On the electrical conductivity of YCrO₃ porous ceramics

D D Malev ¹, ², O Yu Sinelshchikova ³ and V I Popkov ¹
¹ Ioffe Institute, 26 Politekhnicheskaya, St. Petersburg 194021, Russia
² Saint-Petersburg Mining University, 2 21st Line, St. Petersburg, 199106, Russia
³ Institute of Silicate Chemistry, 2 Makarova emb., St. Petersburg, 199034, Russia

E-mail: dm110297@yandex.ru

Abstract. In this work, nanocrystalline yttrium orthochromite (YCrO₃) was synthesized via the solution combustion method using metal nitrates and glycine. The resulting powder was used for sintering YCrO₃ porous ceramics. The SEM, EDX, PXRD and TMA were used to examine structural and morphological features of both the preceramic powder and the sintered ceramics. The electroconductivity of the obtained porous ceramics was investigated in the temperature range from 25 to 1200 °C. YCrO₃ bulk conductivity was found to depend on the microstructure and the pore volume fraction: at temperatures below 400 °C the electrical conductivity was higher than the values for high-density ceramics, while for temperatures above 800 °C the electrical conductivity of the resulting material approaches the values of high-density ceramics (σdc = 1.97×10⁻² S/cm at 1000 °C).

1. Introduction

YCrO₃-based ceramics, which has been successfully applied as a material of electric resistance heaters, recently has attracted the interest of researchers as a multiferroic material with both ferroelectric and magnetic transitions at temperatures of 140 and 473 K, respectively [1-5]. Because of such properties, as well as its high thermal stability, it is proposed to use yttrium orthochromite to create high-temperature electrodes and cathodes for solid oxide fuel cells or SOFCs.

Polycrystalline yttrium chromite can be obtained by the traditional solid-state method from oxides or metal nitrates with final thermal treatment at 1450–1900 °C [4–7]; however, there was an effort to reduce the grain size of ceramics and lower the sintering temperature in the last decade, which has encouraged researchers to use various methods of "soft chemistry" [8–9]. One of these methods is the glycine-nitrate combustion synthesis [10], which allows obtaining highly dispersed YCrO₃ powders at relatively low temperatures [11]. However, unlike the solid-phase method, the final product has a higher specific surface area, which subsequently affects the properties of the final ceramics.

To the best of our knowledge, the effect of porosity on the conductive properties of YCrO₃ has not been studied systematically, although this effect has been investigated extensively for yttrium-stabilized zirconia [11]. Microstructure defects such as grain boundaries, cracks, and especially pores can modify the electrical and magnetic properties of such systems. However, there is no unified theory that could describe the connection between the porosity of a material and its electrical properties, therefore, for most known materials, this relationship is determined experimentally.

The objective of the present work was to obtain porous ceramics of yttrium orthochromite, as well as to study the microstructure and electrical conductivity of the obtained YCrO₃ ceramic. Experimental data were compared with results calculated by the theory of generalized conductivity of heterogeneous
systems by V.I. Odolevsky [12], which has proved to be suitable for calculation of electrical conductivities for materials with a bulk porosity of up to 67%.

2. Experimental

2.1. Materials and methods

YCrO$_3$ powder was obtained by a glycine-nitrate combustion method from a solution of Y(NO$_3$)$_3$·6H$_2$O and Cr(NO$_3$)$_3$·9H$_2$O (99 and 98%, respectively) in a stoichiometric ratio. The glycine was mixed with nitrates in a carbon glass jar with the Y(NO$_3$)$_3$·Cr(NO$_3$)$_3$·2C$_2$H$_5$NO$_2$ = 3:3:10 nitrate ion-to-glycine ratio. The obtained mixture was then heated to evaporate water and to achieve a viscous gel. Heating was continued until a spontaneous exothermic reaction began with the formation of finely dispersed oxide YCrO$_3$. The oxide was collected and grounded into a homogeneous powder, then the fraction of the sample was taken for further analysis, while the rest of the product was then preheated to 600 °C for 6 hours in the air to remove organic species. Desired perovskite powder was mixed with polyvinyl alcohol, cold-pressed into pellets at 500, 750 and 1000 MPa and sintered. The sintering of the sample occurred at atmospheric pressure in two stages: firstly, at a temperature of 600 °C for 2 hours, secondly, for 10 hours at a temperature of 1500 °C. An additional sample was prepared separately with binding and annealed at a temperature of 1500 °C for thermomechanical analysis or TMA.

