ELSEVIER

Thermochimica Acta 257 (1995) 117–125

thermochimica
acta

Thermal behaviour of ammonium polyphosphate–inorganic compound mixtures. Part 2. Manganese dioxide

G.F. Levchik *, S.V. Levchik, P.D. Sachok, A.F. Selevich,
A.S. Lyakhov, A.I. Lesnikovich

*Research Institute for Physical Chemical Problems, Byelorussian State University,
Leningradskaya 14, Minsk 220080, Belarus*

(Received 10 June 1994; accepted 12 November 1994)

Abstract

The chemical interaction between ammonium polyphosphate (APP) and manganese dioxide (MnO_2) was studied by thermogravimetry with linear heating. The products of interaction were collected at successive steps of weight loss and analysed by X-ray diffraction (on crystalline products) or by chemical analysis (on amorphous products).

It was found that MnO_2 starts to interact with APP at the beginning of the thermal decomposition of APP at 270–280°C. At the onset of weight loss of the APP/MnO_2 mixtures, manganese(VI) is reduced to manganese(III) and (II) producing $MnNH_4P_2O_7$ and $Mn(NH_4)_2(PO_3)_4$ respectively. Ammonia, which is partially reduced to nitrogen, is evolved from PP. The formation of $MnNH_4P_3O_9$ and then $Mn_2P_4O_{12}$ is observed on further heating of the mixtures to 560–570°C. The content and ratio of the products of reaction depend on the temperature and the ratio of components in the initial APP/MnO_2 mixtures.

Assignment of the X-ray powder diffraction peaks and an estimation of the lattice parameters have been made on orthorhombic $MnNH_4P_3O_9$ ($a = 7.357(3)$, $b = 12.186(8)$, $c = 9.390(5)$Å, space group P_{mcn}).

Keywords: Ammonium polyphosphate; Linear heating; Manganese dioxide; TGA; XRD

---

1. Introduction

Ammonium polyphosphate (APP) is a typical fire retardant for many synthetic polymers and cellulosic materials [1]. It decomposes on heating, producing polyphos-

---

* Corresponding author.

SSDI 0040-6031(94)02210-0

phoric acid, which can undergo carbonisation with polymers producing char. The evolved gases blow up the viscous polyphosphoric acid which is reinforced by the char and thus an intumescent thermal insulating layer, which can extinguish combustion, is formed. If polyphosphoric acid does not react with the polymer (polyethylene, polypropylene etc.), synergistic organic compounds (e.g. pentaerythritol [2]) are added together with APP to improve the fire retardant properties of the intumescent layer.

Recently we have found that many inorganic compounds which interact at high temperature with polyphosphoric acid can essentially increase the fire retardancy of APP applied to polyamide 6 [3]. For instance, talc, which has no influence on the thermal decomposition of the polymer, interacts with APP to improve the physical mechanical properties of the intumescent char [4,5]. The chemical interaction in the APP/talc system was studied at different temperatures, and it was shown that various magnesium and silicon phosphates can be formed on heating [6].

This work was aimed at studying the interaction of manganese dioxide with APP, as MnO_2 showed good improvement of the fire retardant properties of APP added to polyamide 6 [4].

2. Experimental

Ammonium polyphosphate ($(NH_4PO_3)_n$, $n \approx 700$, Exolit 422 from Hoechst) and manganese dioxide (MnO_2, Russian standard GOST 4470-79, Khimreaktiv) were used. Weight ratios of 3:1 and 6:1 for APP/MnO_2 respectively were chosen for detailed study, as the flame retardant additive APP + MnO_2 showed maximum efficiency in combustion tests in air and in synthetic oxygen/nitrogen atmospheres (oxygen index test), at these ratios.

