University „Alexandru Ioan Cuza” from Iași

Faculty of Chemistry

OXIDES WITH PEROVSKITE-TYPE STRUCTURE. SYNTHESIS, CHARACTERIZATION AND PROPERTIES

Summary of the PhD Thesis

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Motto,

Do not try to do something unless you are sure of yourself, but do not give up simply because someone else is not sure of you.

Stewart E. White

Wish you success, not perfection. Never give up your right to be wrong because then you will lose the ability to learn new things and advance in life.

David Burns

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Keywords:

Sol-gel auto-combustion method, perovskite, IR, XRD, SEM, BET, dielectric properties, catalytic reaction for decomposition of hydrogen peroxide, the oxidation reaction of butanol, photocatalysis

CONTENTS

In this summary i will make a brief cross of the chapters presented in thesis, providing a thorough description of subsections II.1 and III.2.1 respectively, as follows.

I.THEORETIC CONSIDERATION

I.1. Introduction

Metal oxides with perovskite-type structure have attracted the attention of researchers because of the important technological applications due to outstanding physicochemical properties (*Bonilla, 2007*). Many papers reported study on physical and chemical properties of this kind of materials, such as magnetic properties (*García-Landa, 1999; Santos-García, 2013*) and diectric properties (*Nair, 2012; Bharti, 2010*) offer a wide range of technological application perspectives in the industries used in various fields such as catalysis (*Yamazoe, 1990*), fotocatalizǎ. Photocatalysis (*Hatakeyama, 2010*).

These materials were intensively studied in the recent years, especially due to their capacity to incorporate in their structure many elements such as alkaline earth (A-site), transition metal or lanthanide cation (B, B'-site). Therefore, the structure of these materials may be changed, especially due to octahedral tilting (BO_6, $B'O_6$), which building double perovskite-type lattice (*Aguilar, 2008, Blasco, 2009*).

It is a well-known that the properties of double perovskites compounds are strongly influenced by the physical properties, structure and microstructure which are sensitive to the preparation technique. To get materials with perovskite-type oxide structure which meets the requirements for various practical applications was developed sol-gel auto-combustion method (*Vijayakumar, 2009*).

The objective of this thesis was to prepare, using sol-gel auto-combustion method using tartric and citric acid as combustion agents, investigate the structural and dielectric and catalytic properties of the perovskite-type oxides.

I.2.Structure of perovskite-type oxide compounds

I.2.1.Perovskite type - oxides with the general formula ABO_3

First perovskite-type structure was found in natural mineral, $CaTiO_3$, which were assigned the general formula ABO_3 (*Woodward, 1996; Penã, 2001*)(figure1).

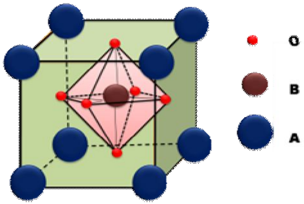


Figure 1. perovskite-type structure, ABO_3/(A = Ca, B = Ti)

Usually, A is a large cation (alkaline metals) surrounded by 12 oxygen anions while B corresponds to smaller heterovalent cations (transition metal or lanthanide cation) surrounded by six oxygen anion (*Woodward, 1996*).

I.2.2. Perovskite type oxides with the general formula $A_2BB'O_6$

The double perovskite type oxides with the general formula $A_2BB'O_6$ are derived from the ABO_3 perovskites, when half of the octahedral coordinated B-site cations are replaced by appropriate B′- cations (*Anderson, 1993*) (figure 2).

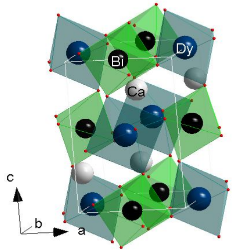


Figure 2. Double perovskite $A_2BB'O_6$ unde A=Ca, B=Dy, B′=Bi structure simulated with DIAMOND programe

As a measure for the deviation from the ideal perovskite structure by substitution of the cations in the positions A, B and B' was added to a factor called tolerance factor defined by the equation 1 (*Penã, 2001*)

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

were: r_A, r_B, r_O = ionic radius of cations and anion *(Shannon, 1976).*

I.3. Synthesis method of the perovskite-type oxides

Various synthesis techniques such as solid state (*Faik, 2012*), co-precipitation (*Jacobo, 2005*), hydrothermal (*Wu, 2010),* combustion (*Prakash, 2002*), microemulsion (*López-Trosell, 2006*), *microwave* (*Zhai, 2012*), sol-gel (*Huang, 2009*), sol-gel autocombustie (*Faik, 2008*) have been reported in the preparation of double perovskite compounds.

