

Influence of Y-ion substitution on structural and electrochemical characteristics of $\text{YCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$

S. Dimitrovska-Lazova^{1*}, S. Aleksovska^{1,2,4}, P. Tzvetkov³,
V. Mirčeski^{1,4}, D. Kovacheva³

¹ University “Sts. Cyril & Methodius”, Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Arhimedova 5, 1000 Skopje, Republic of Macedonia

² Research Center for Environment and Materials, Macedonian Academy of Sciences and Arts, Bul. “Krstе Misirkov” 2, P.O. Box 428, 1000 Skopje, Republic of Macedonia

³ Institute of General and Inorganic Chemistry, Bulgarian Academy of Science, “Acad. Georgi Bonchev”, bl. 11, 1113 Sofia, Bulgaria

⁴ Faculty of Medical Sciences, Goce Delcev University, Stip, R. Macedonia

Received December, 2014; Revised January, 2015

The influence of partial substitution of Y^{3+} with Ca^{2+} in $\text{YCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ perovskite on the crystallochemical and electrocatalytic properties is presented. The perovskites $\text{YCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ and $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ were synthesized by solution combustion method with citric acid as a fuel. The obtained perovskites were analyzed with powder XRD and cyclic voltammetry. The crystal structures of both compounds were determined by Rietveld refinement method. The XRD patterns showed that both perovskites are orthorhombic and crystallize in space group $Pnma$. In aim to obtain a clearer picture for the influence of substitution of Y^{3+} ion with Ca^{2+} ion on the structural characteristics, the lattice parameters and distances and angles were used to calculate several crystallochemical parameters such as, cell distortion, orthorhombic distortion, bond and angle deformation, the tilting angles, bond valences, and global instability index. It was found that the distortion indices and tilting angles are lower for $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ in comparison with $\text{YCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ indicating more stable structure. Taking into consideration the possible application of these compounds as catalysts in direct methanol fuel cells, their catalytic properties towards oxidation of methanol in basic solutions were studied by cyclic voltammetry. The electrocatalytic activity towards oxidation of chloride ions and oxidation of H_2O_2 in phosphate buffer were also investigated.

Key words: perovskites, crystal structure, crystallochemical parameters, electrocatalytic properties.

INTRODUCTION

The perovskite-type oxides (ABO_3) have attracted great scientific attention due to number of specific and important physical and chemical properties. Among the numerous different perovskites, rare-earth cobalt containing perovskites (LnCoO_3 ; $\text{Ln} = \text{Y}$ or lanthanide) are of prominent scientific interest since they exhibit interesting properties such as high electronic conductivity, metal to insulator transition with increasing temperature, significant catalytic activity, specific magnetic properties, etc. [1–5]. Their properties are tightly connected with some characteristics of cobalt ions such as the possibility to change the oxidation state (Co^{4+} , Co^{3+} , Co^{2+})

and also the possibility of altering the spin state of the Co^{3+} ion. Thus, it was found that in LnCoO_3 perovskites, Co^{3+} ion could undergo temperature driven spin-state changes from non-magnetic low-spin (t_{2g}^6) to paramagnetic intermediate-spin ($t_{2g}^5e_g^1$) and finally to paramagnetic high-spin state ($t_{2g}^4e_g^2$), or it could exist in mixed spin state [6–9]. The intermediate-spin state Co^{3+} ion in LnCoO_3 is Jahn-Teller active, which is associated with distortion of the CoO_6 octahedra.

Another well investigated and from applicative point of view the most promising cobalt-containing perovskites, are the systems of general formula $\text{Ln}_{1-x}\text{M}_x\text{CoO}_3$. In these perovskites, the partial substitution of rare-earth elements with divalent cations leads to formation of Co^{4+} ions or oxygen deficiencies [10–13]. A typical example is $\text{Y}_{1/4}\text{Sr}_{3/4}\text{CoO}_{3-\delta}$ which could be prepared as A-site ordered or disordered structure. The A-site ordering leads also

* To whom all correspondence should be sent:
E-mail: sandra@iunona.pmf.ukim.edu.mk

to oxygen vacancies ordering (and *vice versa*), which is connected with modifications of the electronic phases and ferromagnetic transitions [11]. It has been recognized that the physical properties of ABO_3 -perovskites are largely dependent on the oxygen deficiency [11]. The mixed conductivity can be enhanced through the substitution of La^{3+} by Sr^{2+} at A-sites and the substitution of B-cation by other transition metal. The charge imbalance and overall charge neutrality can be maintained by the presence of charged oxygen vacancies and mixed valence state ions at the B sites. These point defects are the origin of the mixed electronic and oxygen ion conductivity [11].

