Composite Materials of Synthetic Mordenite and AgI

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Abstract

Composite materials made up of silver iodide and synthetic mordenite in sodium Na-MD or potassium form K-MD have been prepared by sintering a mixture of silver iodide and Na-MD or K-MD, by modified way of preparation. The prepared composites Na-MD/AgI and K-MD/AgI were characterised by X-ray powder diffractometry and thermal analysis. By integrating certain X-ray peaks quantitative reaction values were obtained. The composite Na-MD/AgI with 19 wt% of AgI content was also characterised by EDS analysis and ac conductivity measurements.

Introduction

Zeolites can include several inorganic salts as guest materials [1]. The inclusion compounds on the basis of zeolites or some composite materials containing silver iodide are interesting with regard to their optical and electrical properties.

It is known from the literature, that sodium mordenite (NaMD), one of the synthetic zeolites, can include AgI and the photosensitive properties of AgI change due to its inclusion into the zeolite [2, 3]. The NaMD–AgI inclusion compound was obtained by sintering a mixture of NaMD and AgI (in air at 500 °C for about 50 h). The inclusion of AgI into the mordenite channels was confirmed by X-ray powder diffraction and the AgI peaks, which appeared in the diagrams of the physical mixture, are not seen in the sintered sample. All peaks for the sintered sample are attributed to the NaMD lattice. Differential thermal analysis of the mordenite–AgI inclusion compound were in a good agreement with X-ray measurements. An exthothermic peak observed for AgI at about 140 °C (146 °C), which corresponds to the phase transition, was not observed in the sintered sample [2].

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 [3].

In our previous papers the composite materials of the potassium form of the synthetic mordenite and AgI (K-MD/AgI) [4] and the potassium form of synthetic zeolite ZSM5 and AgI (K-ZSM5/AgI) [5] were studied and compared. These composites were not prepared by the sintering methods, but by a reaction of the silver forms of synthetic zeolites (mordenite and ZSM5) with a solution of potassium iodide. The attention of our study was focused mainly on the electrical properties of the products prepared. On the basis of ac conductivity data obtained for the composite material K-ZSM5/AgI the AgI forms a thin conductive shell on the surface of the K-ZSM5 particles. But the ac conductivity measurements of composite K-MD/AgI confirmed the absence of continuous conduction pathways of silver iodide around the K-MD particles.

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 ohm^{-1} cm^{-1}, which is about four orders of magnitude larger than the room temperature value. The activation energy for conduction in α-AgI is only 0.05 eV and the structure of α-AgI is so suited for easy motion of Ag^+ ions [6].

The aim of the present study is a preparation of composites of synthetic mordenite and AgI (Na-MD/AgI and K-MD/AgI) by a sintering method, alternating the modes of the preparation, and to characterise them by X-ray powder diffractometry and some of them by EDS analysis and ac conductivity measurements. The methods of preparation of the composites are different

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from the methods that we used in our previous study [4, 5]. After using different modes of sintering we obtained different composites with different properties.

Experimental

Chemicals and materials

In this study we used synthetic mordenite MORSIT SM 315/500 (Slovnaft a.s., Bratislava). The chemical composition of MORSIT SM 315/500 is: Na_2O 5.26%, CaO 0.89%, Al_2O_3 10.99%, Fe_2O_3 0.024%, SiO_2 82.87%. The mordenite 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 (it was denoted as Na-MD).

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

Material preparation

The first step in the preparation of two following series of composite materials in sodium and potassium forms was the preparation of potassium form of synthetic mordenite K-MD and then the preparation of physical mixtures of Na-MD with AgI and K-MD with AgI. The physical mixtures were used also as standards for comparison with the structures and properties of the composites obtained after sintering.

K-mordenite
Thermally activated mordenite in sodium form Na-MD (3.5 g) was mixed with 20 mL of 1 M solution of KI. After 2 h of intensive mixing the heterogeneous mixture was decanted with distilled water and centrifuged (during 2 days). The presence of iodide ions in the water after decanting was checked by adding a solution of 0.1 M $AgNO_3$. The zeolitic product was dried for 1 h at 60–80 °C.

The composite Na-mordenite/AgI

(a) The physical mixture (3 g) of synthetic mordenite in sodium form (Na-MD) and AgI was prepared by cogrinding Na-MD and AgI (19 wt%). The mixture is denoted as Na-MD + AgI.
(b) The composite materials with content of 19% AgI were prepared by sintering of the physical mixture of Na-MD and AgI for 1 h at temperature 450 °C, but also for 12 h at 450 and 500 °C. The composites of Na-MD and AgI are denoted as Na-MD/AgI.

The composite K-mordenite/AgI

(a) Three different kinds of physical mixtures of synthetic mordenite in potassium form (K-MD) and AgI were prepared by cogrinding K-MD and AgI. The content of AgI was 16, 19 and 32 wt%. The mixtures are denoted as K-MD + AgI.

