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Thermal study of double polyphosphates $M^IEr(PO_3)_4$ (M^I is H, NH_4)

Sami Ben Moussa [a], Mokhtar Farid [b], Malika Trabelsi-Ayedi [c,*]

[a] *Departement de Chimie, Institut Supérieur de l'Education et de la Formation Continue 43, Rue de la Liberté, Le Bardo, Tunis 2019, Tunisia*

[b] *Centre de Chimie Appliquée, Institut National de la Recherche Scientifique et Technique BP 95, Hammam-Lif 2050, Tunisia*

[c] *Laboratoire de Physico-Chimie Minérale, Ecole Normale Supérieure, Zarzouna-Bizerte 7021, Tunisia*

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Abstract

A double polyphosphate of ammonium and erbium $NH_4Er(PO_3)_4$ (type IV) has been prepared for the first time. It crystallizes in a monoclinic system and its parameters are $a = 11.02(2)$ Å, $b = 7.70(1)$ Å, $c = 10.39(2)$ Å, $\beta = 107.7(1)^\circ$, $V = 839.9$ Å^3, $d_x = 3.14$, $Z = 4$. The corresponding space group is $P2_1/n$. This compound has been identified as a chain structure by infrared spectra.

A thermal analysis study of two condensed polyphosphates $NH_4Er(PO_3)_4$-IV and $HEr(PO_3)_4$ is presented; TG and DTA curves are given.

Keywords: Ammonium compound; Double polyphosphate; DTA; Erbium compound; Novel; TG

1. Introduction

Since the discovery that double polyphosphates of the type $M^I_x Ln(PO_3)_{3+x}$ ($x = 1$ or 2, M^I is a monovalent element, Ln is a rare earth element) have interesting spectroscopic properties they have become widely used in technology and research on similar compounds containing other rare earth ions is a topic of current interest.

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* Corresponding author.

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In this paper we report and discuss the results of the thermal decomposition of two polyphosphates, $NH_4Er(PO_3)_4$-IV (prepared for the first time) and $HEr(PO_3)_4$ [1].

2. Apparatus and experimental methods

2.1. Apparatus

Four techniques were used to study thermal decomposition.

DTA and TG analysis were employed for the study of thermal properties. The DTA curves were recorded in flowing air on a Rigaku PTC 10A instrument with a heating rate of 5 K min^{-1}. Thermograms were measured using a Setaram 2400 instrument. Measurements were made at a rate of 5 K min^{-1} in air using Pt-Pt/Rh10% thermocouples.

In order to identify the solid phases X-ray diffraction and infrared spectroscopy were used. Diffractograms were recorded on a Philips PW 1050/70 diffractometer. Cu Kα radiation was used. Diffraction measurements were carried out at a rate of $(1/8)^\circ$ min^{-1} per 2θ. Infrared spectra were recorded using a Perkin Elmer IR 783 spectrometer. The wavelength range used was 4000-200 cm^{-1}. Samples were in the form of pellets (2 mg polyphosphate per 300 mg KBr).

2.2. Experimental method

The following procedure was used to study thermal properties. The sample was heated in the DTA unit until a peak was located. When this occurred, heating was stopped and the resulting product was subjected to X-ray and infrared spectroscopic analysis. Heating was then resumed with a new sample of the same compound and treatment as described above was performed for each effect found in the DTA curve.

3. Synthesis and characteristics of $NH_4Er(PO_3)_4$ and $HEr(PO_3)_4$

3.1. Ammonium erbium polyphosphate $NH_4Er(PO_3)_4$

Crystals of $NH_4Er(PO_3)_4$ were synthesized for the first time by mixing di-ammonic phosphate $(NH_4)_2HPO_4$ and erbium oxide Er_2O_3 in stoichiometric proportions. Reagents were ground and melted in a vitrous carbon crucible at 580 K for two weeks. The residue was rinsed with hot water.

The reaction is represented as

$$8(NH_4)_2HPO_4 + Er_2O_3 \longrightarrow 2NH_4Er(PO_3)_4 + 14NH_3 + 11H_2O$$

X-ray data for $NH_4Er(PO_3)_4$ are shown in Table 1. $NH_4Er(PO_3)_4$ (type IV) crystallizes in monoclinic system. It is isostructural with $TlCe(PO_3)_4$ [2]. It belongs to the space group $P2_1/n$ and has lattice parameters $a = 11.02(2)$ Å, $b = 7.70(1)$ Å, $c = 10.39(2)$ Å, $\beta = 107.7(1)^\circ$, $V = 839.9$ Å^3, $d_x = 3.14$, $Z = 4$.

