The National University of Science and Technology POLITEHNICA Bucharest
FACULTY OF MATERIALS SCIENCE AND ENGINEERING
The Doctoral School Materials Science and Engineering

DOCTORAL THESIS

The influence of natural rare earth mixture on zirconia structure with potential applications in solid electrolytes

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Content

ABBREVIATIONS LIST

SOFC – solid oxide fuel cell

AFC – alkaline fuel cell

PEMFC – proton-changing membrane fuel cell

PAFC – phosphoric acid fuel cell

DMFC – fuel cell with methanol

MCFC – fuel cell with molten carbonate

TF-SOFC – thin film SOFCs

ALD – atomic deposition on thin layers

LPG – pulsed laser deposition

PVD – physical deposition in the vapour phase

CVD – chemical deposition in the vapour phase

RF Sputtering – PVD hybrid system (Physical vapour phase deposition)

LSCF – alloy target

YSZ – ZrO_2 based electrolyte (Y_2O_3)

ScSZ – ZrO_2 based electrolyte (Sc_2O_3)

GDC – fluorite, based electrolyte ($Ce_{1-x}Gd_xO_{2-\delta}$)

SDC – fluorite, based electrolyte ($Ce_{1-x}Sm_xO_{2-\delta}$)

YDC – fluorite, based electrolyte ($Ce_{1-x}Y_xO_{2-\delta}$)

LSGM – perovskite, based electrolyte ($La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$)

REE – rare earth

REO – rare earth oxides

REM – rare earth metals

LREE – light rare earths

HREE – heavy rare earths

IOCG – copper-gold deposits of oxide-iron type

D2EHPA – Di-(2-ethylhexyl) phosphoric acid

TR – hydroxide cake

Keywords: *monazite, rare earths, alkaline leaching, solvent extraction, zirconia doped with natural mixture of rare earths, solid electrolyte.*

INTRODUCTION

The thesis: "The influence of natural mixture of rare earths on the structure of zirconia with potential applications in solid electrolytes" proposes a new approach to raw materials in topical areas. Analyzed sequentially, the theme can have two key points: monazite and the use of zirconia as an electrolyte. The doctoral thesis is structured in two parts:

✓ **PART I** consists of chapters I and II, which includes the current state of knowledge, in which an analysis of the specialized literature in the field of the research topic is presented;

✓ **PART II** is represented by chapters III, IV and V in which the own contributions in the addressed field and the obtained experimental results are presented. The experimental part is focused on two research directions, namely: experimental studies on obtaining the natural mixture of REO rare earth oxides from monazite and experimental studies on obtaining and characterizing materials in the form of powders, pellets and thin films based on zirconia doped with 8 % natural mixture of REO**.**

Chapter I, "RESEARCH ON THE DEVELOPMENT OF SOLID OXIDE FUEL CELLS BASED ON ZIRCONIA", presents an analysis of the current state regarding the production of solid oxide fuel cells (SOFC) with an emphasis on the methods of obtaining the electrolyte based on zirconia doped with REO, this being the targeted component in this thesis. This chapter presents the most recent research on synthesis methods and deposition processes approached to obtain these categories of materials, also presenting the most relevant results obtained in this field.

Chapter II, "ANALYSIS OF THE IMPORTANCE OF RARE EARTHS AT THE EUROPEAN LEVEL", presents an analysis of the current state of deposits, the distribution of REE-bearing minerals, the technologies used to extract them from primary sources and the applications in which they are used. Thus, a theoretical foundation is presented regarding the importance of obtaining REE through the most efficient methods**.**

In **Chapter III, "OBJECTIVES AND METHODOLOGY OF THE RESEARCH",** the proposed objectives and research methodology of the doctoral thesis are specified. Furthermore, the methods, equipment, and materials used for obtaining and characterizing powders, compacts, and thin films are indicated.

Chapter IV, "THE OBTAINING AND CHARACTERIZATION OF RARE EARTH OXIDES FROM MONAZITE", aims to obtain rare earth hydroxides from the natural source, namely monazite. The process of extracting rare earths oxides (REO) from monazite from the Jolotca-Ditrău

region, Romania, involves two distinct stages. In the first stage, monazite is treated with sodium hydroxide (NaOH) to extract hydroxides of thorium, uranium and REE. Subsequently, in the second stage, organic solvents are used for extraction, thorium hydroxide being separated from REO by its dissolution. Following these steps, purified REE hydroxides from monazite ore were successfully obtained.

Chapter V, "THE OBTAINING AND CHARACTERIZATION OF MATERIALS IN THE FORM OF POWDERS, COMPACTS, AND THIN FILMS BASED ON ZIRCONIA DOPED WITH A NATURAL MIXTURE OF RARE EARTH OXIDES", it primarily aimed at the study of the synthesis of zirconia-based powders doped with 4 %, 8 % Y_2O_3 and with 8 % natural mixture of (REE= La, Ce, Nd, Sm, Y and Gd). Thus, 3 types of powder were obtained by hydrothermal method: 4ZrY, 8ZrY and 8ZrMZ. The powders obtained were characterized in terms of: chemical composition, thermal stability, phase purity and microstructure, to confirm the feasibility of the process. The study of the behavior of the 3 types of powders during heat treatment followed (Treatment = 1200 °C), thus, 3 types of 4ZrYC powders were obtained; 8ZrYC and 8ZrMZC. The obtained powders were characterized in terms of: chemical composition, microstructure, phase purity and specific surface area.

The next step was to obtain zirconia-based pellets. 18 Types of pressed pellets were obtained for measuring ion conductivity: P1-4ZrY, P2-8ZrY, P3-8ZrMZ. The obtained pellets were sintered (T sintering=1200°C/1300°C/1400°C), characterized by: XRD, SEM, EDX and calculated density by Archimede method. The batch of pellets with the best density was selected (sintering at 1400°C to determine the electrochemical properties.

The last stage was to obtain thin films by the RF-sputtering method. A type of thin film of zirconia doped with the natural mixture of rare earths was obtained, deposited on a silicon substrate which has the following name: F_8ZrMZ.

The thin film obtained was characterized from the point of view of: microstructure, morphology and wetting characteristics

Thus, **the novelty** and **originality** of the doctoral thesis is given by the integration of emerging technologies, a hydrothermal synthesis and the production of thin films (RF sputtering) in order to demonstrate the efficiency of using natural mixtures of rare earths (from natural source - monazite) as dopants in zirconia - based materials with applications in solid oxide fuel cells.

The interdisciplinary character of the thesis emerges from the integration of these methods with the aim of obtaining new materials**.**

For the first time, both the potential of hydrothermal synthesis in obtaining complex powders based on a natural mixture of rare earths and the potential of the RF sputtering process in obtaining thin films, with potential applications in solid oxide fuel cells, will be exploited**.**

CHAPTER III. RESEARCH OBJECTIVES AND METHODOLOGY

3.1. Objectives of the doctoral thesis

The individual extraction of rare earth oxide (REO) from monazite is a challenging process with a significant environmental impact and high energy consumption, which is reflected in high prices. This difficulty is due to the extraction process, involving multiple complex stages, attributed to the similar electronic configurations and physico-chemical properties of REO [3, 157, 164]. The development of technologies for the use of clean and efficient energy as an alternative to fossil fuel resources is an urgent issue, given the continuous increase in demand for new technologies and the challenges associated with global warming [178].

In this regard, a possible research direction would be the development of technologies that enable the use of natural mixtures of rare earths as they are found in ores. Therefore, the **thesis aims** to demonstrate the efficiency of utilizing the natural mixture of rare earth oxides (derived from natural monazite concentrate) instead of individually used rare earth oxides as dopants in the design of zirconia-based electrolytes for Solid Oxide Fuel Cells (SOFC). This is intended to contribute to the efficient utilization of critical raw materials.

To ensure the achievement of the main objective of the doctoral thesis, the following **five specific objectives** were considered:

- **Objective 1:** Elaboration of a literature review on obtaining zirconia doped Solid Oxide Fuel Cells (SOFCs) with rare earth elements;
- **Objective 2:** Elaboration of a literature study on rare earths; current state of research on the importance of rare earths (REE) at European level;
- **Objective 3:** Obtaining the natural mixture of rare earth oxides REO from monazite;

- **Objective 4:** Obtaining and characterizing powder materials based on zirconia doped with 8 % natural mixture of REO;
- **Objective 5:** Obtaining and characterizing zirconia-based pellets and thin films doped with 8 % natural mixture of REO.

3.2. Research methodology

Within the National Institute of Research and Development for Non-ferrous and Rare Metals - IMNR were designed and realized the research methodology, the work plan, the experiments and the actual characterizations, and within the National Institute of Research and Development for Metals and Radioactive Resources - ICPMRR Bucharest was carried out the process of extraction of the REO from monazite.

