



Modification of Properties and Study of Electrical Conductivity of Citrogypsum

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Abstract. Due to a complex chemical composition and microstructure of many functional materials the problem of optimizing their parameters for applied purposes is associated with determining of charge carrier transport mechanisms. To modify the properties of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ we prepared composite samples: $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.95}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.05}$ and $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$. In a dry atmosphere all studied samples also had a specific conductivity of about $10^{-9} \text{ S cm}^{-1}$. It has been established that with an increase in relative humidity (RH) of the environment the specific conductivity increases according to a power law up to $10^{-7} \text{ S cm}^{-1}$. The measurements were carrying out at a constant temperature of 28°C and RH range of 35–90%. To study a proton conductivity of studied compounds a method of impedance spectroscopy was using. Conductivity was measuring in the frequency range 20 Hz–5 MHz. In $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.95}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.05}$ samples and $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$ at above 40% RH granular conductivity was observed, an additional linear section was observed in $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$ samples which is responsible for the conductivity along grain boundaries.

Keywords: Electrical conductivity · Citrogypsum · RH granular conductivity · Grain boundaries · Ferroelectric

1 Introduction

Recently, a role of functional materials has increased in technology and especially in electronics [1, 2]. The physical and chemical properties of functional materials are sensitive to external influences such as temperature, electric field, magnetic field, pressure, humidity, pH value, optical radiation wavelength, adsorbed gas molecules [3, 4]. Functional materials cover a wide range of organic and inorganic materials such as ferroelectric BaTiO_3 , magnetic field sensor $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, surface acoustic wave sensor LiNbO_3 ,

semiconductor light detectors CdS, CdTe, high temperature piezoelectric Ta₂O₅, fast ion conductor Y₂(Sn_xTi_{1-x})₂O₇, high temperature superconductors, etc. The need of the industry stimulates fundamental and applied research aimed at creating new solid-state functional materials, studying their structure and physical properties. Due to a complex chemical composition and microstructure of many functional materials the problem of optimizing their parameters for applied purposes is also associated with the determination of the mechanisms of charge carrier transfer and the study of ion transport processes in solids. This, in turn, led to the discovery of new objects with ionic conductivity. These materials, called ionic conductors, have begun to be actively used in a variety of devices used in electronics and energy. For example, all solid oxide fuel cells, lithium-ion batteries, gas discharge membrane sensors, etc., contain solid crystalline or polymer ion conductors and are never used in single crystal form. It is necessary to understand the features of ion transport in these systems. Even greater relevance to this problem is given by the use of common natural materials as functional materials and materials accumulated in the form of industrial waste, which are a by-product of technological processes. Calcium sulfate dihydrate (CaSO₄ · 2H₂O) is a waste product of the production of food citric acid, called citrogypsum [5]. This by-product cannot be used directly due to its physical properties [6, 7]. This research aims to modify the properties of citrogypsum and find new applications.

2 Materials and Methods

The object of the study was the waste of biochemical production of citric acid—citrogypsum (Belgorod, Russia). Its physicochemical properties are described in detail in [8]. Calcium sulfate dihydrate (CaSO₄ · 2H₂O) as a result of anhydration at 200 °C for 1 h, first transferred to anhydrous gypsum (CaSO₄). Then, as a result of exposure of anhydrous gypsum in the open air in order to gain moisture from atmospheric air for 24 h, semi-aqueous gypsum was obtained (CaSO₄ · 0.5H₂O).

In order to modify the properties of CaSO₄ · 0.5H₂O we prepared composite samples of citrogypsum: (CaSO₄ · 0.5H₂O)_{0.95}–(FeSO₄ · 7H₂O)_{0.05} and (CaSO₄ · 0.5H₂O)_{0.90}–(FeSO₄ · 7H₂O)_{0.10}. Iron sulfate was used as an alloying element (FeSO₄ · 7H₂O). From CaSO₄ · 0.5H₂O and FeSO₄ · 7H₂O stoichiometric samples were prepared using analytical balance LV 210-A with an accuracy of 0.0001 g. Ferrous sulfate was dissolved in water and citrogypsum was added to the resulting solution. The resulting mixture was pressed under a pressure of 22 MPa. After drying in air at room temperature for 2 h, samples were cut out in a parallelepiped form 9.2 × 7.2 × 2.2 mm³ in size. Silver was deposited on large faces by magnetron sputtering using a BH-2000 setup. Contacts for research were fixed by silver-containing glue.

