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STRUCTURAL AND ELECTRICAL PROPERTIES OF THE SELECTED RARE-EARTH OXYCHLORIDES

STRUKTURALNE I ELEKTRYCZNE WŁASNOŚCI WYBRANYCH TLENOCHLORKÓW METALI ZIEM RZADKICH

The preparation and sintering conditions of the selected rare-earth oxychlorides REOCl (Re=La, Nd, Sm, Gd) were determined. The purity of materials phase compositions was confirmed by X-ray diffraction method. Further analysis of the data enabled lattice parameters and average grain size determination. The electrical properties of the single phase REOCl materials were investigated by Electrochemical Impedance Spectroscopy in wide temperature range in atmospheric air. The spectra were analyzed by the equivalent circuit fitting. Basing on the values of equivalent circuits parameters the specific conductivities were calculated and presented in the Arrhenius coordinates. Energies of activation were calculated. The determined structural and electrical properties of four different rare-earth oxychlorides were directly compared.

Keywords: solid electrolytes, Electrochemical Impedance Spectroscopy, rare-earth oxychlorides

Ustalono warunki syntezy i spiekania wybranych tlenochlorków metali ziem rzadkich, a mianowicie LaOCl, NdOCl, SmOCl oraz GdOCl. Czystość składów fazowych materiałów potwierdzono metodą dyfrakcji promieniowania rentgenowskiego. Analiza uzyskanych danych pozwoliła na wyznaczenie wartości stałych sieciowych oraz średniej wielkości ziaren. Własności elektryczne materiałów wyznaczono metodą elektrochemicznej spektroskopii impedancyjnej w szerokim zakresie temperatur w powietrzu atmosferycznym. Do każdego z widm dopasowano układ zastępczy. Na tej podstawie wyznaczono wartości przewodnictw właściwych i sporządzono wykresy Arrheniusa oraz wyznaczono wartości energii aktywacji. Przeprowadzone badania pozwoliły na bezpośrednie porównanie własności strukturalnych i elektrycznych tlenochlorków czterech różnych metali ziem rzadkich.

1. Introduction

The rare-earth oxychlorides REOCl are novel functional materials. According to the literature reviews some of their properties were subjects of preliminary studies e.g. paramagnetical susceptibility and structural stability [1,2].

There are at least four synthesis methods of the materials:

- reaction between ammonium chloride and rare earth oxide (RE)₂O₃ at elevated temperature in the neutral gas atmosphere e.g. nitrogen, helium or argon;
- reaction between gaseous HCl and (RE)₂O₃ in elevated temperature;
- reaction between diluted hydrochloride acid followed by calcination;
- synthesis from the rare earth chlorides in oxidizing atmosphere in elevated temperature.

Up to now only one compound from the whole range of the REOCl namely lanthanum oxychloride (LaOCl) was investigated from the point of view of the electrical properties [3]. The material was synthesized using hydrochloride acid and La₂O₃. Values of electrical conductivities were

determined at different temperatures using Electrochemical Impedance Spectroscopy (EIS). An electrochemical cell was built using LaOCl as a solid electrolyte. Open Cell Voltage (OCV) measurements of the cells were performed in different gaseous atmospheres. It was found that LaOCl is chlorine and oxygen high ionic conductor. Moreover modification of LaOCl by doping with Mg²⁺ or Ca²⁺ ions leads to creation of the additional Cl⁻ anion vacancies and increases total electrical conductivity [3-5].

It is worth to mention that there is a serious need for novel high Cl⁻ ionic conductors. Such materials are inevitable for the Cl₂ potentiometric chlorine gas sensor constructions. LaOCl is a promising candidate as chlorine gas sensing material for potentiometric sensors due to its high chloride ion conduction [3]. Its unique properties such as mechanical, chemical and thermal stability as well insolubility in water make it superior to earlier used Cl⁻ anion conducting chlorides e.g. AgCl, KCl, NaCl. Moreover, in contrast to some of the chloride electrolytes such as BaCl₂ and PbCl₂, it is not toxic and does not cause direct threat for human beings and environment. Therefore LaOCl was used as solid electrolyte

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or auxiliary phase in different potentiometric chlorine gas sensors prototype construction [6-8].

