

New Data on $Zn_2P_2O_7$ Phase Transformations

M. A. Petrova, V. I. Shitova, G. A. Mikirticheva, V. F. Popova, and A. E. Malshikov

Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, Russia

Received November 4, 1994; in revised form March 14, 1995; accepted March 17, 1995

For $Zn_2P_2O_7$ along with the two known polymorphous modifications with monoclinic structure (α and β), we obtained two new metastable modifications, x and y . They form in the course of crystallization of the $2ZnO \cdot P_2O_5$ glass and transform into each other through a monotropic phase transition according to the scheme $glass \rightarrow x \rightarrow y \rightarrow \beta-Zn_2P_2O_7$. The refractive indices of x and y phases are close to each other with $n_{mean} = 1.633$. The picnometric density is equal to $3.68 \pm 0.01 \text{ g/cm}^3$ for x phase and to $3.72 \pm 0.01 \text{ g/cm}^3$ for y phase. © 1995 Academic Press, Inc.

Two polymorphic transformations of zinc pyrophosphate have been known to exist hitherto. These are α and β modifications connected with each other by reversible transformations at 132°C . The high-temperature β modification exists to the temperature of congruent melting 1015°C (1). Keeping in mind the wide possibilities of utilizing phosphate glasses of two-valence elements, it seemed of interest to pay attention to the study of phase transformations taking place during the crystallization of $2ZnO \cdot P_2O_5$ glass.

In the present work the study was made using X-ray phase analysis, DTA, IR spectroscopy, and crystal-optical analysis (in immersion). X-ray diagrams were taken on a Siemens apparatus D-500/HS at room temperature and on a DRON-1 diffractometer with a Pt holder by heating from 20 to 800°C at a rate of $8^\circ/\text{min}$. The heating curves were obtained on a Derivatograph-C at a rate of $7.5^\circ/\text{min}$. The IR spectra were taken on a Specord 751R, the samples being obtained by pressing with KBr.

Zinc pyrophosphate was synthesized by solid state reaction between ZnO (puriss) and $NH_4H_2PO_4$ (special grade high purity). The annealing was performed in glass-carbon and platinum crucibles in a silit furnace in the temperature range $300\text{--}900^\circ\text{C}$. The glass of $2ZnO \cdot P_2O_5$ composition was obtained by melting the zinc pyrophosphate in a Pt-crucible in a silit furnace at 1200°C for 15 min followed by quenching on a steel plate. According to chemical analysis data, the zinc pyrophosphate thus synthesized contained 66.38 mole% ZnO and 33.62 mole%

P_2O_5 , the glass contained 66.26 mole% ZnO and 33.74 mole% P_2O_5 as regards the theoretical composition of $Zn_2P_2O_7$ (66.66 mole% ZnO and 33.33 mole% P_2O_5). No loss of P_2O_5 was observed in the process of glass making.

The crystal-optical investigation of zinc pyrophosphate in immersion samples revealed crystals of isometric form with refractive indices $n_g = 1.716$ and $n_p = 1.684$, and birefringence of 0.032. The X-ray diffraction pattern of $Zn_2P_2O_7$ agrees with the data for $\alpha-Zn_2P_2O_7$ given in (2) as regards the set of interplane distances.

The heating curve for zinc pyrophosphate (Fig. 1a) exhibits two endothermic effects at 130 and 1014°C . The first peak corresponds to the reversible polymorphic transformation which was confirmed by the high-temperature XRD data. The reverse transition $\beta \rightleftharpoons \alpha$ is very rapid, therefore we failed to obtain the β form by quenching. The second peak on the DTA curve at 1014°C is due to the sample melting.