Perovskites with partial substitution of Co^{3+} have also been investigated. Thus, Co^{3+} ions could be partially substituted by Ni [14], by Mn [15] or by Cr^{3+} , which was also a subject of our previous investigations [16–20]. It was found that the magnetic and electrical properties of this type of complex perovskites depends on the spin state of the Co^{3+} ion [14, 15, 21] and the cation–anion–cation overlap [14, 15, 18, 21].

However, the literature data for substituents both in A- and B-sites in Co-containing perovskites are very rare. Therefore, following the trend of investigation of different cobalt containing perovskite compounds, in this work $YCo_{0.5}Fe_{0.5}O_3$ and $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ were synthesized. The main aim of this work was to compare the crystallochemical and catalytic properties of these perovskites and the influence of aliovalent substitution in A-position.

EXPERIMENTAL

The studied perovskites ($YCo_{0.5}Fe_{0.5}O_3$ and $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$) were synthesized by solution combustion method using citric acid as a fuel. The quantity of the fuel was calculated according to the fuel-to-oxidizer ratio, which was set to 1 in order to obtain the highest possible temperature during the reaction. The starting solutions were prepared by dissolving the nitrate salts of constituent metal ions in small quantity of distilled water and the dissolved citric acid was slowly added to this solution. The pH of the reaction solution was adjusted to 7 with addition of NH_4OH . The reaction mixture was placed on magnetic stirrer and it was heated at 80 °C until the evaporation of water. Then the glass baker was transferred on hot plate preheated at ~350 °C when vigorous reaction took place resulting in formation of black spongy powders. The obtained powders were additionally heated for 4 h at 800 °C. In aim to remove the possible impurities and to improve the crystallinity, the resulting powders were washed with diluted HCl and heated at 6 h at 950 °C.

The characterization and structural investigation of the obtained powders were analyzed by powder X-ray diffraction. The XRD patterns were recorded at room temperature on *Bruker D8 Advance* with $CuK\alpha$ radiation and Sol-X detector within the range 10–120° 2θ with step-scanning of 0.02°. The crystal structures were refined by the method of Rietveld [22] using the Fullprof program [23].

The electrocatalytic properties of $YCo_{0.5}Fe_{0.5}O_3$ and $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ perovskites were investigated using cyclic voltammetry. The investigations were performed on μ AUTOLAB, model III. The cyclic voltammograms were recorded on a specially designed paraffine impregnated graphite electrode (PIGE) [24]. The electrochemical cell consisted of three electrodes: PIGE as a working electrode, Ag/AgCl (sat. KCl) as reference electrode, and a platinum wire as auxiliary electrode. The microcrystals of $YCo_{0.5}Fe_{0.5}O_3$ and $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ were deposited on the surface of PIGE by abrasion. The electrochemical activity was investigated at room temperature, in aqueous solutions of different electrolytes: LiCl, KCl, NaCl, $(CH_3)_4NCl$ (all with concentrations 0.5 mol/dm³), HCl (0.3 mol/dm³), KOH (0.1 and 1 mol/dm³), phosphate buffer (pH = 7.35) and buffer in which H_2O_2 (10^{-1} – 10^{-3} mol/dm³) was added. In aim to investigate the possible application of these compounds as catalysts in direct methanol fuel cells (DMFC), the electrocatalytic activity in basic solutions of 1 mol/dm³ methanol was studied.

RESULTS AND DISCUSSION

Crystal structure

The XRD patterns of the synthesized compounds were completely indexed in orthorhombic $Pnma$ space group. Their purity and the crystallinity were improved by subsequent additional heating (Fig. 1).

The results of crystal structure refinements by Rietveld method of the studied perovskites are presented in Table 1 and selected distances and angles are given in Table 2. Both compounds crystallize in $Pnma$ space group with $Z = 4$. The unit cell parameters and fractional atomic coordinates of $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ are close to the values of $YCo_{0.5}Fe_{0.5}O_3$.

The relationships between the unit cell parameters in both compounds are $a > c$ and $a > b/\sqrt{2} > c$, which is typical for *O*-type perovskites, where the main reason for the deformation of the structure, in comparison with the ideal one, is the tilting of the octahedra. As it is well known, the ideal perovskite structure is cubic ($Pm\bar{3}m$) in which the B-cations are surrounded by six anions arranged in corner-