Chemical interaction in the APP/MnO_2 systems at high temperature was studied by thermogravimetry (TG) using a Mettler TA 3000 thermal analyser. Experiments were carried out at a heating rate of $10\,K\,min^{-1}$ in an argon flow of $100\,cm^3\,min^{-1}$. Ceramic holders with which APP and MnO_2 do not react were used.

Solid products of reaction were collected at different steps of weight loss at the temperatures corresponding to the minima on the differential thermogravimetry (DTG) curves. Crystalline products were identified by X-ray analysis using a Carl-Zeiss-Jena diffractometer HZG-4/A, with Cu $K\alpha$ irradiation over a range of 2θ values from 5° to 45°. Cations and anions extracted from the solid products by water were determined by chemical analysis. The anions were separated by thin layer chromatography before identification [7].

Evolved ammonia was trapped by a 0.1 N solution of H_2SO_4 and determined by titration at the end of the heating cycle.

3. Results and discussion

Manganese dioxide decomposes at 470–530°C with the evolution of oxygen, as can be seen by thermogravimetry (see Fig. 1, curve a). The onset of weight loss of APP is

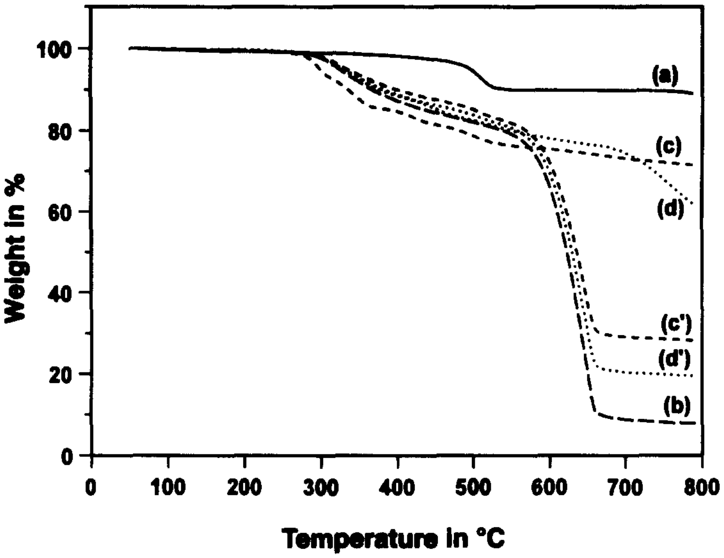


Fig. 1. Experimental (curves a, b, c and d) and calculated (curves c' and d') TG curves of (a) MnO_2, (b) APP, (c, c') mixture APP/MnO_2 = 3:1 and (d, d') mixture APP/MnO_2 = 6:1. Heating rate 10 K min^{-1}, argon flow rate 100 cm^3 min^{-1}.

observed at 280°C (see Fig. 1, curve b). Most of the evolution of ammonia and water from APP occurred below 600°C [8]. Polyphosphoric acid formed on evolution of ammonia underwent condensation with the evolution of water and the formation of pyrophosphoric functionalities. Evaporation of polyphosphoric and ultraphosphoric acids is observed at 600–660°C. The solid residue ($\approx$ 8%), which is stable up to 800°C, is likely to be a compound of phosphorus nitroxide type.

Manganese dioxide added to APP in the APP/MnO_2 ratio 3:1 seems to catalyse the thermal decomposition of APP, as the onset of the weight loss of the mixture (see Fig. 1, curve c) is observed at lower temperatures than that of APP alone (curve b). Furthermore, the weight loss is higher in the temperature interval 270–600°C than that of APP alone. The acceleration of thermal decomposition of APP by MnO_2 at these temperatures is also seen from a comparison of the experimental curve c with the calculated curve c'. The calculated curve was simulated by a computer program assuming that MnO_2 and APP decompose independently. The presence of MnO_2 prevents the volatilization of phosphoric acids above 600°C because the solid residue content at 800°C (72%, for curve c) is greater than expected from the calculated curve c' (28%).

