

INVESTIGATION OF THE THERMAL CONDUCTIVITY OF A SUPERIONIC GEL WITH Na⁺ SUPERIONIC CONDUCTIVITY BASED ON NATURAL AGAR (C₁₂H₁₈O₉)_n

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<https://doi.org/10.5281/zenodo.7707399>

Abstract. *The paper presents the current trends and prospects of one of the new rapidly developing areas of physics - solid state ionics. A brief historical reference is given. The relevance of the study is considered, due to the fact that the solution of some research issues could make a further contribution to the development of this promising direction. The possibility of controlling the thermophysical properties of a superionic gel based on natural agar (C₁₂H₁₈O₉)_n is shown. The measurement technique is presented. Conclusions are given.*

Keywords: *superionic conductors, solid electrolytes, ionic conductivity, ionic gels, controlled thermal conductivity.*

INTRODUCTION. The high ionic conductivity of silver salts was discovered by Michael Faraday in 1833 and proved to be comparable to the electrical conductivity of salt solutions. Faraday proposed the terms "electrolyte" and "ion". Then a similar effect was discovered by Walter Nernst, investigating ceramic compounds of zirconium and predicting to apply this effect to the manufacture of incandescent lamps. Active research of these materials began at the beginning of the 20th century. At first, these phenomena were found only in crystalline substances, the classic representative of which was silver iodide (AgI). When heated (AgI), a sharp increase in electrical conductivity was manifested. It was proved that high electrical conductivity is the result of the movement not of electrons, but of other charged particles - ions, which was similar to the conductivity of salt solutions. Crystalline substances exhibiting high ionic conductivity began to be called *solid electrolytes*, then *fast ionic*, *superionic*, *superionic conductors*, or simply *superionic*.

Currently, the importance of superionics is difficult to overestimate. They are widely used in various technical devices such as ultra-large capacitors (ionistors), timers, reliable storage devices (memory cells), selective sensors, solar panels, household batteries (lithium batteries already known to everyone), fuel cells, ion-selective membranes, information converters. Since 1976, they have been used in pacemakers. Thanks to miniature lithium batteries, they have become more durable. Pacemakers prolong the life of patients with heart failure for a dozen or more years. In addition, superionic materials are used in air purification systems by destroying microbes, to control signal transmission and metabolism in the human body. Based on superionics, the production of high temperature sensors, gas analyzers, and long-lasting batteries has been launched. All listed electrical and electrochemical devices.

Currently, for the needs of functional electronics and the creation of new devices based on superionic materials, it is relevant to create superionic conductors with controlled properties of thermal conductivity and electrical conductivity. Materials of this type are necessary for the creation of thermal keys and other electronic devices. It should be noted that the control of the mechanism of transition of matter to the superionic state has become available. This can be

achieved by increasing the number of structural defects [2], which can be caused by the influence of various factors: heat, deformation, exposure to light and strong electric fields and magnetic fields. In addition, this state can be achieved by introducing defects into the structure, for example, by alloying with impurities. During doping, a phase with an excess of defects is formed, the concentrations of which also create the possibility of transition to a superionic state [3].

Saying about the formation of defects, it is necessary to take into account such factors as the radius of the ion, the ion charge, the coordination numbers of atoms, the presence of other types of defects, the influence of the environment. Different defects can contribute to the conductivity in different ways. In 1973, S. Liang [4] discovered an increase in ionic conductivity by several orders of magnitude in a system consisting of lithium iodide, characterized by relatively low cationic mobility, and finely dispersed aluminum oxide, which is a dielectric. Chemical synthesis of new materials is usually a time-consuming process and not always cost-effective [5]. It is advisable to use natural substances as starting materials and create crystal matrices based on them.

The natural superionic polymer agar (**C₁₂H₁₈O₉**)**n** has interesting properties in this regard. Agar molecules are very long, this is due to the high tensile strength of the gel made from it [6]. Agar-agar is insoluble in cold water. It completely dissolves only at temperatures from 95 to 100 °C, which differs from other natural gels [6]. Its main use is in medicine, as a breeding ground for bacterial reproduction, as well as in research where electrophoresis is used.

