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MELTING TEMPERATURES, CONDITIONS, AND MECHANISMUS OF CYCLO-TETRAPHOSPHATES OF BIVALENT METALS

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ABSTRACT

Differential thermal analysis has been used to follow melting of cyclotetraphosphates of divalent metals. The melting is congruent or non-congruent depending on atmosphere humidity in the sample. Products of the non-congruent melting can be transformed into the original cyclo-tetraphosphates by repeated heating. This paper describes the processes taking place during melting of c-$Zn_2P_4O_{12}$ and c-$Cd_2P_4O_{12}$. The results concerning cyclo-tetraphosphates of other metals are presented in the form of a poster.

INTRODUCTION

Literature data on the problem investigated are incomplete and non-uniform. Melting of cyclo-tetraphosphates of divalent metals is usually described as congruent, sometimes as non-congruent prosesses without giving more detailed data (ref.1).Sometimes the changes taking place during melting of these compounds are only described as modification changes (ref.2,4). Our previous report (ref.3) showed that dicobalt cyclo-tetraphosphate undèrgoes congruent melting in vacuum, whereas in atmosphere containing at least small humidity content the process is non-congruent. The glassy product of non-congruent melting gives back the crystalline cyclo-tetraphosphate on repeated heating. A hypothesis has been proposed that the process is connected by binding (release) of small water amounts into molecules of the condensed phosphates.

MEASURING METHODS

The cyclo-tetraphosphates of Zn(II) and Cd(II) were prepared in our laboratory and purified by acid extraction (ref.5). The DTA measurements were carried out by means of a High-Temperature Differential Thermal Analyzer - VDTA 8 M2 (system "Kiev" constructed by the Institute of Metal Physics of the Academy of Sciences of the Ukrainian S.S.R). The atmosphere in the chamber of the apparatus consisted of either dry or wet helium (0°1 MPa He contained about 2 mg water vapour per 1 dm^3 He).

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Weight changes accompanying the calcination of the samples were followed by thermogravimetry using a Derivatograph Q-1500 apparatus (MOM Budapest, system F.Paulik, J.Paulik, L.Erdey) in the atmosphere of wet argon.

The products of the thermal analyses were submitted to TLC, X-ray diffraction analysis, and IR spectroscopy, and the processes accompanying the calcination were followed visually by means of high-temperature microscopy.

RESULTS AND DISCUSSION

The DTA of Zn(II) and Cd(II) cyclo-tetraphosphates measured under dry He showed distinct exothermic effects of their melting: this occured at 810°C with c-$Zn_2P_4O_{12}$ in accordance with ref.2, but the melting of c-$Cd_2P_4O_{12}$ took place at 800°C, i.e. more than 100°C lower than the value given in ref.2. In the case of c-$Zn_2P_4O_{12}$ was also noticed at 680°C an endothermic effect of irreversible modification change of α_1-modification to α_2-cyclo-tetraphosphate (ref. 4). The DTA of cooling exhibited the corresponding exothermic effects of solidification of the melts of cyclo-tetraphosphates. Repeated DTA of heating and cooling of the same sample showed the respective effect at the same temperatures and in the same extent. The above-mentioned instrumental analytical methods (IAM) proved that the samples after repeated DTA contained the microcrystalline cyclo-tetraphosphates only. Hence, these substances only undergo congruent melting at these conditions.

Figure 1 gives the DTA curves of c-$Zn_2P_4O_{12}$ and c-$Cd_2P_4O_{12}$ in the atmosphere of wet He. The melting takes place at the same temperatures as in the dry atmosphere. However the endothermic effects are somewhat higher. The cooled samples were glassy products. Therefore, practically no effects were observed which would correspond to their solidification during the DTA cooling. The IAM's proved their being composed of molecules of higher linear phosphates and having non-crystalline amorphous character. Ending of there chains (and, hence, their existence) is enabled just by the water molecules present in the atmosphere of the chamber - $/Zn(PO_3)_2/_n.H_2O$, $/Cd(PO_3)_2/_n.H_2O$. Repeated heating of the Cd- and Zn-glasses showed exothermic effects at 600 and 560°C, resp., the latter being less distinct. The IAM's showed that the effects correspond to crystallization of the glasses with formation of the original cyclo-tetraphosphates and with release of the end groups of water molecules