The whole range of REOCl are expected as materials of high applicative qualities. The materials are potential candidates for elements in electrochemical devices. However up to now there was lack of suitable data about the electrical properties of the above mentioned compounds. The main purpose of presented research was electrical properties of selected REOCl (Re=La, Nd, Sm, Gd) examination in wide range of temperatures. First step of the studies consisted in experimental determination of preparation conditions in order to obtain dense sintered bodies of assumed compositions. Initially syntheses were conducted according to the descriptions published elsewhere [1]. The X-ray diffraction method (XRD) was useful in controlling the phase compositions of prepared materials. The LaOCl pure phase was obtained at the first attempt. In case of NdOCl, SmOCl, GdOCl slight modification of synthesis and sintering temperatures were necessary in order to obtain oxychlorides without oxide phases impurities.

2. Experimental

The REOCl samples were prepared by a solid state reaction between RE oxides and ammonium chloride in a static argon atmosphere at elevated temperatures. All the reagents were provided by Acros. In each case the oxides were weighed in order to obtain 3 g of final REOCl product. For each synthesis the double excess of ammonium chloride was used in comparison to the stoichiometric ratio to force the reaction to completeness. The reagents were crushed thoroughly in agate mortar palletized and calcinated in the quartz tube in neutral atmosphere of argon. The mixtures were first heated from room temperature to 450°C for 6 hours and hold at 450°C for 2 hours. The second part of the calcination procedure consisted of heating to final temperature for 4 hours and holding in it for 1 hour. The final calcination temperature depended on kind of rare-earth metal in used $(RE)_2O_3$. According to literature the higher atomic number of rare earth metal into REOCl compound the lower temperature stability of the REOCl phase. Thus usage of too high temperature leads to decomposition of REOCl to $(RE)_2O_3$ and free gaseous Cl_2 . On the other hand, the calcination and sintering temperature has to be high enough in order to force the reaction to completeness as well as to provide good crystallinity of the product. Therefore, preparation conditions impact on chemical composition and physical properties of the final product.

After calcination, the materials were crushed in agate mortar and the pellets of 0.5 g and 10 mm diameter were prepared. The samples were sintered in the neutral atmosphere of argon heated from room temperature to final temperature different for different REOCl for 8 hours followed by holding the pellets for 2 hours at adjusted temperature. The details of the preparation conditions are presented in the next section. TABLE 1 contains the list of prepared batches of materials with enclosed calcination and sintering temperatures. All the prepared pellets were dense and mechanical stable.

From each batch one pellet was crushed in agate mortar for X-ray Diffraction (XRD) measurements in order to determine

the phase composition of the product. The measurements were done in air at room temperature using CuK α radiation (Philips X' Pert) within the 2Θ range 10-90° with the scan rate of 0,008°/s. The experimental data were interpreted using XRD patterns distributed by The International Centre for Diffraction Data – ICDD. The reference numbers of each indicated phase are listed in TABLE 1. Basing on XRD spectra of REOCl single phase probes the constants of elementary cells as well as grain sizes were determined using the broadening of diffraction lines analysis founded on Sherrer's equation.

Electrical properties of four pure oxychloride phase samples were investigated. LaOCl, NdOCl, SmOCl and GdOCl pellets were placed between two silver plates serving as electrodes in the holder for Electrochemical Impedance Spectroscopy (EIS) measurements. The EIS measurements were performed in atmospheric air at temperature range 300-700°C using a frequency analyzer (Solartron model FRA 1260) coupled with Dielectric Interface (model 1296). Frequency range was 0.1 Hz-10 MHz, the amplitude of sinusoidal voltage signal was 20 mV. The experimental data were analyzed using the ZView software (version 2.2, Scribner Associates, Inc.) aided in determination of equivalent circuits' optimal parameters.

3. Results and discussion

First step of the research was preparation of four material batches containing different rare-earth metals (La1, Nd1, Sm1, Gd1). The preparation conditions were selected basing on literature data [1] as well as our previous experience [3, 6, 10]. From every batch one sintered pellet was crushed to powder. Phase compositions of the samples were studied by XRD method. The obtained results are presented in TABLE 1. The La1 specimen contained assumed LaOCl compound without any impurities. La1 spectra showed in Fig. 1 reveals low background indicating fine crystallinity of the material.