The most positive property of gels is their reversibility and high adsorption capacity. They melt when heated and turn back into gel when cooled. Such transformations can be carried out countless times, provided there are no active substances that can hydrolyze agarose molecules or destroy them by oxidation. Such gels are formed due to ionic bonds. These bonds can be broken, for example, only by removing any binding ion. Therefore, natural gels, including agar, can be called ionic chemical gels, since they form ionic bonds and are irreversible. On the other hand, superionic materials are characterized by an increase in thermal conductivity with an increase in temperature. Agar is a relatively fusible compound, which facilitates the alloying process. Thus, by measuring the electrical conductivity and thermal conductivity, combining alloying components, it is possible to easily control the chemical composition and thermophysical and electrophysical properties of this material [7].

METHODS. Currently, the possibility of experimental control of the thermal conductivity of strontium titanate at helium temperatures has already been shown [8]. However, such studies require sophisticated laboratory equipment. To test the possibility of controlling the thermophysical properties of the superionic material, a natural pure agar gel (**C₁₂H₁₈O₉**)**n** was selected. The choice of material is due to the fact that the dissolution temperature of this substance in water is in the range of 95-100 C, and no additional equipment is required for the doping process. Just simple laboratory devices in the form of a Petri dish and a conventional laboratory alcohol lamp for heating the gel are enough. Various concentrations of NaCl were used as an alloying impurity.



Fig.1. Laboratory

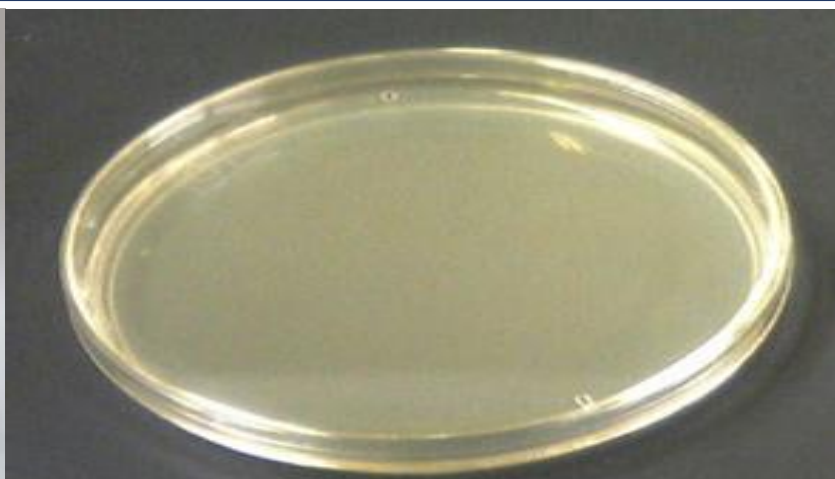


Fig.2. Petri dish alcohol lamp

One of the features of the superionic state is the increase in thermal conductivity with increasing temperature. Therefore, one of the objectives of the study was to study the thermal conductivity depending on the amount of alloying impurities. When selecting alloying impurities, the main emphasis was placed on the rule of the ratio of ion radii [9].

For elements of the same period, during the transition from an alkali metal to a noble gas, the charge of the nucleus increases, and the radii of atoms and ions decrease in small and large periods, ionization potentials, electron affinity and electronegativity increase. As a result, the chemical properties and thermodynamic characteristics change. This is a general pattern of changes in properties in small and large periods, it is most pronounced [9]

Radius ratio	Coordination number	Type of void	Example
< 0.155	2	Linear	
0.155 - 0.225	3	Triangular flat	B₂O₃
0.225 - 0.414	4	Tetrahedral	ZnS, CuCl
0.414 - 0.732	6	Octahedral	NaCl, MgO
0.732 - 1.000	8	Cubic	CsCl, NH ₄ Br

Table 1. Demonstration of the dependence of the type of voids in the crystal lattice on the ratio of the radii of ions (The rule of ionic radii) [9].

Based on this rule, different concentrations of NaCl were used as an alloying impurity. Thermal conductivity was measured by pulse method, at the stage of irregular thermal regime. As calibration studies were carried out on polycrystals of KCl. The samples for research were made in the form of rectangular plates with dimensions of 2x20x20 mm. From polymerized agar gel and polycrystals KCl. A detailed methodology for the study of thermal conductivity is given in [10].