Of all these synthesis, the solid state is the most used in the synthesis of this kind of compounds because it is a relatively simple and uses oxides as reagent to obtain these types of compounds, but ineffective, due to the higher energy consumption of the procedure (*Retuerto, 2006*).

So, we use sol–gel auto-combustion method, for the preparation of the perovskite –type oxides and has been shown to have some advantajes:

- the reagents used in synthesis are inexpensive and readily available (nitrates);
- sintering temperatures are relatively low;
- the equipment used is simple.

Sol-gel auto-combustion method was used for the preparation of double perovskite-type oxide with general formula Ca_2BSbO_6, were B= Dy, Fe, Cr, Al using the tartric acid as chelating and fuel agent, according to the synthesis protocol described in figure 8.

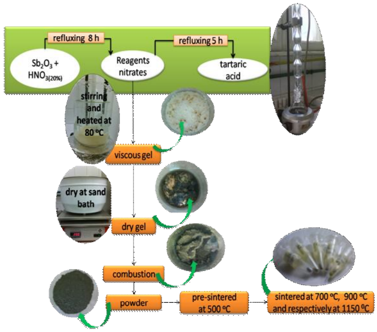


Figure 8. The synthesis flowchart for the preparation of all powders

I.6.4. Perovskite-type catalysts

In literature, polymetallic oxides with simple or double perovskite-type structure [ABO_3or $A_2BB'O_6$ (A = rare or alkaline earth, B and B '= transition metal of 3d, 4d or 5d)] subject this study are presented as materials with a wide range of application in different areas: electrochemistry, superconductivity, biosensors, etc.. and in the field of catalysis. Among the processes catalyzed by this type of compounds can be mentioned: the oxidation of carbon monoxide, of hydrogen, of methane (*Li, 2011*) and chlorobenzene; alkylation reactions and decomposition of alcohol and hydrogen peroxide (*Tejuca, 1989*) and photocatalytics (*Hatakyama 2010*).

PERSONAL CONTRIBUTIONS

II. Synthesis and structural characterization of perovskite-type oxides

II.1. Synthesis and structural characterization of Ca_2BSbO_6, (B = Dy, Fe, Cr, Al) serie

II.1.1. Sol-gel auto-combustion synthesis

For the preparation of Ca_2MSbO_6 (M = Dy, Fe, Cr, Al) double perovskite materials was used sol-gel auto-combustion method with high-purity starting materials as: $Ca(NO_3)_2{\cdot}4H_2O$, $Dy(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $Al(NO_3)_3{\cdot}5H_2O$, Sb_2O_3, HNO_3 and tartric acid, $C_4H_6O_6$ (Sigma-Aldrich) as combustion agent. All reagents used were of analytical quality from Merck production and were used without additional purification. Nitrate solutions were mixed in the appropriate stoichiometric proportion and the molar ratio of tartaric acid / mixed oxide was 3/1.

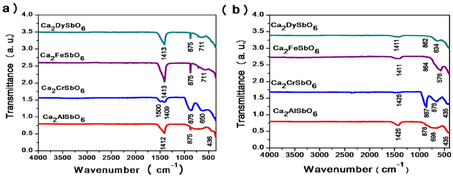
The first step of the synthesis procedure consisted in oxidizing the Sb_2O_3 to antimony (V) oxide with HNO_3 (20%) by refluxing process for 8h (*Brazidil, 1998; Patnaik, 2002*). Consequently, the rest of metallic precursors were added to the as-obtained solution and the refluxing process continued for 5h.

The homogeneous solutions of nitrates were transformed into gels, at 80 °C under continuous stirring, in the presence of the tartaric acid according to the synthesis protocol described in Fig. 8. Subsequently, the gels were heated on the sand bath up to 300°C, until the combustion was clearly observed and powders were obtained. After the combustion process, the powders were grinded and subjected to thermal treatments in four steps: at 500 °C and 700 °C each four 7 hours and at 900 °C for 9 hours in order to complete the double perovskite formation. Finally, in order to achieve pure double perovskite phases, the samples treated at 900 °C were pressed in disks and were sintered at 1150 °C for 9 hours.

