

The Influence of Thermal Treatment on the Nitrate Band Intensities in Infra-Red Spectra of Nitrate Inclusion Complexes of the Zeolite 4A

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Abstract. The changes occurring in the included component in the course of thermal treatment of inclusion complexes of zeolite 4A with alkali nitrates were followed by IR spectroscopy and the results obtained were correlated with the data of TG analysis. An increase in temperature caused changes in the breadth and intensity of the nitrate bands (at about 1450 and 1380 cm^{-1}) and the appearance of a new band at about 1350 cm^{-1} . All the mentioned effects relate to the temperature interval starting from room temperature up to 670 K and are attributed to the increase in the thermal motion of included species in zeolite cages. The activation energy of the coordination change of the nitrate groups in the cage was calculated from the ratio of intensities of the nitrate bands at 1450 and 1350 cm^{-1} and the intensity of the zeolite band at 460 cm^{-1} , originating from a T–O bending vibration as a function of temperature. At temperatures exceeding 720 K decomposition of included nitrate was noticed. Having this in mind, it was concluded that the changes of the band intensities were closely connected with this process.

Key words: Zeolite inclusion complexes, nitrate complexes, IR spectra.

1. Introduction

Zeolites are aluminosilicates which are characterized by a very porous crystal structure. The cations and water molecules that can be substituted by other ions and molecules are present in zeolite cages. The included molecules make contact with the zeolite matrix when adsorption, catalytic, electric and other properties of zeolites are changed. It has also been observed that changes occur in the included component due to the influence of the electrostatic field in the zeolite cage [1,2]. The zeolite crystal structure is well preserved in the majority of included complexes during the process of salt inclusion.

Changes concerning the included component and the zeolite framework [3,4] were discovered during thermal treatment of zeolite inclusion complexes. This paper deals with the influence of the thermal treatment on the included nitrate component. The motion of nitrate groups in the zeolite cage was followed by the changes of the nitrate band intensities recorded in the IR spectra of a solid phase.

2. Experimental

Both the preparation and the chemical composition of the investigated zeolite inclusion complexes have been presented in previous papers [2,5]. On the basis of the relative data, the inclusion complexes containing included sodium and lithium nitrates are characterized by

the following composition:

Formula of unit cell	Symbol
$\text{Na}_{12}A \cdot 10\text{NaNO}_3 \cdot 6.6\text{H}_2\text{O}$	$\text{NaA} \cdot \text{NaNO}_3$
$\text{Li}_{12}A \cdot 9.8\text{LiNO}_3 \cdot 9.3\text{H}_2\text{O}$	$\text{LiA} \cdot \text{LiNO}_3$

(where A is the aluminosilicate part of framework).

The IR spectra of inclusion complexes were recorded within the region from 4000–250 cm^{-1} on a Perkin Elmer 457 spectrophotometer using the KBr pellet technique. The concentration of a sample was 1 mg per 150 mg KBr. The samples were heated for one hour *in vacuo* ($P = 5065 \text{ Pa}$) within the temperature interval from room temperature up to 970 K. The spectra of the samples were then recorded at room temperature. The complex band at about 1400 cm^{-1} characteristic of the nitrate included component, was graphically resolved [6] and analyzed. The graphical resolution was done by the programme for the Hewlett-Packard HP-41C programmable calculator. This further work is aimed at the calculation of the area of these bands and the area of a zeolite band at 460 cm^{-1} (attributed to a $T\text{-O}$ bending vibration) which was utilized as the reference value. In such a way the ratio $P/P_{\text{ref}} = \alpha$ was obtained.

A Du Pont 1090 Thermal Analyzer with TGA 951 Analyzer was utilized. The heating rate was $10^\circ \text{ min}^{-1}$ in a dry nitrogen current.

