Superlattices and Microstructures 98 (2016) 295–305

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Peculiarities of the dielectric response of the silver-modified-zeolite porous microstructure

U. Bunyatova [a], S. Ozturk Koc [b], V.I. Orbukh [c], G.M. Eyvazova [d], Z.A. Agamaliev [d], N.N. Lebedeva [c], İ.C. Koçum [a], B.G. Salamov [e,*], M. Ozer [b]

[a] *Department of Biomedical Engineering, Faculty of Engineering, Baskent University, Baglıca, Ankara 06810, Turkey*
[b] *Physics Department, Faculty of Sciences, Gazi University, Besevler 06500 Ankara, Turkey*
[c] *Baku State University, Institute for Physical Problems, Baku, AZ 1148, Azerbaijan*
[d] *Baku State University, Faculty of Physics, Nano Centre, Baku, AZ 1148, Azerbaijan*
[e] *Azerbaijan Academy of Science, Institute of Physics, AZ0143 Baku, Azerbaijan*

ARTICLE INFO

Article history:
Received 13 May 2016
Received in revised form 26 July 2016
Accepted 25 August 2016
Available online 26 August 2016

Keywords:
Nanoporous materials
Zeolite plate
Frequency
Dielectric properties
Silver modified zeolite

ABSTRACT

The aim of this study was to characterize electrical conductivity and dielectrical properties of the silver-exchanged zeolite - natural clinoptilolite from Western part of Turkey and Azerbaijan in the range of frequencies from 200 Hz to 1 MHz and at room temperature. For a better understanding the effect of concentration and content of silver in the nanoporous zeolite volume on the conductivity, a study of the dielectric properties of an un-modified and silver-modified zeolite plates with different amounts of Ag ions and Ag nanoparticles is performed. Un-modified and three different types of the silver ion-exchanged modified clinoptilolite plates were prepared. It was found, that with increasing silver concentration, resistance of zeolite plate monotonically decreases at the same time a capacitance is increases. It is suggested an explanation of the observed frequency dependence of the capacitance and resistance of zeolite plates on the silver concentrations may be explain on the basis of an electrode-dielectric interface gap model. At the same time, the observed phenomenon can be explained by considering the fact that with increasing content of silver the conductivity increases. These results show that Ag nanoparticles play significant role for performance improvement in plasma electronic devices with zeolite cathode.

1. Introduction

Nanoporous zeolites have three-dimensional framework structures. The zeolite structure is built from TO_4 (T = Si, Al) tetrahedra which are linked together to form a three-dimensional framework of interconnecting pore and channel structure. The conductivity of zeolites is usually associated with ionic conductivity [1,2]. Charge is carried by means of the motion of mobile charge balancing ions in the anion framework. Hydrated zeolites are also known as proton conductors and hydroxyl ion conductors [3]. It is usually presumed that zeolites do not act as electronic conductors [4]. Furthermore, dielectric materials such as zeolites have the ability to store energy upon the application of external electric field [5]. Specific electronic properties of nanopores in zeolite structure make zeolites good candidate materials in the electronic industry, so that silicon-

* Corresponding author.
E-mail address: bala@gazi.edu.tr (B.G. Salamov).

http://dx.doi.org/10.1016/j.spmi.2016.08.040

based technologies could be replaced or supplemented by nanoporous zeolitic materials. The dielectric response of zeolites is one of the key parameters for applications. Such knowledge about zeolites has become important because of their potential application in electrochemical devices.

Conductivity and relaxation properties of various types of zeolites exchanged with monovalent or divalent cations have been extensively studied and results published in the literature [3,6–9]. In particular, it has been shown that both ionic conductivity and dielectric relaxation are due to cation jumps. The analysis of these studies shows that they are often carried out in different experimental conditions, so the obtained results are difficult to compare. It is generally admitted that the dielectric relaxation and conduction phenomena observed at frequencies below 100 MHz (the so-called intermediate frequencies) are related to the movements of cations in the large cavities and channels in which the mentioned cations can be introduced and where they can move between preferred positions. The polarization effects are visible in the frequency dependence of imaginary part of complex permittivity $\varepsilon'' = f(f)$ or in frequency dependence of loss tangent tg $\delta = f(f)$ creating one or more peaks. These peaks can be characterized by critical frequency and the intensity (maximum). It is well known that the absorbed molecules or exchanged cations influence the conductivity and the relaxation properties of zeolites [3,6–8]. In general, there are following aspects which must be taken into account:

- chemical composition of the zeolite with respect to the relation n(Si)/n(Al),
- properties and influence of the exchanged cations,
- the contents of the humidity,
- the temperature of the sample [9].

