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THE STUDY OF HIGH-TEMPERATURE PHASE TRANSITIONS IN AgA AND AgA • $AgNO_3$ FORMS. THERMAL AND X-RAY PROPERTIES

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ABSTRACT

The study of the thermal behaviour of AgA zeolite and the inclusion complex AgA · $AgNO_3$, within the temperature range from room temperature to 1000°C, has been carried out in this paper. Structural transformations have been investigated and followed by X-ray analysis. The high-temperature transformation of the zeolite A structure of the two silver forms was performed throughout the amorphous phase. The recrystallisation process occurring during any further heating causes formation of the same crystal phase $AgAlSiO_4$, identified as Ag-carnegieite, in both cases. AgA zeolite can be directly transformed into Ag-carnegieite while AgA · $AgNO_3$ passes through a metal inclusion complex intermediate phase, and is then transformed into Ag-carnegieite along with the exolution of a metallic silver phase.

INTRODUCTION

Now-a-days, a generally accepted statement is that crystal structure itself is the basic factor in the determination of properties of solid ionic conductors. Activation, as well as the mobility of ionic species, are directly connected with the position and coordination in the crystal lattice. It has only been since recently known that tectosilicate structures, formed by SiO_4 and AlO_4 tetrahedrons, enable a fast movement of ions. Particular attention has been paid to a detailed study of carnegieite [1]. A rather significant number of data concerning a new series of compounds, known as NASICON [2–4], has recently appeared.

The aim of our investigation was to study the synthetic zeolite 4A, as well as the possibilities of its modification. In our previous papers [5,6] it has been shown that structural transformations and the formation of new phases, characterised by extraordinary conducting properties, result from the zeolite when exposed to heating at high temperatures.

The purpose of this paper was to investigate and analyse the changes that occur during the heating processes of AgA zeolite and the nitrate inclusion complex AgA · $AgNO_3$. The properties of the newly formed $AgAlSiO_4$ phase, for which we have found no data in the literature at all, are described in this paper.

EXPERIMENTAL

The preparation of silver zeolite forms, AgA and AgA · $AgNO_3$, is described elsewhere [7,8]. The X-ray powder diagrams were obtained on a Philips diffractometer (PW-1051) using CuK_α radiation and a graphite monochromator, at room temperature. The program POWDER [9] was utilised to calculate the unit cell dimensions.

Phase transformations, as well as the thermochemical behaviour, were investigated by a DuPont 1090 thermal analyser with a high-temperature cell (1200°C) and a TGA 951 analyser in nitrogen atmosphere. The heating rate was 20° min^{-1}. The enthalpy of the $\beta \rightleftharpoons \alpha$ phase transition was determined on the basis of the DSC curve using the program INTERACTIVE DSC V1.1.

RESULTS

Thermal properties

The DTA curve of AgA zeolite shows a series of thermal effects with both endothermal and exothermal characteristics. It can be seen from Fig. 1 that at the very beginning of the curve an endothermal peak of dehydration at 210°C is followed by an exothermal peak at 756°C (739°C) * of high intensity and another of somewhat lower intensity at 922°C (886°C). Another endothermal peak relatively lower intensity at 969°C (966°C) was also noticed on the DTA diagram in the high-temperature region. During the cooling process two exothermal peaks, the first of which was at 711°C (720°C) and the second at 640°C (648°C), were again registered. The situation becomes clearer when both the heating and cooling cycles are repeated several times. It was noticed that the two exothermal peaks registered within the first heating cycle do not appear in the course of a repeated heating process, which certainly indicates the irreversible character of these thermal effects. The first exothermal peak at 756°C (739°C) corresponds to the destruction of the structure of AgA zeolite, as is evident

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* The best representative temperature is the first deviation from the baseline, when using lines in the high-temperature cell.

