Study of the phase behaviour of KH$_2$PO$_4$ with Fe$_2$O$_3$ nanopowder

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The Differential Scanning Calorimetry DSC, Thermogravimetric Analysis TGA and Impedance Spectroscopy Technique were used in this work to study the behaviour of the KH$_2$PO$_4$ with Fe$_2$O$_3$ nanopowders, analyzing their phase behaviour in temperature ranges above room temperature up to 550 K. The KDP polycrystalline samples with Fe$_2$O$_3$ nanopowders show three well defined endothermic peaks before their complete decomposition at higher temperatures, and the TGA results show a weight loss with increasing temperature, starting at the transition point of this peak. These results show a dehydration process before 475 K possibly due to structural changes in the samples.

Keywords: KDP; phase transition; crystal structure.

In this work, we used a mechanical mixing technique to obtain composites with various Fe$_2$O$_3$ (particle size of 10 nm) concentrations in order to study the influence of Fe$_2$O$_3$ on the physical properties of (KH$_2$PO$_4$)$_{1-x}$(Fe$_2$O$_3$)$_x$ system.

2. Experimental

Powder of KH$_2$PO$_4$ (extra pure, Merck) and Fe$_2$O$_3$ (sigma Aldrich) particle size of 10 nm were used as starting materials. The pure salt and the Fe$_2$O$_3$ were weighed in stoichiometric amounts and then were mixed and ground in a mortar during 30 minutes, followed by heating at 320 K during 12 hours. The TGA and DSC analyses were performed using a TA Instruments TGA and MDSC 2920 analyzers, respectively. Both the TGA and DSC measurements were done under a dry nitrogen atmosphere with a flow of 20 ml/min. High-precision ac calorimetric measurements were done with a homemade set-up [9].

3. Results and discussion

Figure 1 shows the DSC heating curves for all the studied (KH$_2$PO$_4$)$_{1-x}$(Fe$_2$O$_3$)$_x$ system samples, recorded at a scanning rate of 5K/min. A DSC well defined endothermic peak after 475 K is observed, which corresponds to the melting point of the material.
The temperature dependence of the sample’s weight loss is plotted in Figure 2 for several samples that were heated at a rate of 5°K/min. It is clearly seen that only the irregular high-temperature DSC peak (Fig. 1) is correlated with a rapid decrease in weight loss in the corresponding sample.

Our results show strong evidence that the dispersed experimental results previously reported for high-temperature phase phenomena observed in KH$_2$PO$_4$ were due to different hydrogen bonds behaviours, which are very sensitive to the thermal history of the sample.

4. Conclusion

The high temperature phase transition occurring upon heating K$_2$HPO$_4$ above room temperature is found to be very sensitive to the degree of disorder induced in its hydrogen bond configuration by the addition of mechanical (grinding) Fe$_2$O$_3$ nanopowders. Strong evidence is found that the controversy concerning the nature of the HTPT at about 475 K was due to sample preparation, such that in well formed KH$_2$PO$_4$, a structural phase transition occurs before its thermal dehydroxylation at higher temperatures.

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1. See, for example, *Ferroelectrics* 71-72 (1987) (Special Issue on KDP Type Ferro- and Antiferroelectrics).
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