2.2. Microstructural analysis

At all stages, the phase composition was examined by X-ray powder diffraction analysis (XRD) and energy-dispersive X-ray spectroscopy analysis (EDS). XRD analysis was performed using Rigaku Corporation SmartLab 3, with Ni-filtered Cu-Kα radiation with a wavelength of 1.5056 Å. X-ray diffraction was recorded in the range from 10 to 100° with a step length of 0.05° and a speed of 0.5 °/min. For elemental characterization, a powder sample was placed on a conductive carbon base, and carbon coating was applied. The microstructure of the sintered ceramics was studied on a polished section with SEM TESCAN VEGA 3. Before the analysis, a ceramic pellet was enclosed in an epoxy coating and polished. To reduce the effect of charge accumulation on the surface of the sample, a carbon base was deposited on two opposite sides of the ceramic sample and brought to a metal stand. Scanning and analysis of the composition were carried out in several areas of the sample, after which the result was obtained by averaging the collected values. TMA analysis was performed on a Shimadzu TMA-60 thermomechanical analyzer. The porosity of the sample was determined using a GeoPyc 1360 density analyzer for bulk density and by the helium pycnometry using Micromeritics AccuPyc 1330 for pycnometric density with subsequent porosity calculation. Values for the theoretical density calculated from lattice parameters of obtained YCrO$_3$. The specific surface area was determined by measuring nitrogen sorption-desorption isotherms (BET) with Micromeritics ASAP 2020.

2.3. Electrical characterization

The conductivity of the obtained ceramics was determined by the two-contact method in a universal direct current cell at RLC meter PM6306 with an operating voltage of 1.0 V in the temperature interval of 25-1250 °C. Before, metal contacts were applied to the end surfaces of cylindrical tablets platinum wire by brazing paste at a temperature of 1000 °C (PPl-2, manufactured by Elma-Pasta LLC). DC conductivity ($\sigma_{dc}$) was calculated by using obtained values for resistance ($R$) according to formula (1):

$$\sigma_{dc} = \frac{1}{d \cdot (R \times A)^{-1}}$$

(1)

where $A$ is the area of the electrodes and $d$ is the thickness of the pellet. The activation energy in straight sections was calculated from the Arrhenius equation (2):

$$\sigma_{dc} = \sigma_0 \exp \left( -\frac{E_a}{kT} \right)$$

(2)
where $E_a$ is the activation energy, $T$ is the temperature, $k$ is the Boltzmann constant and $\sigma_0$ is the pre-exponential factor.

3. Results and discussion

The XRD patterns of the YCrO$_3$ at different stages are shown in figure 1. For further consideration, we have implemented a classification as follows: PWD is denoted to an as-prepared powder sample, while CAL and CER stand for calcined at 600°C powder and ceramic pellet, correspondently. According to the obtained results, for a selected ratio of the starting components, the formation of the yttrium chromite occurs after the combustion stage without the formation of any intermediate phases.

![Figure 1. XRD patterns of the as-prepared powder sample (PWD); sample after calcination (CAL); ceramic pellet (CER); peak diffractogram of ortho-YCrO$_3$ ICSD No. 192859 (Calculated)](image)

Thus, heat treatment at 600 °C does not lead to the formation of a new phase, and the location and intensity of the XRD peaks for PWD and CAL are identical. The location of the peaks for CAL and their intensity agreed with the data for orthorhombic yttrium orthochromite ortho-YCrO$_3$ (ICSD No. 192859) with the $Pnma$ space group. The peak position for the CER ceramic sample remains the same, but there is a remarkable change in intensity, especially for the (200) and (002) peaks, which may be caused by oriented sintering during thermal treatment at 1500 °C. The diffraction pattern was further processed using the Rietveld method to refine the structural parameters of synthesized CAL and CER samples.

