

Nanosized composites of synthetic zeolites and silver iodide as potentially electrochemically active materials

Mária Reháková · Mario Casciola · Silvia Čuvanová ·
Tommy Wadsten · Vladimír Šály · Stanislava Nagyová ·
Ľubica Fortunová · Manolo Sganappa · Juraj Packa

Received: 29 April 2009 / Accepted: 11 July 2009 / Published online: 31 July 2009
© Springer Science+Business Media B.V. 2009

Abstract Zeolitic composite materials made up of silver iodide and potassium form of synthetic zeolites ZSM5 were prepared in different conditions. The composites were characterized by X-ray powder diffraction methods and their electrochemical properties were studied by conductivity measurements. The attention was focused on the composites of synthetic zeolite of ZSM5 and AgI prepared by treating a silver form of synthetic zeolite ZSM5 (Ag-ZSM5) with potassium iodide solution. On the basis of the ac conductivity data it has been inferred that AgI forms a thin conductive crystalline shell on the surface of the K-ZSM5 particles. The sharp conductivity change between 142 and 147 °C is due to AgI undergoing a phase transition from hexagonal to cubic symmetry at 146 °C. The

electrochemical properties of the composites depend on the mode of preparation and on the subsequent thermal treatments.

Keywords Synthetic zeolite · ZSM5 · Silver iodide · Composite · Conductivity · Phase transition · True density

Introduction

Inclusion compounds based on zeolites or some other composite materials containing silver iodide are interesting with regard to their optical [1–6] and electrical properties. Silver–iodide-modified zeolites have application in fields such as semiconductors, photoconductors, information storage and photoelectric conversion materials [5]. Photochromic properties of a hydrated mordenite-AgI inclusion compounds are based on the reversible movements of Ag^+ and I^- ions from the inside to the outside of the lattice and vice versa through the mordenite channels [1].

It has been known for many years that AgI undergoes a phase transition at 146 °C and that the high temperature form, α -AgI, has an exceptionally high conductivity, about $1 \text{ ohm}^{-1} \text{ cm}^{-1}$, which is about four orders of magnitude larger than the room temperature value. The activation energy of conduction in α -AgI is only 0.05 eV and the structure of α -AgI is so suited for easy motion of Ag^+ ions [7]. Moreover, according to the recent data from literature [8, 9], an anomalous increase in ionic conductivity was observed in nanoparticles of AgI. The electrical properties and morphology of the AgI nanoparticles depend on the mode of their preparation, e.g. according to the literature [8] they may be prepared in the form of nano-rods, nano-tetrahedra or nano-plates. The properties of the AgI nano-plates are more extraordinary. The conductivity of the AgI

M. Reháková (✉) · Ľ. Fortunová
Institute of Chemistry, Faculty of Science, P. J. Šafárik
University, Moyzesova 11, 041 54 Košice, Slovak Republic
e-mail: maria.rehakova@upjs.sk

M. Casciola · M. Sganappa
Dipartimento di Chimica, Università di Perugia, Via Elce di
Sotto 8, 06123 Perugia, Italy

S. Čuvanová
Institute of Geotechnics, Slovak Academy of Sciences in Košice,
Watsonova 45, 043 53 Košice, Slovak Republic

T. Wadsten
Development and Research Wadsten, 19150 Sollentuna, Sweden

V. Šály · J. Packa
Faculty of Electrical Engineering and Information Technology,
Slovak University of Technology, Ilkovičova 3, 812 19
Bratislava, Slovak Republic

S. Nagyová
Department of Physics, Electrotechnical Faculty, Technical
University, Letná 9, 042 00 Košice, Slovak Republic

nano-plates is significantly enhanced when compared to the normal microcrystalline specimen and a large hysteresis of 50 °C in the phase transition was observed consistently in both conductivity and differential scanning calorimetry DSC measurements. On cooling the high-temperature α -AgI phase persists down to 100 °C.

