5.1 Introduction

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) or differential scanning calorimetry (DSC) techniques were used by many scientists for the characterisation of nanophase materials.\textsuperscript{1-6} The phase changes occurred in nanocrystalline ZrO$_2$ has been studied using TG/DTA.\textsuperscript{1} Earlier studies on ZrO$_2$ have shown that the crystallisation temperature is dependent on the method and conditions of preparation.\textsuperscript{2} For WO$_3$ microcrystals, the phase transition studies identified a new phase at low temperature.\textsuperscript{5} Grain growth process in nanophase materials was studied using DSC technique.\textsuperscript{3,4} The heat generated during the growth of nanometer sized grains is large enough (due to the high density of interfaces) to be detected by the present-day calorimeters. It is estimated that the heat energy released can be as much as 339 mJ for a grain size of 5nm, while it decreases to 0.7 mJ for a 5$\mu$m grain size. DSC studies on nanostructured Ni foils have shown an additional exothermic peak at 600K which is explained on the basis of grain growth process.\textsuperscript{7} Since the free energy of nanoparticles is higher than that of a coarser grained material, their microstructure and atomic configuration change when exposed to high temperature. These changes are usually accompanied by an exothermic or endothermic peak.\textsuperscript{8}

Nanosized oxide, phosphate, titanate, etc. ceramic powders have been prepared from precursor powders by Pramanik et al.\textsuperscript{9,10} The thermal decomposition behaviour of these systems with temperature and the nanoparticle phase formation from the precursor powder was studied using TG/DTA.\textsuperscript{9,10} Thermal studies of the precursor powders provide data for a
proper calcination profile and to establish a correlation between exothermic heat released and phase formation of the final product. In the sol-gel method of nanoparticle preparation of Co-Bi ferrite and Ni ferrite, the thermal decomposition characteristic of the gel system with temperature was studied using TG/DTA. Thus it is found that nanoparticle phase formation and particle characterisation can be studied with thermal analysis.

In the present study, TGA and DTA analysis of nanoparticles of Ag₃PO₄ and ZnFe₂O₄ was carried out to know about the phase change and grain growth process during annealing of the particles. The formation of FePO₄ nanoparticles from the precursor powder and the phase change occurred during heat treatment of the nanoparticles have been studied using TG and DTA.

5.2 Experimental

Nanoparticles of Ag₃PO₄ (0.01M) and ZnFe₂O₄ (0.1M) were prepared by chemical routes as described in 3.2.1 and 3.2.3 of Chapter 3. Thermal analysis were performed on a TG/DTA instrument, 92-18 SETARAM as described in section 2.3.4 of chapter 2. FePO₄ (1M) nanoparticles were prepared from precursor solution as described in section 3.2.2 of Chapter 3. Thermal analysis of the precursor powder was carried out using TG/DTA instrument in the temperature range 50-850°C. All measurements were carried out in Argon (inert) atmosphere.

5.3 Results and Discussion

5.3.1 Ag₃PO₄ Nanoparticles

Fig 5.1 shows the TGA and DTA traces of nanoparticles of Ag₃PO₄. The TGA trace shows no mass loss of the sample during heat treatment. But the DTA curve shows two endothermic peaks one at 520°C and the other at 559°C. Since there is no mass loss in the TGA curve, the endothermic peak in the DTA curve cannot be attributed to any decomposition of Ag₃PO₄. The peak
at $520^\circ C$ may be due to the melting of nanoparticle $\text{Ag}_3\text{PO}_4$. The theoretical value of the melting point of bulk $\text{Ag}_3\text{PO}_4$ is $849^\circ C$.\textsuperscript{13} In nanoparticle $\text{Ag}_3\text{PO}_4$, the value of melting point may have lowered due to reduced coordination number of the surface atoms, which greatly increases the surface energy so that atom diffusion occurs at relatively low temperature. Moreover it was found that the melting point of gold nanoparticle of size $2.5\text{nm}$ is $700K$ whereas that of bulk is $1300K$.\textsuperscript{14} It is also reported that the melting point of $1.2\text{nm} \text{CdS}$ is $600K$ whereas that of bulk $\text{CdS}$ is $1680K$.\textsuperscript{15} Therefore it can be inferred that the melting point may have lowered.