RESULTS. Figure 3 shows the results of measuring the temperature dependence of the values of the thermal conductivity coefficient of the natural polymer agar.

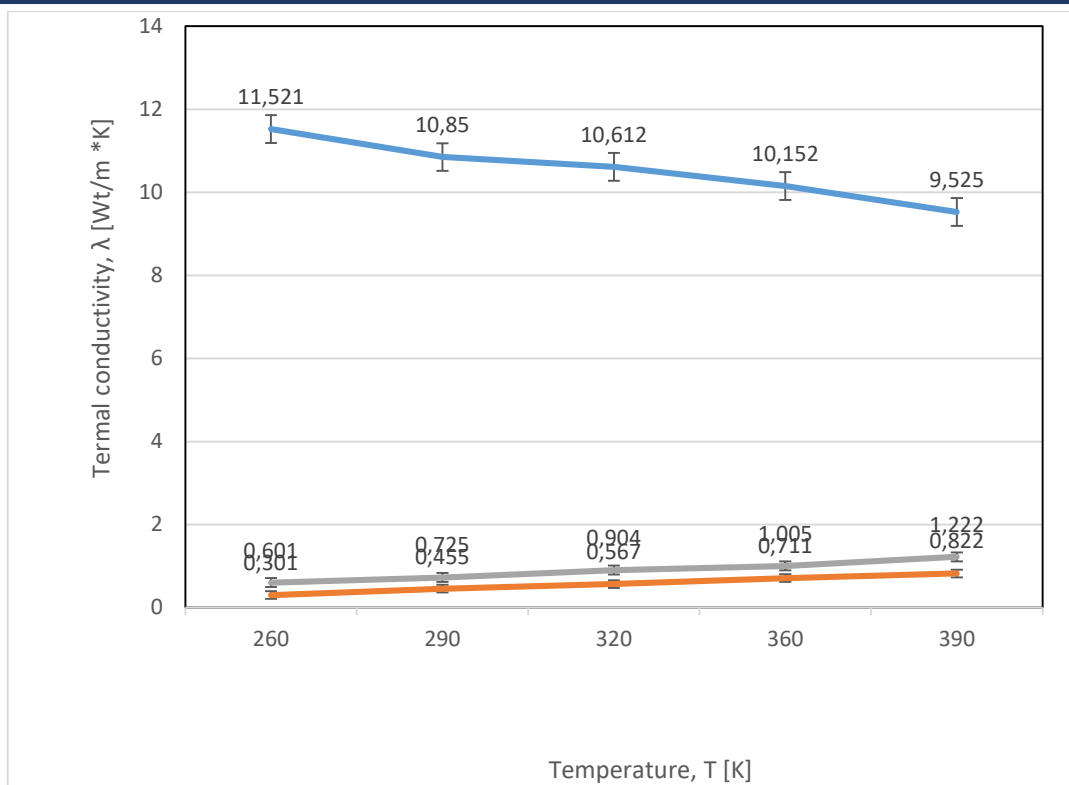


Fig. 1 Temperature dependence of the values of the thermal conductivity coefficient of the polymer agar ($C_{12}H_{18}O_9$)**n** :

- a) the results of calibration measurements on crystals KCl ____
- b) for the thermal conductivity of the pure natural polymer agar ($C_{12}H_{18}O_9$)**n** ____
- c) for the thermal conductivity of the pure natural polymer agar ($C_{12}H_{18}O_9$)**n** doped with (10 volume percent) sodium ____

As can be seen from the above measurement results, when doping NaCl, the values of the thermal conductivity coefficient of the polymer agar ($C_{12}H_{18}O_9$)**n** enriched with Na⁺ ions increase, but the nature of the temperature dependence (linear growth with temperature increase) is unchanged. Similar measurements were carried out with other concentrations of dopant.

DISCUSSION. Studies of the temperature dependence of thermal conductivity were carried out for agar plates polymerized from natural gel, which is a natural superionic polymer material. Since the transition to the superionic state can be considered as the melting of one of the sublattices and the activation of a large number of highly mobile ions, along with the transfer processes, it seems necessary to take into account an additional mechanism of heat transfer due to the diffusion of weakly bound highly mobile ions. Obviously, this mechanism should lead to an increase in thermal conductivity with increasing temperature, as the concentration and mobility of weakly bound ions increase.

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