3. Results and Discussion

The nitrate ion band in the 1400 cm^{-1} region has a complex structure (Figure 1) and so has to be resolved. For the resolution a graphical method was used with the application of an analytical equation [6]:

$$I(\nu) = \frac{I_0}{1 + a \left(\frac{\nu - \nu_0}{\gamma} \right)^2 + b \left(\frac{\nu - \nu_0}{\gamma} \right)^4}$$

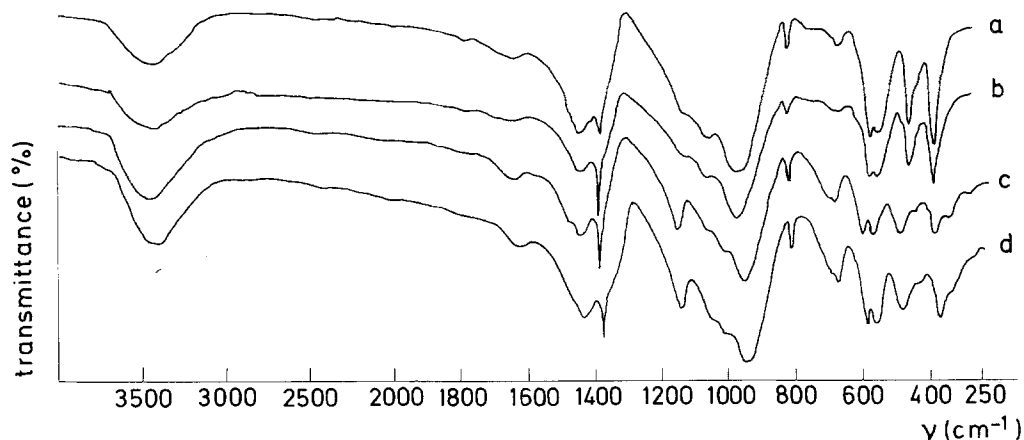


Fig. 1. IR spectra of $\text{NaA} \cdot \text{NaNO}_3$: (a) at 298 K, (b) after heating to 743 K; $\text{LiA} \cdot \text{LiNO}_3$: (c) at 298 K, (d) after heating to 673 K.

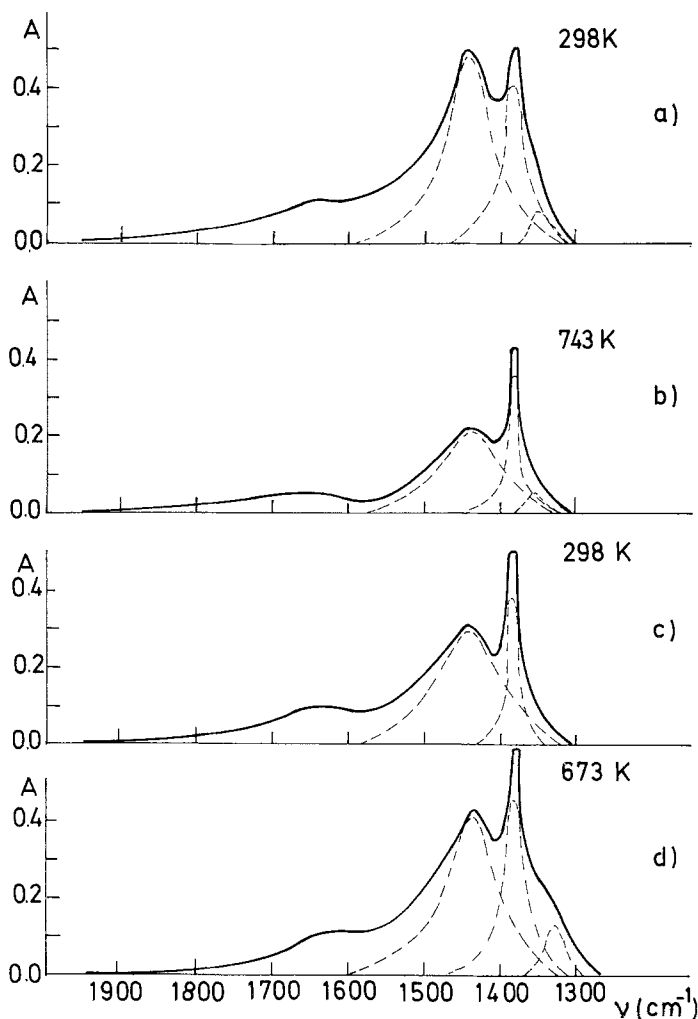


Fig. 2. Graphical resolution of the ν_3 band of nitrate ion for $\text{NaA} \cdot \text{NaNO}_3$: (a) and (b); $\text{LiA} \cdot \text{LiNO}_3$: (c) and (d).

where $I(\nu)$ is the intensity of the band at the wavenumber ν , I_0 is the intensity of the band maximum at ν_0 , 2γ is the band half-width, a and b are constants to be fitted to the band contour where $a + b = 1$. We took $a = 0.9$ and $b = 0.1$ as empirical coefficients which give the best shape of the band in the IR spectra of our systems. Some examples of graphically resolved bands for $\text{NaA} \cdot \text{NaNO}_3$ and $\text{LiA} \cdot \text{LiNO}_3$ are shown in Figure 2.

