J Therm Anal Calorim (2009) 96:917–921
DOI 10.1007/s10973-009-0068-6

Thermal characteristics of pure and neodymium doped calcium hydrogen phosphate single crystals

Valsamma M. Samuel · N. V. Unnikrishnan · M. A. Ittyachen

Received: 20 March 2008 / Accepted: 8 December 2008 / Published online: 19 June 2009

Abstract Single crystals of pure and neodymium doped calcium hydrogen phosphate were grown in sodium meta silicate gels, by the single diffusion gel method. Platelet and needle shaped crystals were obtained. The grown crystals were characterized by different techniques. The thermal behaviour of the crystals was studied using the thermo analytical techniques, which included TG, DTA, DTG and DSC. These studies reveal that the decomposition of the material occurs in one or more stages. The enthalpy value is also calculated.

Keywords Gel growth · Nd^{3+} doping · Thermal analysis

Introduction

The gel method permits the growth of crystals that are difficult to obtain by conventional methods [1]. High temperature techniques are usually expensive and may not be within the reach of every laboratory. Further more, high temperatures become sources of increased thermal stress, as a result of which the crystals may contain more defects. It is therefore, interesting to develop a low temperature technique for the growth of crystals. A room temperature solution technique, popularly known as the gel technique, has been used by a large number of researchers and a good deal of information pertaining to the scientific data of several crystals is available [2–14]. Very little attention however, has been paid to the growth of rare earth doped phosphates at ambient temperatures using the gel techniques, which is not only very simple but inexpensive as well. Neodymium doped crystals were grown by different methods and their thermal and spectral properties were studied [15, 16]. Rare earth phosphate crystals were also grown by flux method and their crystal structure and thermo chemistry were investigated [17–24].

In this paper we report a method of growing pure and neodymium doped calcium hydrogen phosphate (CHP) crystals by controlled diffusion of chemical reaction in silica gel medium. By preventing convection currents and turbulence, and by maintaining chemical inertness, the gel medium provides a three dimensional structure in which the crystal nuclei are delicately held in position for their formation. The aim of the present work was to investigate the effect of neodymium (Nd^{3+}) ion presence during the crystallization of CHP crystals in gels by studying its thermal characteristics.

Crystal growth technique

A single gel, single tube technique was used to grow single crystals of pure and neodymium doped CHP from a solution containing 1 M calcium chloride for pure and 0.9 M calcium chloride and 0.1 M neodymium nitrate for the latter, which serves as the upper reactant. The method involves incorporating one reactant called the lower reactant into the gelling mixture and later diffusing another reactant called the upper reactant into the gel medium. This leads to a very high super saturation condition initiating the nucleation necessary for the growth of crystals. Silica gel is

V. M. Samuel (✉) · N. V. Unnikrishnan · M. A. Ittyachen
School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam, Kerala 686560, India
e-mail: valsageorge99@yahoo.co.uk

Present Address:
V. M. Samuel
Department of Physics, Catholicate College, Pathanamthitta, Kerala 689645, India

optically transparent and therefore crystals may be observed in any stage of the experiment. Furthermore, unlike other gels, the use of silica gel minimizes the effects due to precipitate–precipitate interaction and crystal impact on the walls of the container. Therefore, silica hydro gel is preferred and is the most common gel used for crystal growth experiments. It is obtained by neutralization of sodium meta silicate. Pure sodium meta silicate solution of relative density 1.03 was prepared. Ortho phosphoric acid of 1 M is added gently to the prepared SMS solution with constant stirring. The pH of the resulting solution is adjusted to be 7. The acidified gel was then poured into the test tube. This gel was allowed to set for the desired gelling time—usually 24 h. To this reset gel the upper reactant was poured slowly along the sides of tube. Nucleation starts immediately. Liesegang ring phenomenon was also observed. After 72 h, small needle typed crystals appeared just below the rings. As time passes, the number and size of crystals increases. It takes about three weeks to complete the growth. The crystals are mostly acicular and platelet shaped with an average size of 20 mm × 5 mm × 1 mm.