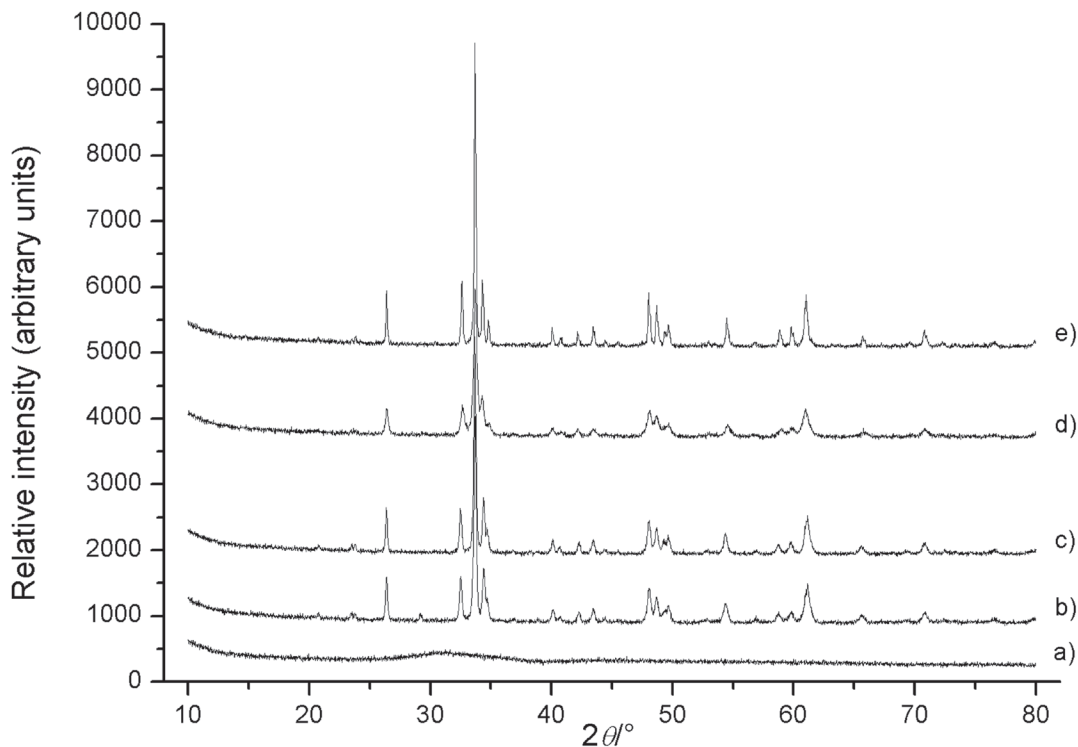


Fig. 1. Powder XRD patterns of: a) as-synthesized $YCo_{0.5}Fe_{0.5}O_3$; b) $YCo_{0.5}Fe_{0.5}O_3$ heated 4h at 800 °C; c) $YCo_{0.5}Fe_{0.5}O_3$ heated 6h at 950 °C; d) $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ heated 4h at 800 °C and e) $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ heated 6 h at 950 °C

Table 1. Unit cell parameters, fractional atomic coordinates and discrepancy factors of the synthesized perovskites

Atoms	Par.	$YCo_{0.5}Fe_{0.5}O_3$	$Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$
	$a/\text{Å}$	5.5087(2)	5.49338(13)
	$b/\text{Å}$	7.4807(3)	7.47863(17)
	$c/\text{Å}$	5.2133(2)	5.22684(13)
Y/Ca	x	0.06816(14)	0.06591(15)
	z	0.9829(3)	0.9842(3)
	B	0.47(3)	0.45(3)
Co/Fe	B	0.19(4)	0.51(4)
O1	x	0.4663(9)	0.4674(9)
	z	0.0999(9)	0.1008(10)
	B	1.18(16)	1.95(16)
O2	x	0.3041(7)	0.3010(8)
	y	0.0539(5)	0.0537(6)
	z	0.6959(8)	0.6978(8)
	B	0.85(14)	1.29(13)
R_1	R_p	15.1	18.8
	R_{wp}	10.9	12.3
	R_{exp}	9.95	10.65
	χ^2	1.21	1.33
	R_B	2.83	4.31

sharing octahedral geometry. This arrangement forms cubooctahedral cavity in which the A-cation is placed [25]. The ideal cubic perovskite structure is not very common and most of the perovskites are of lower symmetry due to the mismatch of the ionic radii ratio with the one in the ideal perovskite struc-

Table 2. Selected distances and angles for $YCo_{0.5}Fe_{0.5}O_3$ and $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$

	$YCo_{0.5}Fe_{0.5}O_3$	$Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$
Y-O1/Å	3.371	3.344
	2.276	2.288
	3.09	3.105
	2.246	2.236
Y-O2/Å x2	2.466	2.463
	2.266	2.275
	3.49	3.462
	2.626	2.634
B-O1/Å x2	1.9502	1.9507
B-O2/Å x2	2.003	1.991
	1.960	1.962
B-O1-B/°	146.06	146.85
B-O2-B/° x2	146.27	147.06

