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THERMAL AND CALORIMETRIC INVESTIGATION ON CRYSTALLINE HYDRATES OF BERILLIUM IODATES

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SUMMARY

By using the DTA - and DSC methods and some data from the I.R. Spectra, the thermal decomposition of $Be(JO_3)_2.4H_2O$, $Be(JO_3)_2.4D_2O$ and $/Be_3(OH)(H_2O)_8/(JO_3)_2.H_2O$, has been studied. On the basis of the results some schemes of this decomposition have been suggested. The availability of hydrogen bonds in the molecular structure of Be $(JO_3)_2.4H_2O$ has been proved.

INTRODUCTION

Up to now, there are known two berillium iodates with the following composition: $Be(JO_3)_2.4H_2O$ /1/ and $/Be_3(OH)(H_2O)_8/(JO_3)_5.2H_2O$/2/.

It is worth-whiwe to examine their thermal and calorimetric behaviours which, respectivewy confirmed by some data of I.R. spectra, couldgive us certain information regading their stricture and could be helpful in investigation of their piezoelectrical properties. By these prerequisities the aim of the present work is in general determined.

For this purpose were recorded the TG-,DTA- and DSC-curves of these compounds, of some intermediate products obtained in the processes of thermal decomposition as well as those of the totally and partially deuterium-substituted analog of $Be(JO_3)_2.4H_2O$.

EXPERIMENTAL

The initial $Be(JO_3)_2.4H_2O$ was produced by the method described in /1/, while the $/Be_3(OH)(H_2O)_8/(JO_3)_5.2H_2O$ - by the method of /2/. By means of recrystallization of $Be(JO_3)_2.4H_2O$ from deuterium oxide, its totally and partially deuterated analogs were produced. The starting materials were kept under nitrogen in order to prevent hyd-

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rolysis processes. The composition of starting materiaws was determined by using the quantity anlysis methods:berilliumby weight as BeO, iodine - iodometrically, water - gravimetrically and by the method of Fisher and the hydroxyl content - by the method of Tchernov /3/.

The derivatograms were recorded by derivatograph of the type MOM , system Paulit-Paulik-Erday at the following conditions: range of 200 mg, heating rate of 10° /min and temperature up to 1000°C; the DSC-curves were recorded by DSC of the firm Perkin-Ewmer at heating rate of 10°/min and temperature from 25 up to 500°C. I.R.Spectra were recorded using infrared spectrograph model UR-10, using KBr disks.

RESULTS AND DISCUSSION

In Fig.1 are given the results from the TG and DTA - curves of $Be(JO_3)_2.4H_2O$ and its totally and partially deuterated products.The respective data from the DSC-curves are shown in Fin.2. Analogical data for $/Be_3(OH)(H_2)_8/(JO_3)_5.2H_2O$ are given in Fig.3 and Fig.4 respectively. The observed, their corresponding enthalpy changes as well as weight changes of the sample under examination, are summarized in Table 1 and Table 2.

Table 1

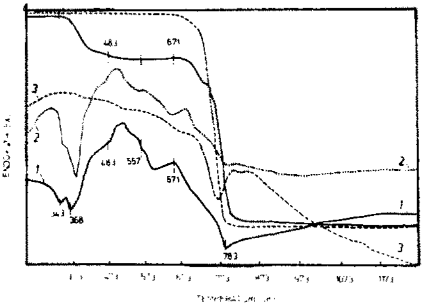
Data from TG- and DSC-curves of $Be(JO_3)_2.4H_2O$ and $Be(JO_3)_2.4D_2O$

