University „Alexandru Ioan Cuza” from Iași

Faculty of Chemistry

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

Summary of the PhD Thesis

Scientific adviser:
Prof. Dr. Mîrcea Nicolaе PALAMARU

PhD Student:
Chim. Simona FERARU

Iași, 2013
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
Acknowledgments

This research work was carried out with financial support funded by the Sectoral Operational Programme Human Resources Development, POSDRU107/1.5/S/78342 project, 2010 - 2013.

With great esteem and appreciation, thank Prof. Dr. Mircea Nicolae Palamaru for patience and trust, not least for the moral and financial support throughout the completion of this scientific research.

Many thanks address to Miss Prof. Alexandra Raluca Iordan, Mister Dr. Samoilă Petrișor, commission members of guidance, who had the patience to guide me throughout the duration of doctoral research.

Thank doctoral fellow Alin, Adrian, Catalin, for for their support in difficult moments encountered throughout doctoral research.

I would also like to thank all the collaborators from the Faculty of Chemistry and Physics of the University "Alexandru Ioan Cuza" Iasi.

Many thanks address to referents and members of the examination for their kindness and acceptance of this PhD thesis analysis and assessments made.
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
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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 dielectric 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), fotocatalizá. 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)(figure 1).

![Perovskite-type structure, ABO$_3$(A = Ca, B = Ti)](image)

**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$_2$BB’O$_6$**

The double perovskite type oxides with the general formula A$_2$BB’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).
Perovskite-type structure oxides. Synthesis, characterization and properties

Figure 2. Double perovskite $A_2B'B'O_6$ 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$_2$B$_2$O$_6$, 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$_3$ or A$_2$BB'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 photocatalysis (Hatakyama 2010).

**PERSONAL CONTRIBUTIONS**

**II. Synthesis and structural characterization of perovskite-type oxides**

**II.1. Synthesis and structural characterization of Ca$_2$B$_2$O$_6$,**

(B = Dy, Fe, Cr, Al) serie

**II.1.1. Sol-gel auto-combustion synthesis**

For the preparation of Ca$_2$MSbO$_6$ (M = Dy, Fe, Cr, Al) double perovskite materials was used sol-gel auto-combustion method with high-purity starting materials as: Ca(NO$_3$)$_2$·4H$_2$O, Dy(NO$_3$)$_3$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, Cr(NO$_3$)$_3$·9H$_2$O, Al(NO$_3$)$_3$·5H$_2$O, Sb$_2$O$_3$, HNO$_3$ and tartric acid, C$_4$H$_6$O$_6$ (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$_2$O$_3$ 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$_2$BSbO$_6$ 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$_2$BSbO$_6$ 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$_2$AlSbO$_6$ and Ca$_2$DySbO$_6$ 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 ($\nu_{as}$) 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$_2$AlSbO$_6$ 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, ($A_{Dy} = 66$, $A_{Fe} = 26$, $A_{Cr} = 24$, $A_{Al} = 13$, $r_{Dy}^{3+} = 0.91\text{Å}$, $r_{Fe}^{3+} = 0.64\text{Å}$, $r_{Cr}^{3+} = 0.61\text{Å}$, $r_{Al}^{3+} = 0.53\text{Å}$) 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 °C 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$_2$BSbO$_6$ double perovskite

The stronger diffraction peak characteristic of double perovskite-type structure are at $2\theta \approx 32^\circ$ attributable to the (112) diffraction planes, confirm the formation of double-perovskites phase for all studied samples. In the case of Ca$_2$CrSbO$_6$ powder, small peaks were observed at $2\theta = 29.6^\circ$ and $30.1^\circ$, suggesting the presence of Sb$_2$O$_4$ (orthorhombic system, COD ID: 1010922) as secondary phase. Can be seen from the analysis of Figs. 11, the theoretical XRD patterns of the Ca$_2$BSbO$_6$ 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)

$$D = \frac{0.94 \cdot \lambda}{\beta_1} \cdot \cos \theta$$
where: $D$ = crystallite size, $\lambda$ = radiation length (1.5405 Å), $\beta_{1/2}$ = half widening of diffraction profile, $\theta$ = diffraction angle.