The mechanism of reactions leading to the formation of the crystals may explain as follows:

$$CaCl_2 \cdot 2H_2O + H_3PO_4 \rightarrow (CaHPO_4) \cdot 2H_2O + 2HCl$$

The chemical reaction employed for the growth of Nd^{3+} doped CHP dehydrates crystals is the same as above with the substitution of Nd ions in the lattice.

$$CaCl_2 \cdot 2H_2O + Nd(NO_3)_3 \cdot 6H_2O + 2H_3PO_4 \rightarrow Nd{:}(CaHPO_4) \cdot 2H_2O + 2HCL + 3HNO_3 + 6H_2O$$

Thermal analysis

The thermo gravimetric analysis provides a quantitative measurement of any mass changes associated with thermally induced transitions. For example TG can record directly the loss in mass as a function of temperature or time for transitions that involve dehydration or decomposition. TG curves are characteristic of a given compound or material due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges [17–25].

In the present investigation TG, DTA, DTG and DSC were conducted. The thermo gravimetric analysis and differential thermal analysis were performed on powdered samples using a Perkin Elmer Thermal Analyzer. The thermo gram was obtained by heating the sample from room temperature to 900 °C in an atmosphere of nitrogen with a heating rate of 15 °C min^{-1}. Differential scanning calorimetric analysis was performed on a Mettler, Toledo, DSC 822 system with a scanning speed of 10 °C per minute.

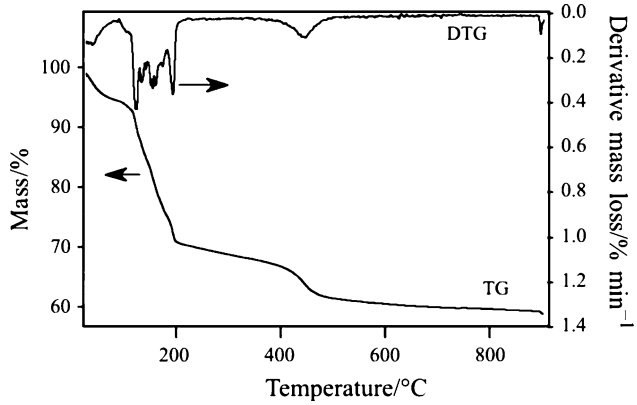

Fig. 1 TG & DTG of CHP

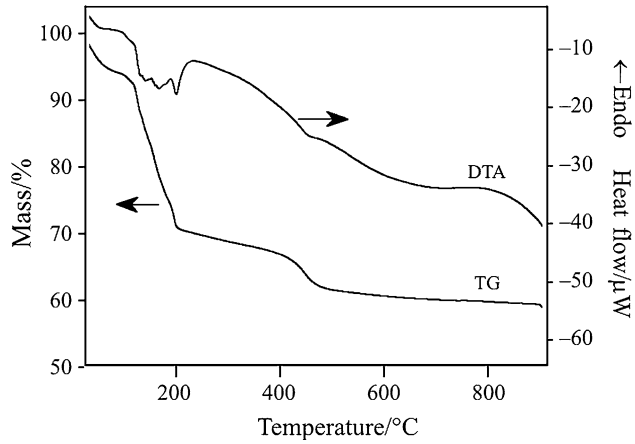

Fig. 2 Heat flow of CHP

Pure calcium hydrogen phosphate (CHP) crystals

The TG & DTG and TG & DTA plots were shown in Figs. 1 and 2, respectively. The TG curve shows the loss of all water molecules in the first step of decomposition, around 200 °C. The loss of water, which is prominent in TG curve, is supported by the first endotherm in DTG curve and which is also prominent in DSC. The sharp downward endothermic peak at the temperature range 350–470 °C corresponds to the decomposition of the sample. The peak temperature 440 °C indicates the temperature at which the reaction is completed. The broad endotherm indicates a slow change in heat capacity. The enthalpy value corresponding to the endothermic peaks are −105.40 and −426.74 mJ. From the figures, it is clear that the crystals decompose into anhydrous crystals at about 200 °C and then slowly decompose into calcium pyrophosphate at about 450 °C. The melting point of calcium pyrophosphate is 1230 °C, therefore it is expected to remain stable up to the end of the analysis i.e. 900 °C. It was found that two water molecules were associated with the crystals. Based on thermo gravimetric analysis and

