a heating rate of $5^\circ\text{C}/\text{min}$ [33, 34].

1.5. Synthesis of Crednerite by Various Processes

The specialized literature presents varied and complex synthesis methods for obtaining CuMnO_2 -type materials as single-phase polycrystalline materials, thin films, and single crystals.

For the production of polycrystalline materials of the crednerite type, synthesis was by the sol-gel method [9], with preparation at low temperatures by exchange reactions [35], or by solid state reactions at high temperatures (950°C) starting from the precursors CuO and Mn_2O_3 in closed quartz tubes under vacuum [36] with an atmosphere of Ar [37] or N_2 [38]. The sol-gel method was used for the preparation of thin films [39] and $\text{Cu}_{1.04}\text{Mn}_{0.96}\text{O}_2$ crystals were obtained by the flux method [40]. In the synthesis of the CuMnO_2 compound at low temperature and pressure by the hydrothermal method [41-43], in the case of obtaining delafossite-type materials based on copper, one of the main difficulties is the stabilization of Cu^+ species in hydrothermal conditions. In aqueous solution at room temperature, Cu^+ is not stable at any pH value and dissociates into Cu^0 and Cu^{2+} .

$\text{Cu}_1 + x\text{Mn}_{1-x}\text{O}_2$ crednerite-type compounds (with $x = 0$ and 0.06) were prepared by the solid state reaction method, as described in [44, 45, 46]. Oxides of CuO and MnO were mixed and ground together, with the mixture obtained having the stoichiometric ratio $(1 + x) \text{CuO} : (1-x) \text{MnO}$, as shown in fig. 1-8. The compounds obtained (for $x = 0$ and $x = 0.06$, respectively) were pressed to give pellet-shaped samples (1 cm in diameter and a few millimetres thick). The pellets were then placed in vacuum-evacuated silicon tubes and heated in an oven at 950°C for 12 hours [47].

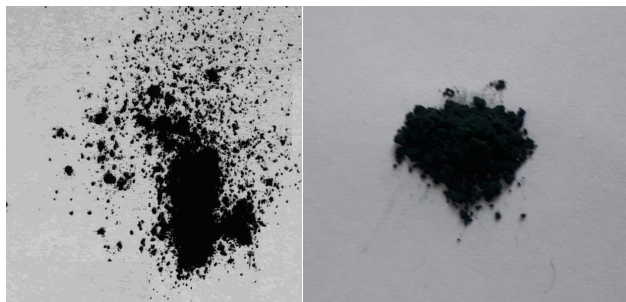


Fig. 1-8. $\text{Cu}_{1+x}\text{Mn}_{1-x}\text{O}_2$ powder-type crednerite samples

1.5.1. Synthesis of materials under vacuum in sealed silica tubes

The synthesis of materials can be performed in a controlled atmosphere of Ar, Ar/H₂, N₂, CO/CO₂, or under vacuum conditions in order to control the stoichiometry and size/shape or obtain single phase compounds. For the synthesis of materials in a vacuum, several approaches can be taken, such as synthesis in a vacuum furnace, or by using sealed silica tubes, as described in the following.

In the first step, the powdered precursors are weighed in stoichiometric proportions, mixed by grinding in an agate mortar, and pressed into pellets (1 cm in diameter and a few millimetres thick) or parallelepiped bars (dimensions: 2 x 2 x 10 mm³). The compression of the powder induces a good diffusion of species during thermal treatment and this step is required otherwise the vacuum inside the tube would not be possible due to the fact that the powder would be drawn into the vacuum pump. The bars or pellets are then placed in an alumina finger, preventing their diffusion in the silica of the powder during synthesis. The alumina finger is then placed in a quartz tube, which is sealed with a vacuum of 10⁻³ mbar. The sealed silica tubes are then placed in a furnace for thermal treatment, performed in a specific sequence for each synthesis (fig. 1-9).

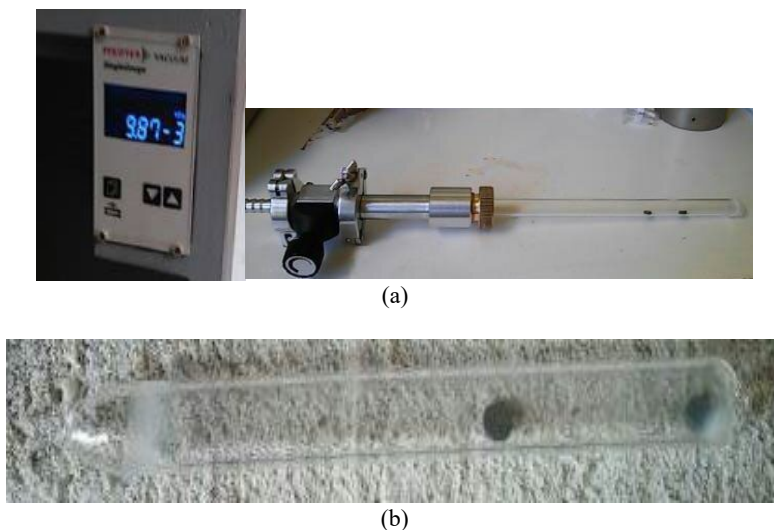


Fig. 1-9. (a) The system used to evacuate the silica tubes under vacuum and (b) a sealed silica tube with 2 pellets inside (without the alumina finger).