The second peak in the DTA curve at $559^\circ C$ may be due to the melting of silver pyrophosphate. It is reported that if $\text{Ag}_3\text{PO}_4$ is kept fused for a long time, it is partly reduced and becomes more fusible, owing to the formation of pyrophosphate.\textsuperscript{13} The theoretical value of the melting point of pyrophosphate is $585^\circ C$. Therefore the endothermic peak at $520^\circ C$ can be attributed to the melting point of nanoparticle $\text{Ag}_3\text{PO}_4$ and that at $559^\circ C$ to silver pyrophosphate.

![Fig. 5.1: TGA and DTA traces of nanoparticles $\text{Ag}_3\text{PO}_4$ (0.01M)](image-url)
5.3.2 FePO₄ Nanoparticles

Fig 5.2 shows the TGA and DTA curves of the precursor powder, which was formed by the flame pyrolysis of precursor solution as described in section 3.2.2. A weight loss of 45% was noted in the TGA trace over the temperature region 50-650°C.

There are three endothermic peaks observed in the DTA curve. The peak at 125°C is due to water loss and the peak at 560°C is due to decomposition of the precursor powder forming crystalline pinkish white ferric phosphate (α-FePO₄). The small endothermic peak at 712°C is due to structural transformation, i.e., α to β transition without any mass loss. Above 650°C there is no considerable weight loss in TGA curve. For bulk FePO₄ crystals the α to β transition temperature reported is 707°C. In the case of iron phosphate obtained from spontaneous precipitation from aqueous solution, the α to β transition temperature is 716°C. In the present study, the α to β transition temperature of nanoparticle FePO₄ is found to be different from that of bulk. The onset value is 712°C and the peak value is 725°C as seen from fig 5.2. This change in temperature may be due to size effect of small particles. The surface to volume ratio of atoms is large in nanoparticles and these atoms have significant influence on the thermal properties of nanostructured materials. The interfacial energy associated with the interface regions in nanoparticles may influence phase transitions in nanophase materials. Hence the phase transitions in nanoparticles may be modified from that of bulk materials.
5.3.3 ZnFe$_2$O$_4$ Nanoparticles

Fig 5.3 shows the TGA and DTA curve of ZnFe$_2$O$_4$ (0.1M) nanoparticles. From TGA curve a weight loss of 20% was observed over the temperature region 50-250$^\circ$C. In this region there is a large endothermic peak in the DTA curve. This may be attributed to the loss of residual water in the powder. From 250$^\circ$C onwards there is a small weight loss $\approx$ 1.5% up to 600$^\circ$C. The endothermic peak starts at the onset temperature of 386$^\circ$C. This corresponds to the crystallization of the spinel phase of ZnFe$_2$O$_4$ nanoparticles.\textsuperscript{19,20} In between 250$^\circ$C and 386$^\circ$C there are very small exothermic peaks which may be attributed to the different arrangement of atoms towards the final spinel-type structure.\textsuperscript{19,20} Again from 450-600$^\circ$C very small exothermic peaks can be observed, which may be due to the starting of grain growth process. At the onset temperature of 685$^\circ$C, a prominent exothermic peak is observed without any mass loss. This peak may be attributed to the recrystallisation and grain growth of ZnFe$_2$O$_4$ nanoparticles.\textsuperscript{7,19} The crystalline phases of the calcined particles were identified and the particle size at each temperature was calculated using XRD pattern shown in fig 3.13 of Chapter 3.
The particle size changed from 6nm to 28nm when the temperature increased from 300°C to 850°C. In nanostructured Ni foils the observed additional exothermic peak was due to grain growth process. Similarly in the present study of ZnFe₂O₄ nanoparticles, the large exothermic peak in the DTA curve may be due to grain growth and recrystallisation of spinel phase. The microstructure and atomic configuration of nanoparticles change when exposed to high temperature since the free energy of these particles is higher than that of bulk crystalline counterpart.

Fig. 5.3: TGA and DTA traces of nanoparticle ZnFe₂O₄ (0.01M)

5.4 Conclusion

High temperature phase changes, grain-growth process and structural behaviour of nanoparticles of Ag₃PO₄, FePO₄ and ZnFe₂O₄ were studied using thermogravimetric analysis. The results were studied based on the factors, which were originated from finite size effect of the particles. Thermal stability of these nanoparticle compounds was understood from TG/DTA analysis.
5.5 References