The doctoral thesis **work plan** consists of two parts that aim to achieve specific objectives.

The first part presents the current state of knowledge, which is divided into chapters one and two, in which the current state of the research theme is presented, based on a laborious documentation of research in the field.

The second part of the thesis is given by the author's personal contribution, divided into chapters three, four and five. In this part are presented the experimental research from the doctoral thesis. Table 3.1 presents the research methodology of the thesis.

During the doctoral thesis was aimed to achieve the following targets:

- ✓ Obtaining from monazite a quantity of **203.8 g** rare earth hydroxides;
- ✓ **3 powder types** based on zirconia doped with 4% Y_2O_3, 8% Y_2O_3 and 8 % mixed natural mixture of REO from monazite: *4ZrY, 8ZrY, 8ZrMZ;*
- ✓ **types of pressed pellets:** *P1-4ZrY_1, P1-4ZrY_2, P1-4ZrY_3, P1-4ZrY_4, P1-4ZrY_5, P1-4ZrY_6, P2-8ZrY_1, P2-8ZrY_2, P2-8ZrY_3, P2-8ZrY_4, P2-8ZrY_5, P2-8ZrY_6, P3-8ZrMZ_1, P3-8ZrMZ_2, P3-8ZrMZ_3, P3-8ZrMZ_4, P3-8ZrMZ_5, P3-8ZrMZ_6.*
- ✓ **18 types of sintered pellets:** *P1-4ZrY, P2-8ZrY, P3-8ZrMZ, T=/1200/1300/1400 °C;*
- ✓ **1 sample type thin film:** *F_8ZrMZ*

In the 8ZrMZ sample, 8 % by weight of Y_2O_3 commonly used as a dopant for SOFC was replaced by 8 % natural REO mixture obtained from monazite.

In the present study, the most relevant investigation methods and techniques were employed to provide results demonstrating the potential use of the natural mixture REO (Rare Earth Oxides). These methods included chemical analysis of powders, microstructure analysis, morphology studies, thermal stability assessments, and specific surface area analysis.

Based on the powder, sintered compacts were produced in three stages (at 1200 °C, 1300 °C, 1400 °C), and their morphology, microstructure, and density were studied. The batch of compacts with the highest density (sintered at 1400 °C) was selected for determining the electrochemical properties. Thin films based on 8ZrMZ were morphologically and structurally characterized. The stages underlying the development of doctoral theses are shown below in Figure 3.1.

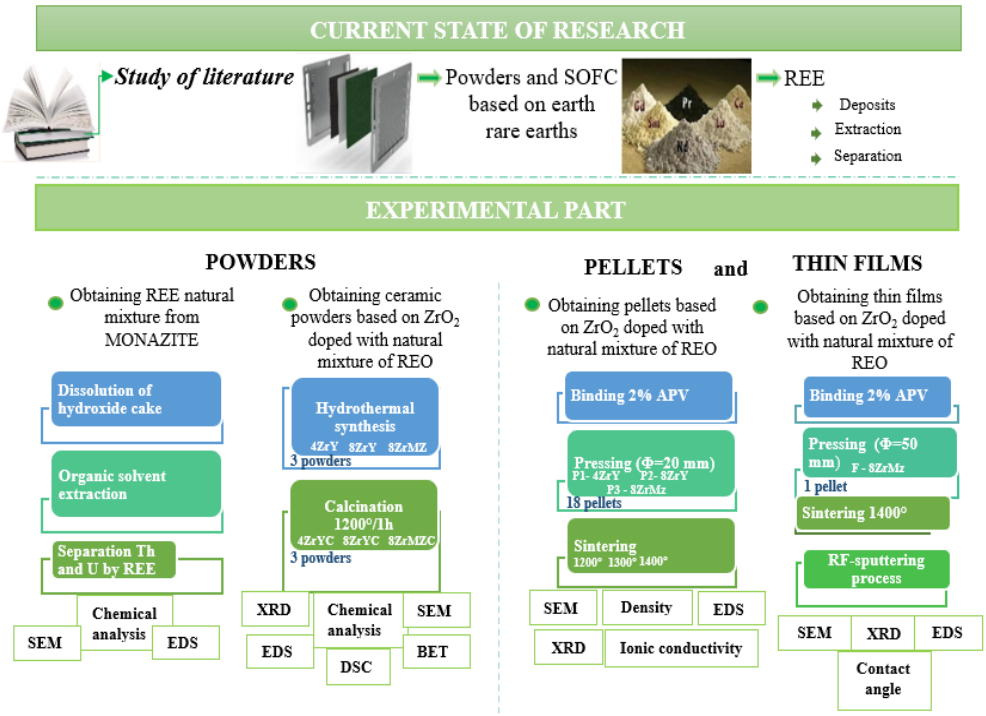

Figure 3.1. Schematic representation of the work plan.

CHAPTER IV. OBTAINING AND CHARACTERIZATION OF RARE EARTH OXIDES FROM MONAZITE

4.1 Methods used to obtain the rare earth oxides from natural sources

Several methods have been proposed for the extraction of Rare Earth Oxides (REO) from monazite, including both chemical and physical methods. The most promising chemical methods

that have been extensively studied are the **alkaline method** (leaching with NaOH) and **liquid-liquid extraction.**

Both methods have shown promising results, but further research is needed to optimize the process and make it more effective [159].

4.1.1 Alkaline method of obtaining REO

In the present study, the factors influencing the leaching efficiency of monazite were determined. These factors include particle size, sodium hydroxide concentration, reaction temperature, and reaction time. Optimal parameters for the alkaline leaching phase were established as fine particle size (0.011 - 0.04 mm), 50% sodium hydroxide solution, a sodium hydroxide to monazite ratio of 1.5:1, a reaction time of 2 hours, and a reaction temperature of 150°C. The results indicated that the efficiency of alkaline leaching increases with decreasing particle size. The resulting reaction mixture exhibits a highly viscous consistency and contains metal hydroxides, sodium phosphate, and excess sodium hydroxide. The mixture was diluted, matured and decanted to remove phosphate ions and excess sodium hydroxide. The reaction mixture was also washed several times to separate the phases in optimal conditions.

4.1.2 Liquid-liquid extraction

The next steps involved dissolving the hydroxide cake, extracting with organic solvents, and separating thorium and uranium from rare earth elements. To obtain a solution containing the elements of interest, the hydroxide cake was completely dissolved in concentrated hydrochloric acid.

The extraction of the key elements was carried out by adding 34% hydrochloric acid (HCl) to the settled suspension. Reaction conditions were maintained at 60°C for 1 hour, with a consumption of 2.3 L HCl per 1 kg of monazite. The resulting solution was characterized by a final free acidity of 3.5 N. To achieve phase separation, the hydrochloric acid solution underwent a maturation process at 80°C for 2 hours, followed by the decantation of residues for 90 minutes. Subsequently, the solution underwent repulping with 3.5 N HCl at a ratio of 1:0.2 S:L, maintaining a temperature between 70-80°C. The washing solution was then mixed with the initial hydrochloric acid solution and subjected to a filtration process to obtain the final product.

Then, the liquid-liquid extraction method was employed to separate thorium from REE. The extraction solvent used, which exhibited high selectivity for Th (IV), was **D2EHPA** in kerosene.

The technological parameters were as follows: 20% D2EHPA extraction agent in organic kerosene, aqueous-to-organic ratio – 1:2, number of extraction stages – 6, and aqueous phase acidity – 3.5N HCl.

The raffinate obtained through extraction with D2EHPA is preserved for the precipitation of lanthanide hydroxides.

Ammonium hydroxide was used for the precipitation of lanthanide hydroxides, and the resulting precipitate was then filtered, dried, and analyzed [159].

4.2 The working methodology

The extraction of rare earth hydroxides (REO) from monazite, Jolotca-Ditrau region in Romania was carried out in two stages (Figure 4.1).