Today, researchers are using this synthesis method for a large variety of materials. Controlled oxygen stoichiometry in the compounds is essential making this a very useful synthesis method for crednerites [48, 49], tungsten bronzes [50], and perovskites [51], for example. For some materials that support a range of chemical compositions, special attention has to be given to the oxygen stoichiometry and sealed silica tubes are used [48].

Polycrystalline $\text{Cu}_{1+x}\text{Mn}_{1-x}\text{O}_{2+\delta}$ ($x = 0-0.10$)-type materials have been reported in the literature, prepared by solid state reactions in closed quartz tubes under vacuum [48, 49]. In a typical synthesis, CuO and MnO powders were weighed in the stoichiometric proportions $1 + x$ CuO and $1 - x$ MnO, ground, and pressed into pellets (1 cm in diameter and a few millimetres thick). These were then placed in quartz tubes sealed under primary vacuum and heated in an oven at $950\text{ }^\circ\text{C}$ for 12 hours [48]. Solid state reactions in sealed silica tubes have also been carried out starting with stoichiometric amounts of Cu, CuO, and Mn_2O_3 in [49] at temperatures ranging from $960\text{ }^\circ\text{C}$ for CuMnO_2 to $1,020\text{ }^\circ\text{C}$ for $\text{Cu}_{1.2}\text{Mn}_{0.8}\text{O}_2$.

1.5.2. The ultrasound-assisted co-precipitation method

In recent years, sonochemistry or ultrasonic cavitation chemistry has emerged as a potential alternative for the synthesis of materials like, for example, ferrites of nano-dimensions [52-56], hydroxyapatite [57], CuO [58], spinels [59], and vaterite-type calcium carbonate [60], etc. This synthesis method is environmentally friendly and allows us to obtain nanosized materials with uniform size distributions that are single phased [61]. In the case of $\text{Ni}(\text{OH})_2$, it has been shown to influence the crystal structure [62].

Sonication of a liquid results in rapid heating, driving cavitation, which involves the implosive collapse of bubbles [63]. The relevant chemical reactions largely take place inside these bubbles [64, 65], which otherwise would require rigorous stirring [66]. In hot spots, where the bubbles are heated intensely, the temperatures are roughly 5,000 °C with pressures of about 500 atmospheres and lifetimes of a few microseconds [64, 67-68].



Fig. 1-10. Ultrasonic device consisting of: 1) sonotrode with a titanium tip; 2) ultrasonic processor; and 3) temperature controller.

In the process of synthesis, the time, temperature, and amplitude of the ultrasound is tested in order to find the best parameters to obtain the desired materials. A typical experimental strategy consists of dissolving

the precursors (acetates, nitrates, etc.) in distilled water before carrying out sonication for several minutes (10, 20, 30... min). Sonication is applied using an ultrasonic probe (1/2in), as shown in fig. 1-10 (Sonics Vibra Cell).

CuMnO₂ nanocrystals were prepared by the ultrasound-assisted co-precipitation method for the first time in [69]. The method consisted of dissolving stoichiometric quantities of Cu (NO₃)₂·3H₂O and Mn (NO₃)₂·4H₂O in a 2.5 M NaOH solution. The mixing of both solutions determined the precipitation, after being subjected to ultrasonic vibration for set periods of time (20, 30, or 40 min) at 80 °C, a frequency of 20 kHz, a pulsation amplitude of 80 %, and a pulsation cycle of 10 s ON/5 s OFF.

1.6. Conclusion

The study of metal oxides is currently a major research direction, both in terms of using new methods of synthesis and the comparative study of the electrical and magnetic performance of samples obtained for use in various applications.

The research conducted and presented in this chapter involved the use of different methods for obtaining metal oxides, including: the classical chemical co-precipitation method; the ultrasonic-assisted co-precipitation method; the direct calcination method; and variants of the hydrothermal method (classical hydrothermal and hydrothermal with the use of dopants). Through the numerous methods used, single-phase or multiphase powder samples were obtained.

These oxide materials samples were analysed both structurally and in terms of surface morphology by X-ray diffraction (XRD), scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX), UV-Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA).

The investigation of the electrical and magnetic properties of the studied nanomaterials was performed to give electrical and magnetic measurements using complex impedance spectroscopy, complex dielectric permittivity, and thermoelectric analysis of the complex conductivity, along with the inductive method of graphing the hysteresis.

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