Crystallographic data from the final refinement as well as the corresponding set of the reliability factors are presented in table 1, according to the calculated discrepancy indexes: profile residual (or reliability) factor, or $R_p$, and weighted profile residual factor, or $R_{wp}$, and goodness-of-fit GoF factor. The lattice parameters obtained for both samples are in agreement with other published results [13,14]. As can be seen, the lattice parameters increased for the ceramic sample; as a result, the unit cell volume increased. This can be explained by both an increase in the number of oxygen vacancies at high temperatures due to the loss of oxygen ions, which further changes the volume of the crystal lattice and leads to the formation of a more stable lattice and crystal grain growth. Additionally, the calculation for theoretical density $\rho_{calc}$ and measurements of bulk density and helium pycnometry allows us to evaluate the open and closed porosity. Thus, significant values of closed porosity indicate that the sintering process continued primarily at the grain boundaries, which allowed the formation of uniformly
distributed pores over the entire volume of the sample. However, there is no definitive relationship between the ratio of open-to-closed porosity and conductivity. As will be indicated later, all analyzed samples demonstrate close values of the activation energy and the electrical conductivity over the full temperature range.

Table 1. Rietveld refinement results of YCrO$_3$-based samples and density/porosity results

| Sample: | Calcined (CAL) | Ceramics (CER) |
|---------|----------------|----------------|
| Phase (chem. name) | YCrO$_3$ (yttrium chromate) | orthorhombic |
| Crystal system | | Pnma (No. 62) |
| Space group | | |
| $\alpha = \beta = \gamma$, deg. | 90 | 90 |
| $a$, Å | 5.5207 | 5.5068 |
| $b$, Å | 7.5344 | 7.5343 |
| $c$, Å | 5.2383 | 5.2510 |
| $V$, Å$^3$ | 217.891 | 217.951 |
| $Z$ | 4 | 4 |
| $\rho_{calc}$, cm$^3$/g | 6.246 | 6.244 |
| $R_p$, % | 4.19 | 7.40 |
| $R_{wp}$, % | 4.71 | 5.72 |
| GoF | 1.53 | 6.06 |
| $\rho_{pycn}$, g/cm$^3$ | 1.6695 ± 0.0066 | 5.8067 ± 0.1979 | 5.3219 ± 0.2509 | 4.9316 ± 0.2465 |
| $\rho_{bulk}$, g/cm$^3$ | - | 2.9425 ± 0.1461 | 2.8145 ± 0.2216 | 2.9277 ± 0.1352 |
| $P_{sum}$, % | - | 52.87 | 54.92 | 53.11 |
| $P_{open}$, % | - | 45.87 | 40.16 | 32.09 |
| $P_{clos}$, % | - | 7.00 | 14.77 | 21.02 |

SEM micrographs of the calcined powder and polished surface of the ceramic sample together with EDS data are shown in figure 2. The micrograph of the polished ceramic showed that the average grain size after the final treatment is about 1 μm; grains have primarily regular polyhedral shape with distinct edges (figure 2c). This result was possible due to the chosen glycine-nitrate synthesis method, which allows one to achieve a powder with a high specific surface with the formation of a large number of micro- and mesopores (figure 2b). Morphological changes of oxide nanocrystals – glycine-nitrate combustion products - accompanying their high-temperature sintering were previously studied in detail in [16-18]. Thus, the specific surface area of the powders after combustion was 14.3±0.1 m$^2$/g, according to the results of the BET analysis, and the average crystallite size calculated by the Scherrer formula is 57.4 nm.

Figure 2. EDS analysis of (a) and SEM micrographs of CAL (b) and CER (c) samples.
We conducted an additional study for the thermal expansion of the CER 500 MPa sample (figure 3). According to the data obtained, an increase in linear dimensions to 0.61% at 1000 °C was revealed for this sample. The value of the coefficient of thermal expansion (CTE) of 6.29·10⁻⁶ K⁻¹ is similar to the published data [13]. Together with the EDS data, we can assume that the loss of oxygen at high temperatures leads to an increase in the size of the crystal lattice.