The X-ray diffraction patterns of α and β modifications of $Zn_2P_2O_7$ obtained by heating are shown in Fig. 2a; the calculated unit cell parameters and density are given in Table 1. The errors in parameters values were determined by the least-squares method using crystalline germanium as the inner standard. The experimental density was determined by the picnometric method in kerosene at 20°C . As seen from Fig. 2a, the α modification differs from the β form by the presence of additional superstructural lines of weak intensity. This can imply that the $\alpha \rightleftharpoons \beta$ polymorphic transformation may probably refer to the second kind of phase transition, the unit cell parameter being a number divisible by 3 along the a -axis and by 2 along the c -axis. As known from the literature (4), this transition is related to the change of P_2O_7 configuration from the curved to the straight line form.

The $2ZnO \cdot P_2O_5$ glass in immersion samples is isotropic, homogeneous in composition, with the refractive index 1.612. The heating curve (Fig. 1b) shows several endo- and exothermic effects. The first endothermic effect of small value at 430°C is due to the glass softening. The next distinct exoeffect at 500°C corresponds to the start of crystallization. The endothermic effect at 1014°C corresponds to the sample melting. Besides these effects,

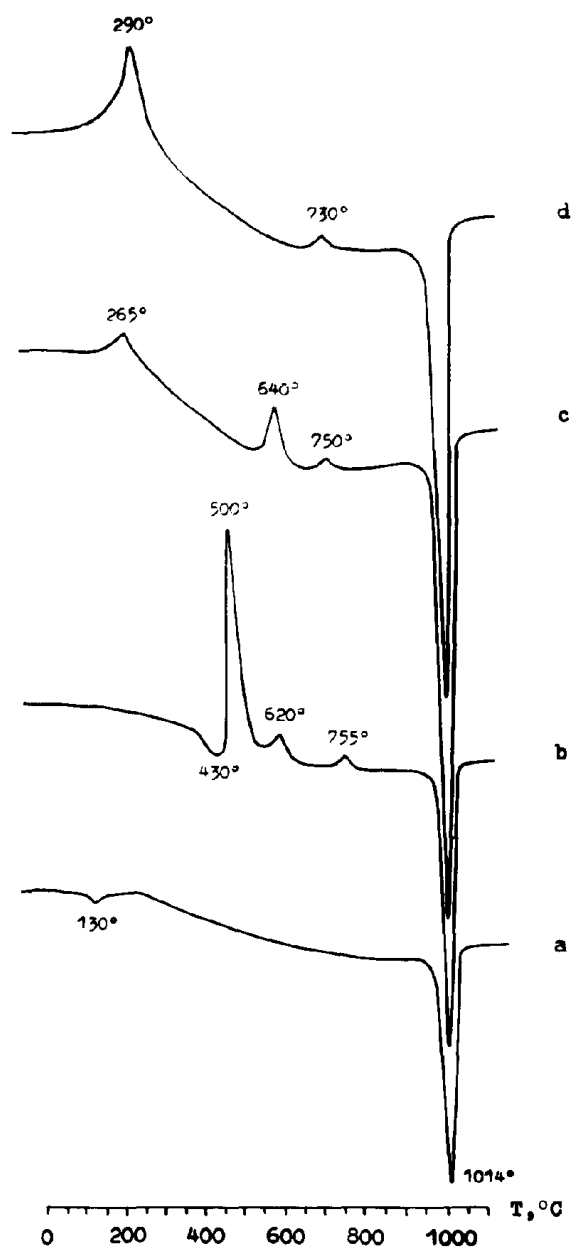


FIG. 1. Thermograms of the compound $Zn_2P_2O_7$ (a) and $2ZnO \cdot P_2O_5$ glass (b) (sensitivity 1/10), as well as of phases x (c) and y (d) (sensitivity 1/5).

two small exoeffects are observed at the heating curves at 620 and 755°C.