Table 1
X-ray data for $NH_4Er(PO_3)_4$-IV [a]

$h\ k\ l$	d_{obs}/Å	d_{calc}/Å	I/I_0	$h\ k\ l$	d_{obs}/Å	d_{calc}/Å	I/I_0
$\bar{1}$ 0 1	8.84	8.63	35	1 2 2	3.097	3.100	30
0 1 1	7.00	6.93	23	0 3 1	3.071	3.075	90
$\bar{1}$ 1 1	6.50	6.45	100	3 0 1	3.015	3.024	37
1 0 1	6.29	6.31	53	$\bar{3}$ 2 1	2.935	2.927	11
2 0 0	5.27	5.25	28	1 0 3	2.898	2.905	9
0 0 2	5.02	4.95	17	3 2 0	2.842	2.839	80
$\bar{2}$ 1 0	4.60	4.62	8	1 1 3	2.790	2.783	23
$\bar{1}$ 1 2	4.50	4.52	8	$\bar{3}$ 2 2	2.771	2.775	6
1 2 0	4.45	4.40	8	0 3 2	2.706	2.708	10
$\bar{2}$ 0 2	4.29	4.31	64	$\bar{2}$ 3 2	2.599	2.588	5
$\bar{1}$ 2 1	4.16	4.23	3	2 3 1	2.549	2.550	11
$\bar{2}$ 1 2	3.99	3.94	18	4 1 0	2.532	2.535	21
1 1 2	3.72	3.72	9	$\bar{3}$ 2 3	2.479	2.474	8
$\bar{3}$ 0 1	3.68	3.67	67	3 1 2	2.450	2.439	13
$\bar{1}$ 0 3	3.46	3.46	46	4 2 1	2.392	2.395	5
$\bar{3}$ 1 1	3.43	3.43	16	$\bar{2}$ 4 1	2.223	2.210	7
$\bar{3}$ 1 0	3.33	3.29	34	0 2 4	2.204	2.204	11
$\bar{2}$ 2 2	3.220	3.224	16	$\bar{1}$ 4 2	2.192	2.192	25
$\bar{3}$ 1 2	3.203	3.195	7				

[a] Space group $P2_1/n$; $a = 11.02(2)$ Å, $b = 7.70(1)$ Å, $c = 10.39(1)$ Å, $\beta = 107.7(1)°$, $Z = 4$, $V = 839.9$ Å^3, $d_x = 3.14$.

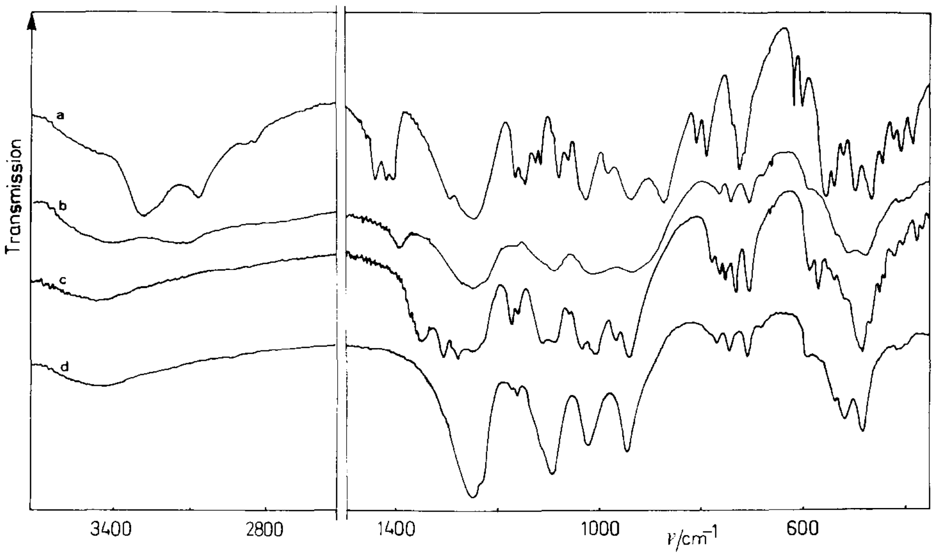

Fig. 1. IR spectra of $NH_4Er(PO_3)_4$-IV at different temperatures: curve a, at room temperature; curve b, heated at 775 K; curve c, heated at 802 K; curve d, heated at 1179 K.