In our previous papers the composite materials of the potassium form of the synthetic zeolite ZSM5 and AgI (K-ZSM5/AgI) [10] were studied. The composite was prepared by a reaction of the silver forms of synthetic zeolites ZSM5 with a solution of potassium iodide. The product was interesting from the point of electrical properties. The composites prepared by the same mode of preparation on the basis of synthetic mordenite exhibited different properties [11, 12]. The results of ac conductivity measurements of the composite K-MD/AgI, prepared on the basis of synthetic mordenite (MD), confirmed the absence of continuous conduction pathways of silver iodide on the surface of the K-MD particles [11].

Our present study of zeolitic composite materials with a content of AgI is aimed at a feasibility to prepare sensors where a steep change of electrical conductivity appears when temperature increases over 146 °C (undesirable in some devices) and is followed by a switching on a signal warning system.

In this stage of study the attention is focused on altering modes of preparation of composite materials made of synthetic zeolite ZSM5 containing AgI. The prepared composites were characterized by X-ray powder diffraction and ac conductivity measurements in various conditions.

Experimental

Material preparation

Chemicals and materials

For our study we used synthetic zeolite ZSM5 (Slovnaft a.s., Bratislava) with chemical composition (without water): $x\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3 \cdot y\text{SiO}_2$ ($x = 0.8 \pm 0.15$, $y = 20\text{--}45$). The ZSM5 was thermally activated for 3 h by heating at continuously increasing temperature in the range from 150 to 400 °C (1 h at 400 °C).

Potassium iodide, silver nitrate and other chemicals were of p. a. purity (MERCK and FLUKA).

Composite of K-ZSM5 and AgI

Composites of K-ZSM5 and AgI (denoted as K-ZSM5/AgI) were prepared by the reaction of silver form of synthetic zeolite ZSM5 (Ag-ZSM5) with a solution of

potassium iodide (KI) [10]. The products obtained by this mode of preparation were additionally heated at different temperature (160, 200, 500, 510–520 °C) for different time 16 and 20 h (four times for 5 h during four days). The samples prepared by this mode will be denoted as K-ZSM5/AgI R (R—it means prepared by the reaction).

The composite of K-ZSM5 and AgI was prepared also by annealing a physical mixture of K-ZSM5 and AgI (content of AgI 19%) at the temperature 450 and 500 °C for 1, 10 and 20 h (the preparation of the last sample was carried out in four steps of 5 h during four days).

Methods

X-ray powder diffraction patterns

X-ray powder diffraction patterns were recorded by two geometrically different techniques applied viz. reflecting and transmission. In the former a Philips X'pert diffractometer with $\lambda = \text{CuK}_\alpha$ radiation and an aluminium sample holder without internal standard was used. With the latter the unit cell parameters and peak amplitudes were obtained by using a Guinier-Hägg focusing camera with strictly CuK_α radiation and photographic recording. Silicon ($a = 5.4309 \text{ \AA}$) was added as internal standard and used for the refinement of the cell parameters. The film strips were measured with an automatic optical reader [13], yielding relative line intensities and geometrical positions. The powder diffraction characteristics were further evaluated with TREOR 90, a trial and error indexing program [14, 15].

The density was determined by the non-destructive gaspychnometric technique with a 1330 Micromeritics instrument.

The dynamic X-ray runs were recorded with a Philips X'pert diffractometer using CuK_α radiation. The sample was heated up to 450 °C and after 1 h at temperature 450 °C it was cooled down to 25 °C. The X-ray measurements were carried out at 25 °C, 300 °C, at 450 °C after 3 min, 450 °C after 1 h. Then the sample was cooled and the measurements were carried out again at 300 °C and 25 °C.