The initiation and formation of double perovskite phase were monitored by IR-spectroscopy, by powder X-ray diffraction (XRD), microstructures of Ca_2BSbO_6 ceramic disks and Specific surface area, S_{BET}, were obtained from N_2-sorption isotherm.

II.1.2. Infrared spectroscopy analysis (IR)

IR spectra of powders treated at 500 °C, depicted in figure 9 (a), the specific bands for M-O stretching vibration in the range of 900-400 cm^{-1} were clearly observed. It should be noticed that the peak attributable to nitrate groups are present in the IR-spectra (around 1450 cm^{-1}), while the bands attributed to the stretching vibration of C=O bond of carboxyl ions (around 2395 cm^{-1}) are disappeared *(Lavat, 2003).*



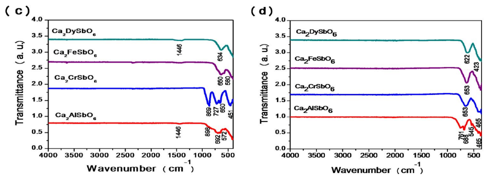


Figure 9. IR-spectra for Ca_2BSbO_6 powders treated at (a) 500°C/7h, (b) 700°C/7h, (c) 900°C/9h and (d) sintered disks at 1150°C/9h

The band attributed to the nitrate groups are less intense for the powders treated at 700°C (figure 9b). After treatment at 900°C (figure 9c) this peak is still observed only in the case of Ca_2AlSbO_6 and Ca_2DySbO_6 powders. The IR spectra of powders sintered at 1150 °C reveal only the specific bands for M-O stretching vibration (figure 9d) confirming the formation of double perovskites oxides phases.

Therefore, from figure 2(d) it can be observed the two strongest bands characteristic for anti-symmetric (υ_{as}) octahedral SbO_6 stretching vibration in the range 688-622 cm^{-1} and the octahedral SbO_6 deformations vibration in the range 465 - 423 cm^{-1}, respectively.

In the case of Ca_2AlSbO_6 powder, two supplementary shoulders, observed at 761 cm^{-1} and at 545 cm^{-1}, are attributed to AlO_6 deformations. The presence of these bands can be explained mainly by the fact that Al is lighter than Fe, Cr, and Dy, (A_{Dy} = 66, A_{Fe} = 26, A_{Cr} = 24, A_{Al} = 13, r_{Dy}^{3+} = 0,91Å, r_{Fe}^{3+} = 0,64Å, r_{Cr}^{3+} = 0,61Å, r_{Al}^{3+} = 0,53Å) and the increase of ionic radius of studied M cations (see Table 1) could determine a shifting towards smaller wavenumber of SbO_6 bands(*Vijayakumar, 2009a*).

II.2.3. X-ray diffraction characterization (XRD)

The recorded and simulated XRD patterns and the crystal structures of the powders sintered at 1150 ºC are shown in figures 11(a-d). The recorded patterns present sharp and well-defined peaks, indicating that the as prepared materials have a highly crystalline nature. Employing the programs SPuDS (*Lufaso, 2001*) and DIAMOND (*Bergerhoff, 1996*) the structural parameters were predicted and the theoretical XRD patterns and crystal structures were simulated. The structural parameters: evaluated by using SPuDS software and crystallite size (*D*) are summarized in Table 2.