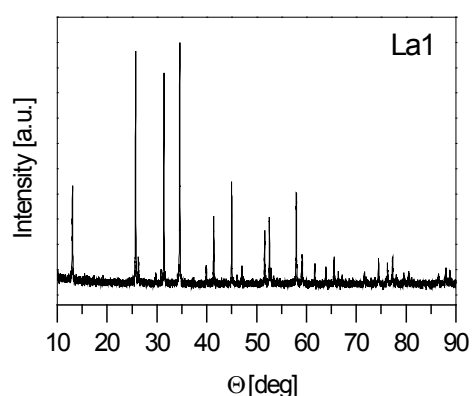


Fig. 1. XRD patterns of La1 sample

The spectra obtained for the rest of the samples are revealed in Fig. 2, 4, 6. In the case of Nd1, Sm1 and Gd1 samples, some amounts of $(RE)_2O_3$ impurity phases were detected indicating too high preparation temperatures which led to partial decomposition of REOCl phases. The regions containing the peaks coming from secondary oxides phases

TABLE 1

Influence of calcination and sintering temperature on phase composition of prepared materials.

Probe label	Assumed Compound	Preparation condition		Obtained composition by XRD	ICDD reference number
		Synthesis final temperature	Sintering final temperature		
La1	LaOCl	830°C	780°C	LaOCl 100%	98-004-0297
Nd1	NdOCl	880°C	830°C	NdOCl 96.7%	98-005-9231
				Nd ₂ O ₃ trigonal 2,3%	98-016-9442
				Nd ₂ O ₃ hexagonal 1%	98-010-0213
Nd2	NdOCl	830°C	780°C	NdOCl 100%	98-005-9231
Sm1	SmOCl	800°C	750°C	SmOCl 95.9%	98-002-6581
				Sm ₂ O ₃ cubic 4,1%	98-002-7998
Sm2	SmOCl	750°C	700°C	SmOCl 100%	98-002-6581
Gd1	GdOCl	720°C	770°C	GdOCl 91.1%	98-005-9232
				Gd ₂ O ₃ cubic 8,9%	00-43-1014
Gd2	GdOCl	720°C	670°C	GdOCl 100%	98-005-9232

are enclosed by red rectangles. The lined fragments close ups are revealed in Fig. 3, 5, 7. The impurity (RE)₂O₃ phases peaks are marked by red asterisks and their positions are additionally showed by perpendicular red lines on the angle axes. In order to obtain pure NdOCl, SmOCl, and GdOCl materials the synthesis or/and sintering temperatures were slightly decreased. In Fig 2, 4, 6 spectra coming from samples Nd2, Sm2, Gd2 prepared with modified conditions are shown. In this cases only assumed REOCl phases were detected. The Gd2 spectra revealed raised background denoting crystallinity deterioration associated with lowered sintering temperature.

