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Calorimetric Investigation of Divalent Metal Diphosphates

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CALORIMETRIC INVESTIGATION OF DIVALENT METAL DIPHOSPHATES

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The heat capacity of Mg, Ca, Sr, Ba, Zn, Co, Ni and Cu diphosphates was studied with a differential scanning calorimeter DSC 111 "SETARAM". Step heating program was used.

Alkali-earth metal diphosphates were synthesized by dehydrating MeHPO_4 . $\text{Mg}_2\text{P}_2\text{O}_7$ and $\text{Zn}_2\text{P}_2\text{O}_7$ were prepared according to standard analytical procedure from MeNH_4PO_4 . For $\text{Co}_2\text{P}_2\text{O}_7$, $\text{Ni}_2\text{P}_2\text{O}_7$ and $\text{Cu}_2\text{P}_2\text{O}_7$ solid-state reactions between MeO and $(\text{NH}_4)_2\text{HPO}_4$ or $\text{NH}_4\text{H}_2\text{PO}_4$ were used. The samples were identified by chemical analysis, x-ray diffraction and DTA.

The heat capacity curves of $\text{Mg}_2\text{P}_2\text{O}_7$, $\text{Zn}_2\text{P}_2\text{O}_7$, $\text{Co}_2\text{P}_2\text{O}_7$, $\text{Ni}_2\text{P}_2\text{O}_7$ and $\text{Cu}_2\text{P}_2\text{O}_7$ exhibit λ -type anomalies which are attributed to $\alpha \rightarrow \beta$ transition in diphosphates accompanied by the change in crystal structures [1]. The transition entropies show that $\alpha \rightarrow \beta$ transformations in $\text{Mg}_2\text{P}_2\text{O}_7$, $\text{Zn}_2\text{P}_2\text{O}_7$, $\text{Co}_2\text{P}_2\text{O}_7$ and $\text{Ni}_2\text{P}_2\text{O}_7$ are of order-disorder type, the number of equilibrium states in β -phase being twice ($\Delta_{\text{tr}}S = R\ln 2$) as much in α -phase. The exception is $\text{Cu}_2\text{P}_2\text{O}_7$ for which transition is accompanied by the change of only one parameter of the monoclinic cell.

The temperature intervals and transition enthalpies of $\text{Ca}_2\text{P}_2\text{O}_7$, $\text{Sr}_2\text{P}_2\text{O}_7$, and high temperature irreversible polymorphic transformations of $\text{Ba}_2\text{P}_2\text{O}_7$ were refined.

1) C.Calvo, Bull. Soc. Chim. France, N 4, p. 1744 (1968).