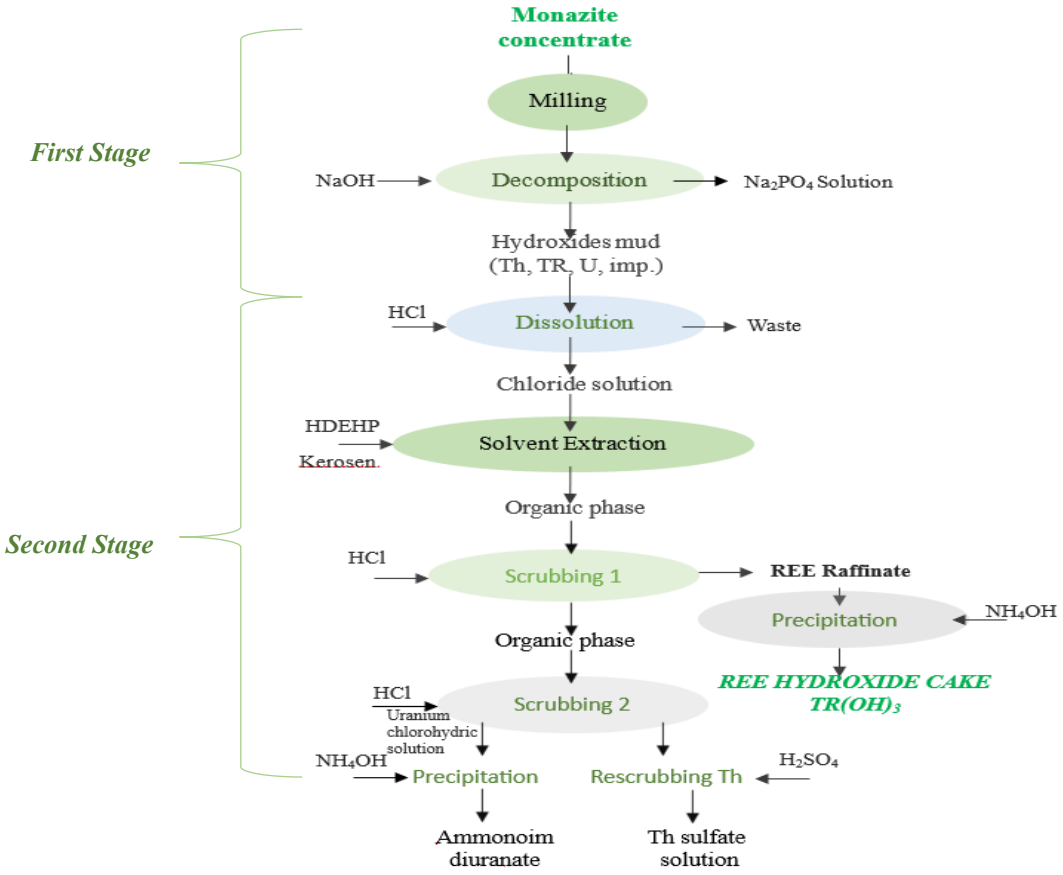

Figure 4. 1. Scheme for obtaining the natural mixture of REO from monazite [159].

4.3 Characterization of the obtained materials

In the first part of the research, the hydroxide cake was successfully obtained, and the results are presented below:

4.3.1 Chemical analysis

Table 4.1 presents the chemical analysis of the monazite concentrate on which the experiments were conducted. The presence of Th, U and REE has been confirmed.

Table 4.1. Chemical composition of monazite concentrate

Sample	U (%)	Th (%)	REE (%)	Si (%)	P (%)	Na (%)	K (%)	Ca (%)	Mg (%)	Zr (%)	Cu (%)	Pb (%)	Zn (%)	Cd (%)	Fe (%)	Al (%)
Monazite Concentrate	**0.1874**	**2.77**	**43.99**	**29.99**	**2.86**	**-**	**0.40**	**2.13**	**0.09**	**5.42**	**0.0076**	**0.10**	**0.0117**	**0.0004**	**0.99**	**0.82**

4.3.2 Granulometric characterization

The test was conducted in a humid environment at a temperature of 200°C, with a concentration of 0.05 mg/ml and 120,000 particles/ml. The measurement lasted for 5 seconds with a frequency of 200 Hz and a rotation speed of 12,000 RPM. Over 95% of the material had a particle size smaller than 6.86 microns, and the average particle size was 4.29 microns. The histogram indicates that the majority of particles fall within the size range of 3-6.86 μm (70%).

4.3.3 Analysis of the sedimentation of precursor materials.

In the second stage, the dissolution of the hydroxide cake (TR) was performed, followed by extraction with organic solvents and separation of thorium from rare earth elements.

Almost all of the Th and U content was extracted with the organic solvent. Regarding the REE content, it is observed that almost all of the quantity from the hydrochloric acid wash is found in the raffinate.

The refined solution was precipitated with ammonium hydroxide and filtered. The result of the chemical analysis is presented in Table 4.4

Table 4.4. Chemical composition of the precipitate obtained

Element	U (%)	Th (%)	REE (%)	Si (%)	K (%)	Ca (%)	Mg (%)	Zr (%)	Cu (%)	Pb (%)	Zn (%)	Fe (%)	Al (%)	P (%)	Na (%)	Cr (%)
Monazite Concentrate	**<0.001**	**0.001**	**30.99**	**0.006**	**<0.002**	**0.36**	**0,08**	**<0.002**	**<0.002**	**0.080**	**0.003**	**2.46**	**0.35**	**0.56**	**0.08**	**0.0076**

The images obtained through scanning electron microscopy revealed granular aggregates formed from fine particles with irregular shapes (Figure 4.13). Semi-quantitative chemical analyses using energy-dispersive X-ray spectroscopy (EDS) for the obtained precipitate confirmed the presence of rare earth elements: La, Ce, Gd, Nd, and Sm. It is important to note that the identification of Au in the samples is attributed to metallization, which is necessary to enhance conductivity during SEM-EDS analysis.

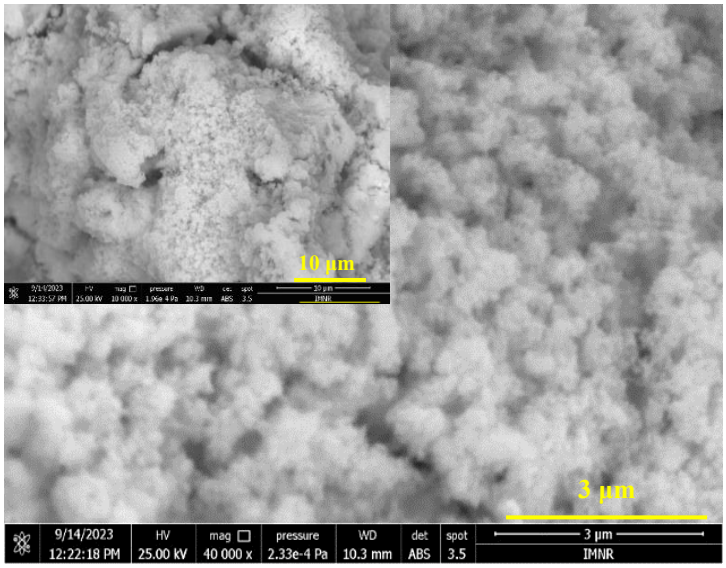

Figure 4.13. Analysis of the SEM of the precipitate obtained.

The X-ray diffraction (XRD) analysis of the obtained precipitate highlighted a cubic phase and a metastable hexagonal phase (Figure 4.16). The main phase of the precipitate is cubic iron oxide with cubic rare earth elements (REE), while the secondary phase is hexagonal lanthanum hydroxide. The major element underwent hydration, and the REE mixture formed a compound with a perovskite-like structure of the type $REFeO_3$.

CHAPTER V. OBTAINING AND CHARACTERIZATION OF MATERIALS IN THE FORM OF POWDERS, COMPACTS, AND THIN FILMS BASED ON ZIRCONIA DOPED WITH A NATURAL MIXTURE OF RARE EARTH OXIDES

5.1 The obtaining of powders based on zirconia doped with rare earth oxides

5.1.1 Hydrothermal process

The synthesis of powders was carried out in a single step using the hydrothermal method, at moderate temperatures (maximum 250°C) and moderate pressures (maximum 40 atm).

The raw material used to prepare a stock solution with a programmed concentration of Zr was zirconium tetrachloride (ZrCl4 99% Merck). Dissolution of the REO precursors in the $ZrCl_4$ solution took place under strong mechanical stirring until a homogeneous transparent solution was obtained.

A 25% NH3 solution was used as a mineralizing agent, added until an alkaline suspension with pH~9 was obtained. pH measurement was continuously performed using a digital pH meter. A Berghof autoclave was used for obtaining the doped powders. Three types of solid precipitates were obtained after completion of the hydrothermal process. These precipitates were subsequently washed and filtered to remove soluble impurities, then dried in an oven until a constant weight was achieved (temperature of 110°C). The process scheme of the hydrothermal synthesis used for obtaining REO-doped powders is presented in Figure 5.1.

The hydrothermal treatment of REO-doped powders occurs in two stages: 1. Dissolution-oversaturation and 2. Crystallization.

The dissolution of precursors in the first stage of the process is influenced by both temperature and pressure. These two variables play an important role in the formation of chemical species in solution, which subsequently react to obtain the desired product.