(b) The composite materials were prepared by sintering of the physical mixture of K-MD with three different contents of AgI (16%, 19% and 32%) for 1 h at temperature 450 °C. The composite with the content of 19% AgI was also sintered for 12 h at temperature 450 °C. The composites of K-MD and AgI are denoted as K-MD/AgI.

Methods

X-ray powder diffraction patterns were recorded by two geometrically different techniques applied viz. reflecting and transmission. In the former a Philips X'pert powder diffractometer with CuK_α 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 ($a = 5.4309$ Å) was added as internal standard and used for the refinement of the cell parameters. The film strips were measured with an automatic optical reader [7], yielding relative line intensities and geometrical positions. The powder diffraction characteristics were further evaluated with TREOR 90, a trial and error indexing program [8, 9].

The dynamic X-ray runs were recorded with a Siemens D5000 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, 300, and 450 °C after 3 min, 450 °C after 1 h. Then the sample was cooled and the measurements were carried out again at 300 and 25 °C.

The ac conductivity measurements were carried out in two laboratories: in Perugia and in Bratislava.

– in Bratislava: pellets 12 mm in diameter and approximately 1.9 mm thick, were prepared by pressing about 250 mg of the material at 6.5 MPa. Two opposite surfaces of the pellet were coated with suspension of graphite. The pellets (prepared by this mode) were heated up to 270 °C and in such way the present water was partially removed. Then they were held over saturated salts solution (RH = 12, 33, 55 and 75%) at room temperature in desiccators and conditioned for 24 h. The electrical measurement was performed keeping the RH and temperature (25 °C) constant and using the HIOKI Z Tester. The parallel capacitance C_p and conductance G_p were measured at applied ac voltage 1 V within the range 50 Hz to 4 MHz.
– in Perugia: pellets, 10 mm in diameter and 1.3–1.5 mm thick, were prepared by pressing about 200 mg of the material at 50 kN cm^{-2}. The two opposite surfaces of the pellet were coated with pressed platinum black or graphite powder mixed with the material in the weight ratio 3:1. The impedance measurements in the range 20 to −20 °C were carried out in a sealed stainless steel cell connected to a Hewlett Packard 4192A Impedance

Analyzer in the frequency range 10 Hz to 10 MHz at a signal voltage lower than 1 V. The pellets were previously equilibrated at room temperature for 2 days at 75% relative humidity. The ac measurements were also performed in the range from 200 to 100 °C by using a cell purged with a flow of dry nitrogen. Before starting the measurements, the pellets were held overnight in the measuring cell at 200 °C.

The silver, iodine and other elements in sodium form of the composite (sintered for 12 h at 490 °C temperature) were determined by EDS analysis using a TESLA BS 340 scanning electron microscope (TESLA ELMI a.s. with a LINK ISIS 300 microanalyser).

Results and discussion

The composites of synthetic mordenite (MD) and AgI were prepared by sintering a physical mixture of the synthetic mordenite with silver iodide. The sintered samples were pale yellow. Our attention was focused mainly at composites with 19 wt% AgI. According to the literature [2] chemical analysis reveals that the maximum AgI content in the cavities of synthetic mordenite is 3AgI per Na-MD unit cell, i.e., 19 wt%.

Two series of composite materials were studied:

1. The first series: the composites Na-MD/AgI based on the sodium form of synthetic mordenite Na-MD were prepared. All sodium composite materials Na-MD/AgI contained 19 wt% of silver iodide. The samples were sintered for 1 and 12 h, at 450 °C temperature, but also at 500 °C.
2. The second series: the composites were based on the potassium form of synthetic mordenite K-MD. The composites K-MD/AgI were prepared from the physical mixture containing K-MD and 19 wt% AgI,

as well as with lower content of AgI (16%) and double content of AgI (32%). The time of sintering was 1 and 12 h at 450 °C.

The composites Na-MD/AgI and K-MD/AgI were characterised by X-ray powder methods. Sodium form of the composites Na-MD/AgI with 19% of AgI (sintered for 12 h at 500 °C temperature) was also analysed by ac conductivity measurements. Presence of silver and iodine in the sample was confirmed by EDS analysis.
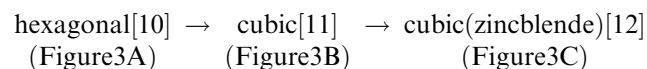
The structure and properties of the composites were compared with the unreacted physical mixtures.

Material characterisation by X-ray powder methods

Very accurate 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 some silver salt.

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. Both methods arrive at the same result i.e., the samples are homogeneous (Figures 1 and 2).