![Figure 3. TMA-analysis of the sample: the increase in the length of the sample, and the CTE data for the full temperature interval.](image)

As one can see from figure 4a, the electrical conductivity values for the obtained ceramics in the low-temperature region (up to 350 °C) is inferior to the literature data (σ_{dc} = 4 · 10⁻⁷ S/cm at 200 °C). As an example, the graph shows the results of studying high-density ceramics (97.6% of the theoretical density) also obtained from nanopowder using hot pressing in the field-assisted sintering at 1300 °C [13], and isostatically cold-pressed and sintered at 1800 °C (with the 94.3% of the theoretical density) [14].

![Figure 4. Temperature dependences: (a) direct current electrical conductivity of synthesized porous ceramics and high-density YCrO₃ - ceramics according to [14] and [15]; (b) dielectric loss tangent measured at 5-25 kHz frequencies for CER-500 MPa.](image)

In this case, the electrical conductivity of the obtained ceramics does not completely obey the generalized theory of conductivity of heterogeneous systems formulated by V. I. Odelevsky [12],
according to which the electrical conductivity $\sigma$ of a porous conductor (with porosity less than 67 vol.%) is in good agreement with the formula (3):

$$\frac{\sigma}{\sigma_b} = 1 - 1.5\theta$$  \hspace{1cm} (3)

where $\theta$ is the bulk porosity, $\sigma_b$ is the electrical conductivity of the non-porous conductor. In our case, a lower values of electrical conductivity at temperature range 400-1000 °C cannot be completely attributed to a high value of porosity ($\theta \approx 53.6\%$, Table 1), which is probably due to the high electrical resistance of intergranular contacts and structural anisotropy of grains conductivity [3]. In this case, the experimental temperature dependence of the bulk conductivity is characterized by the presence of two intervals with different activation energies. In the low-temperature region, including the temperature of the ferroelectric phase transition (200-225 °C), activation energy $E_a = 0.25 \pm 0.02$ eV. In the high-temperature region, $E_a = 0.14 \pm 0.01$ eV. The maximum error of the measured values for the electrical conductivity does not exceed 8%, which is below the average inaccuracy of the measurement method of 15%. At 1000 °C, an average electrical conductivity is $\sigma_a = 1.97 \cdot 10^2$ S/cm. The maximum error of the measured values for the electrical conductivity does not exceed 8%, which is below the average inaccuracy of the measurement method of 15%.

The temperature of the ferroelectric phase transition can also be refined from the temperature dependences of the dielectric loss tangent for the 25 kHz frequency (figure 4b) [1, 5]. Based on the above graphs, it is in good agreement with previous studies.

4. Conclusion

Yttrium orthochromite YCrO$_3$ was prepared by solution combustion method. XRD analysis and EDS data confirmed the successful synthesis of orthorhombic YCrO$_3$. The final powder was then used to obtain porous ceramics, the electrical conductivity of which was measured at temperatures up to 1250 °C. It was found that the high porosity of the sample leads to lower values of electrical conductivity compared to high-density ceramics in the high-temperature region, and it is in a good agreement with Odelevsky theory. However, the difference between the values obtained for porous ceramics and a dense sample in the low-temperature region cannot be explained by Odelevsky theory. This observation suggests that at lower temperatures the conductive properties of porous YCrO$_3$ ceramics depend mostly on the grain connectivity and particle size. In comparison to the conductive properties of dense YCrO$_3$ ceramics, it opens up the possibility of significant material savings. Besides, the proposed relationship between the microstructure of porous ceramics and the obtained conductivity values can be investigated in detail to further reduce the gap between the conductivity values for the high-temperature region. One of the methods for controlling the microstructure can be the alteration of the initial composition for the synthesis of YCrO$_3$ or change of the sintering temperature.

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