At the beginning of the process, when the temperature is raised, the hydrolysis of Y_2 salt precursors and the natural REO mixture produce hydroxides. When the system reaches a higher temperature, the Y_2 hydroxides/natural REO mixture are dehydrated, producing Y_2 oxide/natural REO mixture

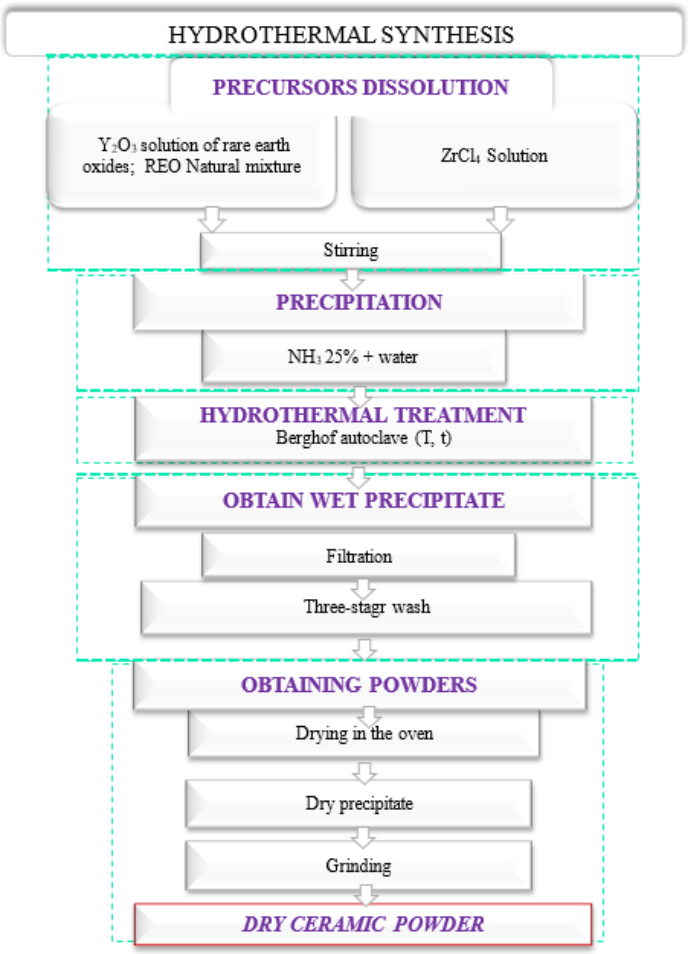

Figure 5. 1. The hydrothermal process scheme for zirconia powders doped with a natural mixture [68].

This is due to the decrease of the dielectric constant of the water and the increased solubility of oxygen due to critical conditions.

In the crystallization phase, particle growth occurs by re-dissolution and precipitation of the pre-existing phases. The growth of kinetically favored intermediate phases and their nucleation can take place after the preferred phase has formed, if the process conditions are maintained for longer periods of time.

The following powders were obtained using the process described above: 2 types of powders with a single rare earth element utilized as dopant: 4ZrY and 8ZrY and 1 type of powder with a natural mix of rare earths obtained from monazite: 8ZrMZ.

The obtained powders were characterized by chemical composition (ICP-OES), morphology and microstructure (SEM), phase purity (XRD) and thermal stability (DSC).

5.1.2 Thermal treatment of the powders

The obtained samples were heat treated at 1200° C, for 60 minutes, which is considered optimal. The resulting powders were characterized by chemical composition (ICP-OES), morphology and microstructure (SEM), phase purity (XRD) and specific surface (BET).

5.1.3 Obtaining and sintering the pellets

The powder and the binder (2% APV, 5% concentration) were mixed in a recipient using a spatula and a few drops of distilled water. Afterwards the resulting slurry was introduced into a centrifugal mixer ARE 250 THINKY for 3 minutes at 2000 rpm. (in order to obtain a homogenous slurry). The slurry was then tried in an oven at 110°C, for ~ 24 hours till it was dried completely. The obtained material was then grinded in order to obtain a fine powder. A hand press was used in order to obtain pellets with about 20 mm diameter. Three types of pressed pellets were obtained, named: P1-4ZrY, P2-8ZrY, P3-8ZrMZ.

The sintering process was done in 3 distinct steps. In the first two steps, the decomposition of the binder took place. According to literature and subsequent research, it is well established that the APV binder undergoes decomposition in a temperature interval situated between 300 and 500° C [15]. In the last step the sintering was performed at the 1200°, 1300° and 1400° temperatures.

5.2 Characterization of powders based on ZrO_2 doped with the natural REO mixture

5.2.1 Results obtained on the powder material

Chemical analysis

The chemical analysis of the hydrothermal synthetized powders is present in table 5.1 and is according to the calculated composition.

Table 5.1. Chemical analysis of powders based on doped ZrO_2.

Sample	Y (%)	Zr (%)	Nd (%)	La (%)	Gd (%)	Sm (%)
4ZrY	6.39	60.5	-	-	-	-
8ZrY	8.81	54.7	-	-	-	-
8ZrMZ	0.067	60.7	0.68	0.78	0.055	0.080

XRD analysis

The XRD spectra of the initial powders and the thermal treated powders are shown in the Figures 5.4 and 5.5. The quantitative phase analysis is shown in Table 5.2.

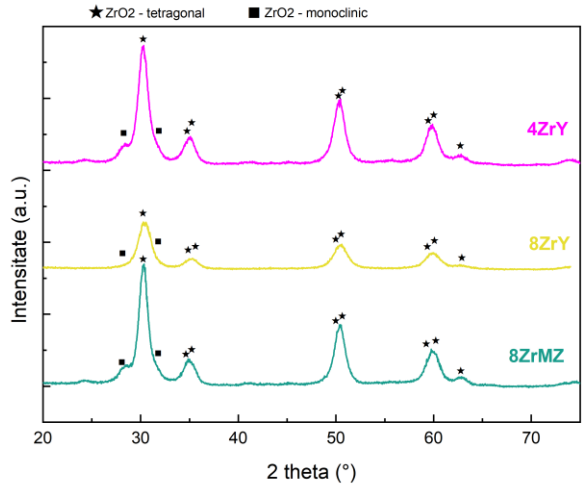

Figure 5.4. XRD analysis results for initial powders.

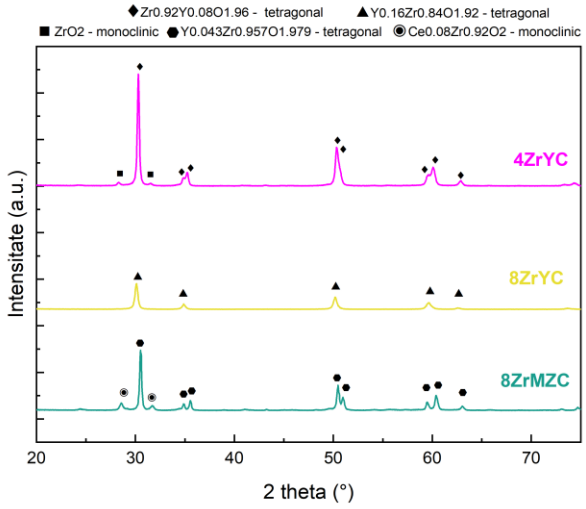

Figure 5.5. XRD analysis results for calcined powders.

Table 5.2. XRD quantitative phase analysis on the obtained powders, initial and after calcination.

Sample	Phase	Formula	The crystallization system	PDF file
4ZrY	Zirconium Oxide	ZrO_2	Tetragonal	PDF 04-013-0070
	Baddeleyite	ZrO_2	Monoclinic	PDF 04-013-6875
8ZrY	Zirconium Oxide	ZrO_2	Tetragonal	PDF 04-013-0070
	Baddeleyite	ZrO_2	Monoclinic	PDF 04-013-6875
8ZrMZ	Zirconium Oxide	ZrO_2	Tetragonal	PDF 04-013-0070
	Baddeleyite	ZrO_2	Monoclinic	PDF 04-013-6875
4ZrYC	Yttrium Zirconium Oxide	$Zr_{0.92}Y_{0.08}O_{1.96}$	Tetragonal	PDF 00-048-0224
	Baddeleyite	ZrO_2	Monoclinic	PDF 00-037-1484
8ZrYC	Yttrium Zirconium Oxide	$Y_{0.043}Zr_{0.957}O_{1.979}$	Tetragonal	PDF 04-010-3269
8ZrYMZC	Yttrium Zirconium Oxide	$Y_{0.16}Zr_{0.84}O_{1.92}$	Tetragonal	PDF 04-016-2113
	Baddeleyite, Ce-bearing	$Ce_{0.08}Zr_{0.92}O_2$	Monoclinic	PDF 04-006-7957

Powders 4ZrY and 8ZrMZ present a majority phase of tetragonal zirconium oxide and a secondary cubic zirconium phase, while the 8ZrY present only the tetragonal phase.