Figures 3 and 4 present IR spectra of the inclusion complexes $\text{NaA} \cdot \text{NaNO}_3$ and $\text{LiA} \cdot \text{LiNO}_3$ after being heated to different temperatures, within the temperature interval from room temperature up to 970 K, respectively. It can be seen in Figure 1 that there is a change neither in the position nor in the intensity of the essential characteristic bands of the zeolite framework. Changes may be noticed in bands which are characteristic of the included nitrate component. The most prominent changes are evident in the bands at 1450 and 1380 cm^{-1} . The band at 1450 cm^{-1} arises from a vibration of a nitrate complex, while the band at 1380 cm^{-1} arises from a vibration of a free nitrate ion [2,7].

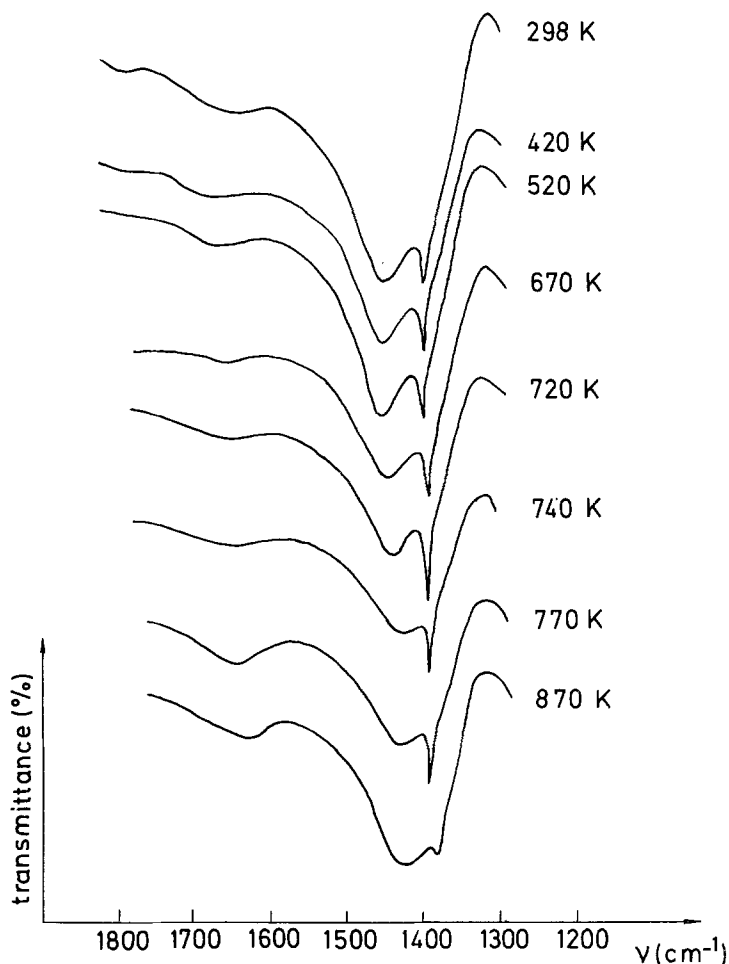


Fig. 3. IR spectra of NaA · NaNO₃ after heating to different temperatures.

As the investigated inclusion complexes are not thermally stable over the whole investigated temperature interval, the changes in the nitrate band intensity are correlated with the data obtained by thermal analysis of these samples (Figure 5). At the very beginning of the TG curves can be seen the mass loss as the result of the dehydration of the inclusion complexes. This is the water that remains after the process of salt inclusion and its content is considerably smaller than that contained in the basic zeolite forms. At temperatures above 770 K for LiA · LiNO₃, and above 870 K for NaA · NaNO₃, the mass loss due to nitrate decomposition takes place.