Table 2
X-ray data for $HEr(PO_3)_4$ [a]

$h\ k\ l$	d_{obs}/Å	d_{calc}/Å	I/I_0	$h\ k\ l$	d_{obs}/Å	d_{calc}/Å	I/I_0
0 0 2	6.61	6.70	51	$\bar{1}$ 1 4	3.08	3.09	7
$\bar{1}$ 1 1	5.61	5.64	18	0 1 4	3.03	3.05	17
$\bar{1}$ 1 2	4.67	4.72	34	1 2 2	3.00	2.98	28
0 0 3	4.55	4.47	17	$\bar{3}$ 1 2	2.89	2.90	28
2 0 1	4.23	4.23	59	$\bar{2}$ 2 2	2.82	2.82	11
1 1 2	4.17	4.15	100	$\bar{3}$ 1 3	2.73	2.70	23
$\bar{2}$ 1 1	4.08	4.05	68	0 0 5	2.67	2.68	8
0 1 3	3.90	3.83	17	$\bar{2}$ 2 3	2.61	2.61	21
$\bar{2}$ 1 2	3.75	3.75	8	0 1 5	2.53	2.52	36
0 2 0	3.69	3.70	53	$\bar{1}$ 2 4	2.49	2.50	74
0 2 1	3.58	3.57	68	0 3 1	2.43	2.43	11
2 0 2	3.52	3.55	89	$\bar{1}$ 3 1	2.38	2.37	19
1 1 3	3.33	3.35	7	$\bar{4}$ 1 2	2.31	2.30	6
0 2 2	3.25	3.24	8	3 1 3	2.25	2.26	13
$\bar{1}$ 2 2	3.12	3.17	8				

[a] Space group $P2_1/a$; $a = 9.79(3)$ Å, $b = 7.41(2)$ Å, $c = 13.71(4)$ Å, $\beta = 102.17(9)°$, $Z = 4$, $V = 972.4$ Å^3, $d_x = 3.31$.

According to infrared spectroscopic analysis of $NH_4Er(PO_3)_4$ (Fig. 1, curve a) bands belonging to ν(N–H) are observed at 3260–3040 cm^{-1} [3–5]. The absorption bands at 1438–1401 cm^{-1} correspond to NH_4 bending [3–5].

The absorption bands which are observed in the ranges 1290–1248 cm^{-1}, 1161–1078 cm^{-1}, 1059–875 cm^{-1} and 808–712 cm^{-1} are respectively assigned to ν_{as}(POO), ν_s(POO), ν_{as}(POP) and ν_s(POP). The absorption bands below 615 cm^{-1} are attributed to δ(POO), δ(POP) and ν(MO). This spectrum is typical of a chain structure.

3.2. *Acid polyphosphate of erbium* $HEr(PO_3)_4$

Crystals of $HEr(PO_3)_4$ were prepared [1] in a vitrous carbon crucible from a mixture of erbium oxide Er_2O_3 and excess phosphoric acid H_3PO_4. The mixture was heated in air at 573 K until crystals were formed. After about a week, the product was taken out and rinsed with hot water. The reaction is described by

$$Er_2O_3 + 8H_3PO_4 \longrightarrow 2HEr(PO_3)_4 + 11H_2O$$

X-ray data is shown in Table 2. The crystalline system of $HEr(PO_3)_4$ is monoclinic with space group $P2_1/a$. The lattice parameters are $a = 9.79(3)$ Å, $b = 7.41(2)$ Å, $c = 13.71(4)$ Å, $\beta = 102.17(9)°$, $V = 972.4$ Å^3, $d_x = 3.31$, $Z = 4$.

The infrared spectrum of $HEr(PO_3)_4$ is reported in Fig. 2, curve. Absorption bands at 1270 and 1225 cm^{-1} are ascribed to δ(POH) [6–9]. The observed bands are attributed as follows:
1270–1225 cm^{-1} to ν_{as}(POO); 1155–1071 cm^{-1} to ν_s(POO); 1050–920 cm^{-1} to ν_{as}(POP); 821–679 cm^{-1} to ν_s(POP); below 602 cm^{-1} to δ(POO), δ(POP), and ν(MO). It can be deduced that $HEr(PO_3)_4$ has a chain structure.

