Synthesis and study of the electrical conductive properties of Cs$_2$Fe$_2$Ti$_6$O$_{16}$ in various gas atmospheres

D A Rogova, O Yu Sinel'shchikova, N V Besprozvannykh, N A Morozov

Institute of Silicate Chemistry, Russian Academy of Sciences (ISC RAS),
2 Makarova emb., St. Petersburg, 199034, Russia

E-mail: polzarogova14@gmail.com

Abstract. In this work, titanate Cs$_2$Fe$_2$Ti$_6$O$_{16}$ with a hollandite-type structure was synthesized by solid-phase synthesis. The electrical conductivity of the obtained ceramics was investigated in the temperature range from 25 to 800 °C in air and in the presence of an argon-hydrogen mixture (3% H$_2$). It was found that the electrical conductivity of the compound under consideration depends on the composition of the atmosphere — the activation energy of conduction changes (0.57 eV in air and 0.91 eV in the presence of hydrogen). The volumetric and grain-boundary contributions to the total resistance of the sample in the gases under consideration are separated by impedance spectroscopy at a temperature of 800 °C.

1. Introduction

The complex oxide Cs$_2$Fe$_2$Ti$_6$O$_{16}$ belongs to the structural type of the hollandite mineral. The framework structure of this compound has a tetragonal (space group I4/m) syngony and is built of (Fe/Ti)O$_6$ octahedra joined together in a zigzag manner along the edges to form blocks, which are “stitched” along the vertices of the octahedra. As a result of this arrangement of polyhedra, square tunnels with a side of 2 × 2 octahedra are formed, containing crystallographic positions in which cesium atoms are located [1]. Initially crystalline ceramics based on cesium hollandites was proposed as an alternative to glass as an immobilization matrix (ie, “Synroc” waste form) for the disposal of nuclear waste due to the better retention of radionuclides in hydrothermal conditions compared to the used aluminoboroslicate glasses [2-5]. Thus, in [1,2] the authors found that materials with a high Cs content showed a significant decrease in the release of Cs from the solid to the liquid phase as a result of leaching or water corrosion. In addition, compounds of hollandite structure, depending on the composition, can be used as catalysts [6] and ionic or mixed conductors [7,8]. At the same time, the electrical properties of a number of titanate hollandites are sensitive to the presence of hydrogen [9], which makes them promising materials for use in hydrogen fuel cells. The study of the electroconductive properties of matrices for the disposal of radioactive waste is important from the technological viewpoint to determine the possibility of using direct electric heating in the synthesis process [10].

Despite a fairly detailed study of the electrophysical properties of potassium hollandites, the study of the electrical conductivity of cesium compounds of this structure is extremely limited; therefore, the goal of this work was to obtain ceramic samples of the hollandite phase of the composition Cs$_2$Fe$_2$Ti$_6$O$_{16}$ by solid-phase reactions and to study its electrical conductivity in air and in the presence of hydrogen.
2. Experimental
The synthesis of the samples was carried out by means of solid-phase reactions from mixtures prepared by mechanical grinding and mixing of oxides and carbonates. The reagents used were: Cs$_2$CO$_3$ (analytical grade), TiO$_2$ (high purity grade), Fe$_2$O$_3$ (high purity grade). Mixing of the initial reagents, taken in stoichiometric ratios, was carried out in a Pulverisette 6 planetary ball mill at a speed of 350 rpm for 20 minutes using a jasper grinding accessory. The initial mixture was pressed into tablets, which were subjected to step firing at temperatures of 650 °C – 21 h and 1050 °C – 17 h (for decompose Cs$_2$CO$_3$ and reduce the loss of cesium), and 1250 °C – 12 h with intermediate grinding and pressing (the pressure was 500 MPa). Calcination was carried out in a SNOL - 6.7/1300 muffle furnace equipped with an electronic temperature controller. The phase composition of the obtained ceramic samples was monitored using X-ray phase analysis (DRON 3M, CuKα - radiation), on the basis of which the parameters of the final firing were selected.

To study the electrophysical characteristics of the synthesized hollandite phases, cylindrical tablets 2–3 mm in height and ~ 10 mm in diameter were used. Before measuring the electrical conductivity, metal contacts were applied to the end faces of the samples by firing an Ag-containing conductive paste (OOO Elma-pastes) at 650 °C. The electrical conductivity was investigated by a two-contact method in the temperature range 50 - 800 °C in air and in an argon-hydrogen mixture (3% H2) at an alternating current with a frequency of 1 kHz, as well as a short-term application of direct current. The voltage applied to the contacts of the measuring cell was 0.12 V (Fluke 6063 LCR meter).

DC conductivity ($\sigma_{dc}$) was calculated by using obtained values for resistance ($R$) according to formula (1):

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

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):

$$\sigma_{dc} = \sigma_0 \exp \left( - \frac{E_a}{kT} \right) \quad (2)$$

where $E_a$ is the activation energy, $T$ is the temperature, $k$ is the Boltzmann constant and $\sigma_0$ is the preexponential factor.