The high-temperature XRD data show that glass crystallization proceeds through several intermediate stages (Fig. 2b). At the first stage, an x phase is precipitated from the glass at 430°C. Its quantity grows with increasing temperature. At 530°C, together with the x phase, another phase denoted by us as y appears in the sample. Further increase of temperature leads to the decrease of

the x -phase content, up to its full disappearance, and to the increase of the y -phase quantity. Above 580°C, the β - $Zn_2P_2O_7$ appears in the sample together with the y phase. The y phase is stable to $\sim 700^\circ C$, and only the β - $Zn_2P_2O_7$ phase exists above 700°C. The high-temperature X-ray diffraction showed that for the $2ZnO \cdot P_2O_5$ glass the exoeffects on the DTA heating curve at 500, 620, and 755°C (Fig. 1b) can be related to the maximum crystallization of x , y , and β - $Zn_2P_2O_7$ phases, respectively. As seen in Fig. 2b, the temperature of the appearance of these phases is lower.

Prolonged isothermal annealing of the glass (24 hr every 10–50°C) in the range 400–700°C permitted more exact definition of the phase transformation temperatures in the series, the glass $\rightarrow x \rightarrow y \rightarrow \beta$ - $Zn_2P_2O_7$ (Table 2). Further increase of the glass annealing time to 140 hr causes no change in phase transition temperatures. Thus, 24 hr annealing is enough for metastable phase equilibria to be established.

A detailed study was made of the thermal behavior of individual crystalline phases x and y by means of DTA, HTXRD, and the method of annealing and quenching. The heating curves of x and y phases shown in Figs. 1c and 1d permit one to establish that the exoeffect at 640°C corresponds to the $x \rightarrow y$ transition, the exoeffects at 730°C and 750°C correspond to the $y \rightarrow \beta$ - $Zn_2P_2O_7$ transition, and the endoeffect at 1014°C is due to the sample (final) melting. Hence it follows that the exoeffects at the heating curve for $2ZnO \cdot P_2O_5$ glass (Fig. 1b) at 620 and 755°C are related to the transitions $x \rightarrow y$ and " y " $\rightarrow \beta$ - $Zn_2P_2O_7$, respectively. In addition to this, the heating curves of x and y phases in the range 260–290°C exhibit an additional exoeffect which is absent on the thermogram for the $2ZnO \cdot P_2O_5$ glass. The nature of the exoeffect was not established by us; the HTXRD data for y phase taken at temperatures from the ambient to 350°C do not reveal any structural changes in this phase.

Subsequent annealing of x and y phases at various temperatures for 24 hr (Table 2) confirm that the above mentioned phase transformations really take place during crystallization of $2ZnO \cdot P_2O_5$ glass and are irreversible.

The data obtained permit us to give schematic representation of $Zn_2P_2O_7$ polymorphic transformations showing the relation between enantiotropic and monotropic transformations (Fig. 3).

The interplane distances (d/n) and the relative intensities (I/I_0) for individual x and y phases are represented in Table 3. By the d/n set, the x and y phases cannot be related to any of the compounds known in the ZnO – P_2O_5 system (ASTM table).

The microscopic data show that these phases belong to the same crystallization type, namely to that of spherulites, the crystallization centers of which lie at the grain