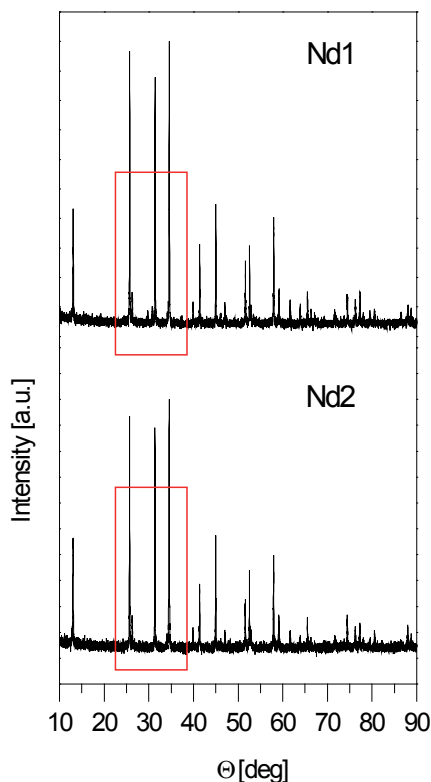


Fig. 2. XRD patterns of Nd1 and Nd2 samples

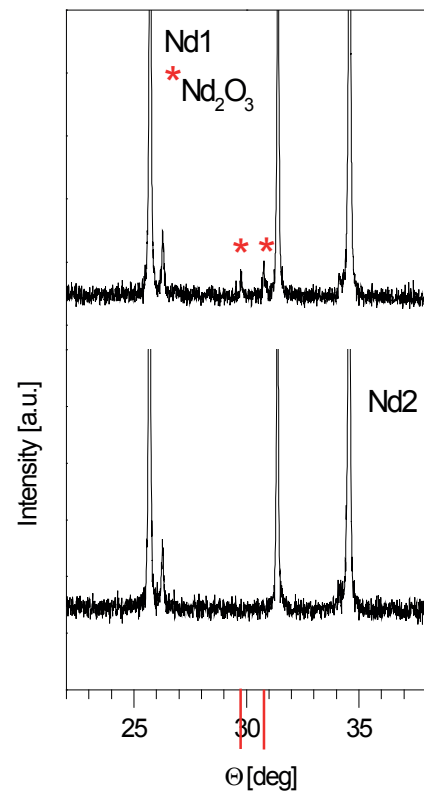


Fig. 3. The fragment of XRD patterns of Nd1 and Nd2 with peaks coming from oxide phase