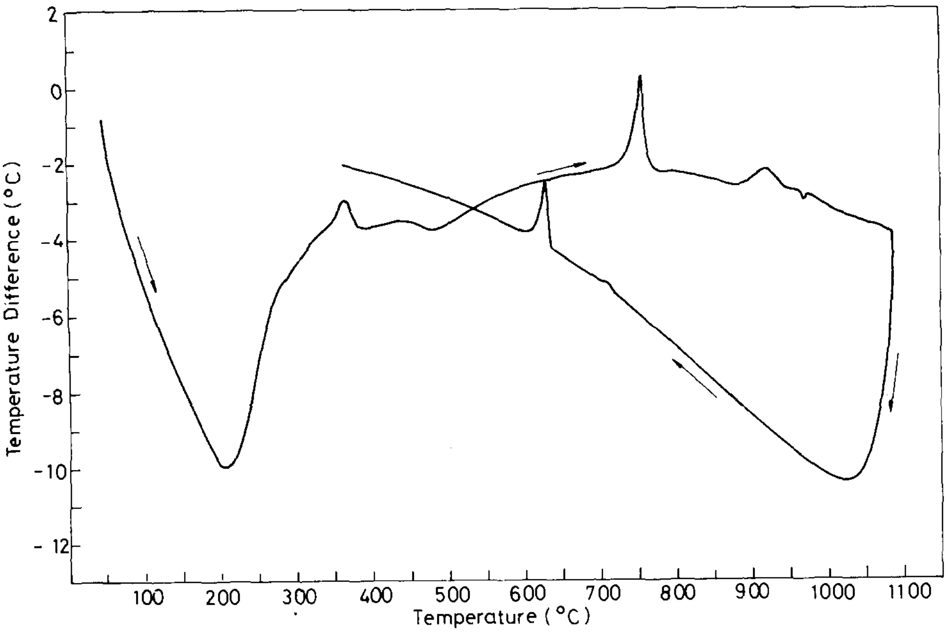

Fig. 1. DTA curve for AgA zeolite.

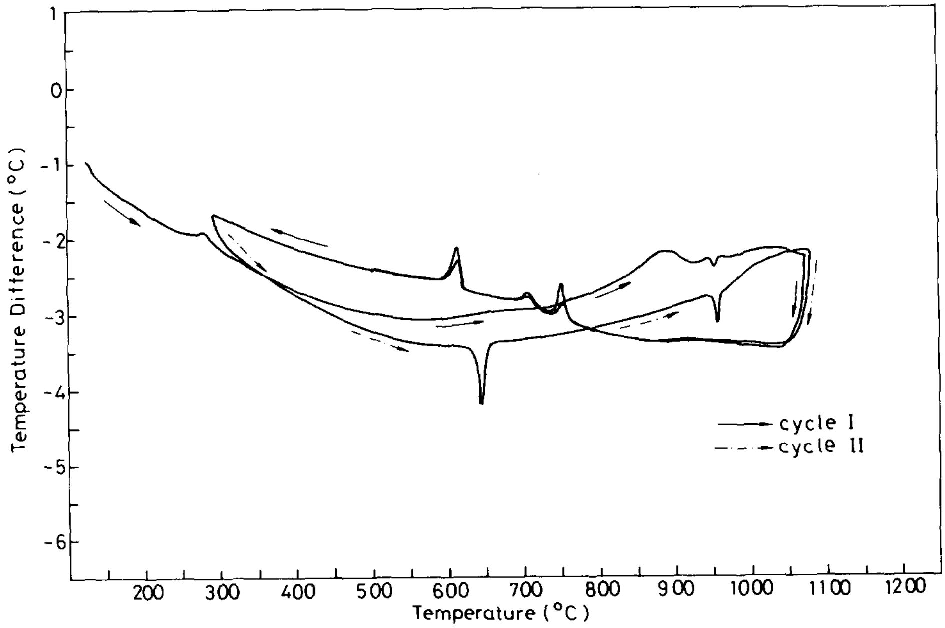

Fig. 2. DTA curve for previously heated AgA at 800°C for 5 min; several cycles of heating and cooling.

from Fig. 2. The same figure illustrates several heating and cooling cycles of the sample, which was previously exposed to the heating process up to a temperature of 800°C (for 5 min), i.e., to a somewhat higher temperature than that at which the first exothermal peak was registered in Fig. 1. In this case the peak at 756°C does not appear. However, the exothermal peak appearing at 922°C is now present in Fig. 2. In the second heating cycle, however, this peak is missing and therefore ascribed to the recrystallisation of the amorphous phase formed after destruction of the zeolite structure. This phenomenon was also checked by X-ray analysis, and it was found that the sample heated at 800°C was amorphous. The recrystallisation carried out at 922°C causes the formation of a new crystal phase that appears in two forms (high temperature alpha and low temperature beta form) characterised by a reversible phase transition at about 640°C. The temperature of the $\beta \rightarrow \alpha$ phase transition determined from the DSC curve is 638.7°C. The corresponding enthalpy of transition is $\Delta H = 17.5$ J g^{-1}.