Conductivity measurements

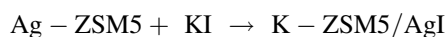
The ac conductivity measurements were performed in two laboratories—in Perugia and in Bratislava:

- the composite material was pressed into pellets at 50 MPa. The two opposite surfaces of the pellets were coated with pressed Pt-black. Impedance measurements in the range 20 to -25 °C were carried out in a

sealed-off stainless steel cell connected to a Hewlett Packard 4192 A Impedance Analyzer in the frequency range 10 Hz to 10 MHz at a signal voltage lower than 1 V. Before the measurements the pellets were equilibrated at room temperature at 53%, 75% and 90% humidity. The ac measurements were also performed in the range from 200 to 100 °C. Before starting the measurements, the pellets were held overnight in the measuring cell at two different temperatures: 200 and 160 °C. Some of the measurements were carried out at temperatures 100 and 150 °C by using a cell with 80% RH – before the measurements the pellets (pressed at 50 MPa) were kept at room temperature and relative humidity 28%. Ag paste was used to prepare electrodes. Goodwill LCR meter 819 was used to measure equivalent capacitance and conductance within the frequency range 10–10⁵ Hz, ac signal 1 V.

Results and discussion

The electrochemical activity of the composite materials prepared on the basis of synthetic zeolite ZSM5 with AgI is expected to depend on the modes of their preparation and on the experimental conditions during the preparation. An interesting composite material was the product prepared by the reaction of silver form of synthetic zeolite ZSM5 (Ag-ZSM5) with a solution of potassium iodide [10]. According to the results of X-ray powder diffractometry the Ag-ZSM5 treated with solution of potassium iodide becomes K-ZSM5 by ion exchange and silver iodide is formed as a separate phase:



The composite K-ZSM5/AgI was also characterized by X-ray photoelectron spectroscopy, electron microprobe analysis and thermal analysis [10, 16]. The results of electron microprobe analysis and XPS revealed the presence of silver and iodine as well as potassium, silicon and aluminum in the composites. The molar ratio of silver and iodine in the composite K-ZSM5/AgI (with content of AgI 11.5%) before heating is the same as in pure AgI within experimental error.

In the present study the composites of ZSM5 and silver iodide were prepared by changing the synthesis procedure. Two series of composite materials were studied:

1. The first series: the composites prepared by the reaction of Ag-ZSM5 with the solution of KI were additionally annealed at different temperatures (160, 200, 500, 510–520 °C) for different time (15, 20 h).
2. The second series: the composite of K-ZSM5 and AgI was prepared also by annealing a physical mixture of

K-ZSM5 and AgI (content of AgI 19%) at different temperatures (450, 500 °C) for different time (1, 10, 20 h).

The properties of the obtained composites were considerably influenced by the conditions of their synthesis as well as by conditions of annealing.

Material characterization by X-ray powder methods

Very accurate X-ray data for the host mineral indicate that it acts as a true zeolite and does not change its cell parameters during these experiments after including silver salt at the annealing temperature.

By using reflecting methods mainly information from the surface is obtained whereas transmission techniques mainly show the matrix character. A homogeneous sample gives thus the same signals, positions as well as amplitudes and both methods arrive at the same results.

In Fig. 1 there are the X-ray diffraction patterns of the sample K-ZSM5/AgI R before annealing and K-ZSM5/AgI R after annealing at 500 °C. These patterns were obtained with the transmission technique. During studying various alterations of composites preparation it was observed that a part of AgI enters into zeolitic cavities in dependence on temperature and time of annealing. We can observe in the X-ray diagrams the decrease of the peak-areas for AgI at $2\theta = 39, 43, 46^\circ$ and at the same time their broadening, i.e. smaller crystallite size. The mean particle size of AgI in the starting sample (K-ZSM5/AgI R before annealing) is around 5 microns and the particle size of AgI is less in the sample after annealing.

