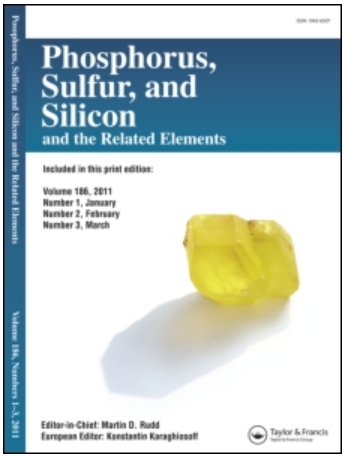

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Calorimetric Investigation of Divalent Metal Diphosphates

G. A. Sharpataya[a]; I. D. Sokolova[a]; Z. P. Ozerova[a]
[a] Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Moscow, USSR

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CALORIMETRIC INVESTIGATION OF DIVALENT METAL DIPHOSPHATES

G.A.SHARPATAYA, I.D.SOKOLOVA, and Z.P.OZEROVA
Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Leninsky prosp. 31, Moscow 117907, USSR

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.

Alkaly-earth metal diphosphates were synthesized by dehydrating $MeHPO_4$. $Mg_2P_2O_7$ and $Zn_2P_2O_7$ were prepared according to standard analytical procedure from $MeNH_4PO_4$. For $Co_2P_2O_7$, $Ni_2P_2O_7$ and $Cu_2P_2O_7$ solid-state reactions between MeO and $(NH_4)_2HPO_4$ or $NH_4H_2PO_4$ were used. The samples were identified by chemical analysis, x-ray diffraction and DTA.

The heat capacity curves of $Mg_2P_2O_7$, $Zn_2P_2O_7$, $Co_2P_2O_7$, $Ni_2P_2O_7$ and $Cu_2P_2O_7$ 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 $Mg_2P_2O_7$, $Zn_2P_2O_7$, $Co_2P_2O_7$ and $Ni_2P_2O_7$ are of order-disorder type, the number of equilibrium states in β-phase being twice ($\Delta_{tr}S = R\ln 2$) as much in α-phase. The exception is $Cu_2P_2O_7$ for which transition is accompanied by the change of only one parameter of the monoclinic cell.

The temperature intervals and transition enthalpies of $Ca_2P_2O_7$, $Sr_2P_2O_7$, and high temperature irreversible polymorphic transformations of $Ba_2P_2O_7$ were refined.

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