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THE THERMOCHEMICAL BEHAVIOUR OF ZEOLITE INCLUSION COMPLEXES

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ABSTRACT

The thermochemical behaviour of nitrate inclusion complexes of zeolites of type A was investigated and DTA curves recorded. An attempt was made to identify thermal effects. Supplementary information was obtained from the IR spectra of the solid phase before and after heating as well as from the process of denitration of inclusion complexes.

INTRODUCTION

The open structure of zeolites allows inclusion of molten salts whereby zeolite inclusion complexes are formed. Salt inclusion may be made into corresponding cationic forms of zeolite obtained previously by an ion exchange reaction from aqueous solutions, or into a commercial zeolite, NaA (where A is the aluminosilicate part), when ion exchange and inclusion occur simultaneously[1, 2]. On inclusion of alkali nitrates and silver nitrate, the structure of the zeolite remains unchanged[3], whereas on inclusion of lithium halides, the structure of the zeolite is destroyed and new phases occur[4].

Salt inclusion into channels and cages of a zeolite offers ample possibilities of modifying the basic zeolite characteristics; cationic capacity increases, new anionic species are introduced, the amount of zeolite water changes and, finally, depending on the included component, structural changes may occur. We have paid special attention to nitrate inclusion complexes in which the structure of zeolite A remains unchanged and which exhibit good properties of solid electrolytes[5–8].

This work is devoted to a study of thermal properties of nitrate inclusion complexes, since solid electrolytes are of interest for work at elevated temperatures.

EXPERIMENTAL

The preparation of inclusion complexes with nitrates of univalent and divalent metals is described elsewhere[3, 9]. The thermochemical behaviour was investigated in the following inclusion complexes.

Symbol	*Formula of unit cell*
$NaA \cdot NaNO_3$	$N_{12}A \cdot 10NaNO_3\ nH_2O$
$AgA \cdot AgNO_3$	$Ag_{12}A \cdot 10AgNO_3\ nH_2O$
$(MgNO_3)NaA \cdot NaNO_3$	$(MgNO_3)_9Na_3A \cdot NaNO_3\ nH_2O$
$(CdNO_3NaA \cdot NaNO_3$	$(CdNO_3)_9Na_3A \cdot NaNO_3\ nH_2O$
$(PbNO_3)NaA \cdot NaNO_3$	$(PbNO_3)_7Na_5A \cdot 3NaNO_3\ nH_2O$

A Robert L. Stone differential thermal analyzer (Model 12) was employed. Sample sizes ranged in weight from 100 to 200 mg, and were heated up to 900 °C at a rate of 10° min^{-1}.

The denitration of inclusion complexes was also followed through the change in pressure on heating under vacuum up to 600 °C. In the course of heating, the temperature was successively increased by 30–50 °C and was maintained at a given value until a change in pressure was observed in the system.

IR spectra of the solid phase (zeolites) were recorded at room temperature in the range 250–2000 cm^{-1} on a Perkin-Elmer grating spectrophotometer, type 457 using the KBr technique.

RESULTS AND DISCUSSION

Figures 1 and 2 show DTA curves of inclusion complexes with nitrates of univalent metals, while Figs. 3–5 show DTA curves of inclusion complexes with nitrates of divalent metals.