To study a proton conductivity of the studied compounds the method of impedance spectroscopy was using. The conductivity was measuring using RLC meter AM-3026 AKTAKOM in the frequency range of 20 Hz–5 MHz at an alternating signal amplitude of 1 V without DC polarization. The measurements were carrying out at a constant temperature of 28 °C and a RH range of 35 to 90%. RH and temperature were measured using AOSONG DHT11 sensor.

3 Results and Discussions

Figure 1 shows the electrical conductivity values of three compositions: semi-aqueous citrogypsum ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and composite samples with the addition of iron sulfate $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.95}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.05}$ and $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$ depending from RH in the range of 35–90% at a temperature of 28 °C.

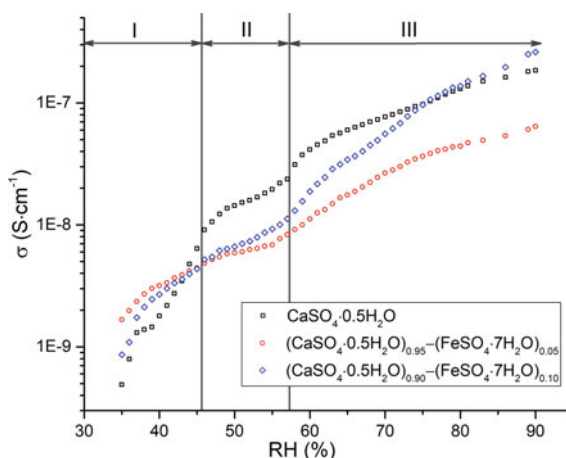


Fig. 1 Dependences of electrical conductivity of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.95}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.05}$ and $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$ on RH at 28 °C

At 35% RH all studied samples have a conductivity of about $10^{-9} \text{ S cm}^{-1}$. With an increase in the RH of the environment the specific conductivity increases according to a power law up to $10^{-7} \text{ S cm}^{-1}$. The dependence of electrical conductivity for all three samples has three linear segments that satisfy the equation:

$$\log_{10} s = a \times \text{RH} + b. \quad (1)$$

The coefficients a and b were determined from the linear plots of the $\log_{10} \sigma$ (RH) dependence and are shown in Table 1.

The proton conductivity of the studied samples was determined from the analysis of the impedance hodographs at 35, 40, 50, 60, 70, 80% RH. We further mean the Faraday impedance and its dependence on the frequency of the alternating current [9]. For all samples at 35% RH the impedance hodograph is a system of straight lines. A typical citrogypsum impedance hodograph is shown in Fig. 2.

The citrogypsum impedance hodograph with increasing humidity remains unchanged. However, for doped samples: $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.95}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.05}$ at RH 40, 50, 60, 70, 80% and for $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$ at 40, 50, 60, 70% RH impedance hodograph is a semicircle. A typical hodograph for doped samples is shown in Fig. 3.