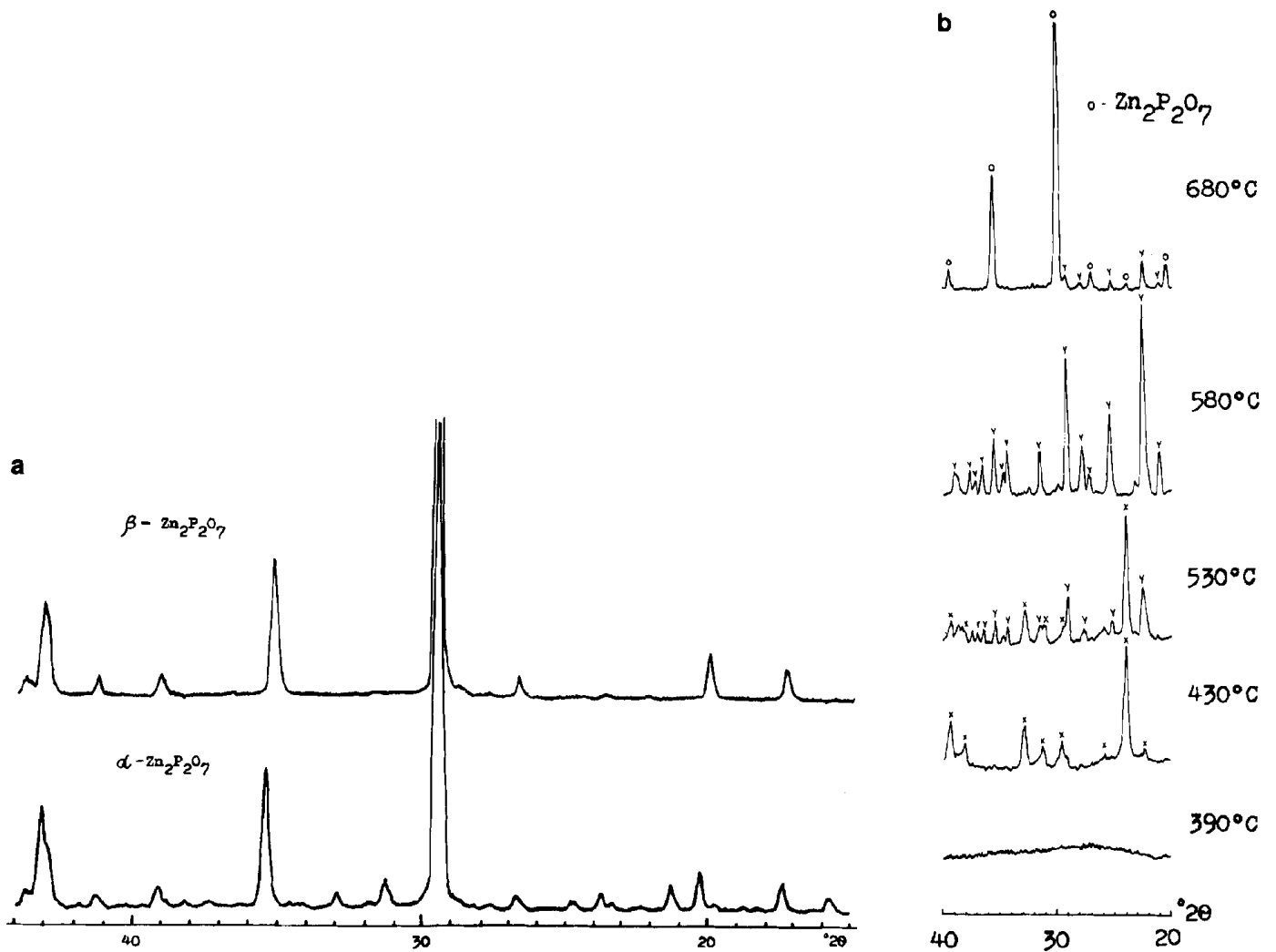


FIG. 2. XRD patterns for the compound $Zn_2P_2O_7$, (a) and $2ZnO \cdot P_2O_5$ glass (b) taken by heating.

TABLE 1
Unit Cell Parameters and Density of α and $\beta-Zn_2P_2O_7$

Compound	Our results		Literature data (2, 3)	
	Unit cell parameters	Density (g/cm ³)	Unit cell parameters	Space group
$\alpha-Zn_2P_2O_7$	$a = 19.617(11) \text{ \AA}$ $b = 8.278(4) \text{ \AA}$ $c = 9.106(4) \text{ \AA}$ $\beta = 100.45(2)^\circ$	$\rho_{\text{calc.}} = 4.18$ $\rho_{\text{meas.}} = 4.08$	$a = 20.068(15) \text{ \AA}$ $b = 8.259(6) \text{ \AA}$ $c = 9.099(8) \text{ \AA}$ $\beta = 106.35(5)^\circ$	$I2/c, Z = 12$
$\beta-Zn_2P_2O_7$	$a = 6.608(2) \text{ \AA}$ $b = 8.279(3) \text{ \AA}$ $c = 4.523(1) \text{ \AA}$ $\beta = 105.43(2)^\circ$	$\rho_{\text{calc.}} = 4.24$	$a = 6.61(1) \text{ \AA}$ $b = 8.29(1) \text{ \AA}$ $c = 4.51(1) \text{ \AA}$ $\beta = 105.40(2)^\circ$	$C2/m, Z = 2$