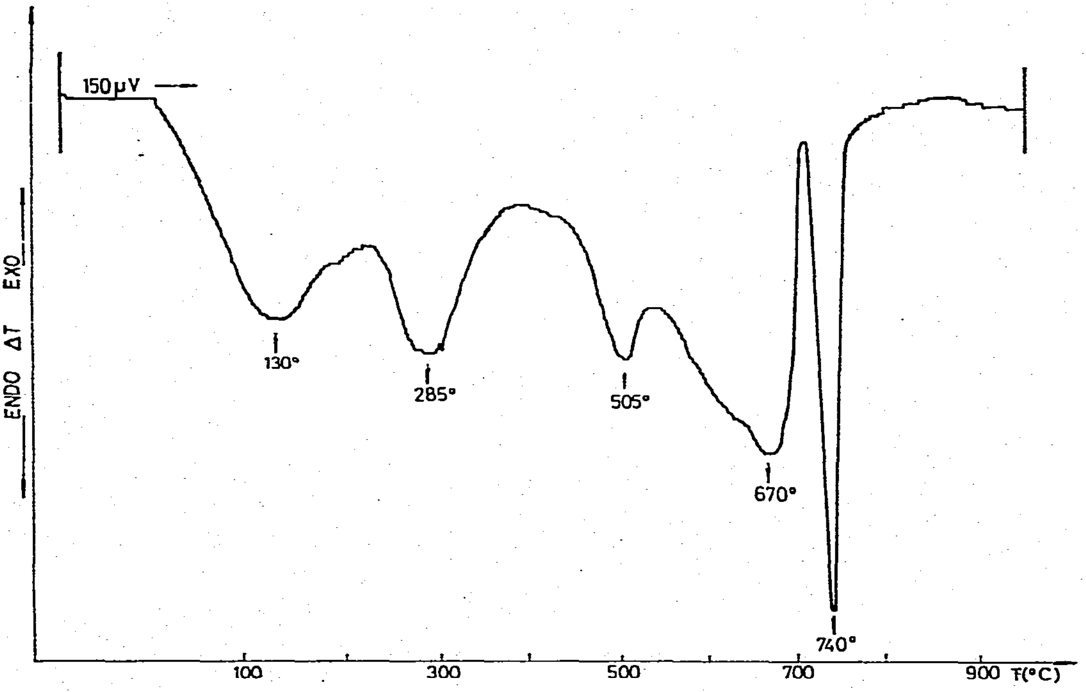

Fig. 1. DTA curve for $NaA \cdot NaNO_3$ inclusion complex.

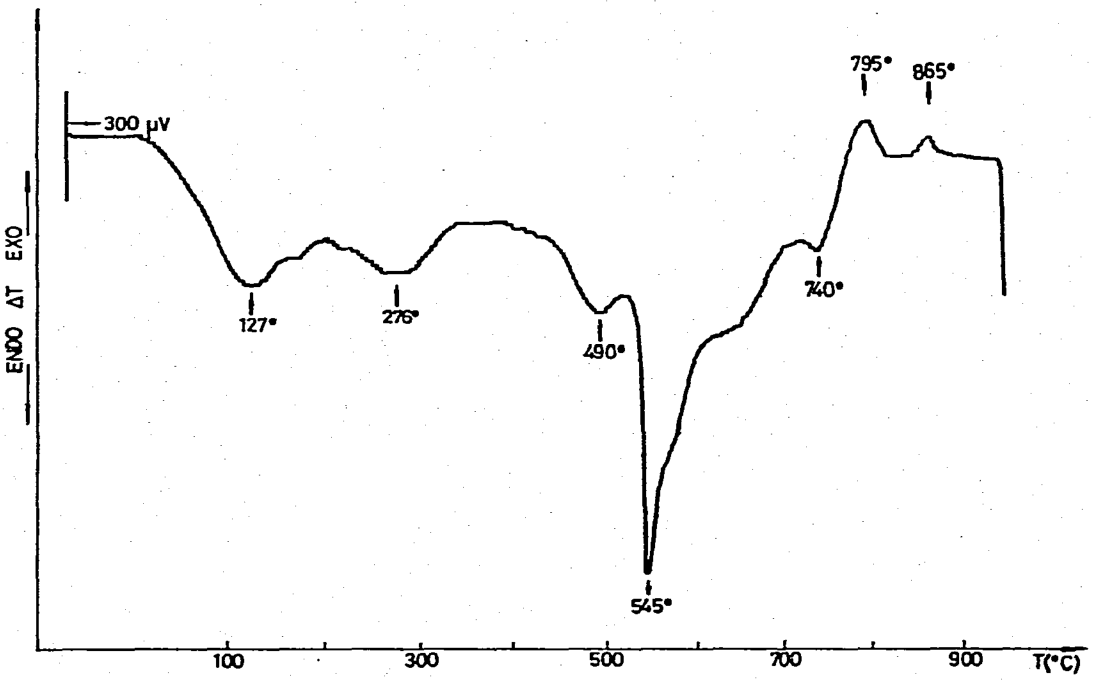

Fig. 2. DTA curve for AgA · $AgNO_3$ inclusion complex.

