

Study of electrical conductivity of fluorine-conducting solid electrolytes based on lead fluoride

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Abstract. Samples of solid electrolytes based on β -Pb F2 doped with ScF3 were synthesized. The dependence $\lg \sigma T$ has been studied from $\frac{1}{T}$ the samples received. Significant changes in electrical conductivity and enthalpy are observed at an impurity concentration of $0,05 \pm 0,02$. It has been established that as the content of ScF3 molecules in a solid solution increases, the number of defective regions increases and at a certain impurity concentration their spatial overlap occurs. The formation of a closed three-dimensional network of the defect phase corresponds to percolation and is accompanied by a change (often sharp) in the conductivity and other properties of solid solutions.

1 Introduction

The modern scientific and technological revolution is closely related to the use of natural and artificially produced materials. Among the latter, a special place is occupied by solid-phase materials, the role of which has increased exceptionally in recent years [1-3]. One of the main reasons for the great interest in ionic crystals is the many applications of these materials in optics, nuclear radiation dosimetry, quantum electronics, radio engineering, and microelectronics [6-11].

The use of solid electrolytes in many cases has significant advantages over solutions or ionic melts, which allows them to be successfully used in new types of current sources, fuel cells, and high-capacity capacitors. The modern era is sometimes called the era of solid-state electronics, based on the widespread use of semiconductors, ferrites and ferroelectrics.

Studies of crystalline fluorides are of significant interest. The unit charge and small size of the fluorine anion can be considered as factors contributing to its high mobility in some compounds even at room temperatures. The variety of crystalline forms of inorganic fluorides allows them to be used as model objects for the search for new highly conductive solid electrolytes.

Due to the above, the importance of synthesis and obtaining the necessary information about the physicochemical properties, including the transport characteristics of nominally

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pure crystals, as well as crystals doped with various impurities, becomes relevant.

In recent years, considerable attention has been paid to the study of the electrophysical properties of fluoride. It is known [12-15] that β -PbF₂ has its own Frenkel disorder in the anion sublattice. At temperatures of 700-1100 K, β -PbF₂ transforms into a superionic state, which is characterized by abnormally high electrical conductivity values.

2 Methods

The electrical conductivity of β -PbF₂ was studied over a wide temperature range using the heterovalent additive method to elucidate the mechanism of ion transfer [16]. In this work, samples of PbF₂ – ScF₃ with a ScF₃ concentration in the range of 0,5 -15 mol% were used in contact with silver. The selected concentration range was chosen based on the fact that lead fluoride with ScF₃ forms solid solutions with a homogeneity region of up to 15 mol %. To obtain the samples, the solid-phase synthesis method was used.

The starting compounds PbF₂ and SeF₃ were dried in vacuum initially at a temperature of 100°C for one hour to remove moisture. Then at a temperature of 200°C for 2 hours to remove traces of acetates, carbonates, etc. Mixtures of PbF₂ and ScF₃ at appropriate ratios were homogenized for 30 minutes in a mortar and then placed in nickel ampoules. The synthesis was carried out in a nickel container (Fig. 1), which was filled with nitrogen. When carrying out the synthesis, a fluorinating atmosphere was used, which ensured stable formation of fluorides without oxide impurities. The synthesis was carried out at a temperature of 720-740°C. Melting point of PbF₂ ~ 824°C. The transition temperature of the α phase to the β phase is \approx 340 0C for 8 hours. The obtained synthesis samples were certified X-ray phase analysis. X ray diffraction analysis was carried out at room temperature.

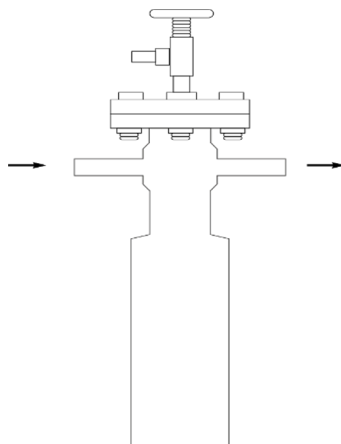
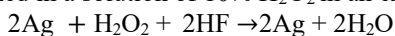


Fig. 1. Container for the synthesis of solid electrolytes PbF₂ –ScF₃

After synthesis, the samples were ground to a powder state and pressed in a mold under a pressure of about $2 \cdot 10^8$ Pa for 3 minutes. The diameter of the tablet was 0,5 cm and the thickness was 125 sm.