TABLE 2
Results of $Zn_2P_2O_7$ Annealing According to XRD Data

Annealing temperature (°C)	Initial sample		
	Glasses	x-phase	y-phase
430	x	x	y
500	x	x	y
550	x + y	x + y	y
580	y	y	y
610	y + $Zn_2P_2O_7$ (traces)	y + $Zn_2P_2O_7$ (traces)	y + $Zn_2P_2O_7$ (traces)
650	$Zn_2P_2O_7$ + y	$Zn_2P_2O_7$	$Zn_2P_2O_7$ + y (traces)
670	$Zn_2P_2O_7$		$Zn_2P_2O_7$

edge, with the crystallization front directed toward the center. The refractive indices of x and y phases are close to each other with $n_{\text{mean}} = 1.633$. The picnometric density is equal to $3.68 \pm 0.01 \text{ g/cm}^3$ for x phase and to $3.72 \pm 0.01 \text{ g/cm}^3$ for y phase.

The absorption spectra for crystalline, vitreous zinc

pyrophosphate and products of its crystallization on heating (x and y phases) are shown in Fig. 4.

The IR spectrum of α - $Zn_2P_2O_7$ corresponds to the one established in (1). It contains the characteristic bands of antisymmetric and symmetric valence vibrations of the terminal PO_3 groups of pyrophosphate anion, $\nu_{\text{as}} PO_3$ with frequencies 1193, 1165, 1113, and 1090 cm^{-1} and $\nu_{\text{s}} PO_3$ in the region of 1055 cm^{-1} ; the deformation vibrations of these groups (σPO_3) are observed below 600 cm^{-1} . The frequencies of valence vibrations of P-O-P bridging bonds (ν_{as} and ν_{s} of POP) are 953 and 725 cm^{-1} , respectively.

The $2ZnO \cdot P_2O_5$ glass contains rather wide bands with the absorption maximum near 920, 750, and 520 cm^{-1} (Fig. 4a).

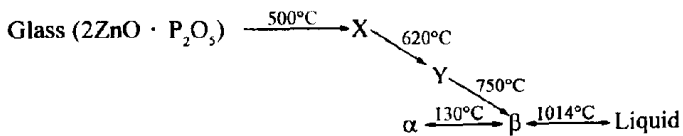


FIG. 3. Schematic diagram of $Zn_2P_2O_7$ polymorphism; temperature values are taken from DTA data.

TABLE 3
XRD Data of x and y phases

x-phase				y-phase			
d/n	I/I ₀	d/n	I/I ₀	d/n	I/I ₀	d/n	I/I ₀
4.56	54	1.810	4	6.18	10	2.466	19
4.34	5	1.708	4	5.18	19	2.398	11
4.01	71	1.653	6	4.63	31	2.341	16
3.73	100	1.625	5	4.58	21	2.225	11
3.44	42	1.562	4	4.24	15	2.162	5
3.02	23	1.537	10	4.03	58	2.111	27
2.88	13	1.4924	12	3.97	100	2.057	8
2.801	16	1.4701	4	3.74	15	2.033	5
2.723	32	1.4504	9	3.54	30	1.977	9
2.450	11	1.4333	6	3.46	28	1.899	7
2.371	14			3.30	12	1.734	4
2.333	22			3.24	20	1.699	4
2.290	32			3.08	64	1.656	4
2.217	6			2.847	24	1.604	6
2.102	9			2.800	11	1.576	8
2.071	6			2.732	11	1.512	21
1.974	23			2.619	20	1.4166	7
1.923	4			2.588	11	1.3711	7
1.863	3			2.537	20		