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

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

were: $\phi$- tilting angle of octahedra,

$\Phi$ – length angle $B – O – Sb$

**Table 2.** Structural parameters obtained from SPuDS software and crystallite size

<table>
<thead>
<tr>
<th>Sample</th>
<th>$r_B^{3+}$ (Å)</th>
<th>$D$ (nm)</th>
<th>$t$</th>
<th>Lattice parameter (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$\beta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_2$DySbO$_6$</td>
<td>0.91</td>
<td>59</td>
<td>0.895</td>
<td>$a = 5.644$</td>
<td>272.63</td>
<td>89.949</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$b = 5.918$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$c = 8.160$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$_2$FeSbO$_6$</td>
<td>0.64</td>
<td>21</td>
<td>0.949</td>
<td>$a = 5.536$</td>
<td>247.45</td>
<td>89.999</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$b = 5.651$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$c = 7.908$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$_2$CrSbO$_6$</td>
<td>0.61</td>
<td>73</td>
<td>0.957</td>
<td>$a = 5.517$</td>
<td>243.57</td>
<td>90.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$b = 5.611$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$c = 7.867$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$_2$AlSbO$_6$</td>
<td>0.53</td>
<td>33</td>
<td>0.982</td>
<td>$a = 5.456$</td>
<td>232.02</td>
<td>90.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$b = 5.493$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$c = 7.741$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 $\beta$ angle value, which determines the distortion from the ideal cubic perovskite structure.

**Table 3.** Interatomic data from SPuDS and tilt angle

<table>
<thead>
<tr>
<th>Samples</th>
<th>$B(III)$ – O (Å)</th>
<th>Sb(V) – O (Å)</th>
<th>$\phi$ (°)</th>
<th>$\phi$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_2$DySbO$_6$</td>
<td>2.268(2)</td>
<td>2.0090(2)</td>
<td>145</td>
<td>17.5</td>
</tr>
<tr>
<td>Ca$_2$FeSbO$_6$</td>
<td>2.026(2)</td>
<td>2.0094(2)</td>
<td>157</td>
<td>11.5</td>
</tr>
<tr>
<td>Ca$_2$CrSbO$_6$</td>
<td>1.991(2)</td>
<td>2.0095(2)</td>
<td>158</td>
<td>11</td>
</tr>
<tr>
<td>Ca$_2$AlSbO$_6$</td>
<td>1.887(2)</td>
<td>2.0095(2)</td>
<td>166</td>
<td>7</td>
</tr>
</tbody>
</table>
From table 3 can be observed that the average $B$ (III) – O bond length and the tilt angle ($\phi$) 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 $\phi = 17.5^\circ$ for Ca$_2$DySbO$_6$ to $\phi = 7^\circ$ for Ca$_2$AlSbO$_6$) 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$_2$BSbO$_6$ ceramic disk sintered at 1150 °C / 9 h are presented in figure 13 (a-d).

![SEM images](image-url)

*Figure 13. SEM images for (a) Ca$_2$DySbO$_6$, (b) Ca$_2$FeSbO$_6$, (c) Ca$_2$CrSbO$_6$, (d) Ca$_2$AlSbO$_6*"

From these micrographs, can be observed nano-sized grains with quasi-spherical shape in case of Ca$_2$DySbO$_6$ (figure 13(a)) and Ca$_2$FeSbO$_6$ (figure 13(b)) materials. SEM image for Ca$_2$CrSbO$_6$ 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$_2$AlSbO$_6$ (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 obținând the following series of compounds $\text{Ca}_2\text{B}_n\text{BiO}_6$ ($B = \text{Dy, Fe, Cr, Al}$), $\text{Ca}_2\text{B}_n\text{BiO}_6$ ($B = \text{Dy, Fe, Cr, Al}$), $\text{Ca}_2\text{Fe}_{1-x}\text{Sm}_x\text{BiO}_6$ ($x = 0; 0.2; 0.4; 0.6; 0.8; 1$), $\text{A}_2\text{DyBiO}_6$ ($\text{A} = \text{Mg, Ca, Sr, Ba}$),
- analysis by infrared absorption spectroscopy and structural characterization by X-ray diffraction confirmed to obtain the title compound,
- the scanning electronic 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 $\text{Ca}_2\text{B}_n\text{BiO}_6$, were $B = \text{Dy, Fe, Cr, Al}$;
- perovskite -type oxide with the general formula $\text{Ca}_2\text{B}_n\text{BiO}_6$, were $B = \text{Dy, Fe, Cr, Al}$;
- perovskite -type oxide with the general formula $\text{Ca}_2\text{Fe}_{1-x}\text{Sm}_x\text{BiO}_6$ ($x=0; 0.2; 0.4; 0.6; 0.8; 1$);
- perovskite -type oxide with the general formula $\text{A}_2\text{DyBiO}_6$ were $\text{A} = \text{Mg, Ca, Sr, Ba}$;
- perovskite -type oxide with the general formula $\text{LaCrO}_3$ and $\text{LaCrO}_3$/support (support = $\text{ZrO}_2$, $\text{TiO}_2$, $\text{Al}_2\text{O}_3$, $\text{SiO}_2$);
- perovskite -type oxide with the general formula $\text{LaCr}_{0.9}\text{B}_{0.1}\text{O}_3/\text{ZrO}_2$ ($B = \text{Mn, Fe, Co, Ni}$).