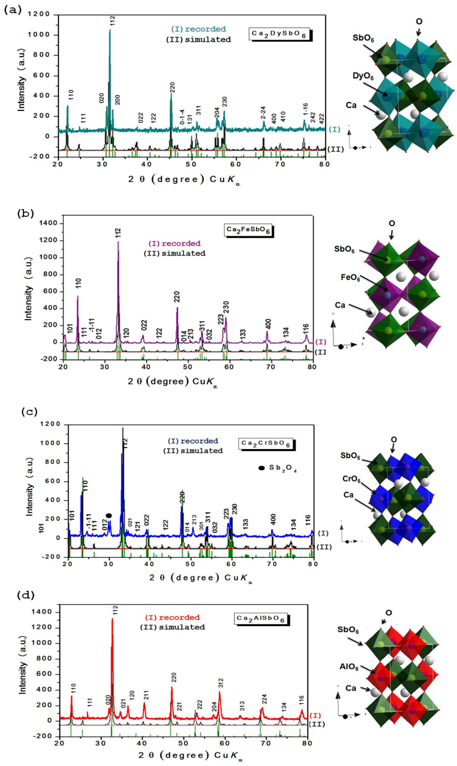


Figure 11. X-ray diffraction patterns of Ca_2BSbO_6 double perovskite

The stronger diffraction peak characteristic of double perovskite-type structure are at 2θ ≈ 32° attributable to the (112) diffraction planes, confirm the formation of double-perovskites phase for all studied samples. In the case of Ca_2CrSbO_6 powder, small peaks were observed at 2θ = 29.6° and 30.1°, suggesting the presence of Sb_2O_4 (orthorhombic system, COD ID: 1010922) as secondary phase. Can be seen from the analysis of Figs. 11, the theoretical XRD patterns of the $Ca_2\textit{B}SbO_6$ double perovskites are in very good agreement with the experimental ones.

The crystallite size was calculated from XDR patterns using Debye-Scherrer formula, described by the Eq. (2)

$$D = \frac{0.94 \cdot \lambda}{\beta_{1/2} \cdot \cos\theta} \tag{2}$$

where: D = crystallite size, λ = radiation length (1.5405 Å), $\beta_{½}$ = half widening of diffraction profile, θ = diffraction angle.

Tilt angle (φ) was calculated using Eq. (9) (*Triana, 2012*) and interatomic coordinates obtained from SPuDS program are summarized in Table 3.

$$\varphi = (180- \Phi)/2$$

were: φ- tilting angle of octhaedra,

ϕ – length andle B – O – Sb

Table 2. structural parameters obtained from SPuDS software and crystallite size

Sample	r_B^{3+} (Å)	*D* (nm)	*t*	Lattice parameter (Å)	*V* (Å^3)	*β* (°)
Ca_2DySbO_6	0.91	59	0.895	a = 5.644	272.63	89.949
				b = 5.918		
				c = 8.160		
Ca_2FeSbO_6	0.64	21	0.949	a = 5.536	247.45	89.999
				b = 5.651		
				c = 7.908		
Ca_2CrSbO_6	0.61	73	0.957	a = 5.517	243.57	90.000
				b = 5.611		
				c = 7.867		
Ca_2AlSbO_6	0.53	33	0.982	a = 5.456	232.02	90.001
				b = 5.493		
				c = 7.741		

From table 2 it can be observed a monotonous decreasing of lattice parameters and, consequently, the cell volume with the increasing of the B-site cation effective ionic radii (r_{Dy}^{3+} = 0.91 Å; r_{Fe}^{3+} = 0.64 Å; r_{Cr}^{3+} = 0.61 Å; r_{Al}^{3+} = 0.53 Å) (*Shannon, 1976*). The increase of the effective ionic radii of M-cation leads to decrease of the tolerance factor value and β angle value, which determines the distortion from the ideal cubic perovskite structure.

Table 3. Interatomic datas from SPuDS and tilt angle

Samples	*B(III)* – O (Å)	Sb(V) – O (Å)	ϕ(°)	φ (°)
Ca_2DySbO_6	2.268(2)	2.0090(2)	145	17.5
Ca_2FeSbO_6	2.026(2)	2.0094(2)	157	11.5
Ca_2CrSbO_6	1.991(2)	2.0095(2)	158	11
Ca_2AlSbO_6	1.887(2)	2.0095(2)	166	7

From **table 3** can be observed that the average *B* (III) – O bond length and the tilt angle (φ) are increasing with the increase of cations effective ionic radii. Instead, the average Sb – O bond length and the average *B*– O – Sb bond angles are decreasing with the increase of this parameter. With the tilt angle decreasing (from φ = 17.5° for Ca_2DySbO_6 to φ = 7° for Ca_2AlSbO_6) the *B*-O bond strength increases and the structure become more stable. It must be mentioned that the tilt angle and tolerance factor give contribution to the ideal cubic structure distortion of the double perovskites (*Fu, 2005*). When the tolerance factor value is smaller than unity, the compound presents a structure with a lower symmetry, different from the cubic one.

II.1.4. Scanning electron microscopy analysis (SEM)

II.1.4.2. Scanning electron microscopy in fracture

SEM images of the Ca_2BSbO_6 ceramic disk sintered at 1150 °C / 9 h are presented in figure 13 (a-d).