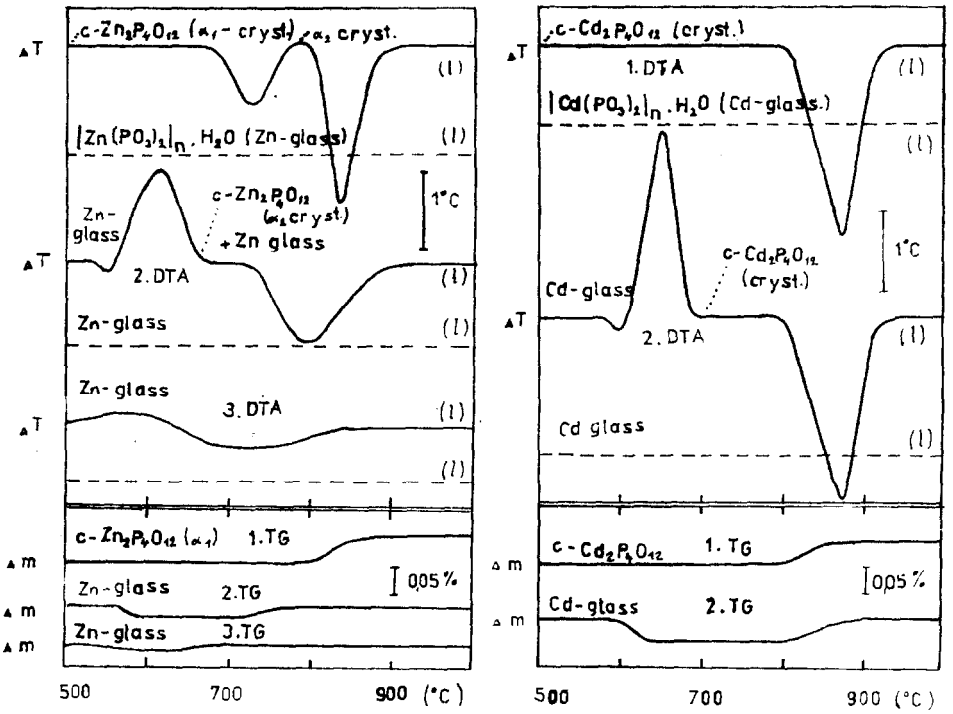

Fig.1. The DTA and TG curves of $c\text{-}Zn_2P_4O_{12}$ and $c\text{-}Cd_2P_4O_{12}$ in the atmosphere (0°1 MPa) of the wet helium (DTA) and wet argon (TG)
DTA-VDTA 8M2 apparatus (system"Kiev"), the heating (cooling) rate 40°C.min^{-1}, the sample weight 100 mg, standard α-Al_2O_3, Mo crucible
TG-Derivatograph Q-1500 apparatus, the heating rate 200C.min^{-1}, the sample weight 2000 mg, sens. of the balance TG 20 mg, Pt crucible.

(the crystalization is only partial with the Zn product - by the formation of α_2-modification $c\text{-}Zn_2P_4O_{12}$). The cyclo-tetraphosphates formed again melt when heated to higher temperatures, which takes place at the same temperature and with the same effect as with the original sample in the case of $Cd_2P_4O_{12}$: hence, the transformations can be considered reversible. With the Zn product the melting effect is smaller and is shifted to lower temperatures. Hence, the melting concerns the eutectic mixture $c\text{-}Zn_2P_4O_{12}$ - $/Zn(PO_3)_2/_n . H_2O$. Repeated heating and cooling processes cause the glass component of the mixture to increase and the effects corresponding to crystallization and melting to gradually vanish. Nevertheless, the melting of the product still takes place, but it is observed at gradually decreasing temperatures - as it was confirmed by observation by means of the high-temperature microscopy.

Participation of water in the process mentioned was confirmed by TG (Fig.1). A weight decrease was recorded during recrystallization of large samples at high sensitivity of TG (transformation of the glasses into cyclo-tetraphosphate). For the Cd product this decrease was 0°4% which corresponds to $n > 80$ in the formula $/Cd(PO_3)_2/_n.H_2O$. Melting of the cyclo-tetraphosphates in wet atmosphere was accompanied by comparable increases of the sample weight corresponding to formation of higher linear phosphates. The weight change was 0°3% with the Zn product whose transformation is not quantitative.(The corresponding weight change was decreased in the same way as the proportion of the product decreased which underwent the transformation on repeated heating and cooling).

CONCLUSION

Melting of $c\text{-}Zn_2P_4O_{12}$ and $c\text{-}Cd_2P_4O_{12}$ in dry atmosphere is congruent at 810 and 800°C, resp. In the case of $c\text{-}Zn_2P_4O_{12}$ undergoes extra irreversible modification change at 680°C. The folowing process take place in wet atmosphere :

$$c\text{-}Cd_2P_4O_{12}(cryst.) \xrightarrow[1/nH_2O]{800^\circ C} \frac{1}{n}/Cd(PO_3)_2/_n.H_2O_{(\ell)} \xrightarrow{840\div25^\circ C}$$

$$\rightarrow \frac{1}{n}/Cd(PO_3)_2/_n.H_2O(glass) \xrightarrow[-1/nH_2O]{600^\circ C} c\text{-}Cd_2P_4O_{12}(cryst.)$$

$$c\text{-}Zn_2P_4O_{12}(\alpha_1\text{-}cr.) \xrightarrow{680^\circ C} c\text{-}Zn_2P_4O_{12}(\alpha_2\text{-}cr.) \xrightarrow[1/nH_2O]{810^\circ C} \frac{1}{n}/Zn(PO_3)_2/_n.H_2O_{(\ell)}$$

$$\xrightarrow{810\div25^\circ C} Zn\text{-}glass \xrightarrow[-x/nH_2O]{560^\circ C} x/c\text{-}Zn_2P_4O_{12}(\alpha_2\text{-}cr.)/ + \frac{1-x}{n}/Zn(PO_3)_2/_n.H_2O_{(glass)}$$

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