The samples K-ZSM5/AgI R before annealing and after annealing at 500 °C have about the same amount of AgI in X-ray crystalline dimensions which is also found by the density calculation (Table 1). A possible interesting point

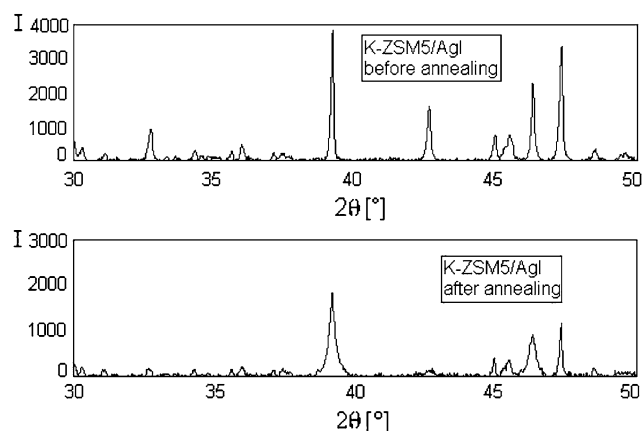


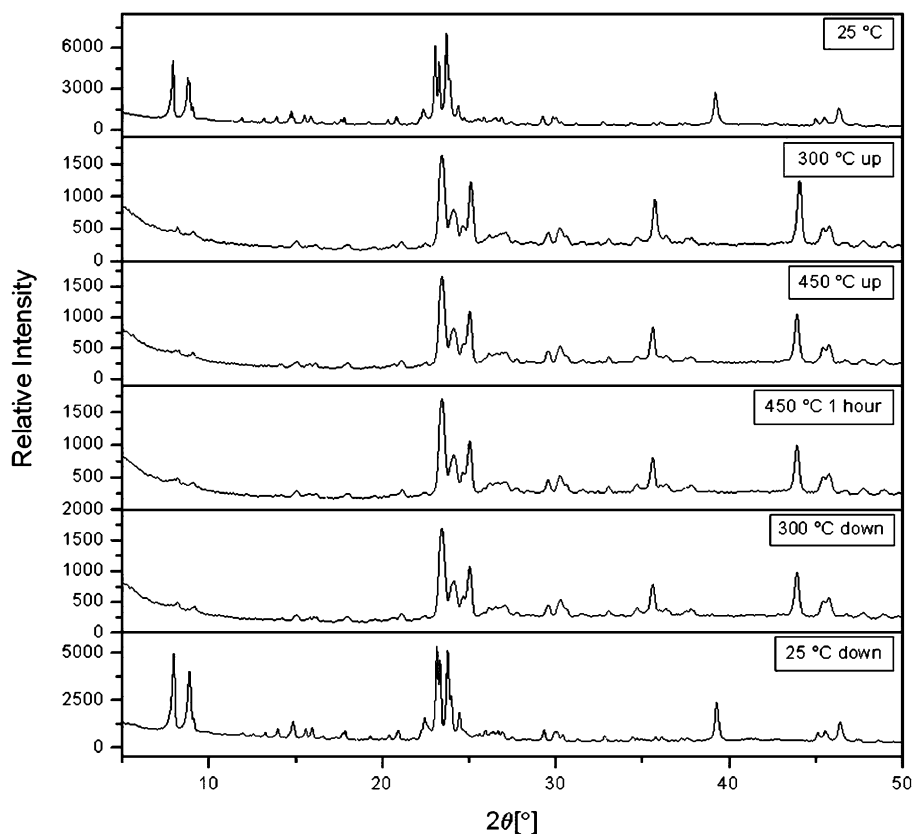
Fig. 1 Transmission X-ray technique of composite K-ZSM5/AgI R before annealing and K-ZSM5/AgI R after annealing at 500 °C

Table 1 The densities of the sample K-ZSM5 and the samples K-ZSM5/AgI R before and after annealing

The samples	Heating time temperature	Density (g cm ⁻³)
K-ZSM5	0 h	2.35
K-ZSM5/AgI R before annealing	0 h	2.66
K-ZSM5/AgI R after annealing	20 h at 500 °C	2.74
K-ZSM5/AgI R after annealing	20 h at 510–520 °C	2.77