It was established that the exothermal peak at 711°C appearing in the cooling process corresponds to the endothermal peak at 969°C in the heating process, as can be clearly seen from Fig. 3. Namely, if the heating process is performed at a temperature below 969°C, at which the peak appears, no peak will be registered at 711°C during the cooling process; only a $\beta \rightleftharpoons \alpha$ phase transition can be seen. The endothermal peak corresponds, according to its position, to the melting point of the metallic silver, while the exothermal peak at 711°C corresponds to the silver solidification. It can be

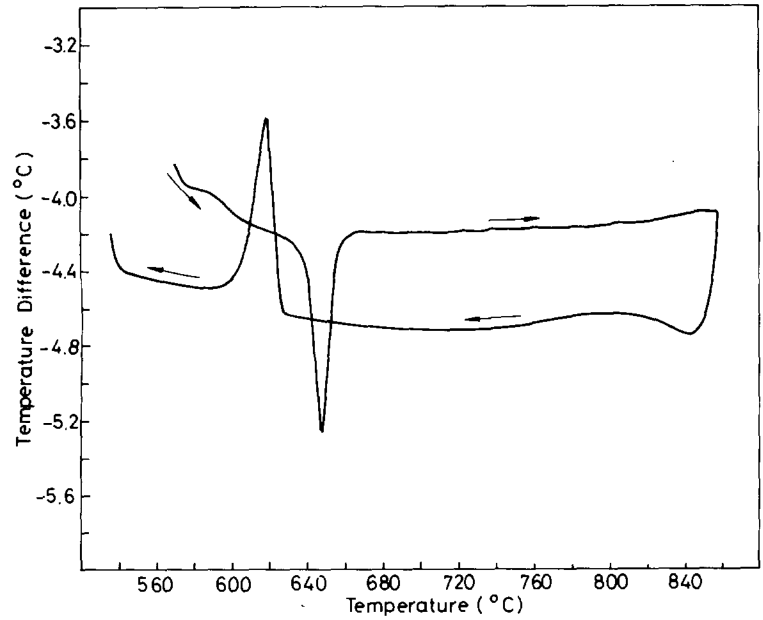

Fig. 3. DTA curve for AgA previously heated to 1000°C, $\beta \rightleftharpoons \alpha$ phase transition is evident.

seen from Fig. 2 that the peak of solidification formed during the cooling process was split, i.e., that the first peak is followed by another one of lower intensity. We have also noticed during our investigations that the very intensity of these peaks both in the heating and cooling processes increases with the number of cycles.

The thermal effects generated during the treatment of the nitrate inclusion complex AgA · $AgNO_3$, containing $AgNO_3$ molecules in channels and cages [8], are presented in Fig. 4. At the very beginning of the first heating cycle, a slight dehydration (water retained during the process of salt inclusion) followed by a wide endothermal peak of nitrate degradation, at about 436°C (368°C), was noticed. The endothermal peak at 687°C (676°C) follows, like the two previous ones, by a mass loss on the TG diagram, which was caused by the degradation of silver oxide formed during nitrate decomposition down to elementary Ag. All the above thermal changes are totally irreversible and the relative peaks do not appear during the repeated heating processes (Fig. 4). It is evident from Fig. 4, however, that besides these effects another two peaks, having reversible character, exist. The first peak already appeared during the first heating cycle, (endothermal peak at 958°C (948°C)) to which corresponds the exothermal peak at 754°C (770°C) occurring in the course of cooling. The second peak is the peak of the reversible phase transition which appears at about 640°C, but during the