Metallic silver was oxidized in a solution of 10% H₂O₂ in an excess of 40% HF.



By gently heating until the water completely evaporated, the dried silver fluoride was pressed into a mold for the tablets PbF₂–ScF₃. Since PbF₂–ScF₃ solid solutions easily react with water, the experiments were carried out in a vacuum. The samples prepared in this way were placed in a quartz cell. Silver metal electrodes were used as electrodes.

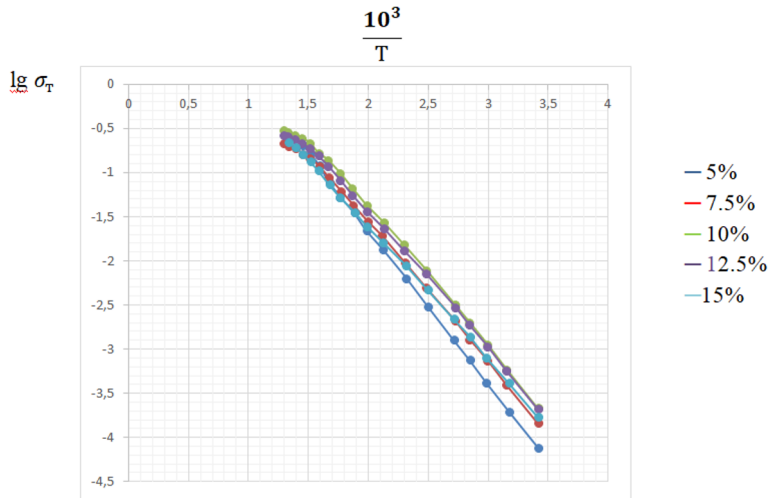


Fig.3. Dependence of the electrical conductivity of lead fluoride-based fuel cells on temperature in the ScF3 concentration range 5- 12,5 mol/l

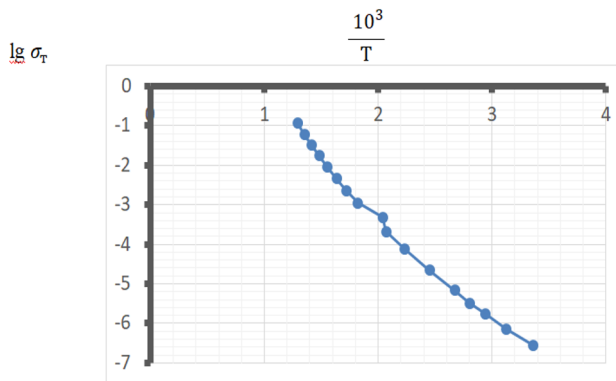


Fig. 4. Dependence of electrical conductivity of lead fluoride on temperature

In this case, the degree of disorder increases exponentially with temperature $T \ll T_C$ and is practically independent of it at $T \geq 1,1 T_C$. The obtained enthalpy of activation of electrical conductivity in section I – 0,20 eV is in good agreement with the data of the study. If we assume that in this region the contribution of the enthalpy of formation of defects is small, then this value coincides with the enthalpy of activation of the mobility of fluorine vacancies in the dissociation region, when the concentration of vacancies is low. This assumption allows us to assume that ion transfer occurs along the vacancy mechanism [18].