* In order to calculate the compositions from the observed parameters some densities are needed, i.e., pure K-ZSM5 = 2.35 g cm⁻³, AgI (hex.form) = 5.69 g cm⁻³ and Ag = 10.5 g cm⁻³, respectively

Fig. 2 Reflecting X-ray dynamic measurements of potassium form of synthetic ZSM5 with AgI at 25 °C and after heating to 300 °C, 450 °C and after cooling down to 25 °C



may be that the standard hexagonal form of AgI seems to change to the cubic type due to the heat treatment. Note the slow increase of the densities (Table 1). In order hopefully to find the explanation to different physical and solid state measurements could be good to add the simple and old-fashioned method, true density [17]. Furthermore this is one of very few non-destructive techniques. At this stage of the investigation even with such new knowledge a complete understanding of the polyphase system does not seem to be simple to explain.

In the sample K-ZSM5/AgI R after annealing at 510–520 °C the crystalline part of AgI is only about 20% compared to the start sample K-ZSM5/AgI R before annealing. Furthermore, the particle size is much less than

before heating: 80% of AgI is distributed in the zeolitic cavities and, as a consequence, must have nanometric size. Such dimensions are not visible by X-ray measurements.

During annealing for longer time (20 h and more) at high temperature over 500 °C, e.g. in the temperature range 510–520 °C a small part of AgI can slowly decompose and iodine evaporates.

The results of X-ray powder diffraction measurements are in a good agreement with the results of XPS [16, S. Čuvanová et al. “unpublished”]. By using XPS method we can obtain information from about 10 nm depth of the sample measured. The XPS results have shown a decrease of the concentration of silver and iodine on the surface. It

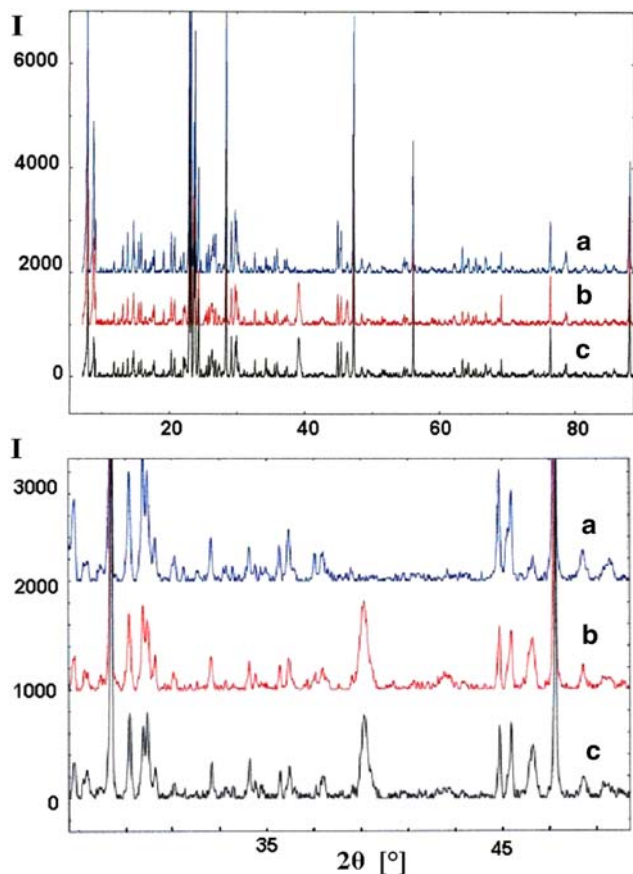


Fig. 3 Transmission X-ray technique of: **a** K-ZSM5, **b** K-ZSM5/AgI prepared by annealing of physical mixture of K-ZSM5 and AgI annealed for 10 h, **c** K-ZSM5/AgI prepared by annealing of physical mixture of K-ZSM5 and AgI annealed for 20 h

indicates that the heating causes diffusion of AgI from the surface into the zeolite.