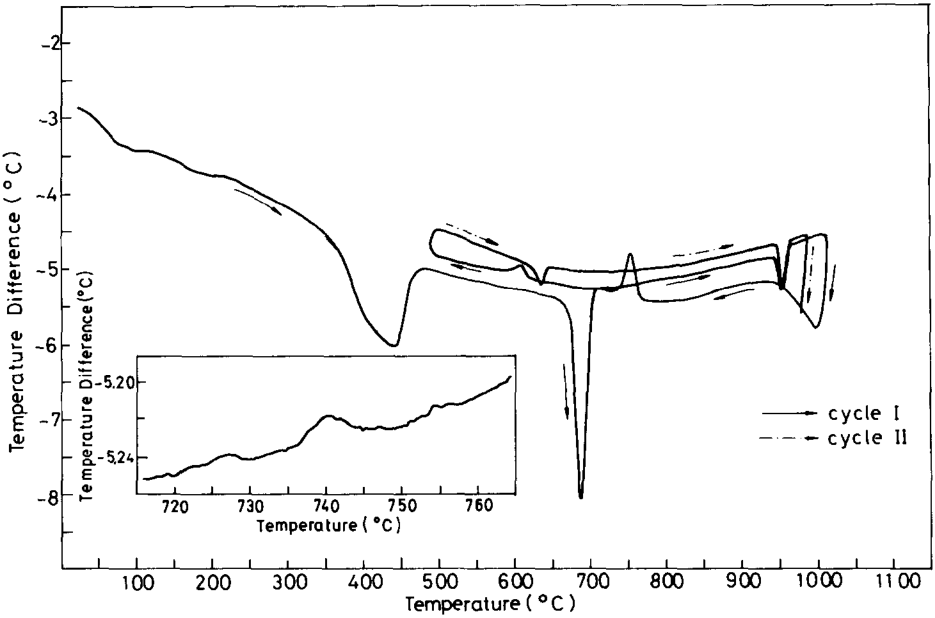

Fig. 4. DTA curve for AgA · $AgNO_3$ inclusion complex, several cycles of heating and cooling in high-temperature range.

repeated heating cycle. A statement can be made, on the basis of the analysis performed, proving that the exothermal peak at 754°C during cooling corresponds to the endothermal heating peak at 958°C, as this very peak does not appear when the sample is heat-treated at temperatures below 958°C.

The nature of these peaks, having a reversible character, is similar to that of heated AgA zeolite. The reversible phase transition at about 640°C corresponds to the $\beta \rightarrow \alpha$ phase transition that also occurs during the thermal treatment of AgA, and is initiated by a newly formed crystal phase appearing after the destruction of the zeolite lattice. The temperature of the phase transition is obtained from the DSC curve and is 639.5°C; the enthalpy of transition is $\Delta H = 8.3$ J g^{-1}. Crystallisation of this phase can be recognised through the exothermal peak at 740°C (736°C) occurring during the first heating cycle as presented by the detail in Fig. 4. A high-temperature endothermal peak at 958°C results from the melting of elemental silver, while the exothermal peak appears during cooling at 754°C within the process of silver solidification. The intensities of the relative peaks are considerably higher when compared to the corresponding peaks of the AgA sample (Figs. 1 and 2), since the inclusion complex AgA · $AgNO_3$ contains a far greater quantity of silver. It can easily be noticed that the exothermal peak of solidification is also split, when it is magnified as in Fig. 5.

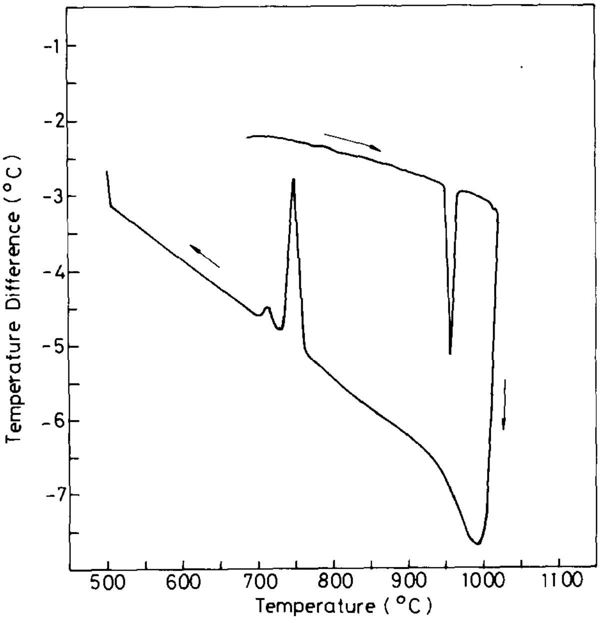

Fig. 5. DTA curve for AgA·$AgNO_3$ in high-temperature range.