Table 1 Thermo analytical data of CHP

Sample	Temperature range in °C	Mass% theoretical	Mass% experimental
$CaHPO_4 \cdot 2H_2O$	Room temperature	100	100
$CaHPO_4$	150–210	79.08	79.25
$Ca_2P_2O_7$	350–470	68.62	68.75

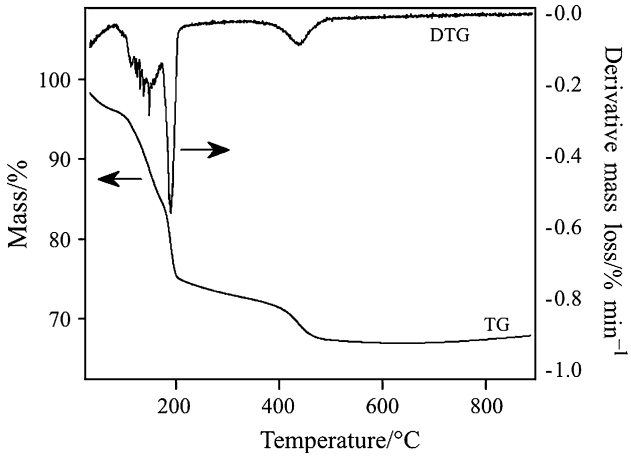

Fig. 3 TG & DTG of Nd:CHP

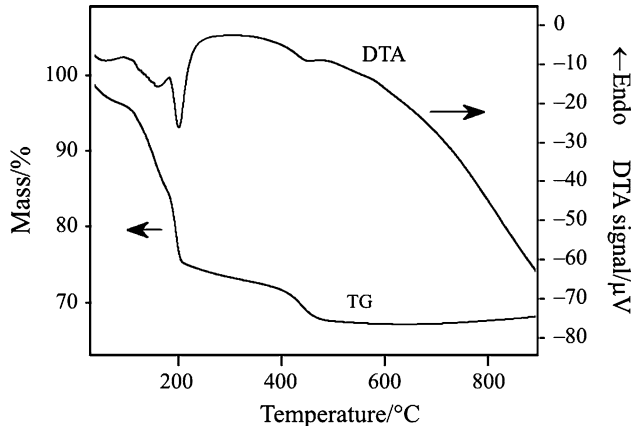

Fig. 4 Heat flow of Nd:CHP

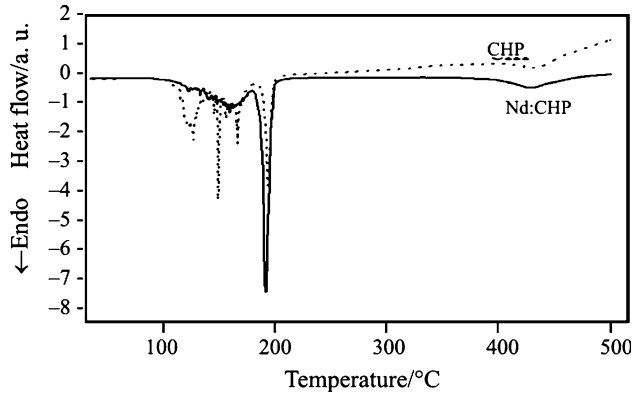

Fig. 5 DSC of CHP & Nd:CHP

differential thermal analysis, the different stages of thermal decomposition of the crystals are as follows, which is in good agreement with the reported values [14].

$$CaHPO_4 \cdot 2H_2O \overset{200^{\circ}C}{\rightarrow} CaHPO_4 + 2H_2O \uparrow$$

$$CaHPO_4 \overset{450^{\circ}C}{\rightarrow} Ca_2P_2O_7 + H_2O \uparrow$$

The thermo analytical data are given in Table 1 along with % theoretical mass loss and experimental mass loss values.