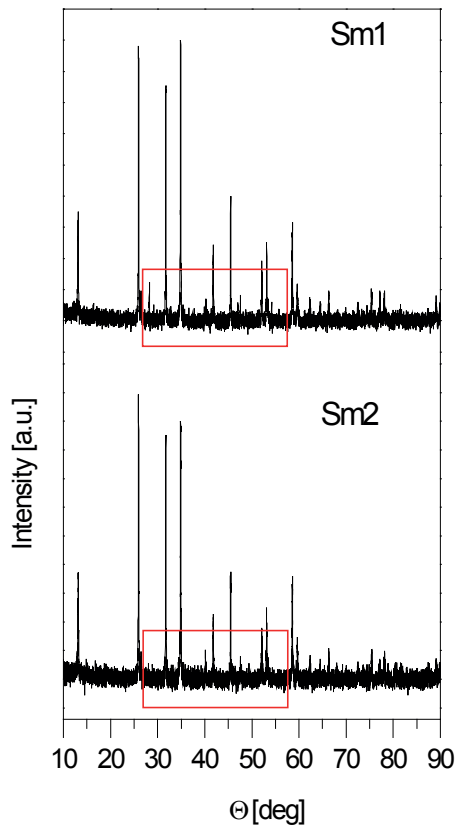


Fig. 4. XRD patterns of Sm1 and Sm2 samples

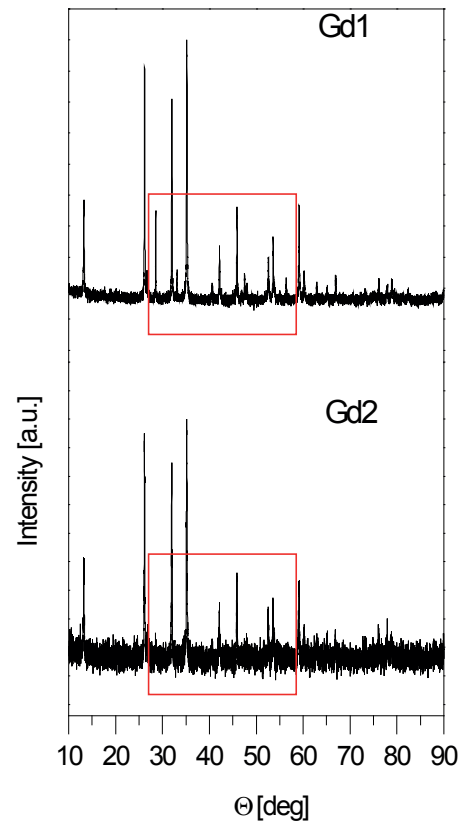


Fig. 6. XRD patterns of Gd1 and Gd2 samples

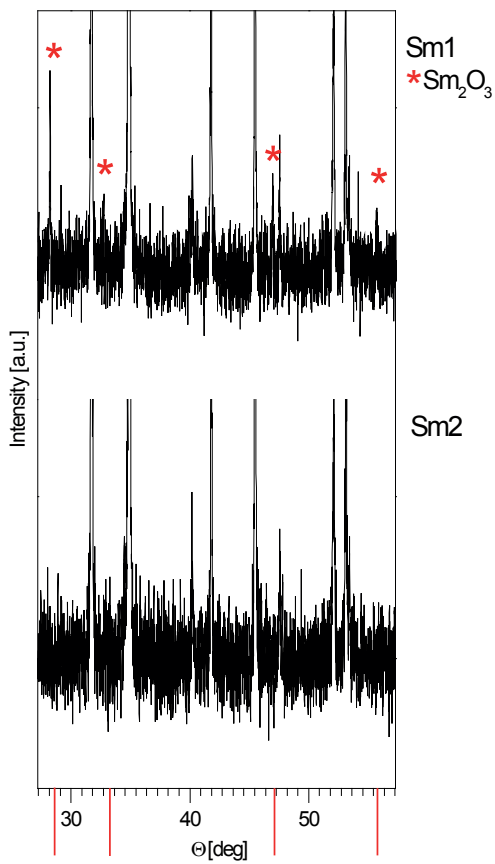


Fig. 5. The fragment of XRD patterns of Sm1 and Sm2 with peaks coming from oxide phase

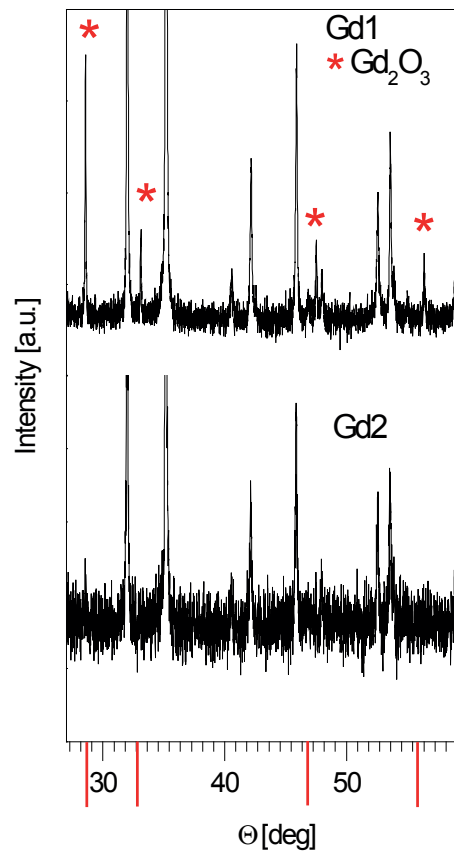


Fig. 7. The fragment of XRD pattern of Gd1 and Gd2 with peaks coming from oxide phase

TABLE 2

Crystallographic data determined by XRD measurements.

Probe label	Composition	Crystallographic data	Lattice parameters	Average grain size
La1	LaOCl	Crystal system: tetragonal Space group: P 4/n m m Space group number: 129	a=0.41208 nm c=0.68823 nm	D(011) ≈ 300 nm
Nd2	NdOCl		a=0.40249 nm c=0.67731 nm	D(011) ≈ 150 nm
Sm2	SmOCl		a=0.39825 nm c=0.67209 nm	D(011) ≈ 110 nm
Gd2	GdOCl		a=0.39500 nm c=0.66654 nm	D(111) ≈ 56 nm

Selected crystallographic data of investigated oxychlorides were determined basing on La1, Nd2, Sm2 and Gd2 spectra. All the REOCl crystallized in tetragonal P4/nmm structure. Calculated lattice parameters as well as average grain sizes are listed in TABLE 2. As it was expected, the lattice parameter values decreases with growing atomic number of the rare-earth metal RE in REOCl. It is related to the fact, that the heavier rare-earth metals are characterized by smaller ionic radius. Average grain size of sintered materials decreases with growing atomic number of the rare-earth metal. What is interesting LaOCl sample is composed from two times bigger grains than NdOCl despite both samples were prepared in comparable conditions. It indicates that the kind of metal is determinant of grain morphology of the sintered REOCl material.

The investigated REOCl electrical properties were studied by EIS method in temperature range 300-700°C in atmospheric air. The measurements were performed on single phase La1, Nd2, Sm2, Gd2 pellets. The exemplary Nyquists spectra obtained at different temperatures are featured in Fig. 8-12.

The LaOCl results vary from results obtained for the rest of the samples. Spectra of LaOCl material shows significant shape changes with growing temperature. At temperatures 300 and 350°C La1 Nyquist plot consists of single semicircle, whereas at temperatures 400-500°C the semicircle in higher frequencies part and arc in lower frequencies are visible. At temperatures 550-700°C high frequencies fragment becomes deformed and low frequency part is nearly rectilinear.