Impedance hodographs were built using a Z2000 impedance meter. The analysis of the experimental Nyquist curves by the method of equivalent circuits was carried out using the program.

3. Results and discussion
As a result of the synthesis, a one-component tetragonal hollandite phase (fig.1) with unit cell parameters was obtained: $a$=10.2285(12) Å, $c$=2.9567(5) Å, $V$=309.34(8) Å$^3$.

![Figure 1. XRD-pattern of synthesized sample of composition Cs$_2$Fe$_2$Ti$_6$O$_{16}$ after firing at 1250 °C. The hkl indices are indicated for reflections related to the tetragonal hollandite phase.](image)
Refinement of the unit cell parameters was performed using the PDWin ver. 2.03 software package (SPE "Burevestnik"), which allows calculating for the selected syngony with known reflection indices. When calculating the parameters, the weight scheme of the least squares method is used. Card No. 152-1333 from the Crystallography Open Database was selected as the source data.

By the nature of the temperature dependence of the electrical conductivity of the sample with the composition Cs$_2$Fe$_2$Ti$_6$O$_{16}$, it can be concluded that it is predominantly ionic, as indicated by the linear temperature dependence of the electrical conductivity and the presence of dispersion of values measured with direct and alternating currents in the range of medium temperatures (up to 400 °C). At a temperature of 650 °C, the synthesized ceramics have a conductivity $\sigma \approx 2.1 \times 10^{-3}$ S/cm in air and $\sigma \approx 7.94 \times 10^{-3}$ S/cm in an argon-hydrogen mixture. When hydrogen is supplied, the slope of these dependences changes, which indicates a change in the activation energy of the charge transfer process. The activation energies were 0.57 eV in air and 0.91 eV in the presence of hydrogen.

**Figure 2.** Temperature dependence of the electrical conductivity of a sample of the composition Cs$_2$Fe$_2$Ti$_6$O$_{16}$ in an atmosphere of air and an argon-hydrogen mixture (3% H$_2$). Measurements on alternating current with a frequency of 1 kHz - solid lines, on direct current - dotted lines.

**Figure 3.** Hodographs of impedance Cs$_2$Fe$_2$Ti$_6$O$_{16}$ measured under air at 800 °C (a), as well as in an argon-hydrogen mixture (3% H$_2$) (b).
The impedance hodographs measured for the synthesized ceramic material at 800 °C in air and in an argon-hydrogen mixture, equivalent circuits and curves modeled on the basis of these circuits are shown in Fig. 3. This temperature was chosen for a more detailed consideration in order to be able to compare the results obtained with the characteristics of hollandites given in [9]. The impedance hodographs obtained at other temperatures in air had a similar appearance, only their sizes changed. As can be seen from the presented graphs, the total resistance in the air atmosphere consists of two distorted (with the center lying below the abscissa axis) semicircles displaced from the point of origin. Resistance \( R_b \), which is responsible for the displacement of these semicircles and does not have a capacitive component, can be attributed to the volume resistance of the grains. The parameters \( R_{gb} / CPE_{gb} \), which determine the size of the high-frequency (closer to the Z-axis) semicircle, according to the values of the capacitive component, correspond to the contribution to the total resistance of grain boundaries, and the low-frequency semicircle \( R_c / CPE_c \) - to the electric double layer formed near the contacts [9,11,12]. The selected values of the parameters of the elements of the equivalent circuit are summarized in Table 1. The greatest contribution to the resistance of the ceramics under consideration in air is made by grain boundaries.

| Equivalent circuit elements | under air | under Ar/H₂ mixture |
|-----------------------------|-----------|---------------------|
| Inductance of the supply current leads | \( L_t, \text{mkH} \) | — | 1.65 |
| Volume resistance of the grains | \( R_b, \Omega \) | 43 | 14.8 |
| Resistance and capacitive component of grain boundaries | \( R_{gb}, \Omega \) | 123 | 4.8 |
| \( CPE_{gb}, F \) | 6 \( \cdot \) 10⁻⁷ | 6 \( \cdot \) 10⁻⁸ |
| \( n_{gb} \) | 0.73 | 0.97 |
| Resistance and capacitive component formed near the contacts | \( R_c, \Omega \) | 49 | — |
| \( CPE_c, F \) | 4 \( \cdot \) 10⁻⁵ | — |
| \( n_c \) | 0.76 | — |

When an argon-hydrogen mixture is supplied at 800 °C, the resistance of the sample is reduced by an order of magnitude. Therefore, in addition to the elements reflecting the behavior of the ceramic under consideration, the impedance includes the inductance of the supply current leads \( L_t \) (reflected in the graphs as negative values - Z”) connected in series with the resistance \( R_b \) and the \( R_{gb} / CPE_{gb} \) block corresponding deviation of the curve from a straight line parallel to the Z” axis (Fig.3b).

