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# Synthesis, characterization and thermal property of $\{Cu_3(PO_4)_2{\cdot}2H_2O; Na_3PO_4; NaHSO_4{\cdot}H_2O\}$

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ABSTRACT

The phosphate compounds of copper and sodium along with sodium hydrogen sulfate monohydrate mixture has been synthesized and characterized with different measurement techniques such as Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA), Fourier Transform Infrared (FT-IR) Spectrometry, C—H—N—S elemental analyzer, Inductively Coupled Plasma -Atomic Emission Spectrometry (ICP-AES), Ultraviolet–Visible and near Infrared (UV–Vis-NIR) Absorption Spectrophotometry and X-ray Powder Diffraction (XRD). The thermal property of this mixture has been studied up to 573 K from 173 K in different thermal cycles with DSC. The specific heat capacity of this mixture has been measured in atmospheric $O_2$ at a rate of 10 K $min^{-1}$ in all cycles. The net specific heat capacity of this mixture is found endothermic in all thermal cycles. So, it can be used as heat storage material as a combination of sensible and latent heat technique.

## 1. Introduction

In many parts of the world, direct solar radiation is considered to be one of the most prospective sources of energy. The researchers are in search of new and renewable energy sources in order to mitigate the energy deficiency. There are different forms of energy sources exist such as mechanical, electrical and thermal. These energy sources can be stored (Sharma et al., 2009). So, one of the options is to develop energy storage devices. These devices are as important as developing new sources of energy. The storage of heat at a temperature level around 400 °C is essential for the continuous production of electricity with solar heat power plants. The materials which are appropriate for this purpose are chemical compounds of metals, metal alloys or intermetallic compounds and metal hydrides (Felderhoff and Bogdanović, 2009; Bogdanović et al., 1990). There are various methods of heat storage such as sensible heat, Latent heat and thermo-chemical (Bogdanović et al., 1990; Bogdanović et al., 2002). Among these methods, the thermal energy is stored in Sensible Heat Storage (SHS) by raising the temperature of solid or liquid. This method utilizes the specific heat capacity and the change in temperature of the material during the process of charging and discharging. Some of the materials used for the storage of sensible heat are listed in Beckmann and Gilli (Beckmann and Gilli, 1984). There are some comparative studies of solar energy storage systems based on the latent heat and sensible heat technique by different researchers as Ghoneim (Ghoneim, 1989). From this study, it was found that latent heat technique is better than sensible heat technique.

Keeping this in mind, the mixture of the phosphate compounds of copper and sodium along with sodium hydrogen sulfate monohydrate has taken into consideration for use as thermal storage material. A number of inorganic metal phosphates are prepared and their structural chemistry is also studied extensively for their potential applications in many fields in recent (Wu et al., 2005; Ouchabi et al., 2016; Onoda and Okumoto, 2011; Onoda et al., 2009; Sekar and Suguna, 2011). Some metal phosphites have been reported for replacing metal phosphate (Rodgers and Harrison, 2000; Harrison et al., 2001; Lin et al., 2004; Gordon and Harrison, 2004). However, none of the phosphate complexes are studied using DSC for evaluation of the thermal property as storage materials.

In this work, the evaluation of thermal storage material is limited to a calorimetric investigation. The objective of this paper is to characterize and study the thermal properties of this mixture for using as thermal storage material.

## 2. Experimental

In a typical synthesis of this salt, the 75 cc solution of $CuSO_4{\cdot}5H_2O$ (0.06 mol) was added in 75 cc solution of $H_3PO_4$ (0.06 mol) with constant stirring under ambient conditions until homogeneous. The above stirred solution was left for 120 h. Then it was neutralised with NaOH. This neutral solution was heated at 323 K for 50 min. It was cooled to room temperature and kept for settle in ambient condition up to 48 h. The suspension was filtered, washed with ethanol and dried in

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desiccators. Highly purify double distilled water was used in all solution preparation. Second distillation was carried out from alkaline $KMnO_4$ using an all-glass distillation apparatus. The DSC of the above dried mixture was performed with Mettler Toledo DSC 822e. The DSC of this mixture was measured at a rate of 10 K/min from 298 K to 573 K and also from 173 K to 303 K in two thermal cycles each. The X-ray crystallography measurement of powder sample was carried out in Bruker AXS D8 Advance. ICP-AES measurement was performed using Thermo Electron IRIS Intrepid II XSP DUO system for Cu, Na, S and P determination. The sample was digested using 10 ml $HNO_3$ of 30%(v/v) and made up to 250 ml using milli-Q water and filtered solution analyzed with ICP-AES system. C—H—N—S measured in Elementar Vario EL III. The IR spectrum was taken with Thermo Nicolet, Avatar 370. Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) for the mixture was performed using Perkin Elmer STA 6000 thermal analyzer at the temperature range of 313 K–999.6 K. The UV–Vis-NIR Absorption Spectroscopy was carried out in Varian, Cary 5000 from wavelength range 224–1976 nm at room temperature in bulk solid state of the mixture. All measurements were performed in ST&IC, Cochin University of Science and Technology, Cochin.