From the dynamic X-ray runs, Figure 3, where the starting material was the physical mixture of potassium form of synthetic mordenite with AgI (K-MD + AgI) and at the end of the X-ray measurements the final material was the composite (K-MD/AgI), it looks as pure AgI undergoes a solid state transformation from

$$\text{hexagonal[10]} \rightarrow \text{cubic[11]} \rightarrow \text{cubic(zincblende)[12]}$$
$$\text{(Figure3A)} \qquad \text{(Figure3B)} \qquad \text{(Figure3C)}$$

But the phase (C) is metastable and goes slowly back to form (A). However, there appears to be some confusion in the literature concerning the polymorphism of AgI. It is stated that there is no good evidence for the cubic
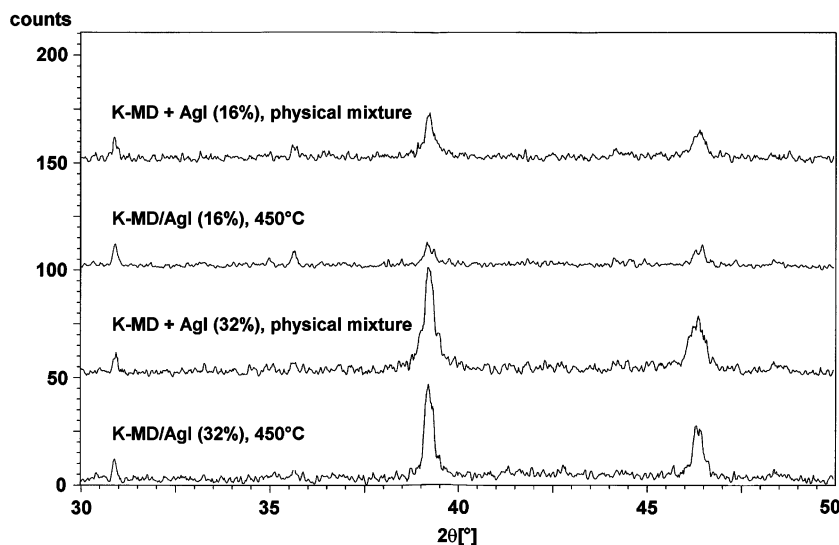

Figure 1. Reflecting X-ray technique of physical mixture K-MD + AgI and composite K-MD/AgI (content of AgI 16% and 32%) sintered for 1 h at temperature 450 °C, AgL-characters at $2\theta = 39°$ and $2\theta = 46°$.
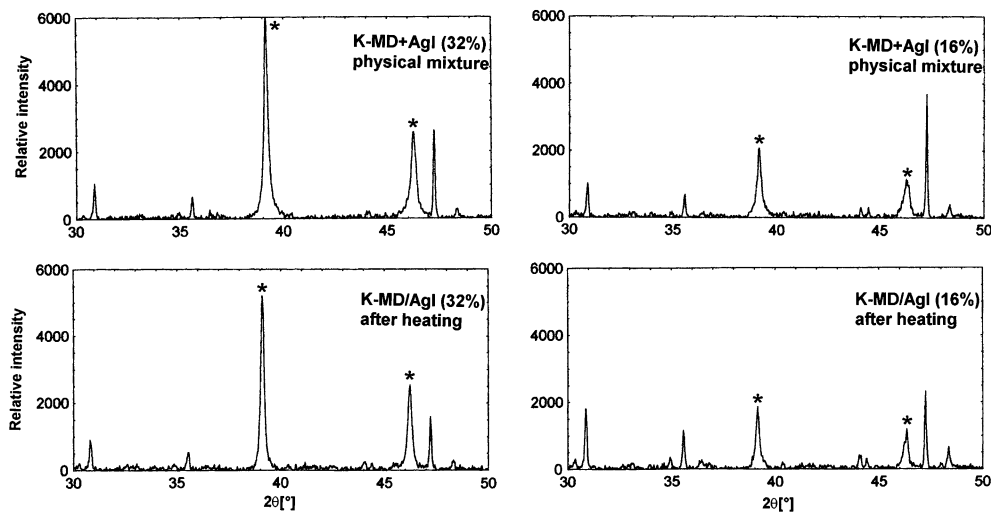
Figure 2. Transmission X-ray technique of physical mixture K-MD + AgI and composite K-MD/AgI (content of AgI 16% and 32%) sintered for 1 h at temperature 450 °C. The two strong peaks are from AgI and the sharp one at $2\theta = 47°$ is the silicon standard.

zincblende structure or for the transition point at 137 °C, and that various structures are obtainable depending on the method of preparation.

In spite of different AgI-structures but with the same density, start phase and reacted phase, three signals have the same angle value and almost the same intensity [see ref 10–12]. These peaks from the transmission runs were normalised and integrated in order to give quantitative information of the AgI-occupancy. The quantitative values here presented are based on one experiment and mean values from three integrated calculations.

In the Figures 1 and 2, there are the X-ray diffraction patterns of the physical mixtures K-MD + AgI and composites K-MD/AgI with two different AgI contents, 16% and 32%. The two K-MD/AgI composites, with 16% and 32% of AgI, give quite consistent decrease of the silver salt, after the 1 h of sintering at the temperature 450 °C. Under these experimental conditions the

zeolite matrix seems to be saturated with 5–6% by weight of AgI.