As the experimental curve d and that calculated, d', for the mixture APP/MnO_2 = 6:1 practically coincide over the range 280–600°C (Fig. 1), it seems that the smaller amount of MnO_2 added to APP does not accelerate the thermal decomposition of APP. MnO_2 prevents volatilization of phosphoric acids above 600°C also in this mixture. However, the residue formed at high temperatures is not so stable as that for the mixture APP/MnO_2 = 3:1, which starts to decompose at 700°C (see Fig. 1, curve d).

Figs. 2(a) and (b) show the experimental TG and DTG curves of the mixtures APP/MnO_2 = 3:1 and 6:1 respectively. Heating was interrupted and the mixtures were analysed by X-ray and chemical analyses. This is indicated on the DTG curves.

The X-ray diffractogram of the solid products collected after the first step of weight loss for the mixture APP/MnO_2 = 3:1 at 320°C is shown in Fig. 3(a). All diffraction peaks are attributable to manganese(III)-ammonium diphosphate ($MnNH_4P_2O_7$) [9]. Thus, in the presence of APP, Mn^{4+} is reduced to Mn^{3+} even at a relatively low temperature, whereas MnO_2 alone decomposes with Mn^{4+} reduction at 470–530°C (see Fig. 1, curve a).

A broad halo which is seen on the base line at 2θ = 30–10° (Fig. 3(a)) is an indication of the presence of amorphous products in the residue. The amorphous phase is soluble in water. In addition to H^+, the cations $NH_4{}^+$, Mn^{2+} and Mn^{3+} were determined by chemical analysis. Various phosphate anions of different degrees of condensation were detected in the water extract. Apart from decreasing contents of Mn^{3+} and $NH_4{}^+$, the

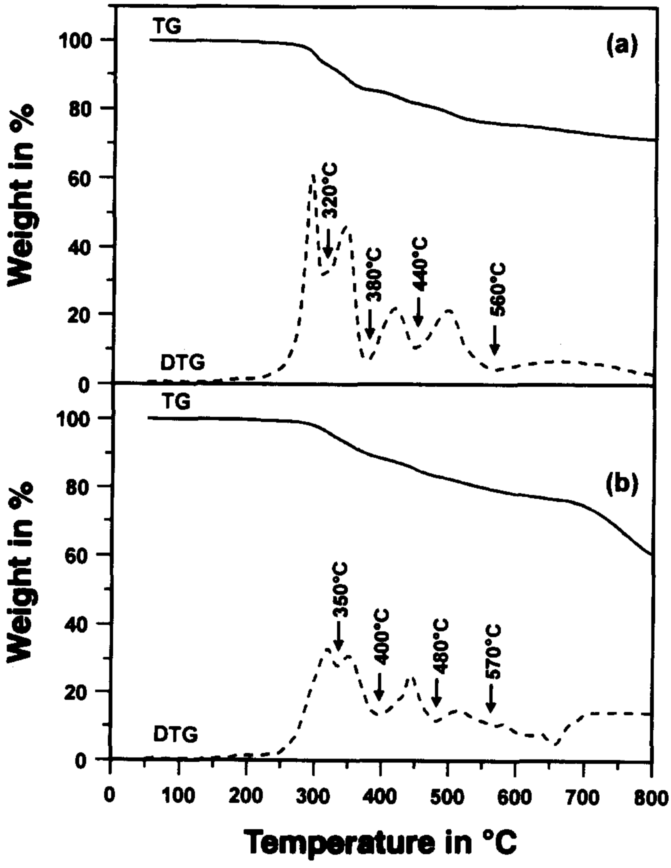


Fig. 2. TG (solid) and DTG (dashed) curves of mixtures with APP/MnO_2 ratio (a) 3:1 and (b) 6:1. Sampling points for analysis of solid residue are shown on DTG curves. Experimental conditions as in Fig. 1.