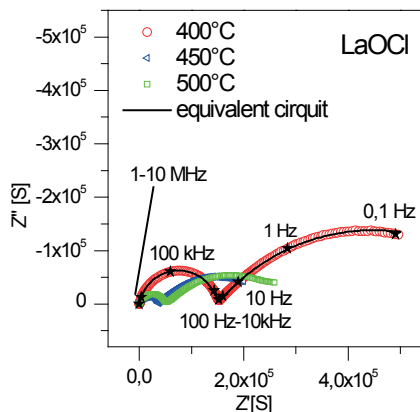


Fig. 8. Complex impedance spectra of La1 sample in temperature range 400-500°C in atmospheric air

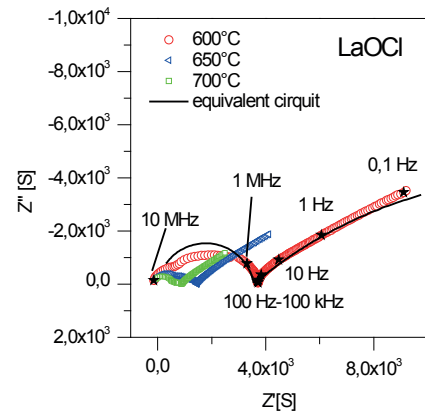


Fig. 9. Complex impedance spectra of La1 sample in temperature range 600-700°C in atmospheric air.

In case of Nd2, Sm2, Gd2 samples obtained Nyquist spectra consisted of single semicircles. At temperatures 600-700°C additional short spurs appeared in low frequencies spectra fragments of Sm2 and Nd2 specimens.

Electrical equivalent circuits were fitted to the experimental data sets. In Fig 8-12 simulated spectra coming from equivalent circuits are plotted using solid lines. For Nd2, Sm2, Gd2 spectra from the whole temperatures as well as for La1 spectra from 300 and 350°C simple parallel equivalent circuits comprised of resistor and Constant Phase Elements (CPE) were fitted. LaOCl more complex spectra at higher temperatures were analyzed by connected in series two parallel equivalent circuits consisted of resistors and Constant Phase Elements.

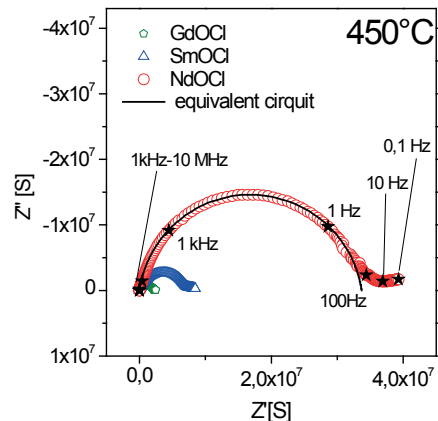


Fig. 10. Complex impedance spectra of Nd2, Sm2 and Gd2 samples at 450°C in atmospheric air

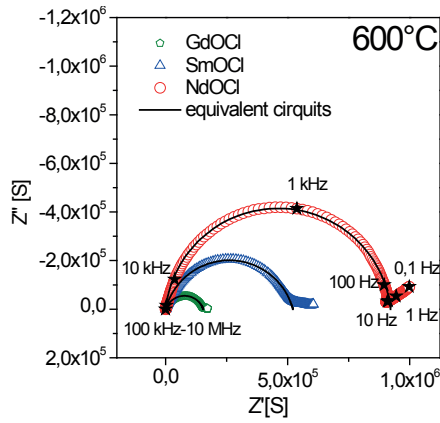


Fig. 11. Complex impedance spectra of Nd2, Sm2 and Gd2 samples at 600°C in atmospheric air

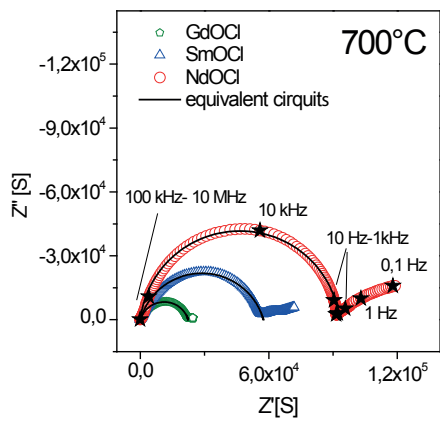


Fig. 12. Complex impedance spectra of Nd2, Sm2 and Gd2 samples at 700°C in atmospheric air

The CPE element was used in a model in place of a capacitor to compensate for non-homogeneity in the system. The CPE is defined by two values, A_0 and n . The impedance in this case is given by relation:

$$Z = 1 / (A_0(i\omega)^n) \tag{1}$$

If n equals 1 the equation is identical to that of a Debye capacitor. In case n equals 0 the CPE is equivalent to resistor. A n value of 0,5 can be used to produce an Infinite Length Warburg element, which occurs when charge carriers diffuse through a material.