In the Figures 4 and 5, there are the X-ray diffraction patterns of the starting physical mixtures and composites of sodium form Na-MD/AgI and of potassium form K-MD/AgI with 19 wt% AgI after sintering for 1 h and also 12 h at temperature 450 °C. In both the composites (in sodium form Na-MD/AgI and in potassium form K-MD/AgI) with 19 wt% AgI after different time of sintering, for 1 and 12 h at the same temperature (450 °C), we can see differences in the intensities of the AgI peaks. The AgI peaks in the composites after 12 h heating are lower compared with the AgI peaks of the composites after 1 h heating.

During studying various alternations of composites preparation it was observed that the amount of AgI entering the cavities depended on temperature and time of heating (sintering). Already an increase by 10 °C and
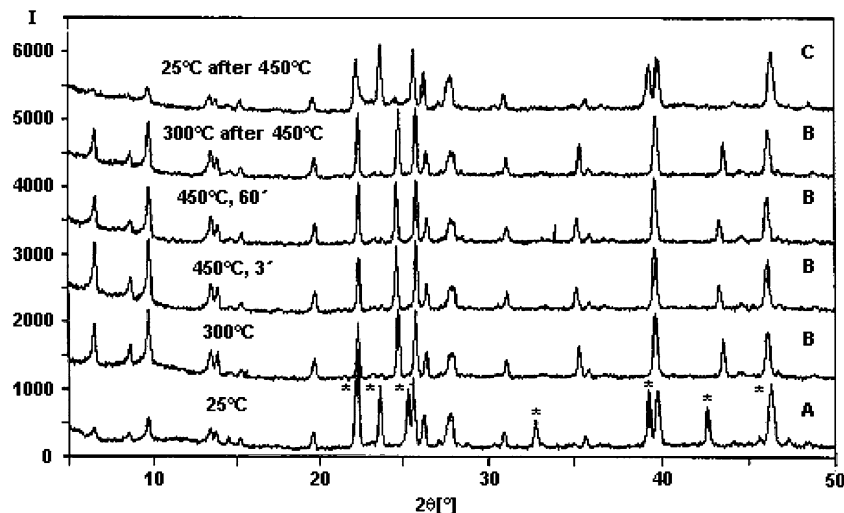

Figure 3. Reflecting X-ray dynamic measurements of potassium form of synthetic mordenite with AgI (A) at 25 °C and after heating to 300 °C (B), 450 °C (B) and after cooling down to 25 °C (C) showing the three polymorphic AgT-phases (A, B, C).
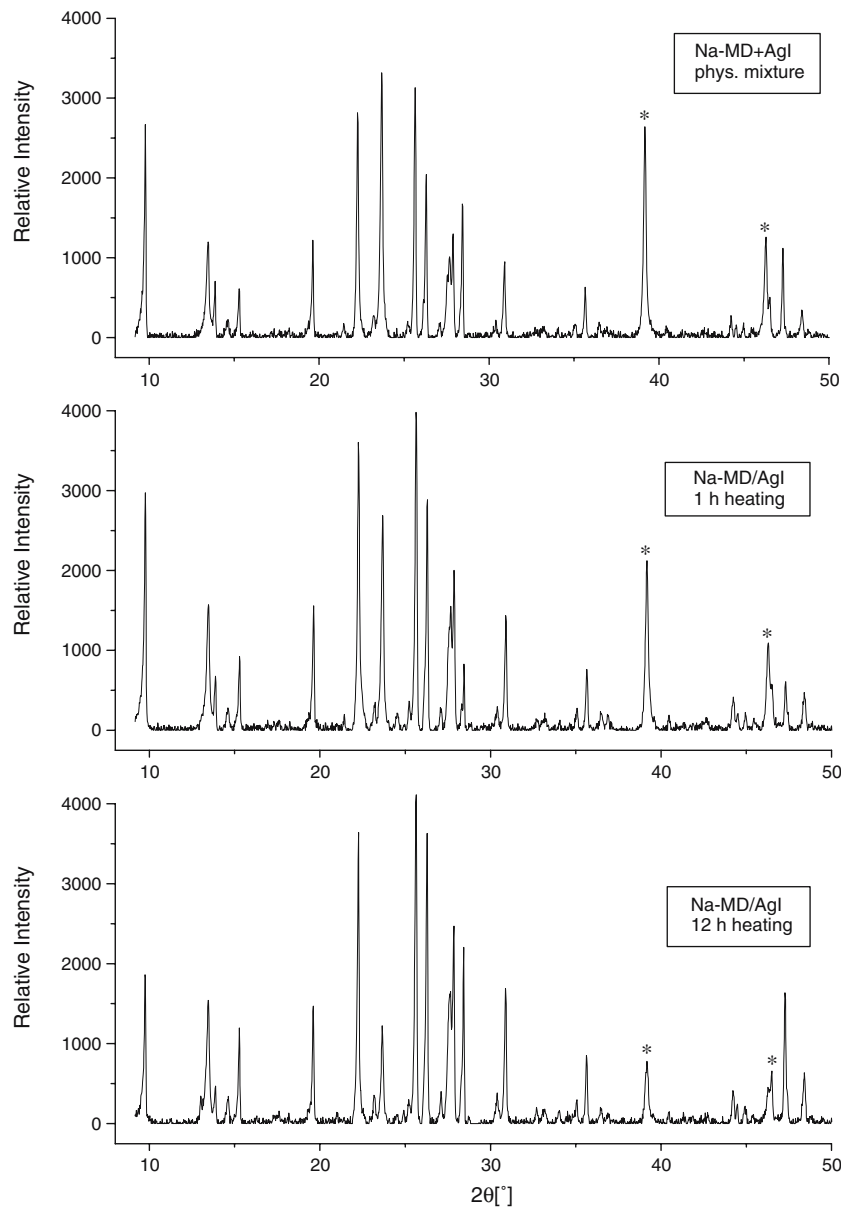
Figure 4. Transmission X-ray technique of physical mixture Na-MD + AgI and composite Na-MD/AgI (content of AgI 19%) after heating for 1 and 12 h at 450 °C.