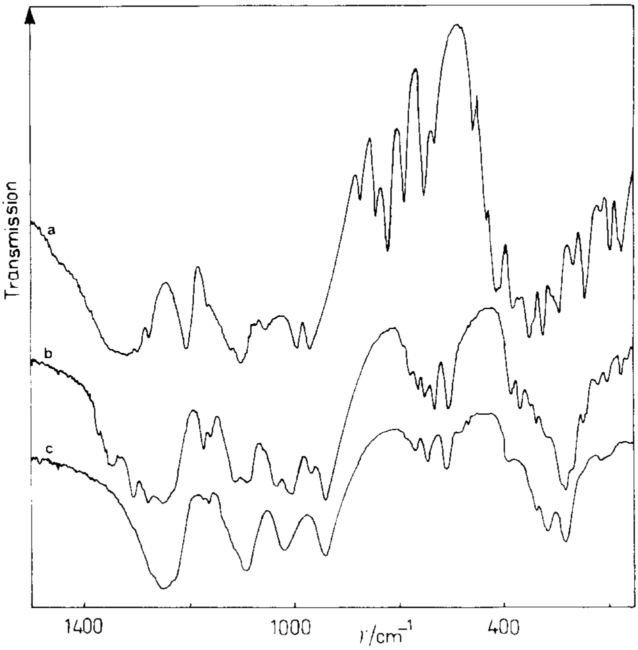

Fig. 2. IR spectra of $HEr(PO_3)_4$ at different temperatures: curve a, at room temperature; curve b, heated at 716 K; curve c, heated at 1079 K.

4. Thermal decomposition of $NH_4Er(PO_3)_4$

The DTA curve of $NH_4Er(PO_3)_4$ (Fig. 3) shows the following effects: the first endo effect was observed at 775 K, a second endo effect occurred at 802 K, and a third endothermic peak appeared at 1155 K.

The thermogram of $NH_4Er(PO_3)_4$ (Fig. 4) reveals that mass loss occurs in three steps. The first loss of 3.46% of initial mass was recorded between 715 and 793 K. The second loss of about 1.68% of initial mass occurred between 793 and 836 K. When the sample was heated above 1193 K, a loss of 7.46% of initial mass was registered.

From the infrared spectrum (Fig. 1, curve b) and X-ray diffractogram it can be seen that at 775 K $NH_4Er(PO_3)_4$ is transformed into erbium polyphosphate $Er(PO_3)_3$-II [10]. We notice that the bands which belong to the region 1438–1401 cm^{-1} are due to the NH_4 bending vibration.

At 802 K the infrared spectrum of the heated product (Fig. 1, curve c) is typical of erbium ultraphosphate ErP_5O_{14}-II [11]. X-ray characteristics of this phase show that erbium polyphosphate $Er(PO_3)_3$-II is still present in the reaction product. We suppose that the infrared absorption bands of ErP_5O_{14}-II mask those of $Er(PO_3)_3$-II. The product obtained at 1179 K is $Er(PO_3)_3$-II (Fig. 1, curve d).