Neodymium doped calcium hydrogen phosphate [Nd:CHP] crystals

The TG & DTG and TG & DTA plots were shown in Figs. 3 and 4, respectively. The DSC plot of CHP& Nd:CHP is shown in Fig. 5. From the figures, it is clear that the crystals decompose into anhydrous crystals at about 190 °C and then slowly decompose into calcium pyrophosphate at about 427 °C. It was found that two water molecules were associated with the crystals. The following chemical reactions are expected to occur during dehydration and decomposition stages.

$$Nd{:}CaHPO_4 \cdot 2H_2O \overset{190^{\circ}C}{\rightarrow} Nd{:}CaHPO_4 + 2H_2O \uparrow$$

$$Nd{:}CaHPO_4O \overset{427^{\circ}C}{\rightarrow} Nd{:}Ca_2P_2O_7 + H_2O \uparrow$$

The theoretically calculated and experimentally observed values of mass% and the corresponding decomposition are given in Table 2. The broad endotherm indicates a slow change in heat capacity. The enthalpy value corresponding to the endothermic peaks are −1371.47 and −479.59 mJ.

Results and discussions

From the TG curves, it is clear that both the materials start decomposing at about 100 °C. The TG curve shows the loss of all water molecules in the first step of decomposition, at about 200 °C in the case of CHP and around 190 °C in the case of Nd:CHP. The loss of water, which is prominent in TG curve, is supported by the first endotherm in DTG curve and which is also prominent in DSC. The

Table 2 Thermo analytical data of Nd:CHP

Sample	Temperature range in °C	Mass% theoretical	Mass% experimental
Nd:$CaHPO_4 \cdot 2H_2O$	Room temperature	100	100
Nd:$CaHPO_4$	150–200	79.08	79
Nd:$Ca_2P_2O_7$	400–480	68.62	68.5

broad downward endothermic peak at the temperature range 395–462 °C corresponds to the decomposition of the sample. The peak temperature 440 °C indicates the temperature at which the reaction is completed in the case of CHP and 427 °C corresponds to Nd:CHP. The broad endotherm indicates a slow change in heat capacity. The enthalpy values corresponding to the endothermic peaks for CHP are −105.40 and −426.74 mJ. The enthalpy value corresponding to the endothermic peaks for Nd:CHP are −1371.47 and −479.59 mJ.

Conclusions

The growth of single crystals of CHP and Nd:CHP was accomplished using single test tube diffusion method. Optimum conditions for growth were worked out. Based on the observations during the growth, the following conclusions can be made.

Gel method is found suitable for growing phosphate crystals. Good quality phosphate single crystals with different morphologies can be grown by gel method. Initial gel pH plays an important role in determining the nature and morphology of the crystals grown. Nucleation control can be achieved by changing a variety of gel parameters such as gel pH, gel density, aging of gel, concentration of feed solutions etc. When neodymium is incorporated no morphological or structural changes take place, but this may be incorporated either by substitution or interstitial ion. Slight changes in the lattice parameters take place when neodymium is incorporated. The above conclusion is confirmed by XRD and other characterization methods.

Based on the observations during the thermal analysis the following conclusions can be made: thermal analysis reveals the decomposition stages of both the crystals. It is found that the decomposition temperature decreases by the substitution of Nd and the enthalpy values also decreases.

Acknowledgements One of the authors (V. M. Samuel) is thankful to the University Grants Commission, Government of India for a fellowship.