Figures 13 and 14 contain plots illustrating the relation between fitted CPE parameters and temperature for the examined specimens. The A_0 values for Nd2, Sm2, Gd2 and La1 for high frequencies are between 10^{-11} - 10^{-9} [S·s⁻¹]. The values of parameter A_0 for La1 in low frequencies are much higher than A_0 in above mentioned cases and strongly depend on temperature. In case of Nd2, Sm2 and Gd2 the parameter n rise with growing temperature. The determined n values are quite high showing the capacitive properties of the materials. In the case of La1, two CPE elements had to be used for fitting the experimental data. One of them is responsible for high frequency spectra part, and the second simulates the data in the low frequency fragments. The n value in high frequency part indicates similar capacitive properties of the LaOCl phase. The data in low frequencies are fitted using Warburg elements as parameter n

can be approximated by 0,5. Obtained results can be interpreted assuming that the silver cations diffuse to LaOCl material. In cases of Nd2, Sm2, Gd2 such processes do not occur.

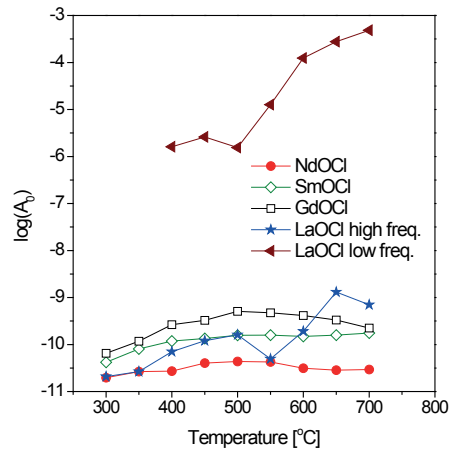


Fig. 13. Values of A_0 parameters in CPE elements used in equivalent circuits

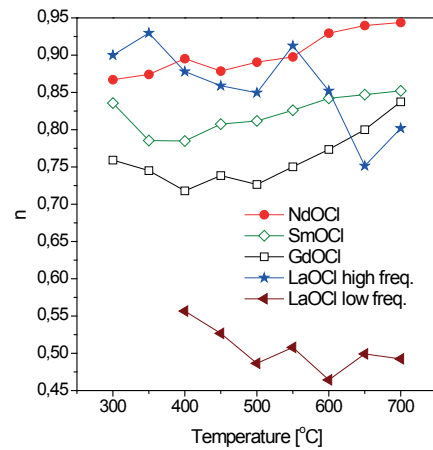


Fig. 14. Values of n parameters in CPE elements used in equivalent circuits

Knowing the geometry of the samples specific conductivities values were calculated. The result were plotted in $\log(\sigma T)$ vs. $1000/T$ coordinates.

In Fig. 15 Arrhenius plots for La1 sample are presented with distinguished results obtained for lower and higher frequencies signal. According to the state of the art the results obtained for low frequencies are mainly depended by ceramic material-metallic electrodes interface properties. The higher frequencies part is influenced by material behavior. In both higher and lower frequencies plots the shifts between linear fragments are observed. It can be interpreted taking into account possible reaction between LaOCl phase and silver electrode which may lead to additional AgCl layer creation followed by melting of arisen AgCl phase above 450°C. This conclusion is also consistent with mentioned above determined values of n parameters used in CPE element for simulation of spectra low frequency part. The values of total electrical conductivities for La1 probe were calculated as:

$$\sigma_{TOTAL} = (\sigma_1 \cdot \sigma_2) / (\sigma_1 + \sigma_2) \tag{2}$$

The Arrhenius plots considered total conductivities for all investigated samples are featured in Fig. 16. For Nd2, Sm2 and Gd2 specimens, the linear dependence is in good agreement with the Arrhenius law. For La1 sample the plot consists of two linear fragments with shift between 400-450°C. Such shift is attributed to the melting of arisen AgCl phase. In each temperature the relation between total conductivities: $\sigma_{\text{TOTAL LaOCl}} > \sigma_{\text{TOTAL GdOCl}} > \sigma_{\text{TOTAL SmOCl}} > \sigma_{\text{TOTAL NdOCl}}$ is preserved.