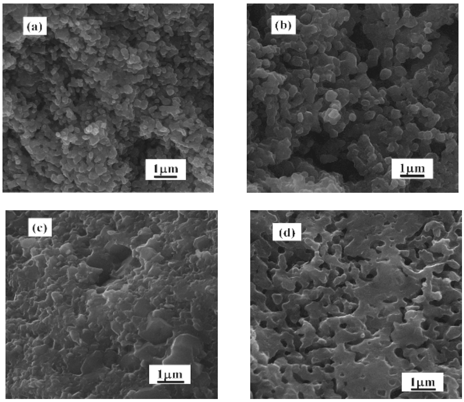


Figure 13. SEM images for (a) Ca_2DySbO_6, (b) Ca_2FeSbO_6, (c) Ca_2CrSbO_6, (d) Ca_2AlSbO_6

From these micrographs, can be observed nano-sized grains with quasi-spherical shape in case of Ca_2DySbO_6 (figure 13(a)) and Ca_2FeSbO_6 (figure 13 (b)) materials. SEM image for Ca_2CrSbO_6 sample (figure 13(c)) shows agglomerated particles with irregular shapes. Smaller grains with plate-like shapes and spongy surface were observed in case of Ca_2AlSbO_6 (figure 13 (d)) double perovskite.

Conclusions

Polymetallic oxides with perovskite-type structure has a wide range of properties so they can be used in various practical applications.

Thesis objectives consist in:

- performed polymetallic oxides with double perovskite-type structure by sol-gel auto-combustion obțінâdu the following series of compounds Ca_2BSbO_6 (B = Dy, Fe, Cr, Al) , Ca_2BBiO_6 (B = Dy, Fe, Cr, Al), $Ca_2Fe_{1-x}Sm_xBiO_6$ (x = 0; 0,2; 0,4; 0,6; 0,8; 1), A_2DyBiO_6 (A= Mg, Ca, Sr, Ba),
- analysis by infrared absorption spectroscopy and structural characterization by X-ray diffraction confirmed to obtain the title compound,
- the scanning eletronic microscopy revealed the microstructure of samples synthesized,
- catalysts are obtained with simple perovskite-type structure and the double perovskite and specific areas of the samples was determined by the BET method,
- catalyst obtained was tested in the reaction of the decomposition of hydrogen peroxide in the oxidation reaction in the reaction of butanol and bleaching of the dye Rhodamine 6G, light in the visible range.

Were made 27 synthesis of polymetallic oxides with perovskite-type structure according to the following series:

- perovskite -type oxide with the general formula Ca_2BBiO_6, were B = Dy, Fe, Cr, Al;
- perovskite -type oxide with the general formula Ca_2BSbO_6, were B = Dy, Fe, Cr, Al;
- perovskite -type oxide with the general formula $Ca_2Fe_{1-x}Sm_xBiO_6$ (x=0; 0,2; 0,4; 0,6; 0,8;1);
- perovskite -type oxide with the general formula A_2DyBiO_6 were A= Mg, Ca, Sr, Ba;
- perovskite - type oxide with the general formula $LaCrO_3$ and $LaCrO_3$/support (support = ZrO_2, TiO_2, Al_2O_3, SiO_2);
- perovskite - type oxide with the general formula $LaCr_{0,9}B_{0,1}O_3/ZrO_2$ (B= Mn, Fe, Co, Ni).

➢ <u>Ca_2BSbO_6, B = Dy, Fe, Cr, Al serie</u>

✓ Synthesis by sol–gel auto-combustion method using tartaric acid as fuel was reported.

- ✓ Disappearance of organic waste were monitored from IR spectra at different thermal treatments.
- ✓ Double perovskite phase formation, were were monitored from XRD patterns at room temperature and was found the best conditions for the synthesis of pure Ca_2BSbO_6 double perovskite materials (B = Dy, Fe, Cr, Al) correspond to a temperature of 1150 °C or higher and a sintering time of 9 h or longer. Experimental diffractograms for all compounds are in agreement with the theoretically simulated diffraction using the DIAMOND program considering the crystallographic data obtained using computer software SPuDs.
- ✓ The investigated cations cause an increase of crystallographic structure distortion as a function of increasing ionic radii. The strongest distortion of octahedral site occurred in Ca_2DyBiO_6 material as a result of the largest ionic radius of the Dy^{3+}cation.
- ✓ SEM micrographs show grains with different morphologies, like quasi-spherical for Dy and Fe containing materials, which lead to higher specific surface area, while spongy porous network with lower BET surface was observed for Ca_2CrBiO_6 and Ca_2AlBiO_6 materials.