longer time of heating resulted in higher amount of AgI entering the cavities. For the potassium form after 12 h at 450 °C it was found that 36 wt% of the AgI was included. For the sodium form it was 42% and by increasing the temperature to 500 °C 66% was included.

When the percentual content of AgI in the started physical mixture of the potassium form of the composite was higher than 19%, there were not already seen any increases in the amount of AgI included in the cavities at the same temperature and time of the sintering.

Conductivity measurements

The conductivity measurements carried out in both laboratories in Perugia and Bratislava checked the differences between the physical mixtures of the synthetic mordenite Na-MD with AgI (19%) and the prepared composite Na-MD/AgI sintered for 12 h at temperature 500 °C.

In Bratislava's laboratory: Using the measured values of G_p and sample geometry, the ac conductivity $\sigma_{ac}(\omega)$ at various frequencies was calculated. The total frequency dependence of the conductivity is expected to take the form

$$\sigma_{ac}(\omega) = \sigma_0 + \sigma'(\omega)$$

where σ_0 is the limit of the conductivity when the frequency $\omega \to 0$. This part is related to the dc conductivity. The frequency dependent part $\sigma'(\omega) = A\omega^s$. The exponent s varies from 0 to 1. Such universal behaviour has been observed on many disordered solids and has been called the universal law by Jonscher [13]. In some cases the dc conductivity σ_0 can be determined using the extrapolation toward low frequencies [14]. An example
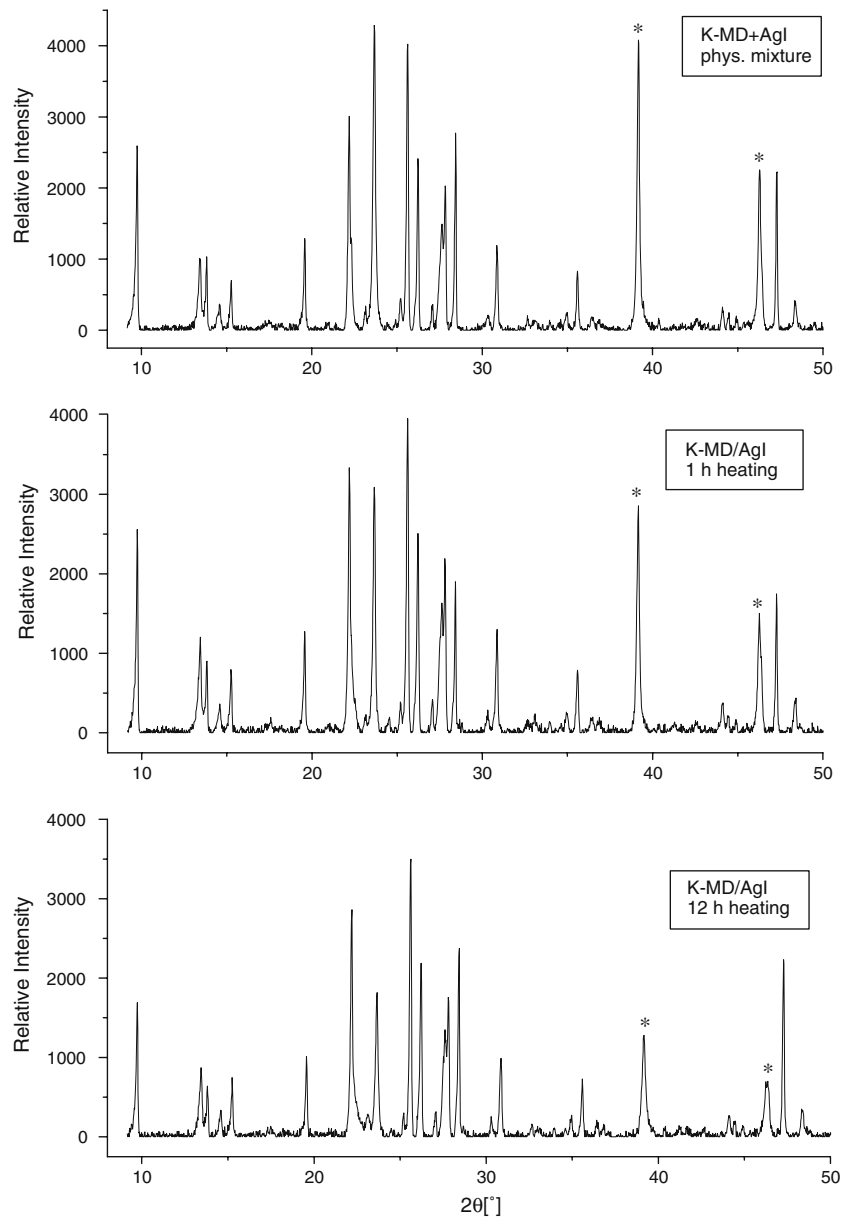
Figure 5. Transmission X-ray technique of physical mixture K-MD + AgI and composite K-MD/AgI (content of AgI 19%) after heating for 1 and 12 h at 450 °C.