To determine the activation energy of the electrical conductivity process E_{act} of dependence $lg \sigma T$ on temperature, the least squares method was used. The activation energy value was calculated from the slope of the straight line $lg \sigma \frac{1}{T}$. The error in determination does not exceed 0,02 eV Coefficients a and b in the equation

$$lg \sigma = a + b \cdot 10^3/T \tag{1}$$

find by formula:

$$a = \frac{1}{m} (\sum y_i - b \sum x_i) \tag{2}$$

$$b = \frac{m(\sum x_i y_i - \sum y_i x_i)}{m \sum x_i^2 - (\sum x_i)^2} \quad (3)$$

Where

$$x = \frac{10^3}{T}; \quad y_i = \lg \tau_i, \quad \tau_i = \tau(T_i)$$

m is the number of pores.

The degree of approximation of the experimental values and the found linear function was determined by the value of the correlation coefficient

$$R = \sqrt{\frac{m \sum x_i y_i - \sum x_i \sum y_i}{[m \sum x_i^2 - (\sum x_i)^2] - [m \sum y_i^2 - (\sum y_i)^2]}} \quad (4)$$

The data obtained indicate that the most significant change occurs at an impurity concentration of 0,05–0,002 ± mol/l.

To explain the behavior of the concentration dependences of the characteristic parameters of solid solutions, a model of “defective regions” is proposed. With the isomorphic introduction of the ScF₃ additive into the crystalline matrix of PbF₂, defective regions are formed containing structural defects in the crystalline structure of fluorite.

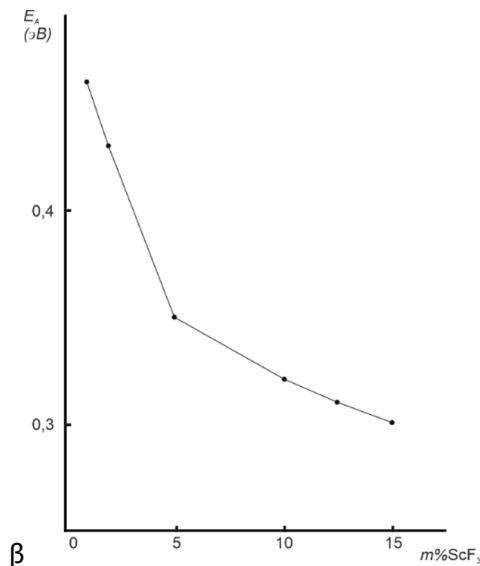


Fig.5. Dependence of activation energy - PbF₂ on the quantitative content of ScF₃

It can be assumed that the defective regions consist of a core containing ScF₃ and fluorine atoms “frozen” by complex formation and a peripheral part that includes a distorted fluorite matrix adjacent to the core. In the periphery there may be fluorine anions weakly bound to the core, and therefore mobile.

Thus the defective region has a composition and local structure that differs from the original matrix. Outside the defect region, both structural distortions of the fluorite matrix and energy disturbances caused by the core are minimized. In other words, we can conditionally assume that non-stoichiometric fluorite-like solid solutions consist of two phases: a PbF₂ matrix and a defect phase.

As the content of ScF₃ molecules in the solid solution increases, the number of defective regions increases and, at a certain impurity concentration x_n , their spatial overlap occurs. The formation of a closed three-dimensional network of the defect phase corresponds to percolation and is accompanied by a change (often sharp) in the conductivity and other properties of solid solutions.

4 Conclusions

A study of the electrical properties of lead fluoride has shown that solid electrolytes based on PbF_3 have their own Frenkel disorder in the anion sublattice. At a temperature of 800 K, $\beta\text{-PbF}_2$ goes into a superionic state. Samples of solid electrolytes based on $\beta\text{-PbF}_2$, doped with ScF_3 , have been synthesized. The dependence of $\log \sigma T$ on $1/T$ of the obtained samples was studied. Significant changes in electrical conductivity and enthalpy are observed at an impurity concentration of $0,05 \pm 0,02$. As the content of ScF_3 molecules in the solid solution increases, the number of defective regions increases and, at a certain concentration of impurities, their spatial overlap occurs. The formation of a closed three-dimensional network of the defect phase corresponds to percolation and is accompanied by a change (often sharp) in the conductivity and other properties of solid solutions.

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