$$S_{BET}^{Ca_2FeSbO_6} = 27m^2/g > S_{BET}^{Ca_2DySbO_6} = 6m^2/g > S_{BET}^{Ca_2AlSbO_6} = 2m^2/g$$
$$> S_{BET}^{Ca_2CrSbO_6} = 1m^2/g$$

- ✓ All the compounds were tested in terms of catalytic activity for test reaction of hydrogen peroxide decomposition studied. The catalytic H_2O_2 decomposition rate is strongly influenced by some important factors like specific surface area, morphology of the material and the agglomeration degree of catalyst grains. Ca_2FeSbO_6 present the best results and larger specific surface.

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SCIENTIFIC ACTIVITY

I. ISI publication list

1. **Simona Feraru**, Petrisor Samoila, Valentin Nica, Alexandra R. Iordan, Mircea N. Palamaru, *Influence of B-site cation nature on dielectric properties in Ca_2XBiO_6 (X=Dy, Fe, Al) double perovskite*, Chemical Papers, 67 (10), **2013**, 1311-1316 (impact factor - **1,097**).

2. **Simona Feraru,** Petrisor Samoila, Adrian I. Borhan, Alexandra R. Iordan, Mircea N. Palamaru, *Synthesis, characterization of double perovskite* Ca_2MSbO_6 *(M= Dy, Fe, Cr, Al) materials via sol–gel auto-combustion and their catalytic properties*, Materials Characterizaţion, 84 (2013) 112 – 119 (impact factor **– 1,880).**

3. **Simona Feraru**, Adrian I. Borhan, Petrisor Samoila, Gigel G. Nedelcu, Alexandra R. Iordan, Mircea N. Palamaru, *Influence of A-site cation on structure and dielectric properties in* A_2DyBiO_6 *(A=Mg, Ca, Sr, Ba) double perovskite*, Australian Journal of Chemistry, (**articol acceptat spre publicare**) (impact factor **– 1,869).**

II. Abstract published in scientific papers

1. **S. Feraru**, P.M.Samoila, A.R. Iordan, M.N. Palamaru. *Synthesis and activity in the catalytic chemical decomposition of hydrogen peroxide of* Ca_2MSbO_6 *serie*. Scientific Session of the students, master and doctoral students "Chemistry - frontier open to knowledge", second edition, Iaşi, 24 june 2011, Acta Chemica Iaşi, SCSMD 201, ISSN 2067-2438, pag. 44-45.

2. **S. Feraru**, P.M.Samoila, A.R. Iordan, M.N. Palamaru. *Sol-gel route of* $Ca_2Fe_{1-x}Sm_xBiO_6$ *(x = 0, 0.2, 0.4, 0.6, 0.8, 1) and catalityc behavior*. Chemistry - frontier open to knowledge", third edition, Iaşi, Acta Chemica Iaşi, Supplement Vol.19, SCSMD 2012, ISSN 2067-2438, pag. 52-53.

3. **S. Feraru**, A.I.Borhan, P.M.Samoila, G.G. Nedelcu, A.R. Iordan, M.N. Palamaru, *Study on structure and dielectric properties of double perovskites* A_2DyBiO_6 *(A=Mg, Ca, Sr, Ba)*, Chemistry - frontier open to knowledge", fourth edition, Iaşi, Acta Chemica Iaşi, Supplement Vol.21, SCSMD 2013, ISSN 2067-2438, pag. 14-15.

III. **List of scientific papers presented at national and international conferences**

1. **S. Feraru**, P.M.Samoila, A.R. Iordan, M.N. Palamaru. *Sol-gel autocombustion technique employed for the* Ca_2MsbO_6 *serie synthesis.* „International Conference of Applied Sciences, Chemistry and Chemical Engineering" Bacău 28-29 April 2011 – http://cisaconf.ub.ro/ (poster)

2. **S. Feraru**, P.M.Samoila, A.R. Iordan, M.N. Palamaru. *Synthesis and activity in the catalytic chemical decomposition of hydrogen peroxide of* Ca_2MSbO_6 *serie.*

"Chemistry - frontier open to knowledge", second edition, Iaşi, 24 iunie 2011 – http://www.chem.uaic.ro/ro/manifestari/programul-sesiunii.html – (poster)

3. **S. Feraru (PhD)**, P.M.Samoila, A.R. Iordan, M.N. Palamaru (PhD Supervisor). *Synthesis and activity in the catalytic chemical decomposition of hydrogen peroxide of Ca_2BSbO_6, $LaCrO_3$, and $LaCrO_3$/support".* Annual Conference of Doctoral School, Iaşi 21-22.10.2011 http://www.docpaideia.ro/index.php?page=news – (oral communication).