TABLE 1

Powder diffraction data for the low-temperature form of Ag-carnegieite

I/I_0	H	K	L	d_{obs} (Å)	d_{calc} (Å)
13	0	1	0	4.256	4.133
100	0	0	4	4.193	4.185
10	0	1	−2	4.048	4.048
12	0	1	2	3.785	3.774
40	1	−1	3	3.673	3.717
63	0	1	−3	3.612	3.614
	1	0	3		3.595
13	0	1	3	3.323	3.327
7	1	0	4	3.170	3.163
	0	1	−4		3.174
29	0	1	4	2.922	2.916
2	1	0	5	2.780	2.777
90	0	1	5	2.577	2.565
67	1	1	0	2.556	2.555
	1	0	−5		2.552
18	1	1	1	2.526	2.526
	1	1	−1		2.525
7	2	−1	2	2.478	2.483
10	0	1	−6	2.458	2.454
8 B	not indexed			2.357	
8	1	1	3	2.326	2.324
10	1	1	−3	2.321	2.321
12	0	1	6	2.276	2.273
20	0	2	0	2.207	2.207
34	1	−1	−6	2.177	2.178
	2	−2	1		2.175
	1	1	−4		2.178
7	0	2	−3	2.117	2.114
12	2	0	3	2.100	2.097
12	0	0	8	2.092	2.092
	0	2	2		2.090
5	2	−2	4	2.057	2.055
11	1	1	5	2.031	2.033
	0	1	7		2.032
	1	1	−5		2.029
7	1	−1	8	2.021	2.019
	1	−2	6		2.018
4 B	1	−1	−7	1.951	
6	0	2	−5	1.920	1.919
4	2	0	5	1.906	1.907
4	1	1	6	1.887	1.886
	0	2	4		1.887
2	1	−2	−5	1.878	1.880
7 B	0	1	8	1.835	
7	0	2	−6	1.807	1.807
5	1	1	−7	1.744	1.744

TABLE 1 (continued)

I/I_0	H	K	L	d_{obs} (Å)	d_{calc} (Å)
10 B	0	2	−7	1.693	
7	1	2	0	1.673	1.674
6	0	1	9	1.664	1.664
	2	1	1		1.664
	0	2	6		1.663
(Plus 15 lines up to $2\theta = 70°$)					

B, Broad reflections were not included in the refinement.

X-ray properties

Silver forms of zeolite AgA and AgA · $AgNO_3$, when heated at 1000°C, were subjected to X-ray structural investigations, as all thermal transforma-