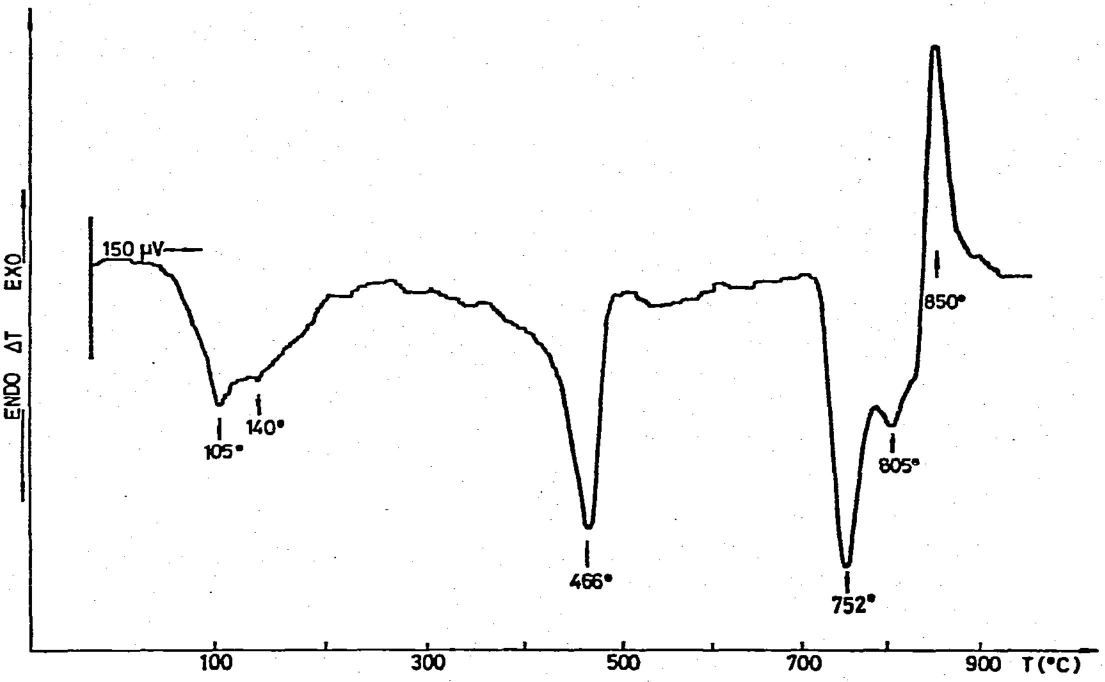

Fig. 3. DTA curve for $(CdNO_3)NaA$ · $NaNO_3$ inclusion complex.

All DTA curves exhibit a number of endothermic peaks in the temperature range up to about 700 °C, whereas at the higher temperatures, exothermic peaks occur in addition to the endothermic peaks. For the identification of the peaks, use was made of literature data on the thermal behaviour of zeolites A, NaA[10, 11], and on the