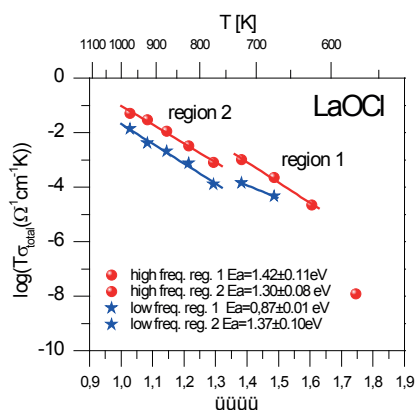


Fig. 15. The dependences of LaOCl conductivity as function of temperature in $\log(\sigma T)$ vs. $1/T$ coordinates

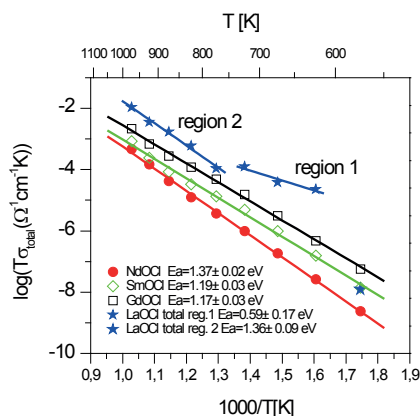


Fig. 16. The dependences of rare earth oxichlorides total conductivities as function of temperature in $\log(\sigma T)$ vs. $1/T$ coordinates

In each case basing on linear Arrhenius dependences the activation energy values were calculated. The energy of activation value for LaOCl in temperature range 300-450°C is much lower in comparison to the comparable values for NdOCl, SmOCl, GdOCl and LaOCl in higher temperatures. It demonstrates that LaOCl compound is much more chemically reactive than the rest of the investigated oxichlorides.

4. Conclusion

Selected rare-earth oxichlorides REOCl (Re=La, Nd, Sm, Gd) were synthesized from rare-earth oxides and ammonium chloride at elevated temperatures in neutral atmosphere of argon. XRD analysis of pure REOCl materials revealed that lattice parameter value as well as average grain size decrease with growing atomic number of rare-earth metal in REOCl compound.

The studied oxichlorides electrical properties were determined by EIS analysis and compared. For NdOCl, SmOCl and GdOCl simple semicircle Nyquists spectra and rectilinear Arrhenius plots were obtained exhibiting ionic conducting processes in the materials. It turned out that in these cases total electrical conductivity grows with decreasing atomic number.

The explanation of the more complicated EIS spectra obtained for LaOCl material requires assumption of the reaction occurring between oxichloride phase and silver electrode material, in which AgCl layer is created. Detailed analysis of the EIS data by equivalent circuit method showed that LaOCl is much more chemically reactive as well as exhibits much higher electrical conductivity in comparison to the rest of investigated REOCl materials in the temperature range 350-700°C.

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REFERENCES

- [1] J. Hölsä, R. Lamminmäki, M. Lastusaari, P. Porcher, R. Sáez-Puche, J. Alloy. Compd. **303-304**, 498-504 (2000).
- [2] Y. Cho, H. Yang, H. Eun, E. Kim, J. Kim, J. Ind Eng. Chem **11**, 707-711 (2005).
- [3] M. Dziubaniuk, P. Pasierb, M. Rękas, Funct. Mater. Lett. **4**, 171-174 (2011).
- [4] K. Okamoto, N. Imanaka, G. Adachi, Solid State Ionics **154-155**, 577-580 (2002).
- [5] N. Imanaka, K. Okamoto, G. Adachi, Angew. Chem. Int. Ed. Eng. **41**, 3890-3892, (2002).
- [6] N. Imanaka, K. Okamoto, G. Adachi, Matter. Lett. **57**, 1966-1969 (2003).
- [7] N. Imanaka, K. Okamoto, G. Adachi, Electrochem. Commun. **3**, 49-51 (2001).
- [8] N. Imanaka, K. Okamoto, G. Adachi, Sens. Actuators B **93**, 233-236 (2003).