Table 1 The values of the coefficients a and b from the Eq. (1)

Sample	a	b	RH (%)
$(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})$	0.1013 ± 0.0055	-12.77 ± 0.22	35–46
	0.0338 ± 0.0018	-9.55 ± 0.09	47–57
	0.0228 ± 0.0006	-8.73 ± 0.05	58–90
$(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.95}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.05}$	0.0386 ± 0.0025	-10.07 ± 0.10	35–46
	0.0175 ± 0.0013	-9.11 ± 0.06	47–57
	0.0266 ± 0.0011	-9.48 ± 0.08	58–90
$(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$	0.0633 ± 0.0058	-11.16 ± 0.23	35–46
	0.0317 ± 0.0020	-9.76 ± 0.11	47–57
	0.0403 ± 0.0011	-10.10 ± 0.08	58–90

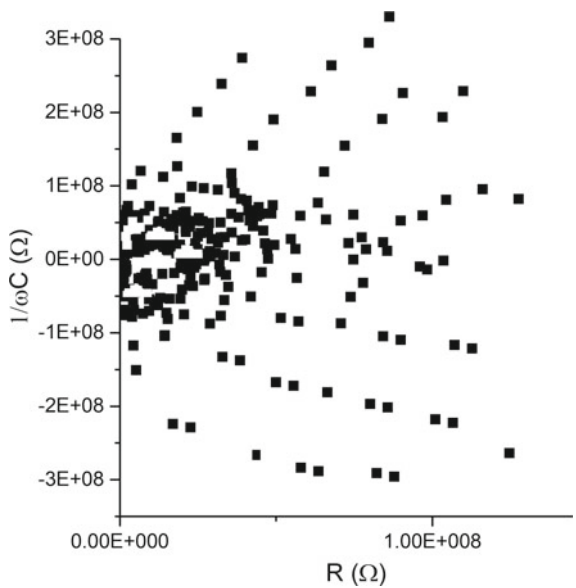


Fig. 2 Typical impedance hodograph $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ at $\text{RH} = 35\%$ and $T = 28\text{ }^\circ\text{C}$

An electrochemical circuit can be described by constructing an electrical equivalent circuit from the simplest elements: resistors and capacitor [8]. According to this model representation the impedance hodograph $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.95}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.05}$ (Fig. 3) will correspond to a parallel connection of resistors and capacitor (Fig. 4) [8].

When the elements of the electrical circuit are connected in parallel, their conductivities add up. Therefore, with a known resistance of a resistor and capacitance of a capacitor for the circuit shown in Fig. 4, the reciprocals of the active and reactive resistances are added.

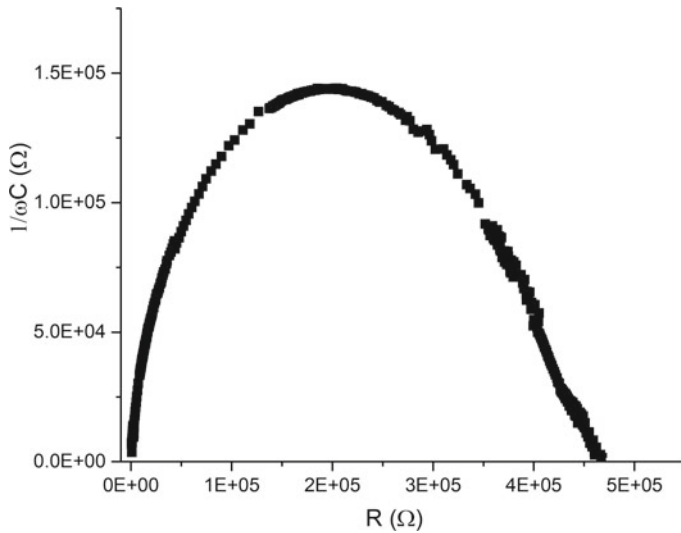


Fig. 3 Impedance hodograph $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.95}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.05}$ at $\text{RH} = 60\%$ and $T = 28^\circ\text{C}$