Table 3. Some crystallochemical parameters of the studied compounds

Crystall. param.	$YCo_{0.5}Fe_{0.5}O_3$	$Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$
Δ_8	4.014	4.042
Δ_{12}	30.64	29.31
Δ_6	0.135	0.074
s	0.055	0.050
d	5.503	4.564
$dist_{orth}$	0.041	0.037
$\theta/^\circ$	16.47	16.57
$\varphi/^\circ$	12.21	11.66
$\Phi/^\circ$	20.40	20.17
BV(Y/Ca)	3.05	3.144/2.431
BV(Co)	2.438	2.456
BV(Fe)	3.39	3.415
GII	0.205	0.178

ture. The distortion of the ideal perovskite structure is manifested by (1) tilting of the BO_6 octahedra; (2) deformation of the BO_6 octahedra and (3) displacement of the B-cation from the center of the octahedra [25]. As was previously mentioned, in the investigated compounds, the tilting of the octahedra distorts the ideal cubic structure to orthorhombic one. Furthermore, considering the ionic radii of calcium and yttrium ions, which are close to each other ($r(Y^{3+}) = 1.109 \text{ \AA}$ and $r(Ca^{2+}) = 1.12 \text{ \AA}$), it would be expected that both compounds will give similar value for the pseudo-cubic unit cell calculated as $a_p = (V/Z)^{1/3}$ [25]. Thus, a_p for $YCo_{0.5}Fe_{0.5}O_3$ is 3.7729 and for $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ is 3.7723.

In order to estimate the influence of the partial substitution of Y with Ca ions on the stability of the perovskite structure, some important crystallographic parameters were calculated (Table 3). Some of these parameters were calculated using the cell parameters, such as: spontaneous strain (s) [26], unit cell distortion (d) [27] and orthorhombic distortion ($dist_{orth}$) [28]. The values of these three parameters show that there is some strain and distortion in the unit cells in both investigated structures. However, the obtained values for $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ are lower, indicating less distortion in its structure.

According to the values of Y-O distances the coordination number of yttrium in these perovskites is 8. This could be also concluded taking into consideration the calculated deformation indices [29] for the coordination polyhedron of the A-cation, which are significantly lower for coordination number of 8 in comparison with one of coordination number of 12. The B-O distances show deformed octahedral

coordination but the values of the deformation indices of the octahedra (Δ_6) indicates that the insertion of calcium ion in the position of Y^{3+} leads towards more regular octahedron (Table 3).

As previously mentioned both perovskites are of O-type, pointing out to the tilting of the octahedra as main reason for deviation of ideal perovskite structure. Therefore, the tilt angles of the octahedra were calculated on the basis of the displacement of the fractional atomic coordinates of the anions from the positions in the ideal cubic structure [25]. It was found that the calculated tilt angles (θ , φ , Φ) in $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ are similar (but lower) with the ones obtained for $YCo_{0.5}Fe_{0.5}O_3$. Finally in aim to obtain clearer comparison between the general stability of the investigated compound, the global instability index (GII) was calculated [30] taking into account the bond valences model [31]. The obtained value for $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ is significantly lower than that for $YCo_{0.5}Fe_{0.5}O_3$, which means that the partial substitution of Y by Ca, leads to perovskite structure with decreased internal stress.

Electrocatalytic properties

Our previous investigations on electrocatalytic properties of some perovskites [20] showed that they can catalyze some redox processes such as oxidation of chloride ions, hydrogen peroxide and methanol. Therefore the electrocatalytic properties of $YCo_{0.5}Fe_{0.5}O_3$ and $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ were investigated by applying cyclic voltammetry at PIGE modified for microcrystals of the perovskite. Firstly, the electrochemical behavior was investigated in contact with the aqueous solutions of chloride ions mentioned in the experimental part. The voltammograms (Fig. 2) were recorded starting from the potential of -1.0 V in a positive potential direction up to 1.5 V , with three different electrodes: blank PIGE electrode, PIGE modified with microcrystals of $YCo_{0.5}Fe_{0.5}O_3$ and PIGE modified with microcrystals of $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$. As can be seen (Fig. 2), a well defined reduction pick at potentials around 0.6 V may be noticed obtained with blank, as well as, with modified PIGE electrode. This reduction pick is preceded by strong oxidation current manifested as an anodic tail on the voltammogram, because the oxidation current is so intensive that it is out of the measuring range of the instrument. It was noticed that if the anodic potential is less than 1.00 V i.e. the value where the oxidation current starts, then the reduction peak disappears. This result points out that the reducible reactant is “*in situ*” formed during the process of oxidation, which is represented by the anodic tail in the voltammogram. Also, the experiments performed with chloride salts of different cations (K^+ , Li^+ , Na^+ or $(CH_3)_4N^+$) but

