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 \((\text{RE}_2\text{O}_3)\) at elevated temperature in the neutral gas atmosphere e.g. nitrogen, helium or argon;
- reaction between gaseous \(\text{HCl}\) and \((\text{RE}_2\text{O}_3)\) in elevated temperature;
- reaction between diluted hydrochloric 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 \((\text{LaOCl})\) was investigated from the point of view of the electrical properties [3]. The material was synthesized using hydrochloric acid and \(\text{La}_2\text{O}_3\). Values of electrical conductivities were determined at different temperatures using Electrochemical Impedance Spectroscopy (EIS). An electrochemical cell was built using \(\text{LaOCl}\) as a solid electrolyte. Open Cell Voltage (OCV) measurements of the cells were performed in different gaseous atmospheres. It was found that \(\text{LaOCl}\) is chlorine and oxygen high ionic conductor. Moreover modification of \(\text{LaOCl}\) by doping with \(\text{Mg}^{2+}\) or \(\text{Ca}^{2+}\) ions leads to creation of the additional \(\text{Cl}^{-}\) anion vacancies and increases total electrical conductivity [3-5].

It is worth to mention that there is a serious need for novel high \(\text{Cl}^{-}\) ionic conductors. Such materials are inevitable for the \(\text{Cl}_2\) potentiometric chlorine gas sensor constructions. \(\text{LaOCl}\) 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 \(\text{Cl}^{-}\) anion conducting chlorides e.g. \(\text{AgCl}, \text{KCl}, \text{NaCl}\). Moreover, in contrast to some of the chloride electrolytes such as \(\text{BaCl}_2\) and \(\text{PbCl}_2\), it is not toxic and does not cause direct threat for human beings and environment. Therefore \(\text{LaOCl}\) was used as solid electrolyte...
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)₂O₃. 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)₂O₃ and free gaseous Cl₂. 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 CuKa 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. Based on XRD spectra of REOCl single phase probes the constants of elementary cells as well as grain sizes were determined using the breadth 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](image-url)

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)₂O₃ 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
Influence of calcination and sintering temperature on phase composition of prepared materials.

<table>
<thead>
<tr>
<th>Probe label</th>
<th>Assumed Compound</th>
<th>Preparation condition</th>
<th>Obtained composition by XRD</th>
<th>ICDD reference number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Synthesis final temperature</td>
<td>Sintering final temperature</td>
<td></td>
</tr>
<tr>
<td>La1</td>
<td>LaOCl</td>
<td>830°C</td>
<td>780°C</td>
<td>LaOCl 100%</td>
</tr>
<tr>
<td>Nd1</td>
<td>NdOCl</td>
<td>880°C</td>
<td>830°C</td>
<td>NdOCl 96.7%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Nd2O3 trigonal 2.3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Nd2O3 hexagonal 1%</td>
</tr>
<tr>
<td>Nd2</td>
<td>NdOCl</td>
<td>830°C</td>
<td>780°C</td>
<td>NdOCl 100%</td>
</tr>
<tr>
<td>Sm1</td>
<td>SmOCl</td>
<td>800°C</td>
<td>750°C</td>
<td>SmOCl 95.9%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sm2O3 cubic 4.1%</td>
</tr>
<tr>
<td>Sm2</td>
<td>SmOCl</td>
<td>750°C</td>
<td>700°C</td>
<td>SmOCl 100%</td>
</tr>
<tr>
<td>Gd1</td>
<td>GdOCl</td>
<td>720°C</td>
<td>770°C</td>
<td>GdOCl 91.1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gd2O3 cubic 8.9%</td>
</tr>
<tr>
<td>Gd2</td>
<td>GdOCl</td>
<td>720°C</td>
<td>670°C</td>
<td>GdOCl 100%</td>
</tr>
</tbody>
</table>

are enclosed by red rectangles. The lined fragments close ups are revealed in Fig. 3, 5, 7. The impurity (RE)_2O_3 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](image1)

![Fig. 3. The fragment of XRD patterns of Nd1 and Nd2 with peaks coming from oxide phase](image2)
Fig. 4. XRD patterns of Sm1 and Sm2 samples

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

Fig. 6. XRD patterns of Gd1 and Gd2 samples

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.

<table>
<thead>
<tr>
<th>Probe label</th>
<th>Composition</th>
<th>Crystallographic data</th>
<th>Lattice parameters</th>
<th>Avarage grain size</th>
</tr>
</thead>
<tbody>
<tr>
<td>La1</td>
<td>LaOC1</td>
<td>Crystal system: tetragonal</td>
<td>a=0.41208 nm</td>
<td>D(011) ≈ 300 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Space group: P 4/n m m</td>
<td>c=0.68823 nm</td>
<td></td>
</tr>
<tr>
<td>Nd2</td>
<td>NdOC1</td>
<td></td>
<td>a=0.40249 nm</td>
<td>D(011) ≈ 150 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=0.67731 nm</td>
<td></td>
</tr>
<tr>
<td>Sm2</td>
<td>SmOC1</td>
<td></td>
<td>a=0.39825 nm</td>
<td>D(011) ≈ 110 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=0.67209 nm</td>
<td></td>
</tr>
<tr>
<td>Gd2</td>
<td>GdOC1</td>
<td></td>
<td>a=0.39500 nm</td>
<td>D(111) ≈ 56 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=0.66654 nm</td>
<td></td>
</tr>
</tbody>
</table>

Selected crystallographic data of investigated oxychlorides were determined basing on La1, Nd2, Sm2 and Gd2 spectra. All the REOCl crystallized in tetragonal P4/ n mm 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 LaOC1 sample is composed from two times bigger grains than NdOC1 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 LaOC1 results vary from results obtained for the rest of the samples. Spectra of LaOC1 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.

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 Constance Phase Elements (CPE) were fitted. LaOC1 more complex spectra at higher temperatures were analyzed by connected in series two parallel equivalent circuits consisted of resistors and Constance Phase Elements.
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:

\[
Z = \frac{1}{A_0(\omega t)^n}.
\]  

If \(n\) equals 1 the equation is identical to that of a Debye capacitor. In case \(n\) equals 0 the CPE is equivalent to a 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 \(10^{-11}-10^{-9}\) \([\text{s} \cdot \text{s}^{-1}]\). 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.

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:

\[
\sigma_{\text{TOTAL}} = (\sigma_1 \cdot \sigma_2) / (\sigma_2 + \sigma_2)
\]  

(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(sT) vs. 1/T coordinates](image1)

![Fig. 16. The dependences of rare earth oxichlorides total conductivities as function of temperature in log(sT) vs. 1/T coordinates](image2)

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 oxychlorides.

### 4. Conclusion

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

The studied oxichlorides electrical properties were determined by EIS 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 REOCI materials in the temperature range 350-700°C.

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### REFERENCES


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