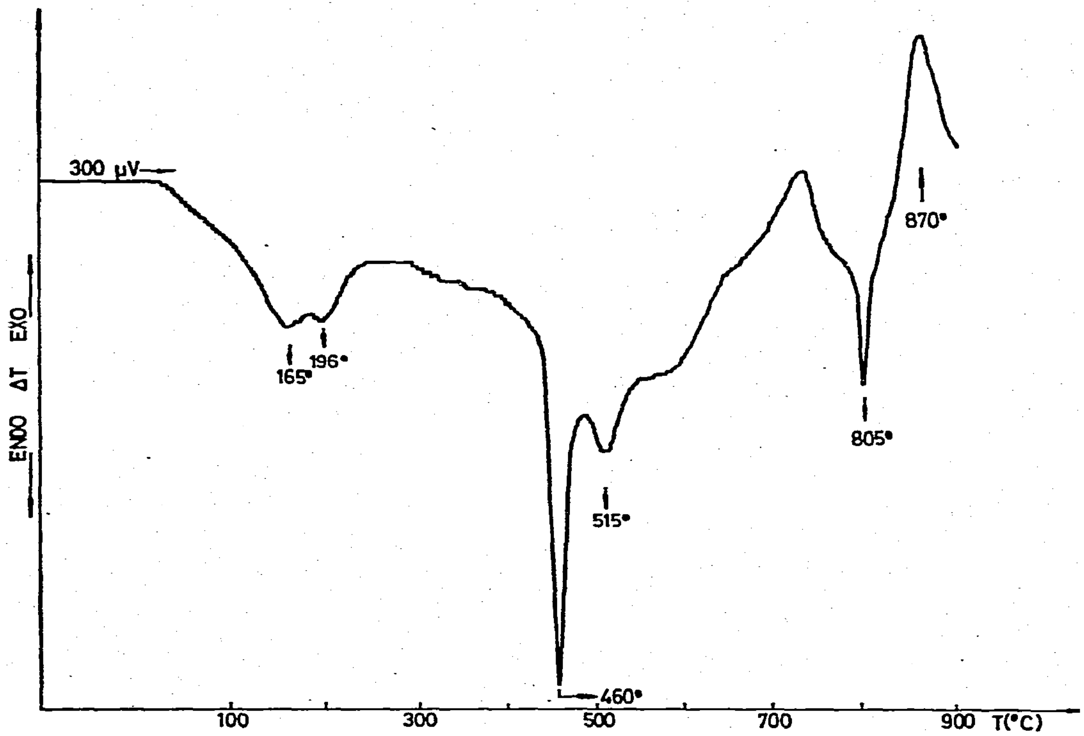

Fig. 4. DTA curve for (MgNO$_3$)NaA · NaNO$_3$ inclusion complex.

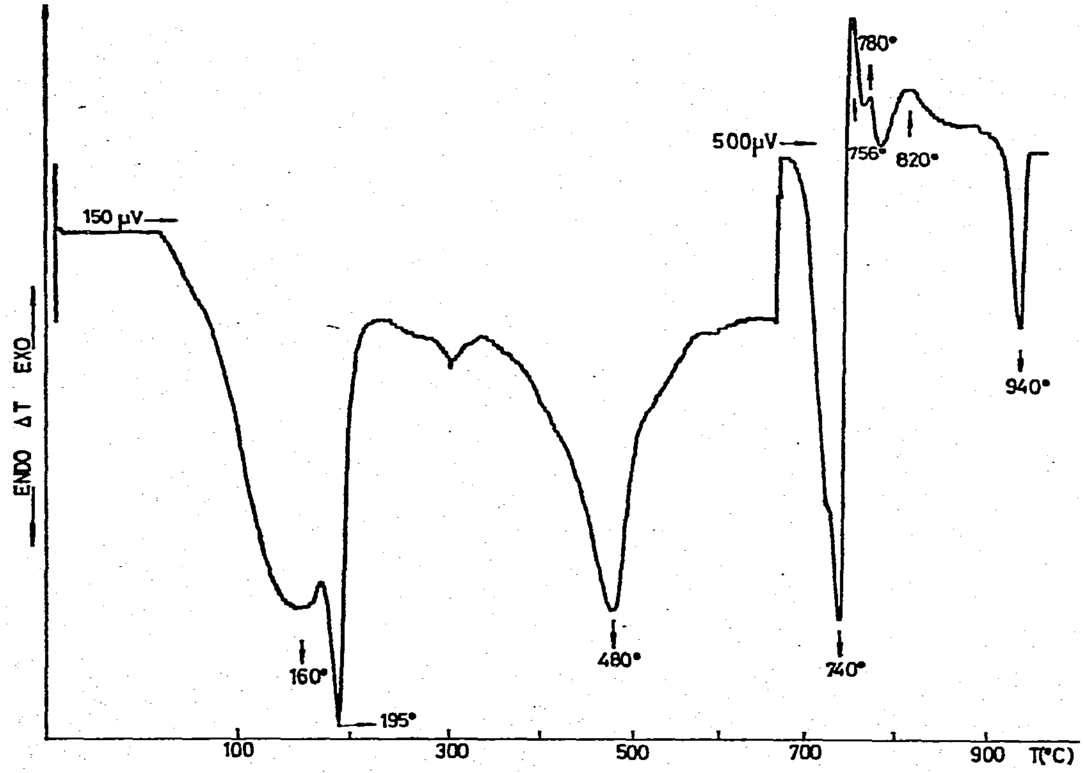

Fig. 5. DTA curve for (PbNO$_3$)NaA · NaNO$_3$ inclusion complex.