No specific peaks for Y/Y_2O_3 were identified in the doped samples, which shows that the dopant has been well incorporated in the crystalline structure of zirconia.

In the calcinated powders 4ZrYC and 8ZrMZC a mainly tetragonal zirconium oxide phase was identified defined by the (hkl) (101) (002) (110) (112) (200) (103) (211) (202) planes, and a secondary monoclinic phase, defined by (hkl) (-111) (111) planes.

Using the Scherrer formula (integral breadth), the average crystallite size along the [111] direction of all crystalline phases that appeared was calculated, denoted as *d*, and for evaluating the microstructure of the samples, the Rietveld method was used, in which they were integrated.

The average crystallite sizes for the 4ZrYC sample are in the range of 23.5-35 nm, for the 8ZrYC sample the average crystallite size is approximately 29 nm, and for the 8ZrMZC sample, the average crystallite sizes are in the range of 16.6-40.8 nm.

SEM analysis

The scanning electron microscopy images show that in all cases crystalline aggregates were formed. The aggregates are irregular in shape and are composed of fine particles of nanometric size. No significant growth of the granules was observed after calcination.

Figure 5.9, presents the morphology of the powder material before and after calcination.

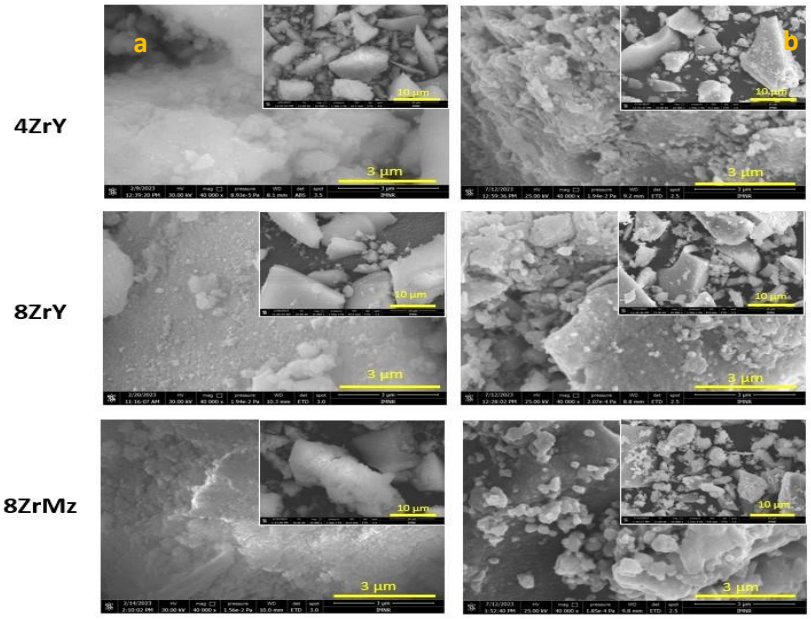

Figure 5.9. Representative SEM images at different sizes for 4ZrY, 8ZrY, 8ZrMZ initial powders (a) and (b) after calcination powders.

X ray energy dispersive spectroscopy (EDS) was utilized in order to determine the semiquantitative composition of the powder samples. The EDS analysis on the initial and calcinated powder confirm the presence of the doping elements. A small quantity of Au was identified, which is due to the applied surface coating in order to improve conductivity.

DSC-TG analysis

The thermal analysis was utilized in order to determine the chemical stability and the phase transformations during the thermal treatment of the hydrothermal obtained powders 4ZrY, 8ZrY, 8ZrMZ.

The DSC-TG graph of the powders heated from room temperature to 1450 ° C is shown in figure 5.13.

DSC-TG measurements performed on the three powder samples show a continuous mass decrease till around 600°C. Additionally, an endothermic peak can be seen at about 85°C. This shows an ongoing dehydration process in the material, which is in accordance with previous studies documented in literature [180].

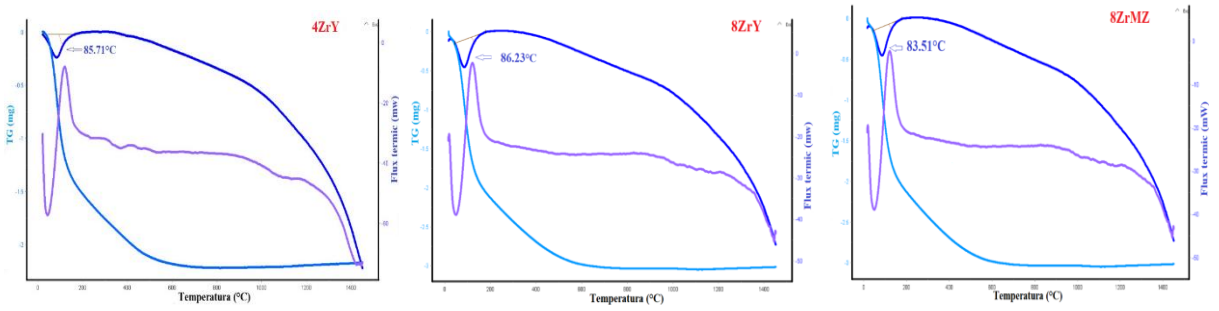

Figure 5.13. DSC-TG analysis of the 4ZrY, 8ZrY, and 8ZrMZ doped zirconia powders

BET analysis

Figure 5.14. presents the adsorption-desorption isotherms for powder samples 4ZrYC, 8ZrYC and 8ZrMZC calcinated at 1200 °C.

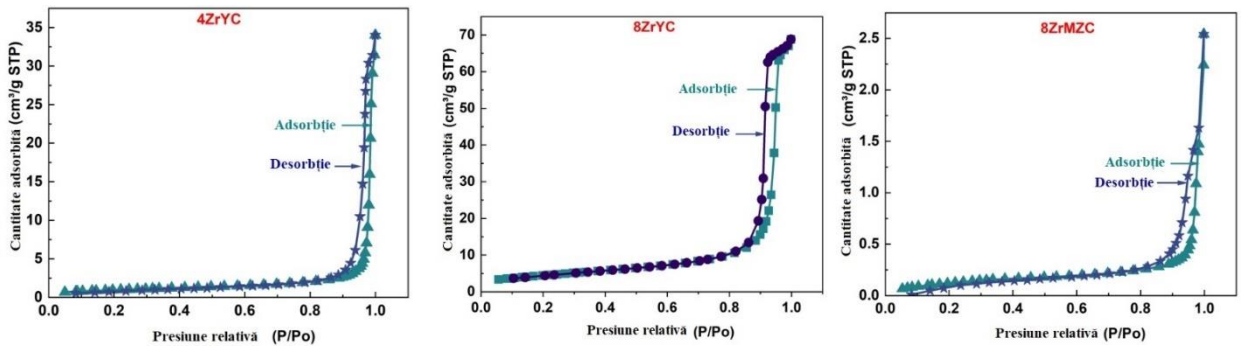

Figure 5.14. Nitrogen Adsorption ± Desorption isotherms for a) 4ZrYC, b) 8ZrYC c) 8ZrMZC, calcinated powders.

The method utilized to determine the specific surface, volume, porosity, and pore size is based on the physisorption of N2 gas at 77 K (-196 °C), with an adsorption-desorption isotherm. The measurements were performed using Micromeritics TriStar II Plus (Micromeritics Instrument Corporation, Norcross, GA, SUA) analyzer.

The calculated surfaces for the Brunauer-Emmett-Teller (BET) method for samples 4ZrYC, 8ZrYC și 8ZrMZ C are 3.4910 m²/g, 16.1432 m²/g and, 0.5047 m²/g. The distribution and pore dimension through the Barrett-Joyner-Helanda (BJH) method is 56.0085 nm (4ZrYC), 26.4404 nm (8ZrYC), 19.4368 nm (8ZrMZC).

TEM analysis

For the investigation of surface morphology and particle dimensions, transmission electron microscopy (TEM) was employed. Samples for TEM were prepared by dispersing them in methanol and placing a droplet of the suspension on a carbon-coated copper grid. TEM images of the samples are presented in Figure 5.14. From the figure, it can be observed that the doped ZrO2 particles are agglomerated and consist of irregularly shaped particles, with the grain size distributed uniformly at ~35 nm for the 4ZrY sample, ~30 nm for the 8ZrY sample, and ~40 nm for the 8ZrMZ sample. This type of morphology is suitable for obtaining sintered pellets that can be used as electrolytes for Solid Oxide Fuel Cells (SOFC).