4. Conclusion
It was found that the investigated complex oxide \( \text{Cs}_2\text{Fe}_2\text{Ti}_6\text{O}_{16} \) shows two orders of magnitude higher electrical conductivity in the air atmosphere (\( \sigma \approx 2.1 \cdot 10⁻³ \) S/cm at 650°C) compared to the values obtained for the previously studied cesium hollandites in [7]. In an atmosphere of an argon-hydrogen mixture (3% \( \text{H}_2 \)) the activation energy of the charge transfer process increases. An analysis of the impedance at 800°C obtained from measurements in the gases under consideration showed a significant decrease in the contribution of the resistance of grain boundaries in the presence of \( \text{H}_2 \).

Acknowledgements
The work was carried out within the framework of the state assignment of the Institute of Silicate Chemistry of the Russian Academy of Sciences with the support of the Ministry of Education and Science of the Russian Federation (topic No. AAAA-A19-119022290092-5).
References

[1] Ladenkov I V 2013 Synthesis, structure and physicochemical properties of ternary titanium-containing oxides formed in the $M_2\text{O}-A_{III}\text{O}_3\text{-TiO}_2$ system (where $M'$ are alkaline elements; $A_{III}$ - Al, Cr, Fe, Ga) Author. dis. for the degree of Doctor of Chem. sciences (N. Novgorod: Nizhny Novgorod State University N.I. Lobachevsky) p 24

[2] Grote R, Zhao M, Shuller-Nickles L, Amoroso J, Gong W, Lilova K, Navrotsky A, Tang M and Brinkman K S 2019 Compositional control of tunnel features in hollandite-based ceramics: structure and stability of (Ba,Cs)$_{1.33}$($Zn,Ti$)$_8$O$_{16}$ J. Mater. Sci. 54 1112–25

[3] Shabalin B G, Titov Yu O, Chumak V V, Vishnevsky O A and Bogachova D O 2011 Immobilization of cesium and strontium in hollandite matrix: synthesis, fazeoutvorennya, izomorfna yemnist' Zbirnyk naukovykh prats' Instytutu heokhimiyi navkolyshn'oho seredovyschya. 19 41-50 (in Ukrainian)

[4] Tumurugoti P, Clark B M, Edwards D J, Amoroso J and Sundaram S K 2017 Cesium incorporation in hollandite-rich multiphasic ceramic waste forms J. Solid State Chem. 246 107-112

[5] Grigor'eva L F, Petrov S A, Sil'neshchikova O Yu, Drozdova I A, Gusarov V V 2007 Kinetics and mechanism of the formation of hollandites in the BaO(CS)$_2$O-Al$_2$O$_3$-TiO$_2$ system from initial mixtures prepared by different methods Glass Phys. Chem. 33 613-619

[6] Watanabe M, Mamoru W, Toshiyuki M, Syoichi Y and Hiroshi Y 1995 Catalytic property of the hollandite-type 1-D ion-conductors: Selective: reduction of NO$_x$ Solid State Ionics 79 376-381

[7] Xu Y, Wen Y, Grote R, Amoroso J, Shuller N L and Brinkman K S 2016 A-site compositional effects in Ga-doped hollandite materials of the form Ba$_x$Cs$_y$Ga$_{2x+y}$Ti$_{8-2x-y}$O$_{16}$: implications for Cs immobilization in crystalline ceramic waste forms Sci. Rep. 6 27412

[8] Weber H-P and Schulz H 1986 Ionic conduction in one dimension: A structural study of the hollandite K$_{1.54}$Mg$_{0.77}$Ti$_{7.23}$O$_{16}$ over the range 133$\leq$T$\leq$919 K J. Chem. Phys. 85 475-484

[9] Cao C, Singh K, Hay Kan W, Avdeev M and Thangadurai V 2019 Electrical properties of hollandite-type Ba$_{1.33}$Ga$_{2.67}$Ti$_{5.33}$O$_{16}$, K$_{1.33}$Ga$_{1.33}$Ti$_{6.67}$O$_{16}$, and K$_{1.54}$Mg$_{0.77}$Ti$_{7.23}$O$_{16}$ Inorg. Chem. 58 4782-91

[10] Remizov M B, Kozlov P V, Vlasova N V, Belanova E A, Rudenko A V, Kataev A A, Red'kin A A, Tkacheva O Yu, Dokutovich V N, Filatov E S and Zaikov Yu P 2018 Thermal and Electrical Conductivity of Molten Alumophosphate and Borosilicate Glass Containing Imitators of High-Active Wastes from SNF Processing Glass Phys. Chem. 44 541-547

[11] 2005 Impedance Spectroscopy. Theory, Experiment, and Applications ed E Barsoukov and J Ross Macdonald (Hoboken, New Jersey: John Wiley & Sons, Inc.) 2nd Edition pp 14-128

[12] Gorshkov N V, Goffman V G, Vikulova M A, Kovaleva D S, Tret'yachenko E V and Gorokhovsky A V 2018 Temperature-dependence of electrical properties for the ceramic composites based on potassium polyanitans of different chemical composition J Electroceram 40 306-315