TABLE 1

INDEX TO SOME DIFFERENTIAL THERMAL ANALYSIS CURVES OF SOME NITRATES[12]

Formula	*Transition temperature (°C)*	*Fusion*[a] *temperature (°C)*	*Decomposition phenomena*[b] *(°C)*
$NaNO_3$	273	304	SB 520; RB 612; SN 710; RN 753; VN 777
$AgNO_3$	169	214	RB 305; RN 469
$Mg(NO_3)_2 \cdot 6H_2O$		107	SN 321; VN 430
$Cd(NO_3)_2 \cdot 4H_2O$		66	SN 345; RN 379
$Pb(NO_3)_2$[c]			RN 478

[a] Temperature at which mass is observed to undergo fusion or hydrate dissolution.

[b] SB = slight bubbling; RB = rapid bubbling; SN = slight nitrous fumes; RN = rapid nitrous fumes; VN = vigorous nitrous fumes.

[c] Present work.

TABLE 2

DENITRATION OF ZEOLITE INCLUSION COMPLEXES

Inclusion complex	*Temperature (°C)*	
	RN[a]	*SN*[a]
$NaA \cdot NaNO_3$	465	560
$AgA \cdot AgNO_3$	465	580
$(CdNO_3)NaA \cdot NaNO_3$	450	
$(MgNO_3)NaA \cdot NaNO_3$	470	580
$(PbNO_3)NaA \cdot NaNO_3$	470	

[a] RN = rapid evolution of nitrous fumes; SN = slight evolution of nitrous fumes.

thermal behaviour of corresponding nitrate salts[12], and of the results obtained by denitration of inclusion complexes as well as of IR spectra of samples heated at definite temperatures. Table 1 shows the thermal changes of corresponding nitrate salts on heating to decomposition.

The dehydration and denitration of inclusion complexes was carried out by heating the complexes to 600 °C. In all cases, the plots of ΔP vs. T exhibit one or two peaks of evolution of brown nitrous fumes in the temperature range 400–600 °C. Table 2 shows the temperature of evolution of nitrous fumes (maxima of ΔP vs. T plots) for the complexes investigated.

By means of the literature data on the thermal behaviour of zeolite A, the endothermic peaks of DTA curves of inclusion complexes up to 200 °C (130°, $NaA \cdot NaNO_3$; 127°, $AgA \cdot AgNO_3$; 105 and 140°, $(CdNO_3)NaA \cdot NaNO_3$; 165 and 195°, $(MgNO_3)NaA \cdot NaNO_3$; and 160 and 195°, $(PbNO_3)NaA \cdot NaNO_3$) were attributed to the process of dehydration. In contrast to the basic form of zeolite which releases water continuously up to 400 °C, in inclusion complexes, well-defined peaks occur and dehydration is terminated earlier, by 200 °C. This process has the character of a reversible process just as in pure zeolite, but a considerably smaller amount of water is involved. Water in inclusion complexes and the question of centers and of the method of bonding are the subject of a special study[13].

The endothermic peak at 285 °C in NaA · $NaNO_3$ inclusion complex is not the result of dehydration because it also appears on the DTA curve of the dehydrated sample. On the DTA curve of the denitrated sample (heated up to 600 °C), this peak is absent (as is the peak at 505 °C). Hence it follows that this endothermic effect is associated with the nitrate component. It is interesting to note that sodium nitrate in this temperature range, 273 °C (Table 1), exhibits an endothermic peak of the $\beta \rightarrow \alpha$ phase transition. The relatively broad endothermic transition in sodium nitrate is considered to be due to the gradual rotation of the nitrate ion during phase transition[12]. In inclusion complexes, there is an indication from IR spectra[3, 9] of limited rotation of the nitrate ion and a lowering of the spectroscopic symmetry group, i.e. D_{3h} makes the transition to C_{2v}, which might bring about an even larger broadening of the endothermic $\beta \rightarrow \alpha$ transition of the nitrate in the inclusion complex. However, if we assume that this peak corresponds to the $\beta \rightarrow \alpha$ transition of the included sodium nitrate in zeolite cages, it remains unexplained how the X-ray structural analysis "does not see" the sodium nitrate phase in the NaA · $NaNO_3$ inclusion complex. Hence the question of a definitive indication of this endothermic peak remains for the present open.