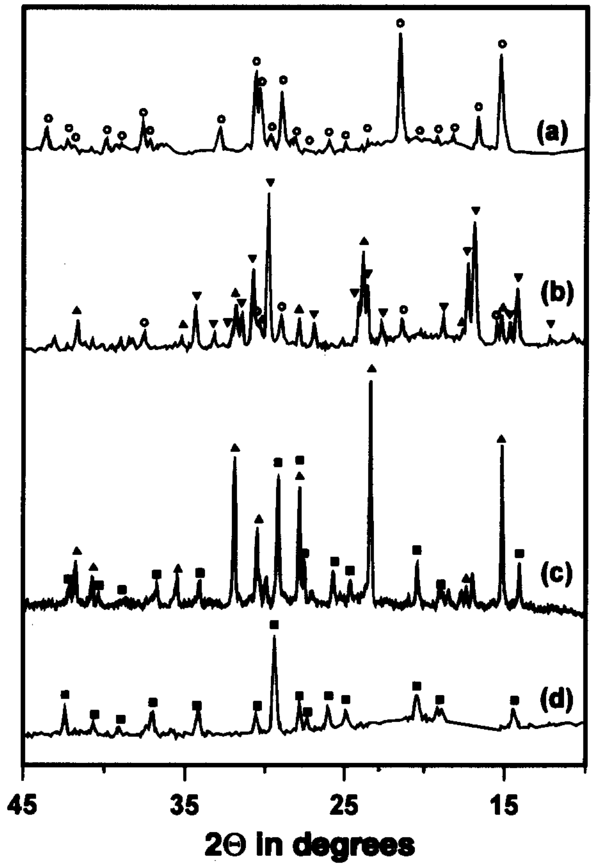


Fig. 3. X-ray powder diffraction patterns of crystalline products of reaction in the mixture APP/MnO_2 = 3:1 at (a) 320°C, (b) 380°C, (c) 440°C and (d) 560°C. Diffraction peak assignments: (M) $MnNH_4P_2O_7$, (V) $MnNH_4P_3O_9$ orthorhombic, (Q) $MnNH_4P_3O_9$ hexagonal, (P) $Mn_2P_4O_{12}$.

composition of the amorphous phase does not change much on increasing the temperature to 560°C.

$MnNH_4P_2O_7$ decomposes on heating to 380°C, because only its most intense peaks remain detectable in the X-ray diffractogram (see Fig. 3(b)). A series of new diffraction peaks appear at this temperature. Some of these peaks are attributed to the hexagonal modification of manganese(II)-ammonium cyclotriphosphate ($MnNH_4P_3O_9$) [10,11], but no suitable assignment could be found in the literature for the remaining peaks, including the most intense.

We prepared a sample which showed only non-attributable X-ray peaks by isothermal heating of the mixture APP/MnO_2 = 3:1 for 0.5–1 h at 350–360°C under nitrogen. By using thin layer chromatography and chemical analysis it was found that the unknown compound also was manganese(II)-ammonium cyclotriphosphate.

Comparison of the X-ray powder diffraction patterns of this new compound with those of known mixed ammonium and bivalent metal cyclotriphosphates showed that it is isomorphic with orthorhombic manganese-ammonium cyclotriphosphate ($MgNH_4P_3O_9$) [12]. Using the crystallographic data of $MgNH_4P_3O_9$ [12] we carried out the indexing of the X-ray powder diffractogram of orthorhombic form of $MnNH_4P_3O_9$ (Table 1). The compound was assigned to the P_{mcn} space group. The lattice parameters $a = 7.3572(26)$, $b = 12.1860(83)$, $c = 9.3904(53)$Å, $Z = 4$ and $V = 841.89(80)$Å^3 were calculated from the diffraction lines.