The changes in the relative intensities of the bands at 1450 and 1380 cm⁻¹ of the inclusion complexes NaA · NaNO₃ and LiA · LiNO₃ with temperature are given in Figure 6. The band intensity at 1450 cm⁻¹ for the inclusion complex NaA · NaNO₃ increases up to 650 K and then decreases with a further temperature rise (Figure 6(a)). The increase of the band intensity at 1450 cm⁻¹ and the concomitant decrease of the band intensity at 1380 cm⁻¹ (Figure 6(b)) can be explained by the change in the coordination of a certain number of free nitrate ions into nitrate complexes, particularly into its bidentate coordination with Na⁺ ions.

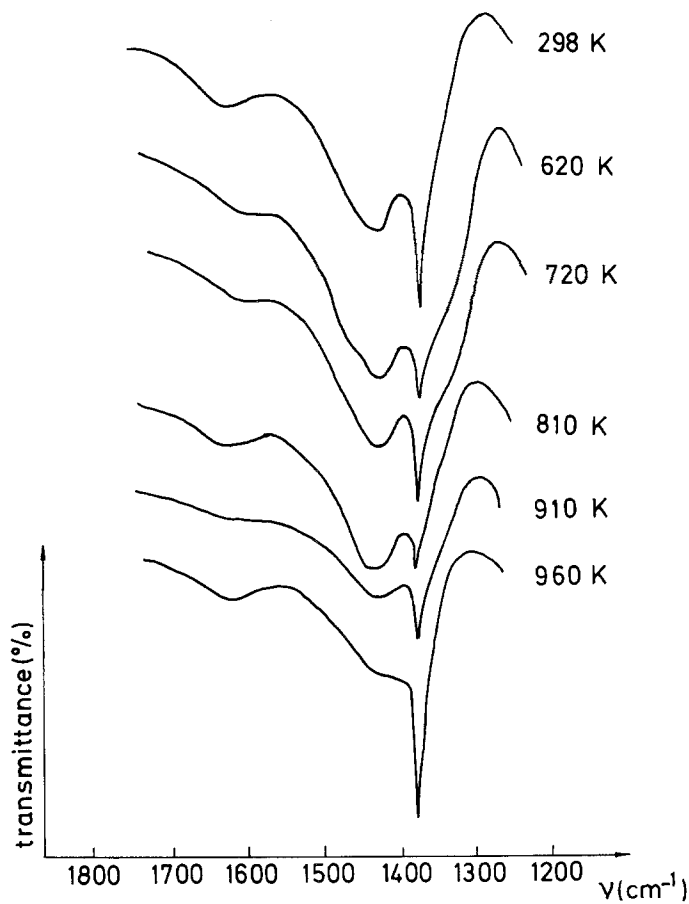


Fig. 4. IR spectra of $\text{LiA} \cdot \text{LiNO}_3$ after heating to different temperatures.

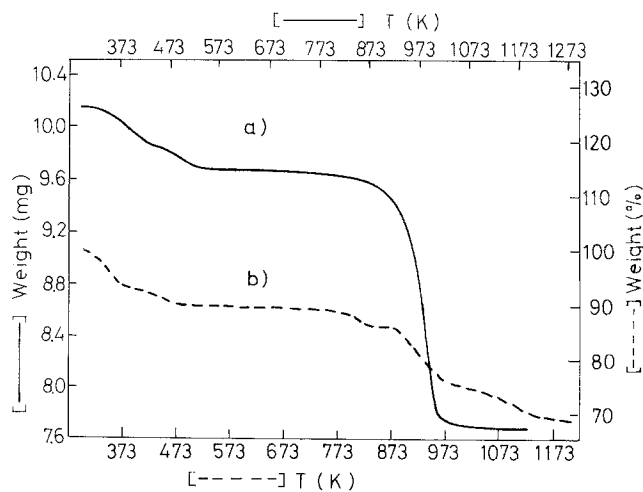


Fig. 5. TG curves of: (a) $\text{NaA} \cdot \text{NaNO}_3$, (b) $\text{LiA} \cdot \text{LiNO}_3$.