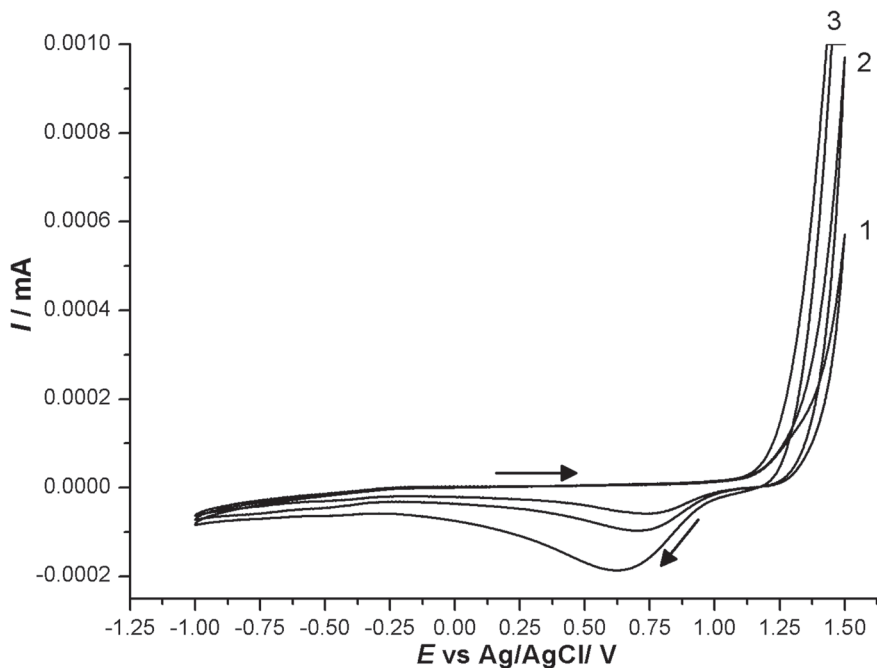


Fig. 2. Cyclic voltammograms in 0.5 mol/dm^3 KCl. 1 – blank PIGE electrode; 2 – PIGE modified with $YCo_{0.5}Fe_{0.5}O_3$ and 3 – PIGE modified with $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$

of same concentration, gave the same voltammetric response, which means that only the chloride anions are involved in the electrochemical redox reaction.

The analysis of voltammograms clearly shows shifting of the reduction peaks obtained with the perovskite-modified PIGEs towards more negative potentials in comparison with the blank PIGE, due to the catalytic effect of both of the investigated perovskites. Furthermore, according to the positions of the reduction peaks, it could be concluded that $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ has more pronounced catalytic properties than $YCo_{0.5}Fe_{0.5}O_3$. Another clue to this conclusion is the increasing of the cathodic peak ($I_{p,c}$), which is most intensive in the case of calcium containing perovskite. These results are confirming that the oxidized chlorine species are *in situ* formed during the anodic process. The oxidation process of chlorides yields, most probably, atomic chlorine or some other chlorine containing species that are adsorbed on the electrode, which afterwards give raise to the reductive voltammetric peak in the corresponding cathodic potential sweep. Thus, because of the catalytic effect of perovskite-modified PIGE (especially in the case of $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$), the quantity of the oxidation products increases and as a consequence the $I_{p,c}$ also increases.

The electrocatalytic properties of the investigated perovskites were also analyzed for oxidation of methanol in basic solution (KOH). This reaction

is of special interest since it takes place in so-called direct methanol fuel cells. In order to investigate the possible application of the studied perovskites as catalysts in this type of fuel cells cyclic voltammograms with modified PIGE were recorded (Fig. 3) in the range of 0.0 to 0.8 V. As electrolyte in these experiments basic solution (1 mol/dm^3 KOH) of methanol (1 mol/dm^3) was used. The comparison of the obtained voltammograms of the blank and of the perovskite-modified PIGEs shows clear electrocatalytic effect. Thus, when the electrode process (oxidation of methanol) is performed with perovskite-modified PIGEs, the onset anodic potential is shifted towards less positive potentials in comparison when it is performed with blank electrode (see the inset, Fig. 3). Again, $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ showed better catalytic activity than $YCo_{0.5}Fe_{0.5}O_3$, which could be also concluded according to the increased $I_{p,a}$.

Finally, the electrocatalytic activity of $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ and $YCo_{0.5}Fe_{0.5}O_3$ towards oxidation of H_2O_2 in phosphate buffer (pH = 7.35) was investigated in the range of -1.0 to 1.5 V. For this purpose, firstly cyclic voltammograms of $YCo_{0.5}Fe_{0.5}O_3$ and $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ -modified PIGE in phosphate buffer were recorded. Afterwards, H_2O_2 was added to the solutions of phosphate buffer and its concentration was subsequently increased from 10^{-3} to 10^{-1} mol/dm^3 (Fig. 4a and 4b).