Further heating of the APP/MnO_2 mixture to 440°C (see Fig. 2(a)) resulted in the quantitative polymorphic transition of the orthorhombic form of $MnNH_4P_3O_9$ to the hexagonal form (see Fig. 3(b)). Such polymorphic transition on heating is known for other compounds of the same class [11]. In addition to $MnNH_4P_3O_9$, manganese(II) cyclotetraphosphate ($Mn_2P_4O_{12}$) [13] was also identified at this temperature, having

Table 1
Experimental and calculated X-ray powder diffraction data of orthorhombic $MnNH_4P_3O_9$

d_{exp}/Å	Relative intensity I/%	*hkl*	d_{calc}/Å
7.437	4	011	7.438
6.294	45	110	6.298
6.088	15	020	6.093
5.228	100	111	5.231
5.111	53	021	5.111
4.695	18	002	4.695
3.957	12	102	3.958
3.765	65	112	3.764
3.725	28	031	3.728
		022	3.719
3.320	17	112	3.319
3.067	18	032	3.072
2.987	96	221	2.986
2.898	51	041	2.898
2.837	23	132	2.835
2.784	8	023	2.784
2.678	10	141	2.696
2.617	27	222	2.615
2.555	7	042	2.556
2.404	11	310	2.404
2.348	7	240	2.346
2.183	4	043	2.183
2.093	8	242	2.099
1.917	24	332	1.919
1.840	18	323	1.840
		400	1.839
1.744	8	333	1.744
1.680	9	314	1.680
1.648	6	431	1.649

been formed by further loss of ammonia from the system APP/MnO_2 = 3:1. The only crystalline phase that remains in the system on heating to 560°C (see Fig. 3(d)) is $Mn_2P_4O_{12}$.

Fig. 4 shows the transformation of the crystalline products of the reaction occurring in the system APP/MnO_2 = 6:1 on heating in an inert atmosphere as monitored by X-ray analysis. The excess of APP favours an easier reduction of Mn^{IV} to Mn^{II}, as manganese(II)-ammonium polyphosphate $Mn(NH_4)_2(PO_3)_4$ is mostly detected after the onset of weight loss at 350°C (see Fig. 4(a)) [14]. Traces of hexagonal manganese-(II)-ammonium cyclotriphosphate are also found at this temperature.

On further heating to 400°C (see Fig. 2(b)), $Mn(NH_4)_2(PO_3)_4$ becomes more crystalline, as is shown by the increased intensities of its peaks (see Fig. 4(b)). Simultaneously, there is an increase in the content of $MnNH_4P_3O_9$ at this temperature. With an excess of APP, in the mixture APP/MnO_2 = 6:1, $MnNH_4P_3O_9$ appears only

