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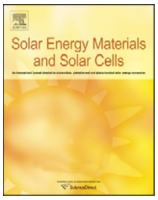

Crystal structures and thermodynamic properties on phase change materials $n\text{-}C_nH_{2n+1}NH_3\cdot H_2PO_4(s)$ ($n=8$, 9 and 10)

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ABSTRACT

Crystal structures of three long-chain *n*-alkylammonium dihydrogen phosphates $n\text{-}C_nH_{2n+1}NH_3\cdot H_2PO_4(s)$ ($n=8$, 9 and 10) (abbreviated as C_8P, C_9P and $C_{10}P$), which may be used as the phase change materials in storage and utilization of solar energy, were determined in layered structures by X-ray crystallography, and the same hydrogen bonding network is observed for these long carbon chain compounds. Low-temperature heat capacities of the compounds were measured by a precision adiabatic calorimeter over the temperature range from 78 to 380 K. Two solid–solid phase transitions were observed for C_8P and C_9P, but only one solid–solid phase transition was observed for $C_{10}P$. The temperatures, molar enthalpies and entropies of the phase transitions were determined based on the analysis of heat capacity curves. Experimental heat capacities for each compound were fitted to two polynomial equations. The smoothed heat capacities and thermodynamic functions ($H_T^o-H_{298.15}^o$) and ($S_T^o-S_{298.15}^o$) of the three compounds were calculated with an interval of 10 K in terms of the polynomial equations.

1. Introduction

The energy problem has become a bottleneck restricting global economic increase. Solar energy is clean, non-pollutive, and convenient to use. Utilization of the solar energy is one of the important ways to solve the problem of energy crisis. But solar radiation energy density on the earth's surface is not high and readily influenced by geography, circadian and seasonal rules. Therefore, the solar energy is discontinuous and unstable because the solar radiation intensity changes constantly. In order to keep the solar thermal power plant continuous operation, we need a heat storage tank to store or absorb the solar energy, then release the stored solar energy when it is in rainy or cloudy days, at nights, and other times with no sunshine. Phase change energy storage materials (abbreviated as PEM) can meet this requirement and satisfactorily solve the problem of storage and effective utilization of the solar energy [1,2]. The goal of PEM is to store the energy from natural source (for example, solar heat) or prevent the equipment from overheating. In solar thermal power plant by using PEM, solar light is gathered in a solar collector and then changed into heat energy [3–5]. A part of the heat energy is used for heating the steam power and another part is stored to ensure continuous power when solar light is insufficient. For example, the American Pipe System Inc. makes the $CaCl_2\cdot 6\,H_2O$ as PEM into the storage heat pipe for storing solar energy and recycling the industrial waste heat. It is well known that the currently developed solid–solid phase change materials with a potential value mainly include polyhydric alcohols, polymers and layered perovskites, among which polyhydric alcohols have the most common use in the practical application. Although the polyhydric alcohols have larger enthalpies of phase changes, they have the higher phase transition temperatures (usually higher than 380 K) and are easily sublimated, which limits their utility especially in storage and utilization of solar energy. The purpose of this article is to find out some suitable materials useful for storage and effective use of solar energy through synthesis, characterization, crystal structures and precision adiabatic calorimetric study on the series of compounds of $n\text{-}C_nH_{2n+1}NH_3\cdot H_2PO_4(s)$ ($n=8$, 9 and 10).

Recently, the compounds of long chain alkylammonium with inorganic and organic acids, whose structure is the same as that of perovskite, are increasingly reported [6] because of the high enthalpies of solid–solid phase transitions. These studies show that these compounds may be used as a kind of nontoxic and environment friendly energy storage materials due to no heavy metals containing in them. However, the crystal structures of the alkyl dihydrogen phosphates are rarely found in literatures, the lattice potential energies and the thermodynamic properties of the solid–solid phase transitions of these compounds are not reported. The lattice potential energy [7–10] is a vital measurement to weigh the bonding ability of the molecules or ions in

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crystal structure, and in relation with many significant physicochemical properties of substances. Heat capacity is one of the most fundamental thermodynamic properties of a substance. Thermodynamic properties of solid–solid phase transitions are indispensable to the applications of the long chain alkylammonium inorganic and organic acid salts used as the PEMs. Adiabatic calorimetry is one of the most reliable methods to obtain heat capacities and various thermodynamic data of substances. It is an important and effective experimental method used to study the solid–solid phase transitions and calculate relevant thermodynamic properties by precisely measuring heat capacities.

