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POLYMORPHIC TRANSITIONS OF SODIUM - MAGNESIUM TRIMETAPHOSPHATE $NaMg(PO_3)_3$

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The existance of the compound $NaMg(PO_3)_3$, which is formed in the binary system $NaPO_3$-$Mg(PO_3)_2$ at the molar ratio of initial metaphosphates 1:1, has been confirmed. The polymorphism and the way of the formation of this compound have been examined.

There is the ternary compound $NaMg(PO_3)_3$ from a group of isomorphic compounds of $NaM^{II}(PO_3)_3$ type (where M^{II} = Ca, Cd, Mg, Zn, Co and Mn) which crystallize in a hexagonal system [1-4], in the binary system sodium metaphosphate $NaPO_3$ - magnesium metaphosphate $Mg(PO_3)_2$. Literature reports on the $NaMg(PO_3)_3$ compound report only its formation and they are different. There is however no information about phase transitions of this compound. We found it necessary to verify the $NaPO_3$ - $Mg(PO_3)_2$ system and to supplement the existing data concerning the $NaMg(PO_3)_3$ compound.

Experimental

In our investigations we used the following commercial reagents: $MgHPO_4 \cdot 3H_2O$ p.a. (Belgium), $NaH_2PO_4 \cdot H_2O$ p.a. (POCh) and 85% H_3PO_4 p.a. (Xenon). We prepared $NaPO_3$, $Mg_2P_2O_7$ and $Mg(PO_3)_2$ in this laboratory. Sodium metaphosphate was produced from $NaH_2PO_4.H_2O$ p.a. by sintering at 450° for 1 h. Magnesium metaphosphate $Mg(PO_3)_2$ was produced from magnesium pyrophosphate $Mg_2P_2O_7$ by treating it with 85% phosphoric acid p.a. with 12% excess. The filtered precipitate was dried at 120° and then heated for 1 h. Magnesium diphosphate $Mg_2P_2O_7$ was synthesized from magnesium hydrogen orthophosphate $MgHPO_4 \cdot 3H_2O$p.a. by sintering at 800° for 1 h.

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Test samples were prepared from $NaPO_3$ and $Mg(PO_3)_2$. The investigations were performed by thermal, microscopic in the reflected light and X-ray analyses. Thermal analysis during heating of 250-500 mg samples was carried out in a derivatograph (MOM, Hungary) under air and argon over the temperature range 20-1500°. The heating rate was 10 deg/min. Standard substance was Al_2O_3. X-ray examinations were performed by powder method in a Guinier camera on a diffractometer HZG-4 by using CuK_α radiation.

In order to identify the polymorphic transitions of the $NaMg(PO_3)_2$ compound the X-ray high-temperature (GPWT-1500 type) unit mounted on a diffractometer (DRON 2,5) was used. The speed of the goniometer was 1/4°-2Θ/min.

Results

Examinations of the system $NaPO_3$-$Mg(PO_3)_2$, which were carried out in this laboratory, confirmed the existence of the compound $NaMg(PO_3)_3$. It was found to melt peritectically according to the reaction: $NaMg(PO_3)_3$ = Lp + $Mg(PO_3)_2$. Figure 1 presents DTA curves of samples from the $NaPO_3$ -$Mg(PO_3)_2$ system with compositions: a) 20 wt.% of $NaPO_3$ - 80 wt.% of $Mg(PO_3)_2$, b) $NaMg(PO_3)_3$ and c) 40 wt.% of $NaPO_3$ - 60 wt.% of $Mg(PO_3)_2$. There are four endothermic effects at: 609, 910, 942 and 980° on DTA curves of the compound $NaMg(PO_3)_3$ which was both molten and sintered for a long time at 900°. The effect at 609° is weak and results from the polymorphic transition of pure compound $NaMg(PO_3)_3$. In neighbouring samples (Fig. 1 curves a and c) this transition is characterized by two thermal effects following one after the other and shifted towards lower temperatures. Therefore, it was concluded that in samples: richer (Fig. 1 curve a) and leaner (Fig. 1 curve c) in $Mg(PO_3)_2$ than the discussed mixed metaphosphate, the polymorphic transition proceeds over the temperature range 550-600°.

At higher temperatures, in the interval 900-950°, on DTA curves of heating, two thermal effects appear and they follow one after the other. They can result from a peritectic reaction proceeding over the temperature range 910-942°. However, the effect at 910° may conceivably have been corresponded to the other, higher thermal polymorphic transition of the compound $NaMg(PO_3)_3$, and the effect at 942° may have been connected with a peritectic reaction of forming the compound $NaMg(PO_3)_3$. As results form Fig. 1 curves a and c, the above discussed thermal effects are also observed

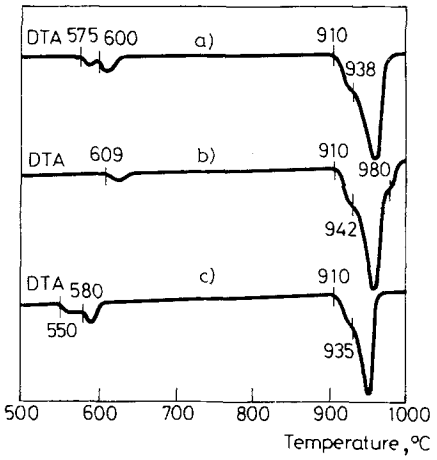

Fig. 1 DTA curves of a) 20% $NaPO_3$; 80% $Mg(PO_3)_2$, b) $NaMg(PO_3)_3$, c) 40% $NaPO_3$; 60% $Mg(PO_3)_2$

in samples with compositions similar to the composition of the $NaMg(PO_3)_3$ compound. The fourth effect observed on DTA curves (Fig. 1 curve b) at 980° is connected with the melting of sample. The authors tried to qualify the character of an effect at 910° univocally. Therefore, high-temperature X-ray examinations of the compound $NaMg(PO_3)_3$ were performed. Apart from those investigations, preparations were sintered and refrigerated from different temperatures. Powder X-ray analysis showed that there is only a low-temperature modification in the obtained sinter. High temperature investigations of the compound $NaMg(PO_3)_3$ did not specify the character of an effect at 910° precisely, because of the small interval of temperature (910-942°) and poor precision of instruments. The obtained results bring to conclusion that the polymorphic transition of $NaMg(PO_3)_3$ at 609° proceeds easily and quickly, therefore the high-temperature modification can not be stabilized at room temperature by refrigeration. It was possible to determine the most favourable conditions of the synthesis of $NaMg(PO_3)_3$ by the correlation of used research methods.

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Zusammenfassung — Es wurde die Existenz der im binären System $NaPO_3$-$Mg(PO_3)_2$ bei einem 1:1 Molverhältnis der Ausgangsmetaphosphate gebildeten Verbindung $NaMg(PO_3)_3$ nachgewiesen. Außerdem wurde die Polymorphie und der Entstehungsweg dieser Verbindung untersucht.