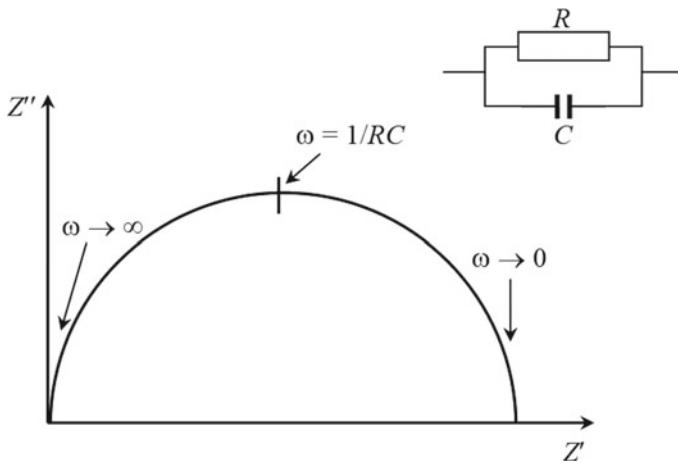


Fig. 4 Impedance for parallel connection of resistors and capacitor [2], axes: Z' and Z'' —active and reactive resistance, respectively

The semicircle in Figs. 3 and 4 indicates ionic conductivity and corresponds to the grain boundary impedance [9] which makes it possible to calculate the capacitance of samples indicated in Table 2.

The right boundary of the semicircle of the impedance hodograph, a typical graph of which is shown in Fig. 3, shifts to the right with increasing RH. This suggests that with increasing RH in the samples the active resistance increases because based on Table 2

Table 2 Capacity of samples of citrogypsum doped with iron sulfate

RH (%)	C (nF)	
	$(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.95}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.05}$	$(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$
40	0.114	0.117
50	0.112	0.103
60	0.108	0.102
70	0.106	0.093
80	0.110	0.109

the capacitance value remains almost constant and does not depend on humidity for both formulations.

For the sample $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$ at 80% RH the impedance hodograph is shown in Fig. 5.

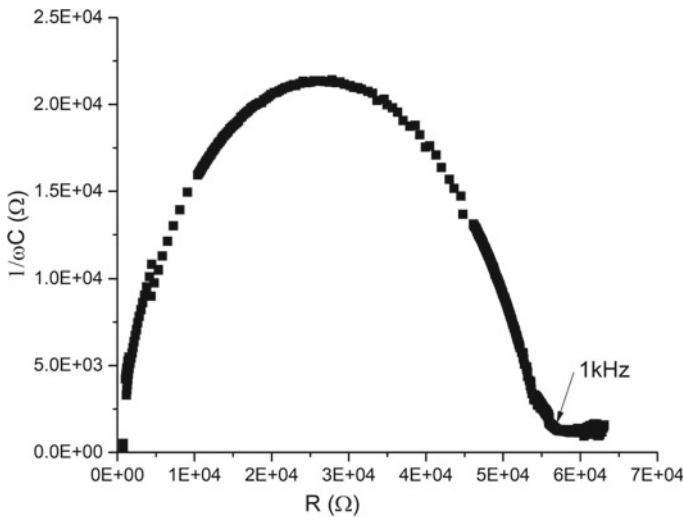


Fig. 5 Impedance hodograph of $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$ at RH = 80% and $T = 28^\circ\text{C}$

The impedance hodograph is a semicircle corresponding to the grain conductivity and a linear segment responsible for the conductivity along grain boundaries [10].

4 Conclusions

Citrogypsum is a material obtained as waste in industrial processes for a production of citric acid and waste disposal is an important environmental issue. In order to expand the field of application of semi-aqueous gypsum ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) an attempt was made

to optimize its parameters for applied purposes and study the mechanisms of charge carrier transfer. In order to modify its properties iron sulfate was used as an alloying element. Composite samples were obtained: $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.95}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.05}$ and $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$. It was found that at 35% RH all the studied samples had a conductivity of the order of $10^{-9} \text{ S}\cdot\text{cm}^{-1}$. With an increase in RH of the environment above 40% the conductivity increased according to a power law up to $10^{-7} \text{ S}\cdot\text{cm}^{-1}$. In samples $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.95}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.05}$ and $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$ granular conductivity was observed at RH above 40%, in the sample $(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O})_{0.90}-(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})_{0.10}$ at above 80% RH is an additional linear region responsible for the conductivity along grain boundaries.

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