The endothermic peak at 276 °C in the AgA · $AgNO_3$ inclusion complex has not yet been positively explained.

At temperatures above 400 °C, according to the results of denitration (Table 2), thermal changes associated with the nitrate component begin, i.e. nitrous fumes are evolved. From the process of denitration of inclusion complexes, it is seen that all the inclusion complexes in the temperature range 400–600 °C exhibit evolution of nitrous fumes. This temperature range mainly coincides with the decomposition range of the corresponding nitrates (Table 1), except for cadmium nitrate which decomposes at a lower temperature, 345 °C, and for sodium nitrate which decomposes at a much higher temperature, 710 °C.

Consequently, the endothermic peaks at 490 and 545 °C for AgA · $AgNO_3$, at 466 °C for ($CdNO_3$)NaA · $NaNO_3$, at 460, 515 and 580 °C (inflection) for ($MgNO_3$)-NaA · $NaNO_3$ and at 480 °C for ($PbNO_3$)NaA · $NaNO_3$ have been attributed to the decomposition of the included nitrate component. It is noticeable that the number of maxima in Table 2 is the same as the number of endothermic peaks on DTA curves in the temperature range 400–600 °C.

On the basis of the data of Table 2, the endothermic peak at 505 °C on the DTA curve of the NaA · $NaNO_3$ inclusion complex has been attributed to the evolution of nitrous fumes, as has the inflection at 620 °C, which brings about the asymmetricity of the endothermic peak at 670 °C.

From the IR spectra of inclusion complexes which were heated to 600 °C, it is

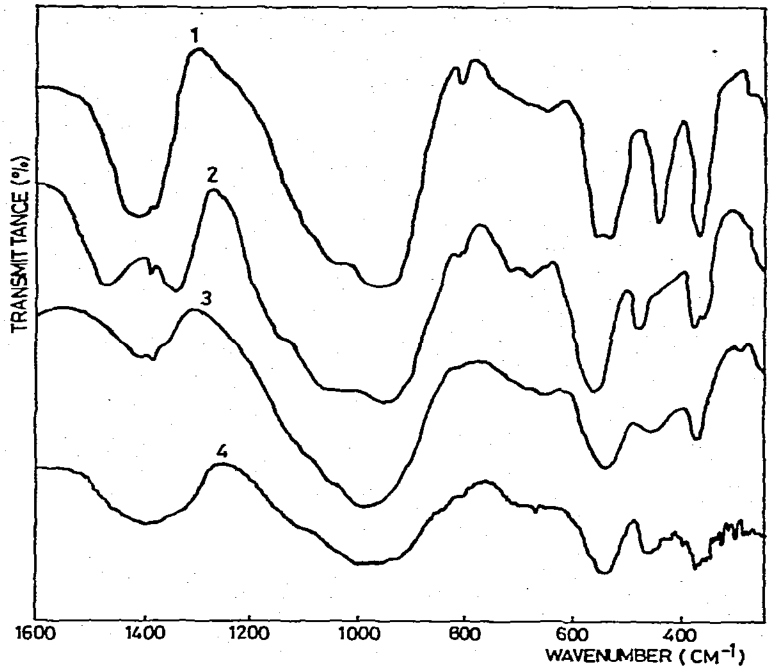

Fig. 6. Infrared spectra of inclusion complexes after heating to 600 °C. 1, NaA · $NaNO_3$; 2, $(CdNO_3)$-NaA · $NaNO_3$; 3, $(MgNO_3)$NaA · $NaNO_3$; 4, $(PbNO_3)$NaA · $NaNO_3$.

seen that the structure of zeolite A remains preserved in all the inclusion complexes and that the relative intensities of the nitrate bands decrease, although the bands are still preserved. The NaA · $NaNO_3$ inclusion complex is the first to undergo structural destruction at 670 °C, whereby there occur two new phases, sodalite and the low-temperature phase carnegieite, β-carnegieite, which is also cited as β-crystobalite-like structure[14]. At 740 °C, the NaA · $NaNO_3$ inclusion complex has a very sharp endothermic peak which means a definitive decomposition of the nitrate component (Table 1). However, X-ray structural analysis of this inclusion complex[14] has shown that at higher temperatures there occurs one more phase, nepheline. The exothermic peak of nepheline generation is overlapped by the strong endothermic peak of nitrate decomposition, and the alkali component present (Na_2O which is produced by nitrate decomposition) is responsible for the occurrance of the nepheline phase. Otherwise, nepheline in pure zeolite, NaA, occurs only at temperatures of 900–1000 °C[10, 11].