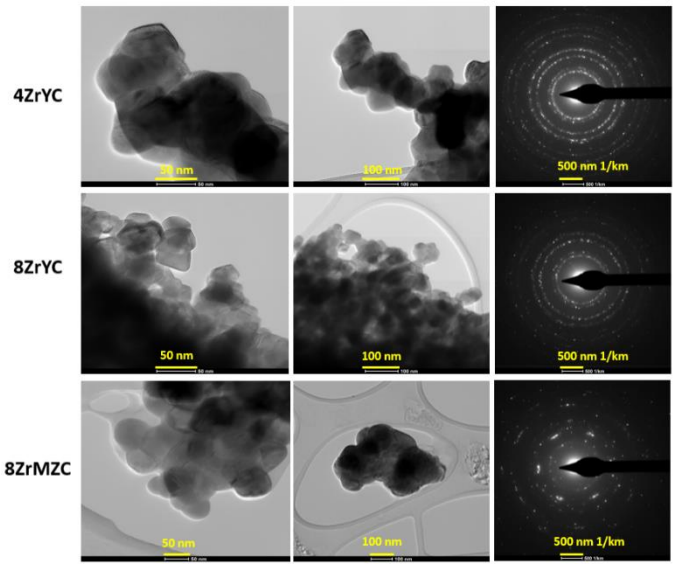

Figure 5. 15. TEM representative images for samples 4ZrYC, 8ZrYC, 8ZrMZC after calcination.

5.2.2 Pellets

SEM analysis

The morphology of the sintered pellets at different temperatures is presented in Figure 5.16.

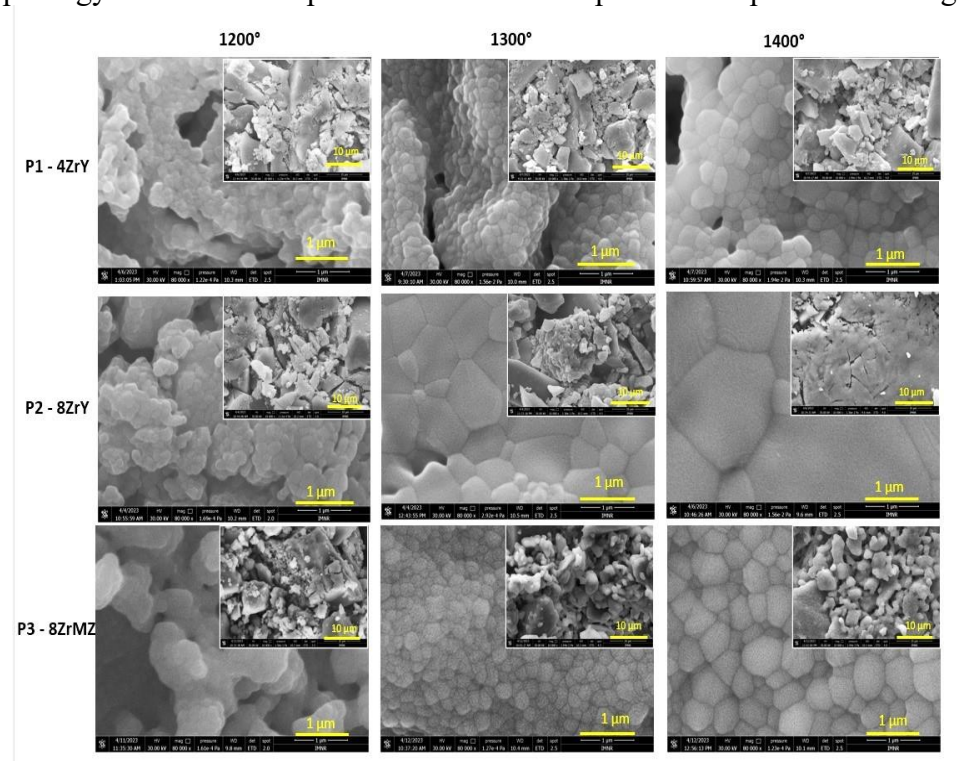

Figure 5.16. Representative SEM images at different magnifications for the pellets P1-4ZrY, P2-8ZrY, P3-8ZrMZ sintered at different temperatures.

Samples P1-4ZrY and P2-8ZrY sintered at 1200 °C, present porosity, with grain sizes between 172 and 216 nm for sample P1-4ZrY, and grain sizes between 200 and 222 nm for sample P2-8ZrY.

With increasing the sintering temperature, the grain size also increases:

For sample P1-4ZrY: (T sintering =1300°C): grain sizes vary between 243 nm and 425 nm; (T sintering =1400°C): grain sizes vary between 280 nm and 628 nm.

For sample P2-8ZrY: (T sintering =1300°C): grain sizes vary between 350 nm and 1.4 μm (micrometric); (T sintering =1400°C): grain sizes vary between 585 nm and 2 μm.

For samples sintered at 1200 °C P1-4ZrY and P2-8ZrY, the increase of dopant (from 4% to 8%) didn't have a significative impact upon the grain growth.

Sample P3-8ZrMZ, sintered at 1200 °C, did not show a uniform granulation begin formed. Instead, the sample presents an interconnected grain structure, with the presence of porosity. The particles have sizes ranging from 328 to 432 nm.

Increasing the sintering temperature led to the formation of a uniform grain structure for sample P3-8ZrMZ: At T sintering =1300°C: grain sizes vary between 276 and 317 nm, and for T sintering =1400°C: grain sizes vary between 550 and 700 nm.

Density

For samples P1-4ZrY, P2-8ZrY, sintering at 1400°C proved to be the most efficient in order to obtain higher density pellets. Sample P3-8ZrMz, has a slightly lower density than the others, which is probably due to the impurities present in the doping material.

According to literature [18], samples that are sintered below 1400°C do not achieve the necessary density due to a greater number of pores and large pore sizes. As the temperature increases to 1400°C, a denser microstructure is obtained, and only a small portion of the structure consist of closed pores. At temperatures higher than 1450°C, an over-sintering effect was observed, confirmed by the presence of cracks at the grain boundary and an increase in the size of pores which can be attributed to the increase in residual stress within the material.

As such, 1400°C was chosen as the optimal sintering temperature for this paper. Next, the samples sintered at 1400°C were characterized through XRD, and the crystallite dimension as well as the ionic conductivity was measured on these samples.

XRD analysis

The spectra resulting from the XRD analysis of the sintered pellets at a temperature of 1400°C are presented in Figure 5.22, and the quantitative phase analysis is provided in Table 5.5.

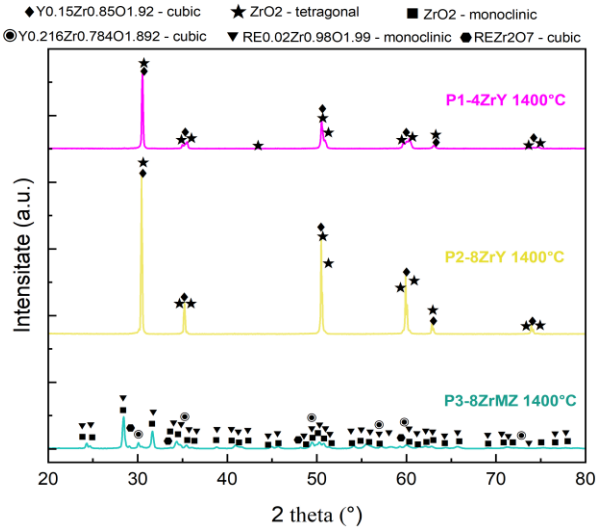

Figure 5.22. XRD analysis results for sintered pellets at 1400°C.

Table 5.5. Quantitative phase analysis for sintered pellets at 1400 temperature

Sample	Phase	Formula	Crystallization system	PDF file
P1-4ZrY 1400	Yttrium Zirconium Oxide	$Y_{0.15}Zr_{0.85}O_{1.92}$	Cubic	PDF 04-024-8010
	Zirconium Oxide	ZrO_2	Tetragonal	PDF 04-005-4207
P2-8ZrY 1400	Yttrium Zirconium Oxide	$Y_{0.15}Zr_{0.85}O_{1.92}$	Cubic	PDF 04-024-8010
	Zirconium Oxide	ZrO_2	Tetragonal	PDF 04-005-4207
P3-8ZrMZ 1400	Gadolinium Praseodymium Zirconium	$RE_{0.02}Zr_{0.98}O_{1.99}$	Monoclinic	PDF 04-024-8698
	Baddeleyite	ZrO_2	Monoclinic	PDF 04-004-4339
	Yttrium Zirconium Oxide	$Y0_{.216}Zr_{0.784}O_{1.892}$	Cubic	PDF 04-024-6811
	Gadolinium Lanthanum Zirconium Oxide	$REZr_2O_7$	Cubic	PDF 04-020-2892

The structures observed through XRD for the hydrothermally treated samples correspond, based on the ICDD database, to specific forms of ZrO_2. In the case of samples P1-4ZrY 1400, P2-8ZrY 1400, and P3-8ZrMZ 1400, after sintering, phases of ZrO_2 with the presence of yttrium are identified. The phase transition towards the stabilized form is influenced by the Y content, with a reduction in the proportion of the monoclinic phase due to the addition of rare earth elements.