The dynamic X-ray runs of the physical mixture of potassium form of synthetic zeolite ZSM5 with AgI (K-ZSM5 + AgI) are shown in the Fig. 2. The starting material was heated from 25 °C up to 300, then 450 °C and

after 1 h at temperature 450 °C it was cooled down to 300 and 25 °C. According to the results of dynamic X-ray runs the start at 25 °C and the end at 25 °C after cooling are very similar. Only a small amount of AgI has entered into the zeolitic cavities. The integral intensity ratio of the diffraction lines of the sample at 25 °C before heating and after heating in the range 22–26°2θ are different. AgI converts from hexagonal low temp phase to the metastable cubic, 5.05 Å, phase.

Figure 3 shows X-ray powder diffraction patterns of K-ZSM5 and K-ZSM5/AgI prepared by annealing (10 and 20 h) of physical mixture of K-ZSM5 and AgI. The differences of the integral intensity ratio of the selected diffraction lines of K-ZSM5 and AgI (e.g. at 2θ = 39 and in the range 30–33°2θ, 44.5–47°2θ) indicated that a part of AgI enters into the zeolite. The changes are more visible after heating for 20 h.

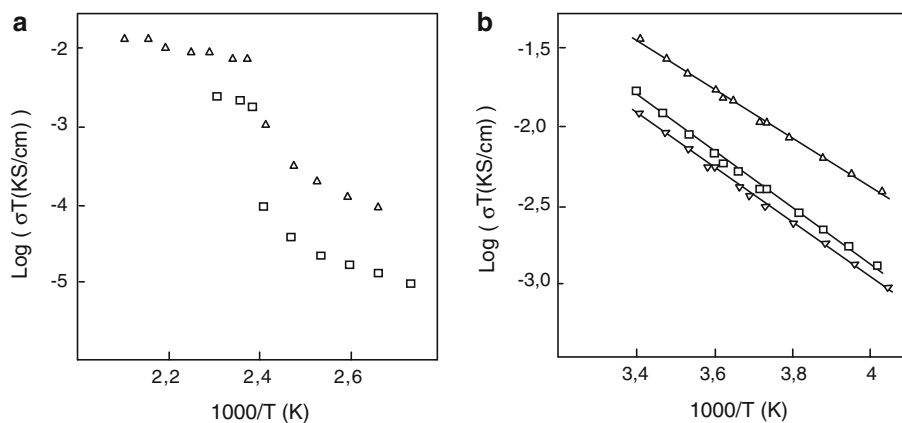
In spite of several different analyses we have not yet completely understood the X-ray phenomena presented in this paper but we work on it.

Conductivity measurements

On the basis of the ac conductivity data [10] for the composite material K-ZSM5/AgI R (R—prepared by the reaction) as well as for K-ZSM5, Ag-ZSM5, microcrystalline AgI and a physical mixture of AgI and K-ZSM5 it has been inferred, that in the composite material AgI forms a thin conductive shell on the surface of the K-ZSM5 particles.

By changing the synthesis procedure, we prepared composites with different properties. The composite prepared by the reaction of Ag-ZSM5 with the solution of KI and additionally annealed at different temperatures exhibited change of the properties (Figs. 4a, 5, 6). In particular, Fig. 4a shows that an increase in the annealing temperature from 160 to 200 °C results in an overall increase in the composite conductivity and in a smaller conductivity

Fig. 4 Arrhenius plots for conductivity of composite K-ZSM5/AgI R; the measurements were taken **a** in air after heating for 15 h at 160 (□) and 200 °C (Δ), **b** in the range from 20 to –20 °C, after equilibration at different relative humidities (Δ 90%, □ 75%, ▽ 53% RH). All measurements were carried out at decreasing temperature