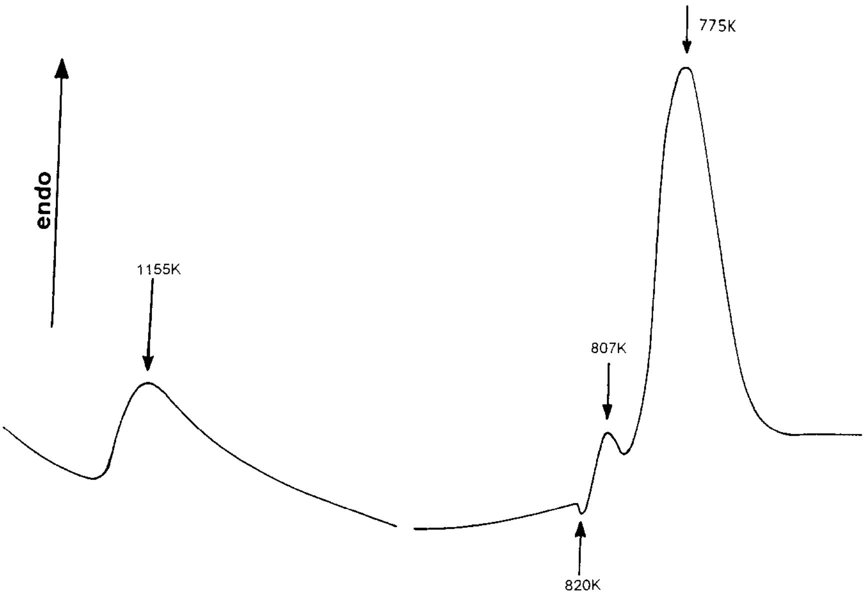

Fig. 3. DTA curve of $NH_4Er(PO_3)_4$-IV at a heating of 5 K min^{-1} in flowing air.

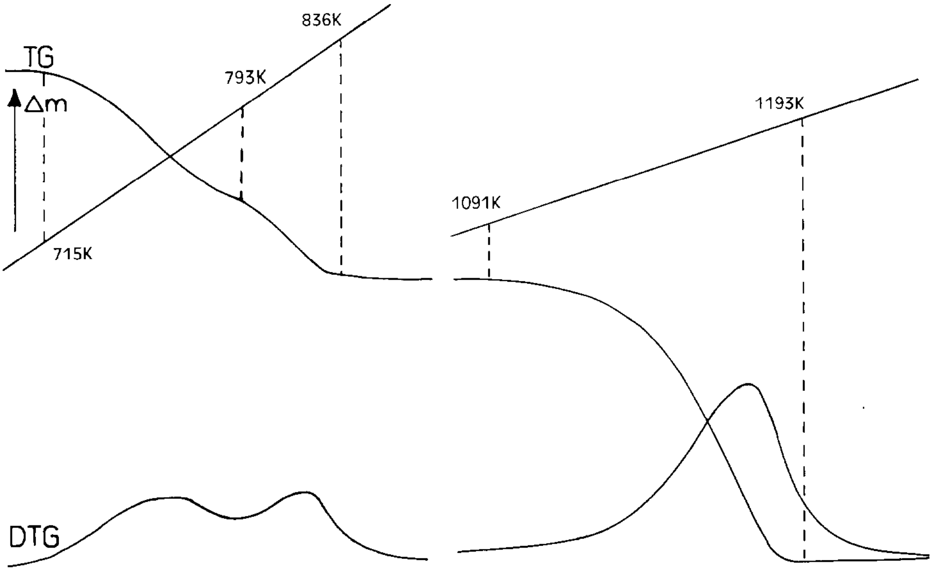

Fig. 4. TG and DTG curves of $NH_4Er(PO_3)_4$-IV at a heating rate of 5 K min^{-1} in flowing air.

Taking into account the previous outcome the following conclusions may be drawn:

(i) The first transformation of $NH_4Er(PO_3)_4$ into $Er(PO_3)_3$-II at 775 K is simultaneously accompanied by formation of an amorphous phase towards X-rays and a removal of volatile compounds which is attributed to loss of 0.5 molecule of ammonia and 0.5 molecule of water. Theoretical calculation (3.49%) is close to experimental results (3.46%).

(ii) At 802 K the resulting product contains both erbium ultraphosphate ErP_5O_{14}-II and erbium polyphosphate $Er(PO_3)_3$-II. The other half of the ammonia molecule is lost. The agreement between experimental result (1.68%) and theoretical calculation (1.69%) seems relatively good.

(iii) The end product of thermal decomposition at 1179 K is erbium polyphosphate $Er(PO_3)_3$-II. The compound ErP_5O_{14}-II undergoes transformation into $Er(PO_3)_3$-II with loss of phosphoric anhydride P_2O_5. Deviation between theory (14.6%) and the experimental result (7.46%) presumably indicates that (apart from decomposition of ErP_5O_{14}-II into $Er(PO_3)_3$-II) an amorphous phase appears.

5. Thermal decomposition of $HEr(PO_3)_4$

The DTA curve of $HEr(PO_3)_4$ (Fig. 5) indicates one endo effect at 716 K and another at 1079 K.

The TG curve of $HEr(PO_3)_4$ (Fig. 6) exhibits two steps. Between 708 and 757 K the thermogram displays a loss of 1.52% of initial mass. The mass loss beginning at 948 K has a value of 6.14% of initial mass.