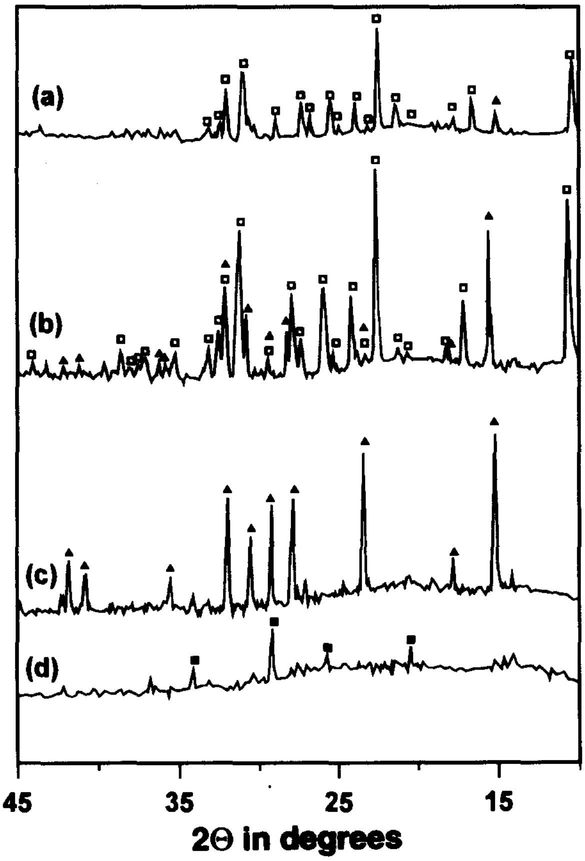
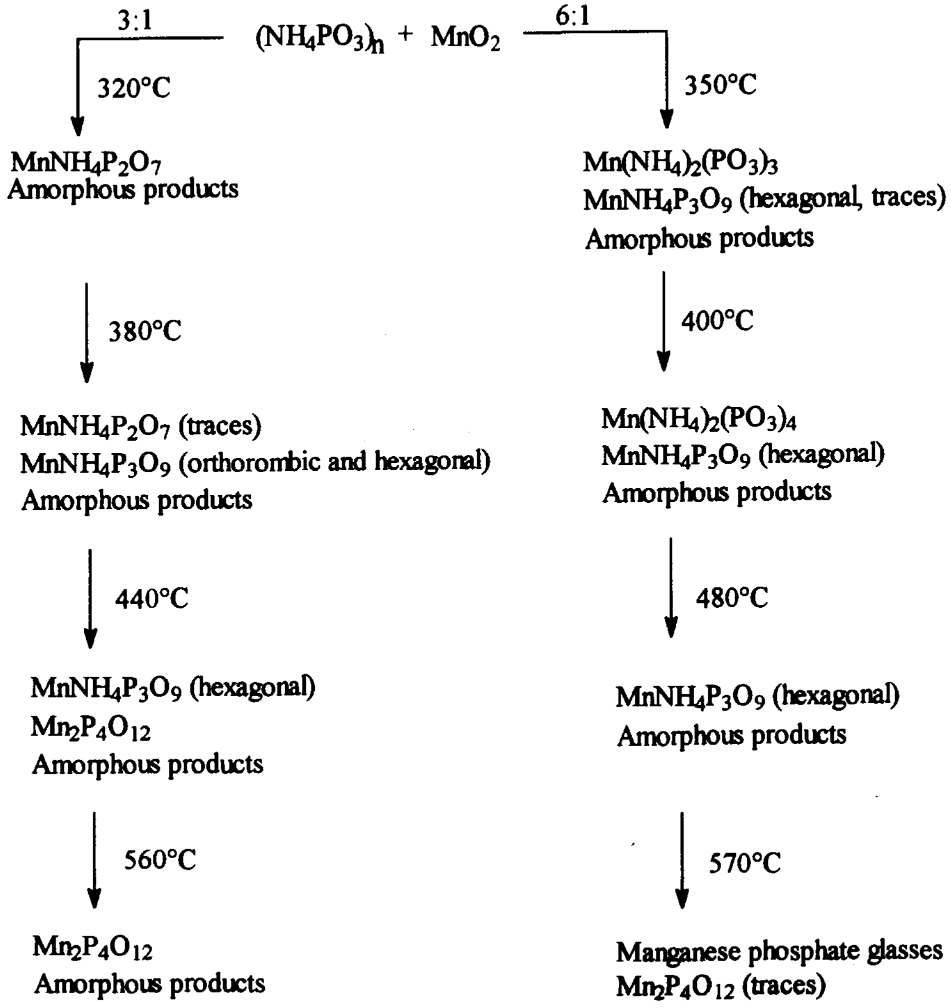


Fig. 4. X-ray powder diffraction patterns of crystalline products of reaction in the mixture APP/MnO_2 = 6:1 at (a) 350°C, (b) 400°C, (c) 480°C and (d) 570°C. Diffraction peak assignments: (O) $Mn(NH_4)_2(PO_3)_4$; other attributions as in Fig. 3.

in the hexagonal form, and the orthorhombic modification was not detected at any temperature.