References

1. Henisch HK. Crystal growth in gels. New York: Dover Publications, Inc; 1996.
2. Shittole SJ, Saraf KB. Growth and study of some gel grown group II single crystals of iodate. Bull Mater Sci. 2001;24(5):461–8.
3. Shittole SJ, Saraf KB. Growth, structural and microtopographical studies of calcium iodate monohydrate crystals grown in silica gel. Cryst Res Technol. 2002;37(5):440–5.
4. Bhavsar DS, Saraf KB. Morphology of PbI_2 crystals grown by gel method. Cryst Res Technol. 2002;37(1):51–5.
5. Desai CC, Ramana MSV. Nucleation density and electrolytic growth of lead hydrogen phosphate single crystals in silica gels. J Cryst Growth. 1990;102:191–6.
6. Bhat S, Kotru PN. Growth of neodymium heptamolybdate crystals in silica gels at ambient temperatures. Mater Sci Eng B. 1994;23:73–82.
7. Kusumoto H, Kaito T, Yanagiya S, Mori A, Inoue T. Growth of single crystals of $PbBr_2$ in silica gel. J Cryst Growth. 2005;277:536–40.
8. Patel AR, Venkateswara Rao A. Crystal growth in gel media. Bull Mater Sci. 1982;4(5):527–48.
9. Joseph KC, Joshi MJ. The study of different parameters affecting Liesegang rings formation during the growth of calcium hydrogen phosphate dehydrate crystals. Indian J Phys. 2002;76A:159–63.
10. Kijowska R. Ca-substituted europium(III) phosphate monohydrate obtained through crystallization from phosphoric acid solution. J Alloys Comp. 2004;363:138–42.
11. Joshi VS, Joshi MJ. FTIR spectroscopic, thermal and growth morphological studies of calcium hydrogen phosphate dihydrate crystals. Cryst Res Technol. 2003;38:817–21.
12. Ravikumar RVSSN, Chandrasekhar AV, Reddy BJ, Reddy YP, Ikeda K. X-ray powder diffraction, DTA and vibrational studies of $CdNH_4PO_4{\cdot}6H_2O$ crystals. Cryst Res Technol. 2002;37:1127–32.
13. Kijowska R. X-ray diffraction and Ir-absorption characteristics of lanthanide orthophosphates obtained by crystallization from phosphoric acid solution. J Mater Sci. 2003;38:223–8.
14. Kijowska R. Thermal decomposition of lanthanide orthophosphates synthesized through crystallization from phosphoric acid solution. Thermochim Acta. 2003;404:81–8.
15. Zhuang N, Lin Z, Hu Z, Zhang L, Wang G. Crystal growth and spectral properties of Nd^{3+}:$Sr_2La_{0.667}(VO_4)_2$ crystal. J Cryst Growth. 2005;277:32–6.
16. Li X, Lin Z, Zhang L, Wang G. Growth, thermal and spectral properties of Nd^{3+}doped:NaGd $(MoO_4)_2$ crystal. J Cryst Growth. 2006;290:670–3.
17. Dabhi RM, Joshi MJ. Thermal studies of gel grown zinc tartrate spherulites. Indian J Phys. 2002;76A(2):211–3.
18. Denisova TI, Grinenko SB, Kuznetzova LS. Thermal stability of organosilica and their forms modified by ions of copper(II). J Therm Anal Cal. 2006;86(1):97–9.
19. Czakis-Sulikowska D, Radwańska-Doczekalska J, Czylkowska A, Markiewicz M, Broniarczyk A. New complexes of Mn(II), Co(II), Ni(II) and Cu(II) with 2,2′- or 2,4′-bipyridine and formates (synthesis, thermal and other properties). J Therm Anal Cal. 2006;86(2):327–35.
20. Martins TS, Matos JR, Vicentini G, Isolani PC. Synthesis, characterization, spectroscopy and thermal analysis of rare earth picrate complexes with L-leucine. J Therm Anal Cal. 2006;86(2):351–7.

21. Pistofidis N, Vourlias G, Pavlidou E, Chrissafis K, Stergioudis G, Polychroniadis EK, et al. A combined characterization of zinc hot-dip galvanized wireswith DSC, XRD and SEM. J Therm Anal Cal. 2006;86(2):417–22.
22. Abdel-Rehim AM. Thermal and XRD analysis of Egyptian galena. J Therm Anal Cal. 2006;86(1):393–401.
23. Bolbukh YN, Tertykh VA, Gawdzik B. TG and DSC studies of filled porous copolymers. J Therm Anal Cal. 2006;86(1):125–32.
24. Day M, Victoria Nawaby A, Liao X. A DSC study of the crystallization behaviour of polylactic acid and its nanocomposites. J Therm Anal Cal. 2006;86(3):623–9.
25. Wendlandt WWM. Thermal analysis. 3rd ed. NY: Wiley; 1964.