## 3. Results

### 3.1. FT-IR analysis

The FT-IR spectrum is displayed in Fig. 1. The vibrational bands of phosphate anion are observed at 1048, 991 and 560 $cm^{-1}$. These bands are assigned to the asymmetry stretching ($\upsilon_{as}$), symmetry stretching ($\upsilon_s$) and bending ($\delta_s$) of $PO_4^{3-}$ ion respectively. These bands are assigned according to the literature of Onmura et al. and Abadzhieva et al. (Onmura et al., 1998; Abadzhieva et al., 1994). The bands at 1640 and 3373 $cm^{-1}$ are assigned to water bending and asymmetry stretching vibration of O—H, ($H_2O$), respectively (Periasamy et al., 2009). This indicates the presence of crystalline hydrate. The vibrational bands below 700 $cm^{-1}$ are assigned to the symmetric and asymmetric bending of $SO_4^{2-}$ group. Here, the symmetric ($\delta_s$) and asymmetric bending ($\delta_{as}$) of $SO_4^{2-}$ group is assigned to 390 and 620 $cm^{-1}$ respectively (Periasamy et al., 2009). The asymmetric stretching ($\upsilon_{as}$) of $SO_4^{2-}$ group is assigned to 1120 $cm^{-1}$. This band appears as a shoulder to 1048 $cm^{-1}$ band. (Periasamy et al., 2009).

**Table 1**
Crystal data and experimental details of the title mixture.

| | |
|---|---|
| Molecular formula | $\{Cu_3(PO_4)_2{\cdot}2H_2O; NaHSO_4{\cdot}H_2O; Na_3PO_4\}$ |
| Molecular mass | 718.62 gm |
| Scan axis | Gonio |
| Start position [°2Th.] | 3.0000 |
| End position [°2Th.] | 80.0019 |
| Step size [°2Th.] | 0202957 |
| Scan type | Continuous |
| Measurement temperature [K] | 298.00 |
| Anode material | Cu |
| K-Alpha1 [Å] | 1.54060 |
| K-Alpha2 [Å] | 1.54439 |
| K-Beta [Å] | 1.39222 |
| K-A2/K-A1 Ratio | 0.50000 |
| Generator settings | 35 mA, 40 kV |

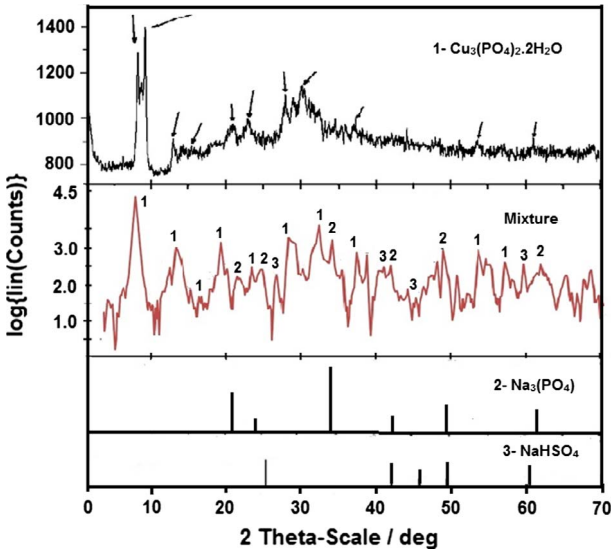


**Fig. 2.** The compared XRD patterns of $Cu_3(PO_4)_2{\cdot}2H_2O$; $Na_3PO_4$; $NaHSO_4{\cdot}H_2O$ at room temperature.

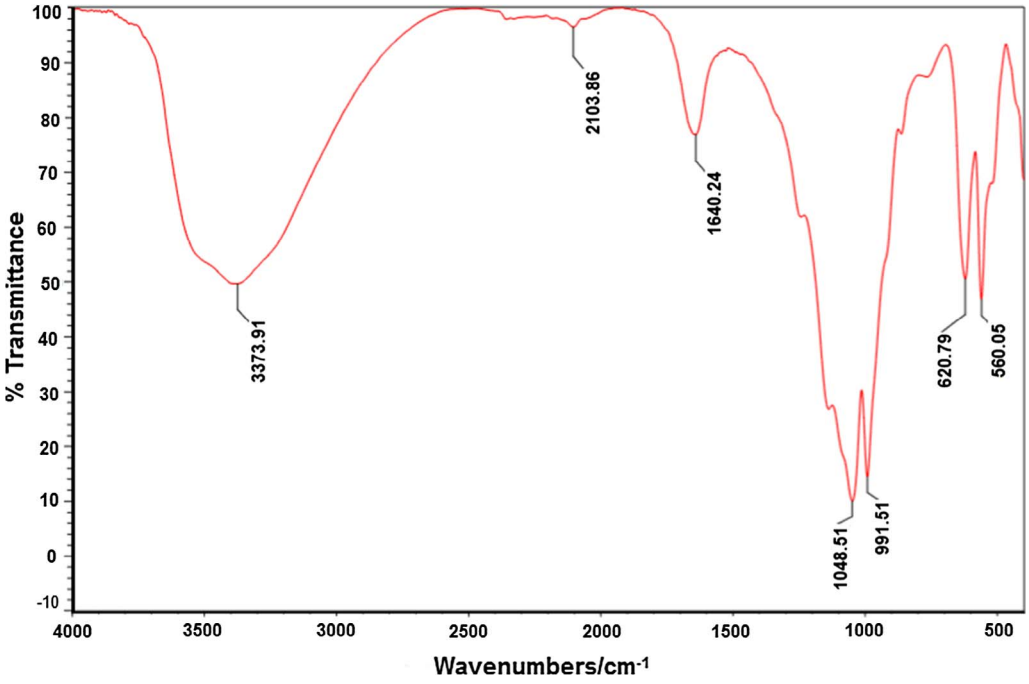


**Fig. 1.** FT-IR spectrum of $Cu_3(PO_4)_2{\cdot}2H_2O$; $Na_3PO_4$; $NaHSO_4{\cdot}H_2O$.