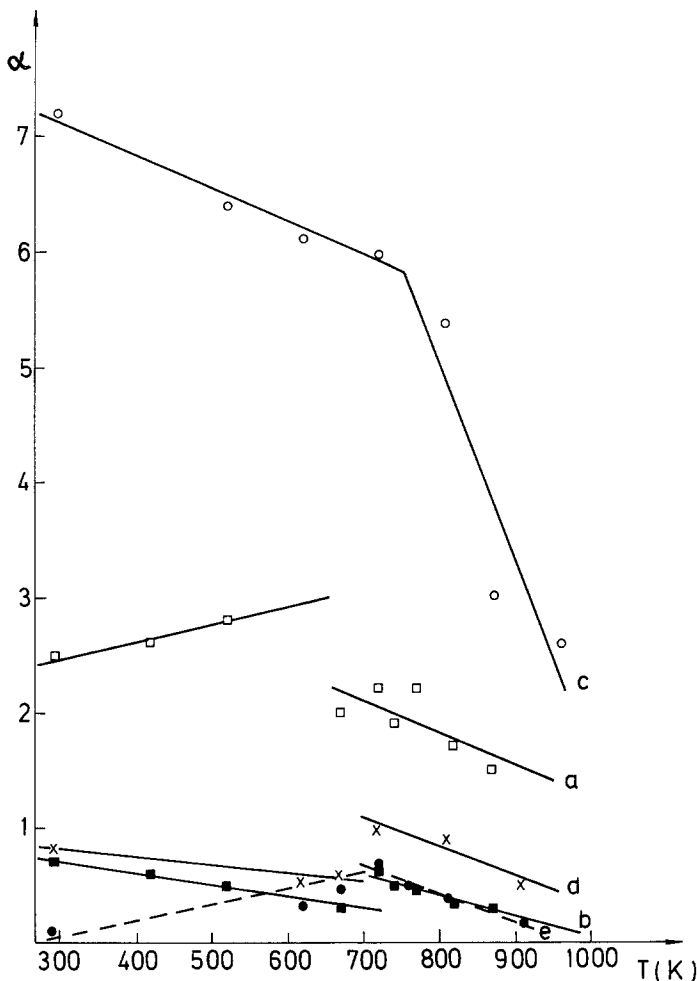


Fig. 6. Ratio of bands intensities (α) as a function of temperature: (a) $\text{NaA} \cdot \text{NaNO}_3$: 1450 cm^{-1} (\square) and (b) 1380 cm^{-1} (\blacksquare), (c) $\text{LiA} \cdot \text{LiNO}_3$: 1450 cm^{-1} (\circ), (d) 1380 cm^{-1} (\times) and (e) 1350 cm^{-1} (\bullet).

For the $\text{LiA} \cdot \text{LiNO}_3$ inclusion complex the included nitrate occurs mainly in bidentate coordination with Li^+ cations while a smaller quantity is found as a free nitrate ion. As can be seen from Figures 6(c) and (d), the band intensity at 1450 and 1380 cm^{-1} decreases with increasing temperature. The occurrence of a band at 1350 cm^{-1} , which is attributed to the unidentate coordination of nitrate ion [2,7], as well as the increase of this band's intensity with temperature increasing up to 720 K , indicates a change of nitrate ion coordination (Figure 6(e)). This, in fact, means that a certain number of nitrate groups, following the rise in temperature, change their coordination into a unidentate coordination with Li^+ ion. According to Figure 6(c) and (d), this change is mainly performed from bidentate into unidentate coordination of nitrate groups. It is also with the $\text{LiA} \cdot \text{LiNO}_3$ inclusion complex that at high temperatures, namely at those exceeding 770 K (Figure 6(c)) decomposition of nitrate takes place and consequently this is manifested as the basic process in the case when a change of nitrate band intensity is concerned. The process of decomposition, i.e.,