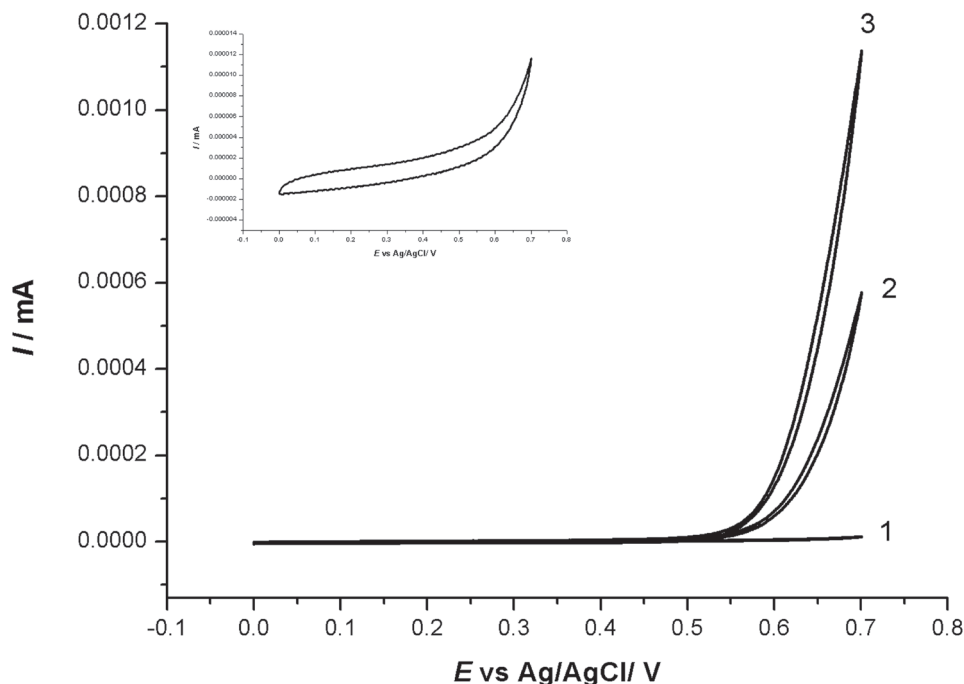


Fig. 3. Cyclic voltammograms in 1 mol/dm³ KOH + 1 mol/dm³ CH₃OH. **1** – blanc PIGE electrode; **2** – PIGE modified with $YCo_{0.5}Fe_{0.5}O_3$ and **3** – PIGE modified with $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$. Inset: Enlarged voltammogram of blanc PIGE electrode

As can be seen, both investigated perovskites show catalytic activity towards oxidation of H_2O_2 in phosphate buffer. Again, this can be concluded on the basis of the onset starting anodic potential when formation and liberation of O_2 starts. This potential is shifted towards less positive potentials when perovskite-modified PIGEs were used in comparison with blank electrode. Obviously, the Ca-substituted perovskite shows more pronounced electrocatalytic

effect than $YCo_{0.5}Fe_{0.5}O_3$. The repeated experiments with different concentrations of H_2O_2 confirmed this conclusion.

It was previously found that Co-containing perovskites are very good catalysts for number of reactions [4]. However, in all three electrolyte solutions $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ showed better catalytic activity than $YCo_{0.5}Fe_{0.5}O_3$. The possible explanation for the better electrocatalytic activity of

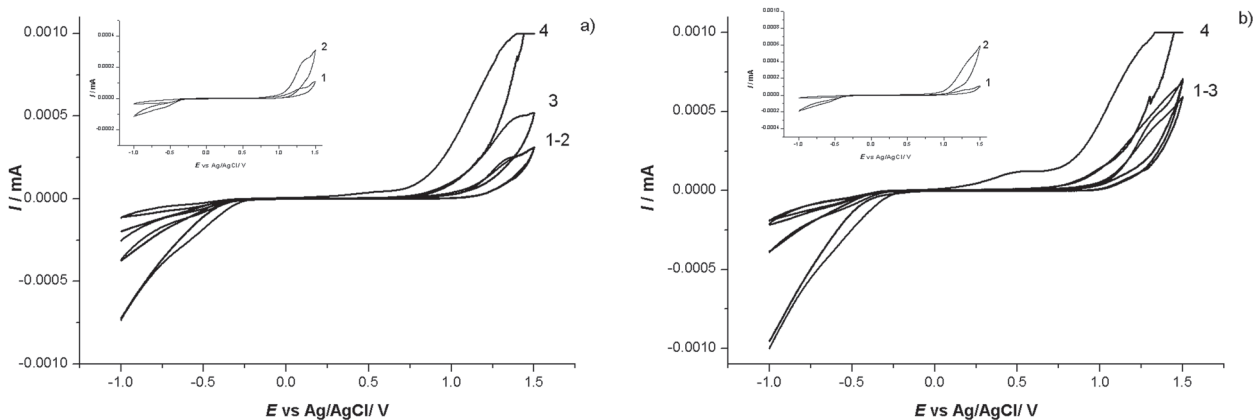


Fig. 4. Cyclic voltammograms of a) $YCo_{0.5}Fe_{0.5}O_3$ and b) $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ in: **1** – 0.1 M phosphate buffer; **2** – phosphate buffer + 10^{-3} M H_2O_2 ; **3** – phosphate buffer + 10^{-2} M H_2O_2 ; **4** – phosphate buffer + 10^{-1} M H_2O_2 . Inset: **1** – blanc PIGE electrode in phosphate buffer + 10^{-3} M H_2O_2 and **2** – modified PIGE in phosphate buffer + 10^{-3} M H_2O_2

$Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ in the investigated electrolyte systems in comparison with $YCo_{0.5}Fe_{0.5}O_3$, is connected with the structure of Ca-containing perovskite. Namely, the partial substitution of Y^{3+} -ions with Ca^{2+} ions leads to oxygen vacancies in the structure. It is supposed that the point defects in the structure, lead to mixed type of conductivity – electronic and ionic – of the modified electrode that facilitates the electrocatalytic process.