The crystal sizes of the sintered pellets were calculated using the model described for the powders obtained after the hydrothermal treatment.

Electrochemical Properties

Figure 5.29 presents Nyquist plots for samples P1-4ZrY, P2-8ZrY, and P3-8ZrMZ at temperatures ranging from 500 to 800 °C. An equivalent circuit with two resistors, R1 and R2, and two capacitors, C1 and C2, was employed. This technique utilizes electrical properties to separate the individual effects of components (mass and grain size). The complex impedance, Z, consists of Z' (resistive component) - the real part, and Z'' (capacitive component) - the imaginary part of the impedance.

In the case of sample P3-8ZrMZ, a semicircle is prominent in the temperature range of 500-700 °C, and at 800 °C, a second semicircle begins to appear. Since only one semicircle is observed, it is closely related to the grain contribution, indicating a distinct electronic property in conductors [18].

For samples P1-4ZrY and P2-8ZrY, the Nyquist plot shows the appearance of two overlapping semicircles, indicating the contribution of both grains and their boundaries. As the temperature increases, it is evident that the semicircle becomes more complete. With the temperature rise, there is a tendency for impedance values to decrease towards higher frequencies.
The NOVA 2.1 software was utilized to adjust the parameters of each element in the mixed circuit.

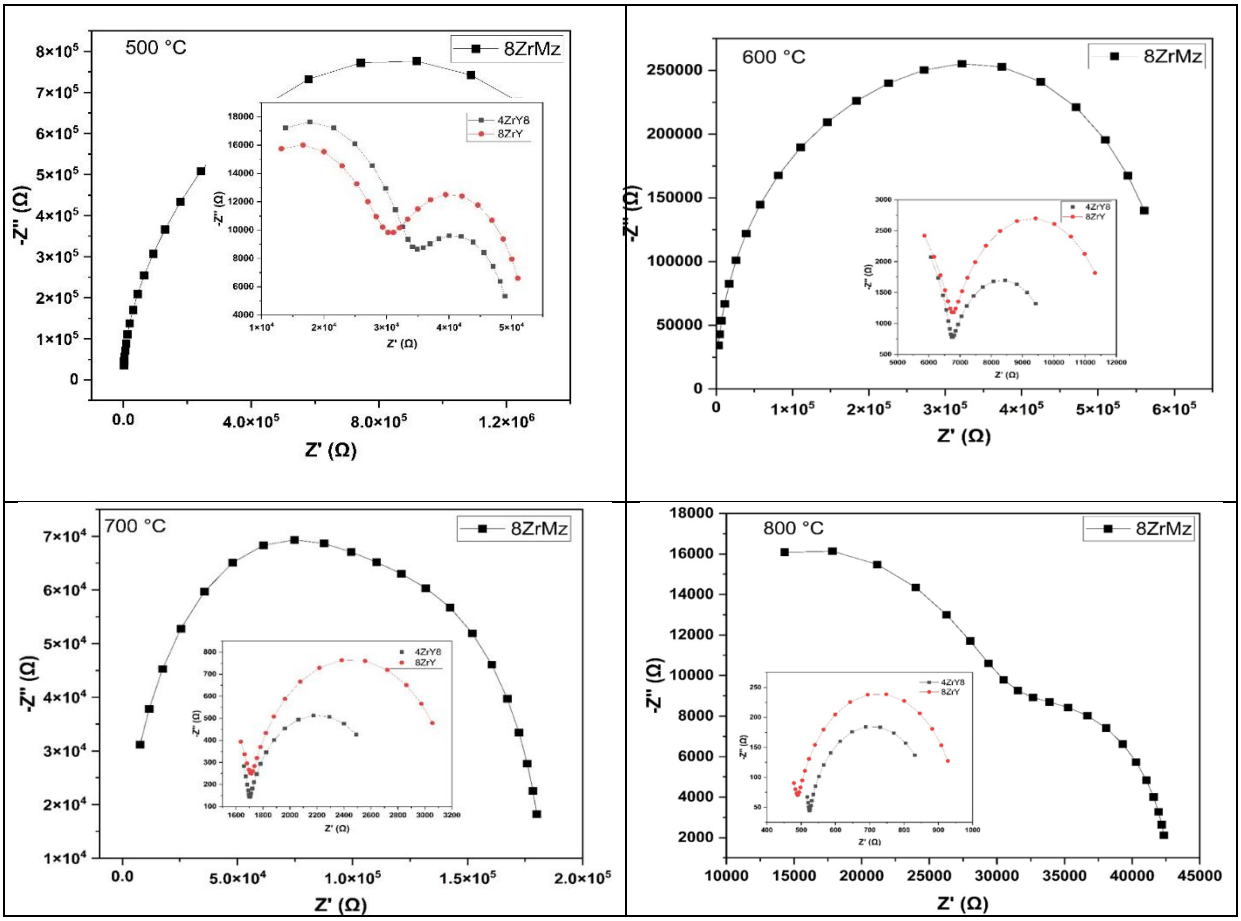

Figure 5.29. Nyquist Charts for samples P1-4ZrY, P2-8ZrY, P3-8ZrMZ, 500-800° C.

The first parallel circuit corresponds to the resistance of grain contribution (R1) and the capacitance of grains (C1). The second parallel circuit, R2 and C2, represents the resistance of grain boundaries and corresponds to the capacitance of grain boundaries. The values of grain and grain boundary resistances decrease with increasing temperature for all ceramics. This may indicate the existence of a thermally activated conduction mechanism, both within the grains and at their boundaries [19].

5.3 Obtaining thin films through the RF Sputtering method

The target used for RF sputtering was 8 mol% yttria-stabilized zirconia with an 8% rare earth mixture obtained from monazite (8ZrMZ), with a diameter of approximately 50 mm and a thickness of 5 mm. This target was obtained by pressing the powder, followed by calcination.

The pellets were bonded to a copper metal support using a thermally conductive epoxy resin with silver (Ag), aiming to prevent overheating and cracking of the pellets. Silicon plates were employed as substrates, which were subsequently cleaned and degreased in an ultrasonic bath with alcohol. Afterward, they were mounted and attached to the mounting support using Kapton tape. During the process, the silicon substrate was rotated to ensure a good homogeneity of thickness and film quality. Material deposition was achieved by sputtering the target with argon plasma.

The vacuum reached before deposition was $5*10^{e-6}$ Torr, while the working vacuum was $2 * 10^{e-3}$ Torr. The distance between the target and the substrate was fixed at 10 cm. The deposition power was 100 W, and the Ar flow rate was 50 ml/min. The entire deposition process lasted for 2 hours.

5.4 Characterization of thin films

SEM analysis

The thin films obtained through the RF sputtering technique were created for future research in the context of obtaining thin films for potential low-temperature Solid Oxide Fuel Cell (SOFC) applications. Figure 5.35 is the SEM image of the thin film sample F_8ZrMZ, deposited on a silicon substrate through the RF sputtering process.

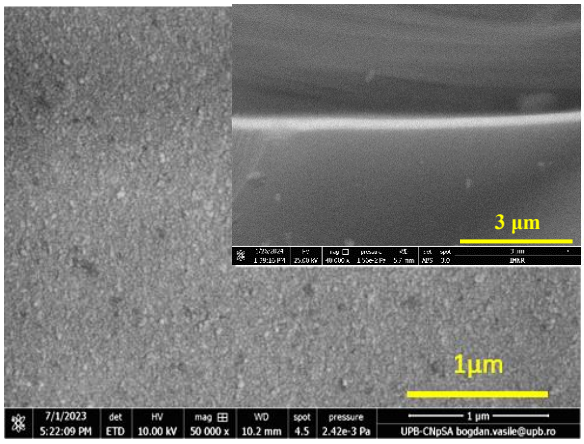

Figure 5.35. Surface and section SEM image of thin film F_8ZrMZ deposited on a silicon substrate by RF sputtering process.

The picture shows that the obtained film is continuous, dense and uniform. The grain size is between about 13 and 22 nm, and the layer size is about 333 nm.

XRD analysis

The spectrum resulting from the XRD analysis on the thin film is shown in Figure 5.39.