X-ray diffraction and infrared spectroscopic studies of the resulting compounds have shown that $HEr(PO_3)_4$ converts at 716 K into ErP_5O_{14}-II (Fig. 2, curve b) which converts into $Er(PO_3)_3$-II (Fig. 2, curve c) at 1079 K.

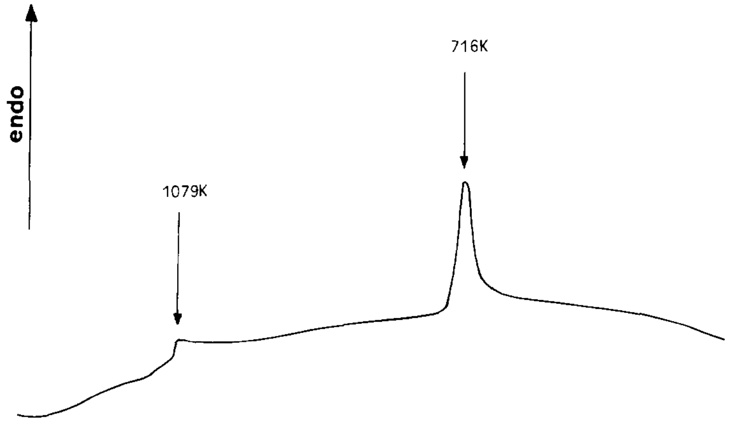

Fig. 5. DTA curve of $HEr(PO_3)_4$ at a heating rate of 5 K min^{-1} in flowing air.

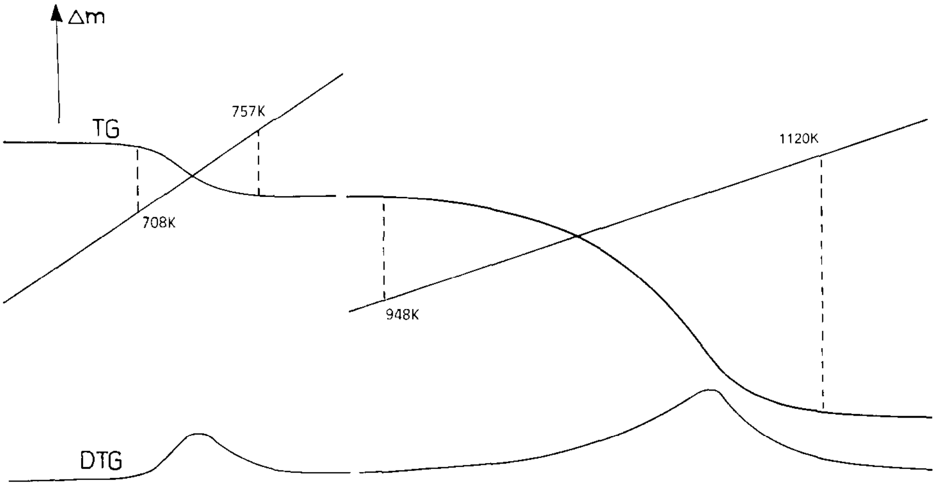

Fig. 6. TG and DTG curves of $HEr(PO_3)_4$ at a heating rate of 5 K min^{-1} in flowing air.

From these results we have found that the thermal decomposition of $HEr(PO_3)_4$ displays two transformations. The first one occurs at 716 K and corresponds to a conversion of $HEr(PO_3)_4$ to ErP_5O_{14}-II. The mass loss may be attributed to the loss of 0.41 molecule of water. The remaining 0.09 molecule of water expected by theoretical calculation is gradually lost between 757 and 948 K. The compound ErP_5O_{14}-II decomposes at 1079 K into $Er(PO_3)_3$-II with a loss of mass which is attributed to the removal of phosphoric anhydride P_2O_5. The theoretical result (14.65%) is not concordant with experiment (6.14%), indicating that probably an amorphous phase is simultaneously formed with decomposition of ErP_5O_{14}-II.

6. Conclusions

Crystals of $NH_4Er(PO_3)_4$ have been synthesized and the corresponding X-ray diffraction patterns have been indexed. Vibrational spectra of $NH_4Er(PO_3)_4$ and $HEr(PO_3)_4$ are given. Thermal studies of these polyphosphates have been undertaken and show that before melting they decompose to give ErP_5O_{14}-II and $Er(PO_3)_3$-II, both of which have been isolated.

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