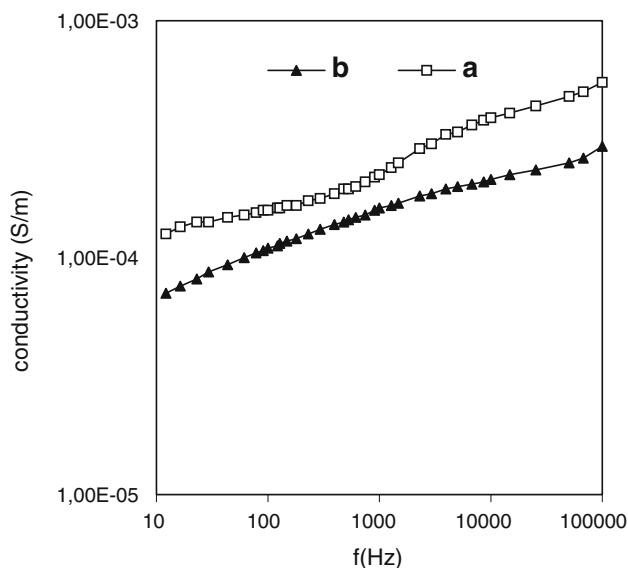


Fig. 5 Frequency dependence of conductivity. Room temperature, RH = 28%, **a** K-ZSM5/AgI R annealed at 500 °C, **b** K-ZSM5/AgI R before annealing

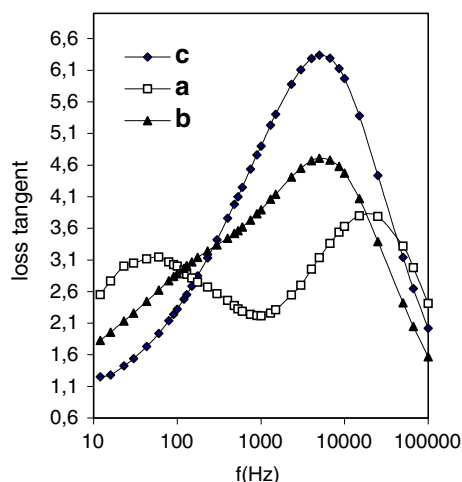


Fig. 6 Frequency dependences of loss tangent. Room temperature, RH = 28%, **a** K-ZSM5/AgI R annealed at 510–520 °C, **b** K-ZSM5/AgI R before annealing, **c** K-ZSM5

change associated with the transition from α -AgI to β -AgI. As a consequence, the conductivity of the composite annealed at 200 °C is by an order of magnitude higher than that of the composite annealed at 160 °C at temperatures below 146 °C, and only by a factor of 3 above 146 °C. The σ value of K-ZSM5/AgI R annealed at 200 °C and measured at 150 °C is $1.7 \times 10^{-5} \text{ Scm}^{-1}$ in air and increases up to $1.0 \times 10^{-3} \text{ Scm}^{-1}$ in the presence of water vapour with 80% RH.

The water present in hydrated zeolites gives rise to the typical relaxation peak in loss tangent versus frequency in the range between 10 Hz and 10 MHz. Its intensity is

dependent on the stage of the humidity [18]. The peak presence is in contrast with the measurements at temperatures over 100 °C when water escapes to the certain amount and loss tangent dependence is commonly without typical polarization peak.

K-ZSM5/AgI R shows also another peak closer to the low frequency end of loss tangent versus frequency dependence (Fig. 5). As one can see, its intensity increased when K-ZSM5/AgI R underwent the annealing. It is important to emphasize that all curves in Fig. 6 were obtained for samples stored at RH = 28% for at least 24 h.

On the other hand, the composite of K-ZSM5 and AgI prepared directly by sintering a physical mixture of K-ZSM5 and AgI at the temperature 500 °C for 20 h was not interesting from the point of its electrical properties. The ac conductivity did not show any increase above 146 °C thus indicating the absence of continuous conductive shells on the surface of the K-ZSM5 particle.