of the obtained results is reported in Figures 6 and 7. The frequency dependence of the conductivity is shown separately for the Na-MD + AgI in Figure 9 due to the better resolution. The fitted parameters are also presented. The calculated values of the exponent s are given in Table 1.

In the case of physical mixture Na-MD + AgI the curve $\sigma_{ac}(\omega)$ could be divided into three areas with different value of the exponent s.

The influence of humidity on the conductivity of the samples is shown in Figure 8. The water present in zeolites can be bonded to the framework or to the compensating cations of the zeolite or the water molecules are free and create clusters with the properties depending on the surrounding space. In such way both, the
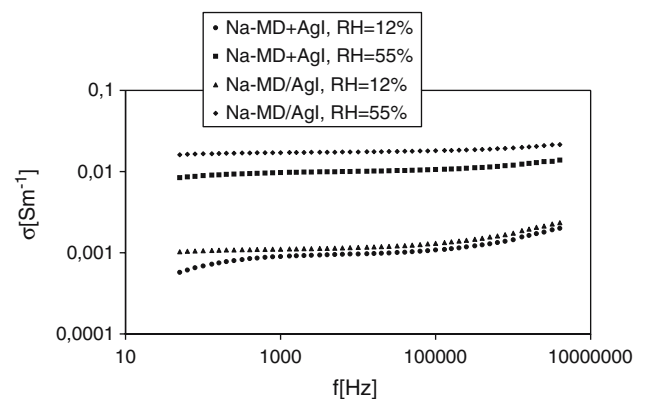

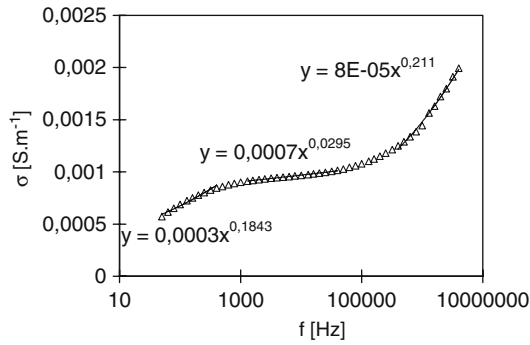*Figure 6.* Frequency dependence of the ac conductivity of the measured samples.

Figure 7. Frequency dependence of the ac conductivity of the sample Na-MD + AgI and the calculation of parameter *s* (RH = 12%).

dielectric polarisation and electrical conductivity in hydrated zeolites is the result not only of the hopping of cations between different sites but of the movement of water molecules itself, as well. On the other hand the present water affects the movement of cations in the cavities of the zeolite [15]. If the water molecules occupy the empty sites, the cation to jump need additional energy. This fact results in the dependence of conductivity of the hydrated zeolite on the content and the character of the present water.

Among the three different samples (Na-MD, Na-MD + AgI and Na-MD/AgI) the highest conductivity was measured on the composite Na-MD/AgI at the humidity RH = 55%.

In Figure 9, there are shown the complex impedance diagrams measured and calculated when RH = 33%. In the minima of the plots the value Z'_{min} was estimated and the conductivities σ_{min} in this points calculated. The results are given in Table 2. The highest value of the conductivity σ_{min} was calculated again for the sintered sample Na-MD/AgI.