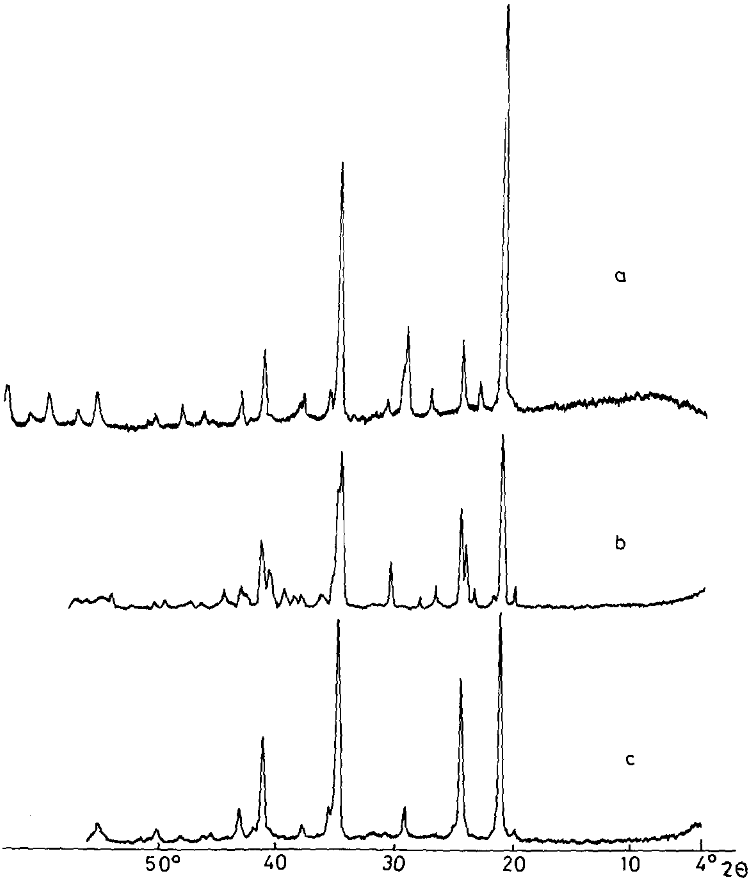

Fig. 6. X-ray diffractograms of: (a) carnegieite; (b) Ag-carnegieite; (c) silver-exchanged form of carnegieite.

TABLE 2

Unit cell parameters for the low-temperature forms of Ag-carnegieite and carnegieite

	Low-temperature form of Ag-carnegieite	Low-temperature form of carnegieite [17]
a (Å)	5.023 (3)	5.0347 (6)
b (Å)	5.074 (3)	5.0822 (7)
c (Å)	16.982 (9)	16.910 (2)
α(°)	98.30 (3)	99.00 (1)
β(°)	81.62 (4)	81.50 (1)
γ(°)	119.20 (4)	119.09 (1)
V (Å^3)	372.4	

tions of the starting forms are completed and obtain their stationary phases at temperatures below this.

The X-ray diagrams of phase powder formed in the course of the phase transformation of AgA zeolite at 1000°C is given in Fig. 6b. An identical X-ray diagram was obtained during heat-treatment of the inclusion complex AgA · $AgNO_3$, but this time with the presence of a metal silver phase. In both cases the transformation of the aluminosilicate framework is carried out through an amorphous phase. The measured and indexed powder diagram of newly formed $AgAlSiO_4$ phase, which we could not identify in the ICPDS file, is given in Table 1. The dimensions of a unit cell were calculated by the method of least squares and the results are presented in Table 2.

DISCUSSION

The distribution of Ag^+ ions and water molecules, and the atoms of aluminosilicate framework of AgA zeolite up to a temperature of 600°C, is well known from previously published papers [10,11]. On the basis of the results obtained during the investigation of the thermal treatment of AgA zeolite, it can be concluded that at a temperature of 756°C the crystal lattice of A zeolite transforms into the amorphous state. Further increase in temperature causes recrystallisation into one crystallographically well-defined phase composition $AgAlSiO_4$ (Table 1). We did not succeed in the identification of this phase. But, this $AgAlSiO_4$ phase, according to position and intensity of reflections on X-ray powder diagram, is very similar to low carnegieite form which is formed during destruction of NaA zeolite structure [12–14], Fig. 6a. This similarity, as well as that between the ionic radii of Ag^+ and Na^+, made us presume the crystal lattice of the $AgAlSiO_4$ phase obtained to be isomorphous with that of β-carnegieite. Bearing this in mind, we called the $AgAlSiO_4$ phase β-Ag-carnegieite, temporarily, as similar phases (Ca-carnegieite) [15] have been quoted in the literature. To prove this presumption concerning isomorphism, we made an ion-exchange reaction with β-carnegieite in the silver nitrate melt. The X-ray diagram of such exchanged β-carnegieite (Fig. 6c), where an amount of $Na^+ \rightleftharpoons Ag^+$, exchange was complete (99%), is identical with that of the powder of Ag-carnegieite formed during the phase transformation of AgA zeolite. Some insignificant differences certainly result from a superstructure which is also marked with β-carnegieite [1,15]. The result obtained by the calculation of dimensions of the Ag-carnegieite unit cell (Table 2), starting from data for the β-carnegieite unit cell [16], speak in favour of isomorphism. Somewhat greater differences existing between d_{obs} and d_{calc}, as well as errors of standard deviations, indicate the possible higher symmetry of β-Ag-carnegieite. However, verification of the mentioned presumption requires thorough research and X-ray investigation on a single crystal.