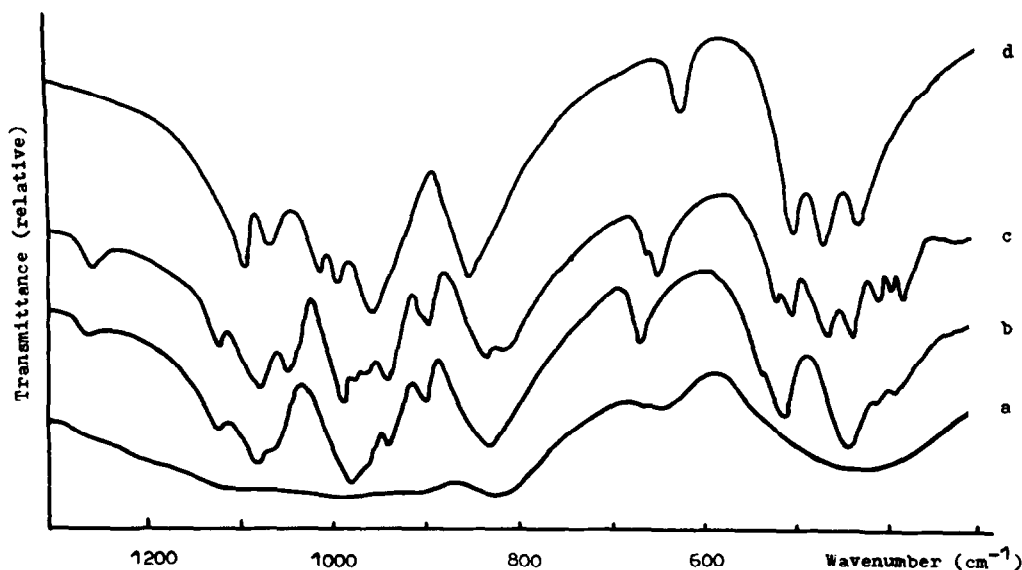


FIG. 4. IR absorption spectra of $2ZnO \cdot P_2O_5$ glass (a), x (b), y (c) phases, and α - $Zn_2P_2O_7$ (d).

The IR spectra of crystalline x and y phases (Figs. 4b and 4c) differ significantly from the α - $Zn_2P_2O_7$ (Fig. 4d) spectrum, but they are rather similar to each other. The difference consists in the number of absorption bands and in the presence of high-frequency bands with values of about 1360 and 1220 cm^{-1} in the spectra of x and y phases. Based on the IR spectra of x and y phases and on their comparison with spectra of the other compounds, one can assume that mixed anionic groups of the $[P_3O_{10}] \cdot [PO_4]$ -type formally corresponding to the $[P_2O_7]$ pyro-group are present in the structures of those phases. This is possible due to the tendency toward condensation typical of phosphates, but this assumption needs structural investigation.

CONCLUSIONS

For $Zn_2P_2O_7$ along with the two known polymorphous modifications with monoclinic structure (α and β), we obtained 2 new metastable modifications which we called x and y . They form in the course of crystallization

of the $2ZnO \cdot P_2O_5$ glass and transform into each other through a monotropic phase transition according to the scheme $\text{glass} \rightarrow x \rightarrow y \rightarrow \beta$ - $Zn_2P_2O_7$.

X-ray, IR—spectroscopic, and crystal-optical characteristics of these phases have been determined. The temperature-concentrational limits of x and y phases have been found.

ACKNOWLEDGMENT

This work was conducted with the financial support of Corning Incorporated.

REFERENCES

1. F. L. Katnack and F. A. Hummel, *J. Electrochem. Soc.* **105**(3), 125–133 (1958).
2. B. E. Robertson and C. Calvo, *J. Solid State Chem.* **1**(2), 120–133 (1970).
3. C. Calvo, *Can. J. Chem.* **43**(5), 1147–1153 (1965).
4. A. N. Lazarev, T. F. Tenisheva, and M. A. Petrova *Izv. Akad. Nauk. SSSR. Neorg. Mater.* **1**(8), 1379–1381 (1965).