In Perugiás laboratory: The dependence of conductivity on temperature was investigated on pellets made of Na-MD/AgI and Na-MD + AgI, previously stored at 75% RH, room temperature. The Arrhenius plots (log(σT) versus $1/T$, Figure 10) show that the conduc-

Table 1. Exponent *s* calculated for the measured samples. In the case of Na-MD + AgI three various areas could be recognised

Material	Parameter *s*			
	RH (%)	Low frequencies	Medium frequencies	High frequencies
Na-MD	12	0.0157		0.1980
	33	0.0197		0.2491
	55	0.0100		0.0836
	75	0.0137		0.1632
Na-MD/AgI	12	0.0169		0.1871
	33	0.0170		0.2048
	55	0.0108		0.0564
	75	0.0169		0.1908
Na-MD + AgI	12	0.1843	0.0295	0.2110
	33	0.1875	0.0322	0.2540
	55	0.0571	0.0157	0.0903
	75	0.1985	0.0310	0.2258

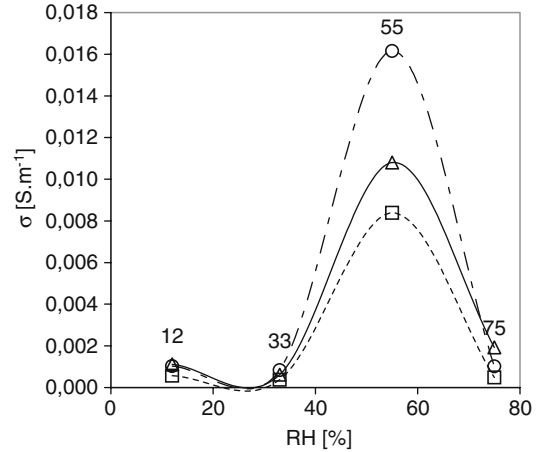*Figure 8.* The conductivity of the measured samples at various humidity (Δ Na-MD, o Na-MD/AgI, □ Na-MD + AgI). The connecting lines serve for better orientation only.

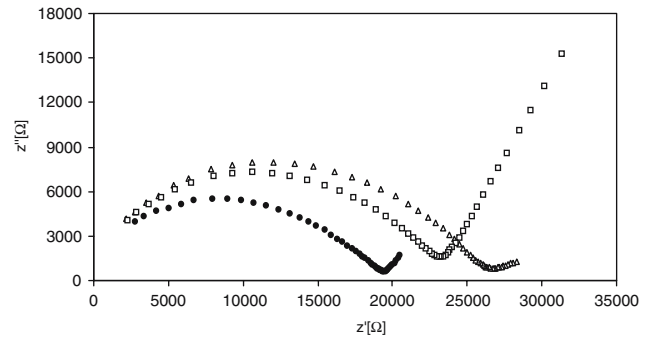*Figure 9.* Complex impedance diagrams of the measured samples at RH = 33%. Δ Na-MD, □ Na-MD + AgI, • Na-MD/AgI.

Table 2. The values Z'_{min} and σ_{min} calculated from the plots shown in Figure 9

Sample	Z'_{min} (Ω)	σ_{min}
Na-MD	26700	6.55×10^{-6} S cm^{-1}
Na-MD + AgI	23100	6.24×10^{-6} S cm^{-1}
Na-MD/AgI	19400	8.87×10^{-6} S cm^{-1}

tivity of Na-MD/AgI is higher than that of Na-MD + AgI by a factor of 3 in all the investigated temperature range. Therefore, within the experimental error, both systems are characterised by the same activation energy, $E_a = 51 \pm 1$ kJ mol^{-1}, obtained by parameterisation of the Arrhenius equation ($\sigma T = A \exp(-E_a/RT)$).