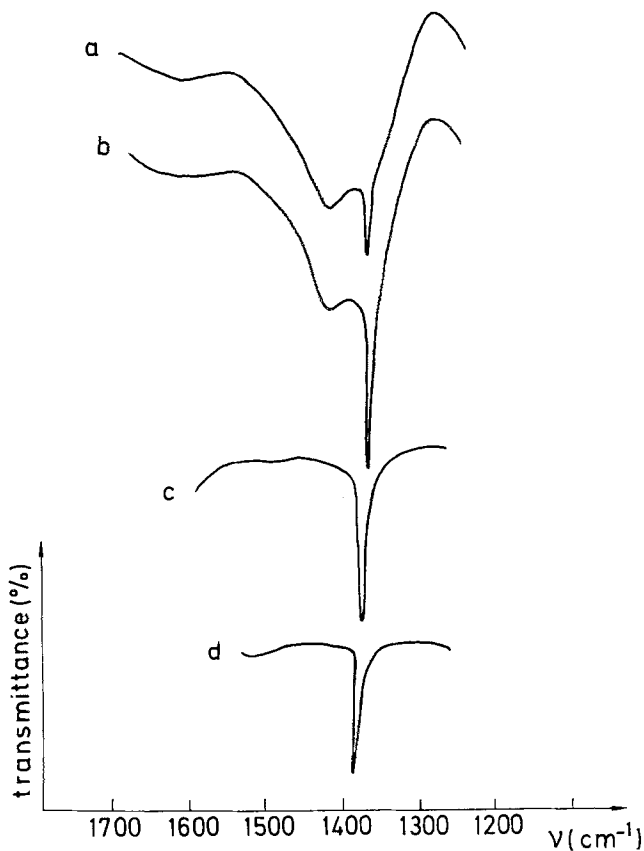


Fig. 7. IR spectra of: (a) $\text{NaA} \cdot \text{NaNO}_3$ after heating to 740 K, (b) $\text{NaA} \cdot \text{NaNO}_3$ after heating to 770 K, (c) NO_2 sorbed on NaA zeolite, (d) NaNO_3 solid.

denitration, is far quicker with the $\text{LiA} \cdot \text{LiNO}_3$ inclusion complex when compared to $\text{NaA} \cdot \text{NaNO}_3$, as can be seen from Figure 6. However, during the denitration process, the increase in the band intensity at 1380 cm^{-1} can be observed at certain temperatures causing in such way the discontinuity on curves b and d in Figure 6. We have explained this phenomenon as an interaction of NO_2 , formed during the decomposition of nitrate, with oxygen from a zeolite framework which gives a coordination of a free nitrate ion. This was experimentally proved by sorbing nitrous oxide, obtained during the thermal decomposition of sodium nitrate on NaA zeolite. The observed IR spectra are compared to the spectrum of pure sodium nitrate in Figure 7.

At a temperature of 970 K, the process of denitration of the inclusion complexes is complete and the nitrate bands disappear from the IR spectra.

Both the change in band intensity and shape, as a function of temperature, indicates, in principle, the motion of the nitrate groups in the zeolite cages. The broadness of the bands characteristic for a nitrate ion, at high temperature, is particularly marked in the $\text{LiA} \cdot \text{LiNO}_3$ inclusion complex and clearly points to the thermal activation and increase in mobility of the included component. For $\text{NaA} \cdot \text{NaNO}_3$, the increase in temperature is followed by the

change in coordination of a certain quantity of free nitrate ions into nitrate ions with bidentate coordination. In the case of the $\text{LiA} \cdot \text{LiNO}_3$ inclusion complex, where a nitrate ion is mainly present as a bidentate complex, the rise in temperature causes the change in coordination and transfer into a unidentate complex. This change concerning nitrate group coordination clearly indicates that the movement, i.e., rotation, of a nitrate group in a cage is being observed. As mentioned above, the increase in intensity of the band at 1450 cm^{-1} and the concomitant decrease of the band at 1380 cm^{-1} , for the $\text{NaA} \cdot \text{NaNO}_3$ sample, are observed. This increase in intensity can be represented by a relationship of the form $\alpha = \beta \exp(-E/RT)$, where $\alpha = P/P_{\text{ref}}$. The activation energy of 0.7 kJ mol^{-1} , from the $\log \alpha$ vs. $1/T$ plot, using the least squares method, has been calculated. In the same way from the data for curve Figure 6(e), an activation energy of 8.4 kJ mol^{-1} is obtained. The activation energies are calculated from the data in the temperature range from room temperature up to 720 K , and concern the coordination change of the nitrate groups in zeolite cages in $\text{NaA} \cdot \text{NaNO}_3$ and $\text{LiA} \cdot \text{LiNO}_3$, respectively.

Having in mind the complementary results given in this work, a conclusion on both the thermal stability of nitrate and nitrate complexes can be made. For the $\text{LiA} \cdot \text{LiNO}_3$ inclusion complex the decomposition of the nitrate ion occurs first (Figure 6(d)), and then the decomposition of bidentate and unidentate nitrate complexes follow (Figures 6(c) and (e)). For $\text{NaA} \cdot \text{NaNO}_3$, according to the IR spectra, the bidentate nitrate-complex is decomposed first, above 670 K , and then at temperature exceeding 720 K , the nitrate is decomposed. However, in the TG thermogram these processes could not be distinguished as the denitration process occurs very quickly and would be manifested by a rapid mass loss.

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