To optimize the conductivity and the relaxation properties process of zeolites, the knowledge of dielectric properties is needed. Under various conditions a number of works is devoted to study on dielectric spectra of zeolites. In Ref. [10] authors studied the dependence of the dielectric properties of the zeolite on the type of primary ion or alkaline cations incorporated in a zeolite, i.e. ion controlling ion-migration polarization. At the same time, the temperature dependence of the dielectric permittivity at different frequencies is studied. It is established that the experimental results are satisfactorily described by a model of two-component system of the zeolite - air pores. Effect of water on the dielectric properties of the natural zeolite Ca-clinoptilolite have been studied in Ref. [11]. It is shown that relaxation of water and its various concentrations influenced on the dielectric spectra in the clinoptilolite - water system. It has been established, that the contribution of water on the dielectric properties of the zeolite, i.e. water bound in the pores and water in the free volume is different. In Ref. [12] shown that modification of the natural zeolite clinoptilolite by some ions increases its dielectric permittivity, at the same time ion exchange by another ions decreases of the dielectric permittivity may be observed in relation to un-modified samples. In a previous study [13], the dielectric properties at room temperature of natural zeolite powders and plates have been studied. In our earlier work [14] dielectric spectra of natural zeolite clinoptilolite are studied at room temperature and 85% air humidity (at atmospheric pressure). The measurements were carried out on samples of high density (natural plate) and low density (unpressed powder). We have shown that the frequency dependence of both real and imaginary parts of the dielectric permittivity is characterized by approximately the same relaxation time of about 10^{-5} s. Moreover, the dielectric spectra are determined by fluctuations of alkali-metal ions associated with the water molecules inside the zeolite pores. In Ref. [15] the dielectric permittivity of natural clinoptilolite has been measured for the first time in the wide frequency range up to microwave frequencies ($\omega = 4{,}5 \times 10^{10}$ radn/s). On the basis of these measurements are an approximation of the frequency dependence of the dielectric constant in the range of 10^2–10^6 Hz. In Ref. [16] dielectric spectra of natural zeolite composites prepared by using zeolite and silicon powders are studied. The maximum dielectric permittivities were detected depending on the concentration Si powder at different frequencies. It was found that a stable decrease of the dielectric response with increasing concentrations of Si if the concentration of Si powder is more than 9%.

In microelectronics conductivity of the natural zeolites usually associated with ionic conductivity [17,18]. The aluminosilicate framework of zeolites has a negative charge, which is balanced by the cations of alkali-earth metals and water molecules connected weakly with the pores and cavities of the framework. Hydrated zeolites are also known as proton conductors [3]. Normally, as a rule, it suggests that electronic conduction [19] is not realized in zeolites. In addition materials such as zeolites have the ability to store energy upon application of an external electric field [5]. Special electrical properties of the nanopores of the zeolite structure make them good candidate materials in microelectronics [20], gas sensors [21], solar cells [22], functional fillers in composites [23] and plasma light sources with low energy consumption [24]. Thus, it should be noted that the zeolite is actively used as an element of the electrical circuit. However, a systematic study of the zeolite as an electrical circuit element has not yet been carried out. Clinoptilolite is the most abundant natural zeolite and is characterized by large, intersecting, open channels of ten- and eight-membered tetrahedral rings [21]. The channels are occupied by ion-exchangeable cations and water molecules. Keeping this in mind we have investigated the frequency dependence of the dielectric permittivity, conductivity of natural zeolite and its modifications. In this study above mentioned measurements for un-modified and silver-modified zeolite plates with different amounts of silver ion (Ag^+) and silver nanoparticles (Ag^0) is performed. We chose the silver-modified nanozeolite because it is widely used in various fields of microelectronics, medicine and biology [25–28].

In recent years, different studies are conducted for natural zeolite modified by ions and nanoparticles various metals, not only for medical purposes, but also as an element of the electrical circuit. Silver is a very useful material in microelectronics due to its excellent electrical and thermal conductivity, photosensitivity and antimicrobial properties. These processes can be