Measurements were also carried out at high temperature on anhydrous samples. In order to achieve complete dehydration, the pellets were heated overnight in the measuring cell at 200 °C under a dry argon flow. The conductivity was then determined at decreasing temperature from 200 to 100 °C (Figure 11). Differently from the low temperature results, in this case the composite and the physical mixture exhibit very close conductivity values and slightly, but significantly, different activation energy (67 and 62 kJ mol^{-1}, respectively).
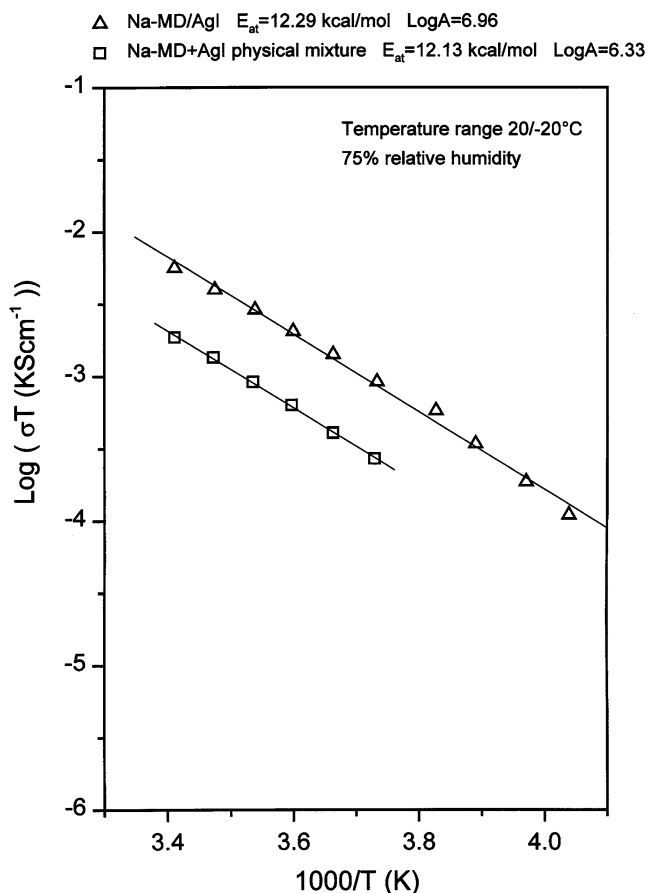
△ Na-MD/AgI E_{at}=12.29 kcal/mol   LogA=6.96
□ Na-MD+AgI physical mixture E_{at}=12.13 kcal/mol   LogA=6.33

Temperature range 20/-20°C
75% relative humidity

Figure 10. The Arrhenius plot for the conductivity of physical mixture Na-MD + AgI and composite Na-MD/AgI in temperature range from 20 to −20 °C.

△ Na-MD / AgI E_{at}=15.92 kcal/mol   LogA=4.09
□ Na-MD + AgI physical mixture E_{at}=14.82 kcal/mol   LogA=3.48

Temperature range 200°-100°C

Figure 11. The Arrhenius plot for the conductivity of physical mixture Na-MD + AgI and composite Na-MD/AgI in temperature range from 200 to 100 °C.

The absence of discontinuity in the Arrhenius plot of the composite in the correspondence of the AgI phase transition at 146 °C indicates that not included AgI does not give an appreciable contribution to the pellet conductivity and that, in particular, does not form continuous pathways on the surface of Na-MD particles, as it was found for the AgI/K-ZSM5 composite [5].

On the basis of the low and high temperature results it can be concluded that the inclusion of AgI (or inclusion of silver and iodide ions) in Na-MD alters to some extent the electrical conductivity of the zeolite. But it is still not quite clear in which form the AgI is built in the host channels.

Conclusion

The saturation of mineral matrix with AgI depends on experimental conditions, mainly on time and temperature of sintering. By using different geometrical diffraction methods it is further noticed that the samples are homogeneous. The mineral acts as a true zeolite host, by not changing its lattice dimensions during the high temperature inclusion of the guest molecule AgI. There seems to be more space in the Na-mordenite than in the K-mordenite.
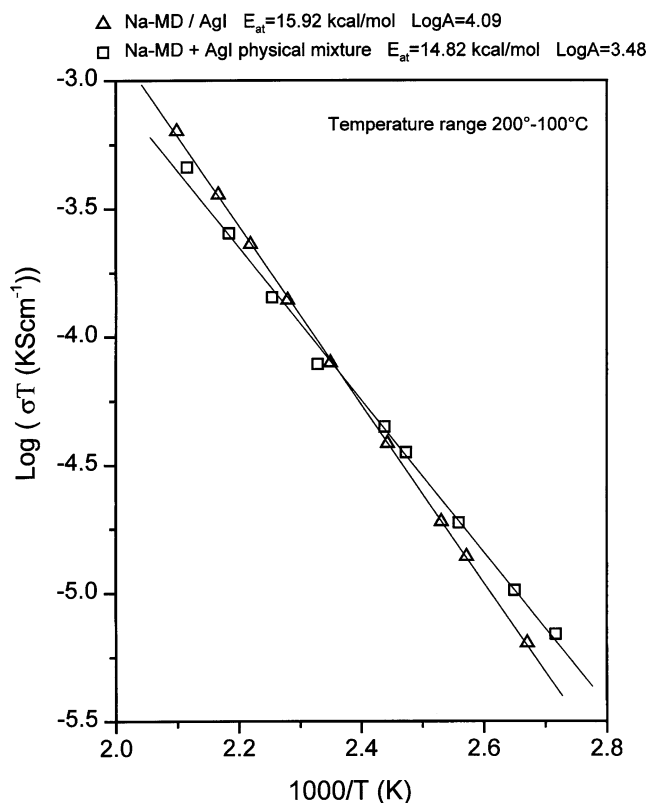
It is still not quite clear in which form AgI is built in the host channels.

The changed properties of the composites of sodium form of synthetic mordenite with AgI in comparison with their physical mixture were checked also by the ac conductivity measurements.

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