CONCLUSION

The perovskites $YCo_{0.5}Fe_{0.5}O_3$ and $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ were successfully obtained by solution combustion method using citric acid as a fuel. The refinement of crystal structure using the Rietveld method showed that the unit cell parameters and the fractional atomic coordinates of the two compounds are very similar. Calculated crystallochemical parameters revealed that insertion of calcium ion in the position of Y^{3+} leads toward smaller deformation of octahedron. Also, the calculated tilting angles are a little bit lower for $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$. This distortion of the unit cell (d and $dist_{orth}$) is also lower in Ca-containing perovskite, as well as, the value of global instability index.

The investigation of the electrocatalytic properties of the studied compounds with cyclic voltammetry revealed that both compounds catalyze the reaction of oxidation of chloride ions; the oxidation of methanol in basic solution and the oxidation of H_2O_2 in phosphate buffer. It was found that in all three investigated systems, $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ showed better catalytic activity than $YCo_{0.5}Fe_{0.5}O_3$. This could be explained by the formation of oxygen vacancies in this structure, which probably lead to mixed type of conductivity (electronic and ionic) of the modified electrode that facilitates the electrocatalytic process.

Acknowledgement: The financial support of the BAS-MANU Collaborative Project “Structural characterization and investigation of electrical and catalytic properties of new synthesized complex perovskites” is gratefully acknowledged.

REFERENCES

1. Z. Shao, S. M. Haile, *Nature* (London), **431**, 170 (2004).
2. Y. Wang, N. S. Rogado, R. J. Cava, N. P. Ong, *Nature* (London) **423**, 425 (2003).
3. W. Kobayashi, S. Ishiwata, I. Terasaki, M. Takano, I. Grigoraviciute, H. Yamauchi, M. Karppinen, *Phys. Rev. B* **72**, 104408 (2005).
4. M. A. Peña, J. L. G. Fierro, *Chem. Rev.*, **101**, 1981 (2001).
5. S. Yáñez-Vilar, A. Castro-Couceiro, B. Rivas-Murias, A. Fondado, J. Mira, J. Rivas, M. A. Señaris-Rodríguez, *Z. Anorg. Allg. Chem.*, **631**, 2265 (2005).
6. K. Knížek, Z. Jiráček, J. Hejtmánek, M. Veverka, M. Maryško, G. Maris, T. T. M. Palstra, *Eur. Phys. J. B*, **47**, 213 (2005).
7. J.-Q. Yan, J.-S. Zhou, J. B. Goodenough, *Phys. Rev. B*, **69**, 134409 (2004).
8. F. H. M. Cavalcante, A. W. Carbonari, R. F. L. Malavasi, G. A. Cabrera-Pasca, R. N. Saxena, J. Mestnik-Filho, *J. Magn. Magn. Mater.*, **320**, e32–e35 (2008).
9. J.-S. Zhou, J.-Q. Yan, J. B. Goodenough, *Phys. Rev. B*, **71**, 220103R (2005).
10. S. Fukushima, T. Sato, D. Akahoshi, H. Kuwahara, *J. Appl. Phys.*, **103**, 7 (2008).
11. Y. Liu, X. Y. Qin, *J. Phys. Chem. Solids*, **67**, 1893 (2006).
12. G. Ch. Kostogloudis, N. Vasilakos, Ch. Ftikos, *Solid State Ionics*, **106**, 207 (1998).
13. A. J. Barón-González, C. Frontera, J. L. García-Muñoz, J. Blasco, C. Ritter, S. Valencia, R. Feyerherm, E. Dudzik, *Physics Procedia*, **8**, 73 (2010).
14. R. Z. Yarbay, H. E. Figenand S. Z. Baykara, *Acta Phys. Polonica A*, **121**, 44 (2012).
15. M. M. Farhoudi, X. L. Wang, *IEEE Transactions on Magnetism*, **41**(10), 3493 (2005).
16. S. Dimitrovska-Lazova, D. Kovacheva, S. Aleksovska, M. Marinšek, P. Tzvetkov, *Bulg. Chem. Comm.*, **44**, 235 (2012).
17. S. Dimitrovska-Lazova, D. Kovacheva, P. Tzvetkov, *Bulg. Chem. Comm.*, **44**, 245 (2012).
18. M. Pecovska Gjorgjevich, S. Aleksovska, M. Marinšek, S. Dimitrovska-Lazova, *J. Am. Ceram. Soc.*, **97**(12) 3864 (2014).
19. M. Pecovska Gjorgjevich, S. Aleksovska, S. Dimitrovska-Lazova, *Physica Macedonica*, **61**, 21 (2012).
20. S. Dimitrovska-Lazova, V. Mirčeski, D. Kovacheva, S. Aleksovska, *J. Solid State Electrochem.*, **16**, 219 (2012).
21. H. Taguchi, *J. Solid State Chem.*, **122**, 297 (1996).
22. H. M. Rietveld, *J. Appl. Crystallogr.*, **2**, 65 (1969).
23. J. Rodriguez-Carvajal, *Physica B*, **192**, 55 (1993).
24. F. Scholz, U. Schröder, R. Gulaboski, *Electrochemistry of immobilized particles and droplets*, Springer, Berlin, 2005.
25. R. H. Mitchell, *Perovskites: Modern and Ancient*, Almaz press – Thunder Bay, 2002.
26. J. A. Alonso, M. J. Martínez-Lope, C. de la Calle, V. Pomjakushin, *J. Mater. Chem.*, **16**, 1555 (2006).
27. S. Sasaki, C. Prewitt, R. Liebermann, *Am. Mineral.*, **68**, 1189 (1983).
28. G. Huo, D. Song, Q. Yang, F. Dong, *Ceram. Int.*, **34**, 497 (2008).
29. R. D. Shannon, *Acta Crystallogr.*, **A32**, 751 (1976).
30. A. Salinas-Sanchez, J. L. Garcia-Muniz, J. Rodriguez-Carvajal, R. Saez-Puche, J. L. Martinez, *J. Solid State Chem.*, **100**, 201 (1992).
31. I. D. Brown, *Acta Crystallogr.*, **B53**, 381 (1997).