The process of thermal transformation of $AgA \cdot AgNO_3$ differs, to a certain degree, from the already described AgA zeolite. It is initiated at a temperature of 436°C by the process of nitrate decomposition, after which the framework of A zeolite still remains stable in the form of a metal inclusion complex, the formation and behaviour of which have been previously described [17]. This structure, however, being less stable than that of AgA zeolite, can be destroyed at temperature of about 687°C. The exothermal peak of structural collapse, which can be clearly seen at 739°C for AgA zeolite, is not registered at all for the $AgA \cdot AgNO_3$ inclusion complex. We are ready to explain this phenomenon in the following way. Namely, $AgA \cdot AgNO_3$ when exposed to thermal treatment passes through the phase of a metal inclusion complex. Within this temperature range, the DTA shows a rather outstanding peak caused by decomposition of silver oxide down to metallic silver, which is endothermal according to the nature of the process. We are of the opinion that this thermal effect covers the exothermal peak of structural collapse of the zeolite framework. The present silver is partly built into the structure of α-Ag-carnegieite, partly forms a metallic silver phase, and partly forms Ag crystallites at the surface of the α-Ag-carnegieite phase. The metallic silver phase is characterised by a melting peak at 958°C in the DTA diagram and is also present as a metallic silver phase in the X-ray powder diagram.

As to the phenomenon of a peak splitting in the cooling process (Fig. 5) it can now be considered as the result of the different locations of silver, as has been already discussed. The first peak of solidification at 754°C originates from the metallic silver phase, while the second one, at 711°C, results from silver crystallites. Wishing to support this statement, we underline the fact that one peak only, of silver solidification, at 711°C, appears in the cooling process, within the thermal treatment of AgA up to 1000°C (Fig. 1). During a prolonged time of heating at high temperatures (Fig. 2), however, a migration of silver was noticed. Silver, having left the carnegieite phase transfers into the metallic silver phase to which an exothermal peak at 754°C in the cooling process corresponds. This phenomenon is even more prominent with the AgA · $AgNO_3$ sample where a far greater quantity of silver is present after destruction of the zeolite structure. The increase in intensities of the relative peaks indicates the possible migration of silver from the carnegieite phase into the metallic silver phase.

A more precise determination of the distribution of silver and its nature requires additional investigation.

REFERENCES

1 R.D. Shannon and T. Berzins, Mater. Res. Bull., 14 (1979) 361.
2 R.D. Shannon, Phys. Chem. Miner., 4 (1979) 138.
3 J.A. Kafalas and R.J. Cava, in P. Vashishta, J.N. Mundy and G.K. Shenoy (Eds.), Fast Ion Transport in Solids, Elsevier, New York, 1979, p. 419.
4 U. v. Alpen, M.F. Bell, R. Bräutigam and H. Laig-Hörstebrock, in P. Vashishta, J.N. Mundy and G.K. Shenoy (Eds.), Fast Ion Transport in Solids, Wiley, New York, 1979, p. 443.
5 N. Petranović and M. Šušić, Zeolites, 3 (1983) 271.
6 N. Petranović, Sci. Ceram., 12 (1984) 735.
7 R.M. Barrer and W.M. Meier, J. Chem. Soc., (1958) 299.
8 M.V. Šušić, N.A. Petranović and D.A. Mioč, J. Inorg. Nucl. Chem., 33 (1971) 2667.
9 O. Lindqvist and F. Wengelin, Ark. Kemi, B, 28 (1968) 179.
10 Y. Kim and K. Seff, J. Phys. Chem., 82 (1978) 1071.
11 Y. Kim and K. Seff, J. Am. Chem. Soc., 100 (1978) 6989.
12 A.S. Berger and L.K. Yakovlev, Zh. Prikl. Khim., 38 (1965) 1240.
13 G.T. Kokotailo and S.L. Lawton, Proc. 3rd Int. Conf. on Molecular Sieves, Zürich, 1973, p. 144.
14 M. Ristić, N. Petranović, M. Šušić, V. Petrović and R. Dimitrijević, Sci. Ceram., 10 (1980) 359.
15 R.D. Shannon, C.M. Foris and I.R. Barkley, Mater. Res. Bull., 15 (1980) 1467.
16 R. Klingenberg, J. Felsche and G. Miehe, J. Appl. Crystallogr., 14 (1981) 66.
17 N. Petranović and R. Dimitrijević, Stud. Surf. Sci. Catal., 12 (1982) 45.