From the DTA curves of other inclusion complexes $(CdNO_3)$NaA · $NaNO_3$, AgA · $AgNO_3$ and $(PbNO_3)$NaA · $NaNO_3$, it is seen that all have an endothermic peak at 740–750 °C. We have already noted that the IR spectra of inclusion complexes heated to 600 °C still exhibit the presence of nitrate bands (Fig. 6), although according to the literature data, at this temperature thermal decomposition has ended in all the quoted nitrates except sodium nitrate. This endothermic effect on the DTA curves of inclusion complexes has been attributed to the decomposition of an ion pair, i.e. of a complex nitrate ion which was identified in the quoted inclusion complexes[9, 15]. The metal–nitrate interaction in univalent metals is especially pronounced in silver[16] and in divalent metals such as magnesium and cadmium[9]. In IR spectra, it is seen that at a temperature above 600 °C there remain just the bands of the complex nitrate MNO_3^+ (where M is a divalent cation), the bands at about 1480 cm^{-1} and 1330 cm^{-1}, and the band at about 1440 cm^{-1} for the ion pair of nitrate and univalent metals. The magnesium nitrate inclusion complex contains the complex ion $MgNO_3^+$, whose bands also remain above 600 °C in the IR spectrum (Fig. 6), but on the DTA curve of this complex there is seen only an inflection at 770 °C which brings about the asymmetricity of the peak at 805 °C. In view of the known thermal instability of magnesium nitrate, it is possible that, above 600 °C, this inclusion complex contains only a minor part of nitrate in the form of $MgNO_3^+$; this is also indicated by the relative intensity of the bands of the complex nitrate ion in the IR spectrum (Fig. 6).

At a temperature above 800 °C, the basic form of zeolite undergoes a structural destruction via two exothermic processes of which the first corresponds to the transition to an amorphous phase, while the other corresponds to the transition to a high-temperature phase of carnegieite, α-carnegieite (which, at room temperature, is identified as β-carnegieite, since on cooling it undergoes the $\alpha \rightarrow \beta$ transition at 676 °C). At about 1000 °C, nepheline again occurs via an exothermic effect. Above 750 °C, all our inclusion complexes except $NaA \cdot NaNO_3$, which was discussed earlier, exhibit one or two exothermic peaks of a definitive destruction of the structure of zeolite A and production of new phases: $AgA \cdot AgNO_3$ at 795 and 865 °C, $(CdNO_3)NaA \cdot NaNO_3$ at 850 °C, $(MgNO_3)NaA \cdot NaNO_3$ at 870 °C, and $(PbNO_3)NaA \cdot NaNO_3$ at 756, 780 and 820 °C. In the cadmium and magnesium nitrate complexes, besides exothermic peaks there is also an endothermic peak at 805 °C, and in the lead nitrate inclusion complex at 940 °C. From the IR spectra of inclusion complexes, it is evident that, after heating above 750 °C, the part of the spectrum between 750 cm^{-1} and 250 cm^{-1} is completely changed. The following structural changes have been observed: appearance of two new phases, sodalite and β-carnegieite at ~800 °C in $AgA \cdot AgNO_3$; appearance of nepheline at ~810 °C in $(CdNO_3)NaA \cdot NaNO_3$; appearance of sodalite at elevated temperature, 870 °C, in $(MgNO_3)NaA \cdot NaNO_3$, and appearance of sodalite at 750 °C in $(PbNO_3)NaA \cdot NaNO_3$. These structural changes cannot be definitively explained without supplementary X-ray structural data.

In conclusion, we would stress that nitrate inclusion complexes exhibit a thermal stability limited by the presence of the nitrate component. As an upper limit of thermal stability, we could take a temperature of 450 °C for inclusion complexes with nitrates of univalent metals, and 400 °C for those of divalent metals. As regards structural changes, according IR spectra they are stable as denitrated zeolites up to 600 °C.

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