Phase transition	T,K	°C	ΔH kJ/mol	Δm, % experimentally determined	Δm, % calculated
$Be(JO_3)_2.4H_2O_{(s)} \rightarrow Be(JO_3)_2.4H_2O_{(L)}$	340	67	55,22	-	-
$Be(JO_3)_2.4H_2O_{(L)} \rightarrow Be(JO_3)_2 + 4H_2O_{(g)}$	360-444	87-170	41,68	16,1	16,7
$Be(JO_3)_2$ - stable	483-613	210-340			
$Be(JO_3)_2 = BeO + J_2O_5$	631	358,7	-115,4	77,34	77,04
$Be(JO_3)_2.4D_2O_{(s)} \rightarrow Be(JO_3)_2.4D_2O_{(L)}$	366	93	53,04	-	*
$Be(JO_3)_2.4D_2O_{(L)} \rightarrow Be(JO_3)_2 + 4D_2O_{(g)}$	430-451	157-178	20,24		18,22
$Be(JO_3)_2$ - stable	482-615	209-342	-	-	-
$Be(JO_3)_2 \rightarrow BeO + J_2O_5$	631	358,7	-116,56	76	74,82

Table 2

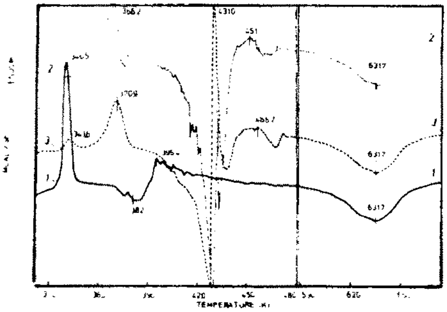
Data from TG- and DSC-curves of $/Be_3(OH)(H_2O)_8/(JO_3)_5.2H_2O$

Phase transition	T,K	°C	ΔH kJ/mol	Δm,%	
				experimentally determined	calculated
$[Be_3(OH)(H_2O)_8](JO_3)_5.2H_2O_{am} \rightarrow$ $[Be_3(OH)(H_2O)_8](JO_3)_5.2H_2O_{cr}$	427,8	154,6	52,32	-	-
$[Be_3(OH)(H_2O)_8](JO_3)_5.2H_2O \rightarrow$ $[Be_3(OH)(H_2O)_8].(JO_3)_5 + 2H_2O_{(g)}$	429	156,7		4,44	3,27
$[Be_3(OH)(H_2O)_8](JO_3)_5 =$ $= [Be_3(OH)_3](JO_3)_3 + 2HJO_3 +$ $+ 8H_2O_{(g)}$	435-448	162-175	-33,84	14,3	15,3
$2[Be_3(OH)_3](JO_3)_3 = 2Be(JO_3)_2 +$ $+ 2HJO_3 + 4BeO + 2H_2O$	452,5	179,5	60,97	-	-



DTA-,TG-curves of:

Fig 1. 1. $Be(JO_3)_2.4H_2O$
2. $Be(JO_3)_2.4D_2O$
3. $Be(JO_3)_2$



DSC-curves of:

Fig 2. 1. $Be(JO_3)_2.4H_2O$
2. $Be(JO_3)_2.4D_2O$
3. $Be(JO_3)_2.xH_2O.yD_2O$

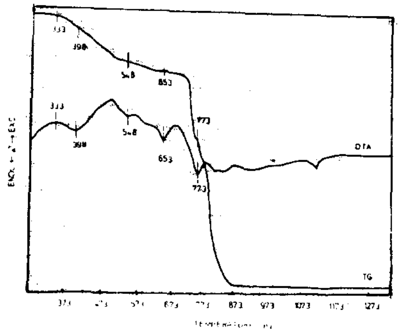


Fig.3. DTA-,TG$[Be_3(OH)(H_2O)_8](JO_3)_5.2H_2O$

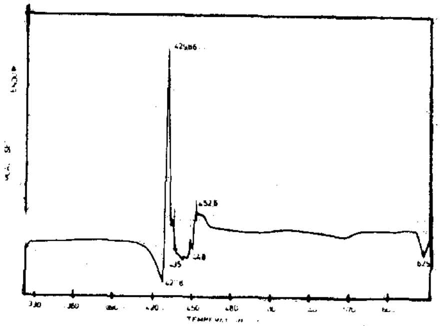


Fig 4. DSC$[Be_3(OH)(H_2O)_8](JO_3)_5.2H_2O$

As the data from Table 1 and Table 2 show, $Be(JO_3).4H_2O$, respectively $Be(JO_3)_2.4D_2O$ undergo analogical phase transitions, but the temperatures at which these transitionas are observed in the deuterated compound, are higher. It is interesting that in the DSC-curves of the two compounds (Fig.2), before the endothermic peak of dehydration, an exothermic one can be observed. That exothetmic peak of dehydration, an exothermic one can be observed. That exothermic peak for the deuterated compound is markedly sharp, passes abruptly one and is shifted at higher temperatures. These dependences exist and in the partially deuterium-substituted compounds. The exothetmic peak observed in the DSC-curves and which is missing in the respective DTA-curves, could be explained by the different conditions at which these curves were recorded and which were favorable to the simultaniousness of the processes of dehydration from the melt, of crystallization of the dehydrated salt in the crystallization water produced and evaporation of the latter, taking place in the system. It is quite possible, structural transformations in the melt to take place too. The total change of the enthalpy for the endo- and exothermic peak is ΔH_{395}=41,68 kJ/mol for $Be(JO_3)_2.4H_2O$ and ΔH_{451}= = 20,24 kJ/mol. The higher temperatute, at which fussion takes place and dehydration begins, points to a higher stability of $Be(JO_3)_2.4D_2O$, resulting from the stronger hydrogen bonds, existing in its structure. The availability of these bonds is proved by the I.R.Spectra of these compounds.

The observed split in the endothermic peak of dehydration of $Be(JO_3)_2.4D_2O$ is due to the value of the heavy water heat of evaporation, which is higher than of the normal water is. The character of the DSC-curve of the partially deuterium-substituted $Be(JO_3)_2$. $4D_2O$ (Fig.2), curve 3) is in support of that too. In Fig.1(curve 3) is given the DTA-curve of the produced and separated $Be(JO_3)_2$.Since, in this curve the endo- and the exothermic peaks within the range from 483 up to 631 K are missing, it may also de accepted as a prove that these thermal effectc are connected with the dehydration of the starting compounds. The separated $Be(JO_3)_2$ is identified and proved not only by the quantitive analysis methods, but by recording and its I.R.Spectra, where valence and deformation vibrations of the crystallization water, were missing.

The endothermic peak observed at 631,7 K(358,7°C), having $\Delta H_{ph.tr.}=-116,56$ kJ/mol, is due to the thermal decomposition of $Be(JO_3)_2$ to BeO and J_2O_5. The latter, as the TG- and the DTA-curves show, is decomposed to O_2 and J_2 which evaporate and then the $\Delta m= 77,34\%$ may be read out.

$Be(JO_3)_2$ is stable in the temperature range 210-340°C. Thes compound is obtained as an intermediate product during the thermal decomposition of periodates |4| and is identified by us Fig.1(curve 3).

On the basis of the results and the information in the Fig.2 and Fig.3, the most probable scheme of thermal decomposition of $|Be_3(OH)(H_2O)_8.$ $.(JO_3)_5 2H_2O$ is suggested (Table 2). The enthalpies of phase transitions and their corresponding weight reduction, are read out. From the scheme suggested it may be seen that the phase transitions observed are accomponied by structural transformations passing through the stable $[Be(OH)_3]^{3+}$-ion. Its decomposition results in a comsiderable heat effect ΔH= 60,97 kJ/mol. The HJO_3,produced due to the decomposition, undergoes a step dehydration to J_2O_5.

Since the thermal peaks observed are within a narrow temperature interval, there is no possibility to separate all intermediate phases, a circumstance which shouwd had give us more detailed information on the mechanism of the thermal dissociation of the compounds under research.

C O N C L U S I O N S

The examinations carried out, show that the thermal decomposition of the two compounds is taking place by a rather complex scheme, wherein $Be(JO_3)_2.4H_2O$ does not undergo any changes up to 64°C(340 K), $Be(JO_3)_2.4D_2O$ - up to 93°C(366 K) and $|Be_3(OH)(H_2O)_8|.$ $(JO_3)_5.2H_2O$ -up to 154,6°C (427 K). The hydrogen bonds availbility in the molecular structure of the two compounds is awso proved.

R E F E R E N C E S

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