4. **Simona Feraru**, Petrişor Mugurel Samoilă, Alexandra Raluca Iordan, Mircea Nicolae Palamaru. *Dublu perovskiţi cu Bi. Sinteză şi caracterizare.* Scientific Session organized on the occasion of university days, 28.10.2011, Iasi – http://www.chem.uaic.ro/files/File/2011-2012/zu-2011/program-zilele-universitatii-2011(10).pdf – (oral communication).

5. **Simona Feraru**, Petrişor Mugurel Samoilă, Alexandra Raluca, Mircea Nicolae Palamaru. *Sinteza şi studiul proprietăţilor catalitice a perovskitului $LaCrO_3$ suportat.* Scientific Session organized on the occasion of university days, 28.10.2011, Iasi–http://www.chem.uaic.ro/files/File/2011-2012/zu-2011/program-zilele-universitatii-2011(10).pdf – (poster).

6. **S. Feraru**, P.M.Samoila, A.R. Iordan, M.N. Palamaru. *Synthesis and study of electric and catalityc behavior of double perovskite-type $Ca_2B(III)BiO_6$, were B(III) = Fe, Al and Dy*. „International Conference of Applied Sciences, Chemistry and Chemical Engineering",Sixth Edition – Aplril 24-27/ 2012, Bacau, Romania – http://cisaconf.ub.ro – (poster).

7. **S. Feraru**, P.M.Samoila, A.R. Iordan, M.N. Palamaru. *Sol-gel route of $Ca_2Fe_{1-x}Sm_xBiO_6$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) and catalityc behavior.* Sesiunea de comunicări ştiinţifice a studenţilor, masteranzilor şi doctoranzilor "Chimia – hem. er deschisă spre cunoaştere", ediţia a III-a, Iaşi, 26 mai 2012 – http://www.chem.uaic.ro/files/File/2011-2012/smd-26-mai-2012/program-final-conferinta-26-05-2012(3).pdf - (poster).

8. **S. Feraru**, P.M.Samoila, A.R. Iordan, M.N. Palamaru. *Synthesis and study of catalytic properties of bulk and supported $LaCrO_3$.* University "Alexandru Ioan Cuza" Days, Conference of Faculty of Chemistry, 2012.- http://www.chem.uaic.ro/ro/manifestari/zu2012.html – (oral communication)

9. **S. Feraru**, P.M.Samoila, A.R. Iordan, M.N. Palamaru. „Synthesis, characterization and properties of Ca_2BBiO_6 series", *"Al. I. Cuza" University, Faculty of Chemistry, 11 Carol 1 Bd., R-700506, Iasi, Romania.* Annual Conference of Doctoral School, University Alexandru Ioan Cuza from Iaşi, 19-20 October 2012, POSDRU 107/1.5/S/78342 project (oral communicaton)

10. **S. Feraru**, P.M.Samoila, A.I. Borhan, A.R. Iordan, S. Cucu-Man, M.N. Palamaru. Photocatalityc behavior of $Ca_2Fe_{1-x}Sm_xBio_6$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) double perovskite-type oxide. „International Conference of Applied Sciences, Chemistry and Chemical Engineering" Bacău 16-18 May 2013 – http://cisaconf.ub.ro/ (poster)

11. **S. Feraru**, A.I.Borhan, P.M.Samoila, G.G. Nedelcu, A.R. Iordan, M.N. Palamaru, *Study on structure and dielectric properties of double perovskites A_2DyBiO_6 (A=Mg, Ca, Sr, Ba)*, „Chemistry - frontier open to knowledge", ediţia a IV-a, Iaşi, http://www.chem.uaic.ro/files/File/2011-2012/smd-26-mai-2012/program-final-conferinta-28-06-2013(3) (oral communication)