The composites obtained by the same mode of preparation by using different synthetic zeolites exhibited different properties [11, 12], e.g. the ac conductivity of the composite K-MD/AgI, prepared on the basis of synthetic mordenite (MD), did not show any discontinuous conductivity change that can be ascribed to the β to α transition in AgI [11]. Therefore the formation of continuous conduction pathways of silver iodide on the zeolite surface seems to be associated to some extent with specific surface properties of ZSM5.

Conclusion

The electrochemical activity of the composite materials based on synthetic zeolite and AgI depends on the structure of the zeolitic framework and on the modes of their preparation. Among the investigated materials, the only composites based on Ag-ZSM5 and obtained by ion exchange of K^+ for Ag^+ exhibited a temperature dependence of conductivity resembling that of silver iodide. In addition, the conductivity is strongly affected by the annealing temperature of the composite and the time.

Acknowledgements This work was supported by the Slovak Research and Development Agency under the contract No. APVV-51-035505 and the Slovak Grant Agency for Science VEGA grant No. 1/0107/08.

References

- Hirono, T., Kawana, A., Yamada, T.: J. Appl. Phys. **62**, 1984 (1987)
- Hirono, T., Kawana, A., Yamada, T.: J. Appl. Phys. **63**, 1196 (1988)

3. Kodaira, T., Ikeda, T., Takeo, H.: *Chem. Phys. Lett.* **300**(3–4), 499 (1999)
4. Zhai, Q.-Z., Qiu, S., Xiao, F.-S., Zhang, Z.-T., Shao, Ch.-L., Han, Y.: *Mater. Res. Bull.* **35**, 59 (2000)
5. Zhai, Q.-Z., Hu, W.-H., Guan, X., Jiang, T.-S., Qiu, S., Zou, M.-Q.: *J. Solid State Chem.* **169**, 81 (2002)
6. Kodaira, T., Kubota, T., Okamoto, Y., Koshizaki, N.: *Eur. Phys. J. D* **34**(1–3), 63 (2005)
7. West, A.R.: *Solid State Chemistry and its Applications*, p. 474. John Wiley and Sons, New York (1989)
8. Guo, Y.-G., Lee, J.-S., Maier, J.: *Solid State Ion.* **177**(26–32), 2467 (2006)
9. Keen, D.: A type-II superionic transition in silver iodide, <http://www.isis.rl.ac.uk/crystallography/keen/Science%20AgI.htm>, 5 June 2007
10. Reháková, M., Casciola, M., Krogh Andersen, I.G., Bastl, Z.: *J. Incl. Phenom.* **25**, 303 (1996)
11. Reháková, M., Casciola, M., Massinelli, L., Krogh Andersen, I.G., Bastl, Z.: *J. Incl. Phenom.* **31**, 131 (1998)
12. Reháková, M., Čuvanová, S., Wadsten, T., Šály, V., Nagyová, S.: *J. Incl. Phenom.* **58**(1–2), 151 (2007)
13. Werner, P.E.: *J. Phys. E. Sci. Instrum.* **13** (1980)
14. Farkas, L., Werner, P.E.: *Z. Kristallogr.* **151**, 141 (1980)
15. Werner, P.E., Erksso, L., Westdahl, M.: *J. Appl. Crystallogr.* **18**, 367 (1985)
16. Čuvanová, S., Reháková, M., Bastl, Z., Pollicino, A., Nagyová, S., Fajnor, V.Š.: *J. Therm. Anal. Calorim.* **84**(3), 721 (2006)
17. Archimedes, Mathematician Syracuse, 287–212 BC
18. Šály, V., Mikloš, P.: *Proceedings of DISEE 2000, 13th International Conference, Dielectric and Insulating Systems in Electrical Engineering, Častá-Píla, Slovakia*, p. 192, September (2000)