ВЛИЯНИЕ НА ЗАМЕСТВАНЕТО НА Y-ЙОНИ ВЪРХУ СТРУКТУРНИТЕ И ЕЛЕКТРОХИМИЧНИ ХАРАКТЕРИСТИКИ НА $YCo_{0.5}Fe_{0.5}O_3$

С. Димитровска-Лазова^{1*}, С. Алексовска^{1,2,4}, П. Цветков³,
В. Мирчески^{1,4}, Д. Ковачева³

¹ Университет „Св. Кирил и Методий“, Институт по химия, Факултет Природни науки и математика, Архимедова 5, 1000 Скопие, Република Македонија

² Изследователски център за околна среда и материали, Македонска академия на науките и изкуствата, Бул. „Кръсте Мисирков“ 2, п.к. 428, 1000 Скопие, Република Македонија

³ Институт по обща и неорганична химия, Българска академия на науките, „Акад. Георги Бончев“, бл. 11, 1113 София, България

⁴ Медицински факултет, Университет „Гоце Делчев“, Шип, Република Македонија

Постъпила декември, 2014 г.; приета януари, 2015 г.

(Резюме)

Представено е влиянието на частично заместване на Y^{3+} от Ca^{2+} в структурата на $YCo_{0.5}Fe_{0.5}O_3$ върху кристалохимичните и електрокаталитични свойства. Съединенията с химичен състав $YCo_{0.5}Fe_{0.5}O_3$ и $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ имат перовскитова структура и бяха получени по метода на изгаряне от разтвор с използване на лимонена киселина за гориво. Получените фази бяха характеризирани с прахова рентгенова дифракция (XRD) и циклична волтаметрия. Кристалната структура и на двете съединения беше уточнена по метода на Ритвелд. Праховите дифрактограми показват, че двете съединения кристализират в орторомбична пространствена група $Pnma$. С цел да се получи по-ясна представа за влиянието на заместването на Y^{3+} от Ca^{2+} йони върху структурните характеристики, параметрите на елементарната клетка и разстоянията и ъглите в структурата бяха използвани за изчисляване на няколко кристалохимични параметъра като деформация на клетката, орторомбично изкривяване, деформация на дължината на връзки и ъгли, наклон на октаедрите, сума от валентните връзки и глобален индекс на нестабилност. Беше установено, че пресметнатите индекси на деформация и ъгли на наклон между октаедрите са по-малки за $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ в сравнение с $YCo_{0.5}Fe_{0.5}O_3$, което е показател за по-стабилна структура. Като се има предвид възможното прилагане на тези съединения като катализатори в директни горивни клетки, работещи с метанол, техните каталитични свойства по отношение на окисление на метанол в алкални разтвори бяха изучени с циклична волтаметрия. Беше изпитана също тяхната електрокаталитичната активност спрямо окисление на хлорни йони и H_2O_2 в разтвори на фосфатен буфер.