- $\text{Ca}_2\text{B}_n\text{BiO}_6$, $B = \text{Dy, Fe, Cr, Al}$ serie

✓ 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 $\text{Ca}_2\text{BSbO}_6$ double perovskite materials ($\text{B} = \text{Dy}, \text{Fe}, \text{Cr}, \text{Al}$) 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 $\text{Ca}_2\text{DyBiO}_6$ material as a result of the largest ionic radius of the $\text{Dy}^{3+}$ 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 $\text{Ca}_2\text{CrBiO}_6$ and $\text{Ca}_2\text{AlBiO}_6$ materials.

$$S_{\text{BET}}^{\text{Ca}_2\text{FeSbO}_6} = 27 \text{ m}^2 / \text{g} > S_{\text{BET}}^{\text{Ca}_2\text{DySbO}_6} = 6 \text{ m}^2 / \text{g} > S_{\text{BET}}^{\text{Ca}_2\text{AlSbO}_6} = 2 \text{ m}^2 / \text{g}$$

$$> S_{\text{BET}}^{\text{Ca}_2\text{CrSbO}_6} = 1 \text{ m}^2 / \text{g}$$

- All the compounds were tested in terms of catalytic activity for test reaction of hydrogen peroxide decomposition studied. The catalytic $\text{H}_2\text{O}_2$ decomposition rate is strongly influenced by some important factors like specific surface area, morphology of the material and the agglomeration degree of catalyst grains. $\text{Ca}_2\text{FeSbO}_6$ present the best results and larger specific surface.

**References**


Perovskite-type structure oxides. Synthesis, characterization and properties


(Fu, 2005) Fu W.T, Ijdo D.J.W, X-ray and neutron powder diffraction study of the double perovskites Ba₂LnSbO₆ (Ln= La, Pr, Nd and Sm), Journal of Solid State Chemistry 178 (2005) 2363
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(López-Trosell, 2006) López-Trosell A, Schomäcker R, Synthesis of manganite perovskite Ca$_{0.5}$Sr$_{0.5}$MnO$_3$ nanoparticles in w/o-microemulsion, Materials Research Bulletin 41 (2006) 333
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Perovskite-type structure oxides. Synthesis, characterization and properties


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 Ca₂XBiO₆ (X=Dy, Fe, Al) double perovskite, Chemical Papers, 67 (10), 2013, 1311-1316 (impact factor - 1,097).


II. Abstract published in scientific papers

2. **S. Feraru**, P.M.Samoila, A.R. Iordan, M.N. Palamaru. *Sol-gel route of Ca$_2$Fe$_{1-x}$Sm$_x$BiO$_6$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) and catalytic behavior. Chemistry - frontier open to knowledge”, third edition, Iaşi, Acta Chemica Iaşi, Supplement Vol.19, SCSMD 2012, ISSN 2067-2438, pag. 52-53.


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


7. **S. Feraru**, P.M.Samoila, A.R. Iordan, M.N. Palamaru. *Sol-gel route of Ca$_2$Fe$_{1-x}$Sm$_x$BiO$_6$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) and catalytic behavior*. Sesiunea de comunicări științifice a studenților, masteranzilor și doctoranzilor “Chimia – hem. er deschisă spre cunoaștere”, ediția a III-a, Iași, 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).


10. **S. Feraru, P.M.Samoila, A.I. Borhan, A.R. Iordan, S. Cucu-Man, M.N. Palamaru.** Photocatalytic behavior of Ca$_2$Fe$_{1-x}$Sm$_x$BiO$_6$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) double perovskite-type oxide. „International Conference of Applied Sciences, Chemistry and Chemical Engineering” Bacău 16-18 May 2013 – [http://cisaconf.ub.ro/](http://cisaconf.ub.ro/) (poster)