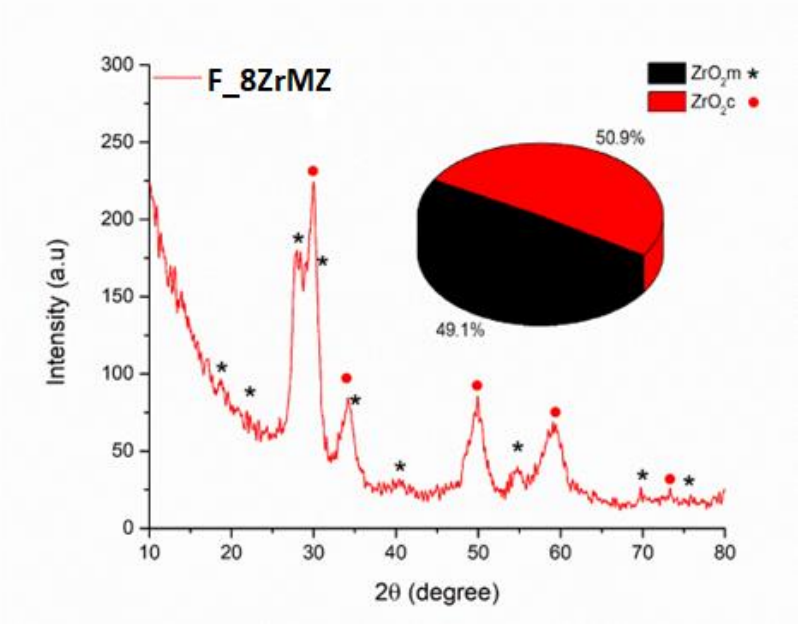

Figure 5.39. XRD spectrum for thin film F_8ZrMZ deposited on a silicon substrate by RF sputtering process.

Rietveld analyses revealed a quantity of 50.9% crystallized ZrO2 in the cubic system (PDF 00-049-1642) and 49.1% crystallized ZrO2 in the monoclinic system (PDF 00-007-0343). Zirconia thin films obtained through RF sputtering highlight the development of zirconia phases depending on the sputtering power and pressure. Preferential growth of zirconia layers is observed. At low power and high pressure, a columnar structure develops, while high power and low sputtering pressure favor the growth of randomly oriented polycrystalline structures.

Analysis of Contact Angle

The wettability and surface free energy of the thin films were investigated based on contact angle (CA) measurements with two wetting agents (water and ethylene glycol (EG)).

The average contact angle value on the F_8ZrMZ sample in the water working environment was 95.51°, and in the ethylene, glycol working environment, it was 72.71°. The surface free energy was calculated as 23.44±2.91 m N/m, indicating that the surface is hydrophobic

CONCLUSIONS, PERSONAL CONTRIBUTIONS AND RESEARCH DIRECTIONS

Conclusions

The aim of the doctoral thesis, titled "The Influence of Natural Rare Earth Mixture on the Structure of Zirconia with Potential Applications in Solid Electrolytes," was to analyze the possibility of using naturally occurring mixed rare earth mixtures, exactly as extracted from monazite, as dopants for ZrO2, with potential applications in solid oxide fuel cells. The use of natural mixtures of rare earth oxides as dopants could have a fundamental impact on their efficient use, avoiding increased costs and environmental issues associated with separating them into individual chemical elements.

The first step involved obtaining the naturally blended purified rare earth element (REE) hydroxide mixture. These elements were successfully extracted from the monazite ore originating from the Jolotca-Ditrău area, Romania, using the described procedures. The total recovery efficiency for the entire dissolution process with HCl of the hydroxide cake was 46.09% for REE, while the total removal efficiency for Th was 99.98%, and for U, it was 99.73%.

The extraction of Th from the HCl solution was performed using the D2EHPA/kerosene mixture as a solvent. From 1 kg of monazite ore, after precipitation with ammonium hydroxide, 203.8 g (46.28%) of REE hydroxides were obtained, and approximately 0.22 g of Th hydroxide was retained in the organic solution.

The next step involved the use of the natural mixture obtained in the synthesis process. For this purpose, zirconia doped with the natural mixture of rare earths (8ZrMZ) was synthesized using hydrothermal synthesis. The samples 4ZrY and 8ZrY were synthesized under the same conditions, serving as standards in commercial SOFCs.

The powders obtained, both the initial ones and those calcined, consist of granular aggregates composed of fine particles exhibiting tetragonal and monoclinic symmetry. It was noted that when the specific surface area of the fine zirconia powder increases from approximately 0.5 to 16 m^2/g (corresponding to a decrease in the average particle size), the densification rate improves, while an increase in grain growth was also observed. The crystal size of these powders

do not differ from the particle size calculated based on selected-area electron diffraction (SAED) measurements.

The study of the sintered compacts was conducted in the temperature range of 1200-1400°C. All the samples studied exhibited theoretical densities higher than 96% for the compacts sintered at 1400°C, with grain sizes ranging from 280-2000 nm. Semi-quantitative EDS analysis of the sintered compacts confirmed the presence of the dopant elements considered in the synthesis.

The sintered compacts at 1400°C were used for the electrochemical study through impedance spectroscopy and X-ray diffraction. Comparing the Nyquist spectra for zirconia doped with REE sintered P3-8ZrMZ with P1-4ZrY and P2-8ZrY shows a clear difference between the conductivity mechanisms in the temperature range between 500 and 800°C.

There are two possible reasons for the lower ionic conductivity properties of zirconia doped with the natural REE mixture (P3-8ZrMZ) compared to zirconia doped with 4% and 8% yttrium: 1) the presence of impurities resulting from mixed doping with REE after the removal of thorium and uranium from the monazite concentrate, especially iron and silicon (approximately 0.5%), known to have a negative impact on ionic conductivity properties; 2) the ratio of REE in the dopant composition affects ionic conductivity due to the association of structural defects in complex defects.

The last step involved obtaining thin films through the RF sputtering technique. The target used for RF sputtering was zirconia stabilized with 8% rare earth mixture obtained from monazite (F_8ZrMZ). This target was obtained by pressing the powder, followed by calcination. The thin films thus obtained consist of cubic and monoclinic zirconia, with a grain size ranging from approximately 13 to 22 nm, having a continuous, dense, uniform, and hydrophobic surface.

Consequently, the highlighted results above emphasize that the use of zirconia doped with a natural mixture of rare earths has potential for applications in SOFCs if an efficient method of rare earth extraction from ore is pursued.

ORIGINAL CONTRIBUTIONS

Original contributions were made at each stage, starting with the comprehensive literature review, followed by the experimental steps: extraction of the natural mixed rare earth element mixture, development of ceramic powders, obtaining sintered pellets, and finally, the production of thin films in the last stage.

Listed below are the original contributions, extensively described throughout the PhD thesis:

- ✓ Elaboration of a *literature study* on the fabrication of Solid Oxide Fuel Cells (SOFC) based on ZrO2 doped with rare earth elements, focusing on areas of interest such as the impact of SOFC in the field of energy with an emphasis on the transition to green energy, types of fuel cells, materials used for solid electrolytes, zirconia, and sintering methods.
- ✓ Development of a *literature study* on rare earth elements; the current state of research on the importance of rare earth elements (REE) at the European level, focusing on areas of interest such as rare earth elements and their applications, deposits and distribution, minerals carrying rare earth elements, and methods for extracting rare earth elements from monazite.
- ✓ **Demonstrating the extraction potential of the natural mixed REO blend from monazite** for obtaining rare earth hydroxides used as dopants for stabilizing zirconia. Obtaining the natural mixed REO blend was a crucial step in conducting the experiments.
- ✓ **Demonstrating the potential use of the natural mixed REO blend for obtaining a ZrO_2-based powder material** (8ZrMZ) and a ZrO_2-based pellet material (P3-8ZrMZ) with promising properties for use in the development of Solid Oxide Fuel Cells (SOFC**).**
- ✓ **Demonstrating the feasibility of the natural mixture of rare earth oxides** for obtaining a type of thin film.

Future research activities

- To improve the electrochemical properties of REE-doped ZrO2, an additional purification of the initial REE mixture will be conducted to remove impurities, specifically Si and Fe, that affect ionic conductivity. The purified mixed REE hydroxides will then be used as dopants, following the procedures outlined in this thesis, and the electrochemical properties will be measured in the temperature range of 400-800°C.
- Additional studies will be conducted to map the influence of multiple REE concentrations on ionic conductivity properties. An active factorial experimental plan will be proposed, utilizing purified REE hydroxides, to assess the ionic conductivity of each compound and generate a "digital twin" of ZrO2-based materials doped with the natural REE blend.
- After obtaining the powders, they will be sintered using the spark plasma sintering (SPS) method, as it offers several advantages over conventional sintering methods. SPS allows for rapid processing with quick heating and cooling cycles, lower sintering temperatures, and more uniform heating, resulting in improved **densification** and **fine microstructures**.

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