Further loss of ammonia by $Mn(NH_4)_2(PO_3)_4$ at 400–480°C results in its quantitative transformation to hexagonal $MnNH_4P_3O_9$ (see Fig. 4(c)). $MnNH_4P_3O_9$ decomposes on heating to 570°C and, in the excess of polyphosphoric acids, produces highly hygroscopic manganese-phosphate glasses. Only traces of manganese(II) cyclotetraphosphate were found at this temperature (Fig. 4, curve d).

Thus, taking into consideration the above results, the proposed scheme of chemical transformations of the solid products in the APP/MnO_2 mixtures is given in Scheme 1.



Scheme 1. The proposed scheme of chemical transformations of solid products in the APP/MnO_2 mixtures.

The addition of MnO_2 to APP results in a decrease in the amount of evolved ammonia. By trapping NH_3 in H_2SO_4, it was found that both mixtures under study produce 12–15% less ammonia on heating to 600°C than the same amount of APP decomposing independently. Taking into consideration that NH_4^+ was not detected in the crystalline (see Scheme 1) or in the amorphous products, we must assume that oxidation of the evolved ammonia occurs with the production of Mn^{VI} or Mn^{III} [15].

As can be seen from Scheme 1, the mixture $APP/MnO_2 = 3:1$ loses ammonia more easily on heating than the mixture with the components in the ratio 6:1. This phenomenon most likely explains the behaviour of these mixtures in thermogravimetry, where $APP/MnO_2 = 3:1$ shows less stability at the initial stages of degradation than the other system.

The reactions of APP with inorganic additives can result in the formation of different phosphates. The composition of the products depends on the chemical nature of the additive, the initial ratio of the components and the temperature. The results obtained in this work will be used to clarify the mechanism of the fire retardant action of APP in the presence of inorganic additives in polymers.

References

[1] H.L. Vandersall, J. Fire Flammability, 2 (1971) 97.

[2] G. Camino, G. Martinasso, L. Costa and R. Gobetto, Polym. Degradation Stab., 28 (1990) 17.

[3] G.F. Levchik, S.V. Levchik, A.F. Selevich and A.I. Lesnikovich, Byelorurussian Patent 00076-01, 1993.

[4] S.V. Levchik, G.F. Levchik, A.F. Selevich, G. Camino and L. Costa, Proceedings of the 2nd Beijing International Symposium/Exibition of Flame Retardants, Beijing, October 11–15, p. 197–202.

[5] S.V. Levchik, G.F. Levchik, G. Camino and L. Costa, J. Fire Sci. (in press).

[6] G.F. Levchik, A.F. Selevich, S.V. Levchik and A.I. Lesnikovich, Thermochim. Acta (in press).

[7] E.A. Prodan and I.L. Shashkova, Vesti Akad. Nauk. BSSR, Ser. Kim. Nauk, 4 (1978) 79.

[8] G. Camino, L. Costa and L. Trossarelli, Polym. Degradation Stab., 6 (1984) 243.

[9] J.D. Lee and L.S. Brown, J. Chem. Soc. Ser. A, (1968) 559.

[10] R. Masse, J.-C. Grenier, M.-T. Averbuch-Pouchot, D. Tranqui and A. Durif, Bull. Soc. Fr. Mineral. Crystallogr., 90 (1967) 158.

[11] R. Masse, J.-C. Grenier and A. Durif, Bull. Soc. Chim. Fr., (1968) 1741.

[12] J.-C. Grenier and R. Masse, Bull. Soc. Fr. Mineral. Crystallogr., 91 (1968) 428.

[13] Th. Hinsch, W. Guse and H. Saalfeld, J. Cryst. Growth, 79 (1986) 205.

[14] T.M. Averbuch-Pouchot and A. Durif, Mater. Res. Bull., 4 (1969) 397.

[15] Z.A. Konstant and A.P. Dindune, Phosphates of Bivalent Metals, Zinatne, Riga, 1987 (in Russian).