In this paper, the crystalline compounds C_8P, C_9P and $C_{10}P$ are synthesized, and their crystal structures are characterized by X-ray crystallography. Lattice potential energies of the title compounds are obtained based on the data from crystal structures. Low-temperature heat capacities of the series of compounds are measured by a precision automatic adiabatic calorimeter over the temperature range from 78 to 380 K and the thermodynamic properties of the solid to solid phase transitions and thermodynamic functions for these compounds are derived.

2. Experimental section

2.1. Synthesis of the three compounds

n-Octylamine, *n*-nonylamine, *n*-decylamine (all of them are purchased from J & K Scientific Ltd., China) and phosphoric acid (0.98 in mass fraction) chosen as reactants, and anhydrous ethyl alcohol used as the solvent are all of analytical grade. The reactants are accurately weighed at the molar ratio of $n[(C_nH_{2n+1}NH_2)\,(n=8,\ 9\ \text{and}\ 10)]:n(H_3PO_4)=1:1$, in which phosphoric acid is slightly excessive and slowly dissolved in anhydrous ethyl alcohol. The mixtures are heated by an electric jacket and stirred under boiling and refluxing for 4 h. The final solutions are laid aside, and several days later, the colorless transparent crystals are obtained. The crystals are recrystallized for three times with anhydrous ethyl alcohol and washed by ether for three times. Finally, the samples are placed in a vacuum desiccator at $T=300$ K to dry in vacuum for 6 days, then they are put into the weighing bottles and preserved in a desiccator. The actual mass fraction purities of the samples are >0.995 by a chromatographic method (HPLC). The HPLC method with differential refraction detector is used for the measurement, and the method of area normalization is available for analyzing the purity of the compounds. HPLC measurements for each compound are carried out in parallel for three times and the average value is taken as the result. The HPLC pattern verifies that each compound has only one component (single peak). The phosphate contents of the compounds are determined by chemical analysis. Elemental analysis (C, H, and N) is carried out on a Vario EL III CHNOS instrument made in Germany.

2.2. X-ray crystallography

The crystals are glued to the fine glass fibers and then mounted on the Bruker Smart-1000 CCD diffractometer with Mo-Kα radiation, $\lambda=0.71073$ Å. The intensity data are collected in the φ–ω scan mode at $T=(298\pm2)$ K. The empirical absorption corrections are based on multi-scan. The structures are solved by the direct method and the differential Fourier synthesis, and all non-hydrogen atoms are refined anisotropically on F^2 by the full-matrix least-squares method. All calculations are performed with the program package SHELXTL [11,12].

2.3. Adiabatic calorimetry

A precision automatic adiabatic calorimeter is used to measure heat capacities of these compounds over the temperature range $78\le(T/\text{K})\le390$. The calorimeter is established in the Thermochemistry Laboratory of the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and performance of the adiabatic calorimeter and the procedures of heat capacity measurements have been described in detail elsewhere [13–15]. The ideal adiabatic condition is required between the calorimetric system and it's environment when the adiabatic calorimeter is applied to measure heat capacities of the substance. The heat convection between the sample cell and it's surroundings is eliminated by high vacuum pump system. The sample cell, inner adiabatic shield, the middle shield and the outer shield are suspended each other from the top of the calorimeter and the electric leads are made from very thin copper wires (diameter of the wire is less than 0.1 mm), which can eliminate heat conduction as much as possible. In addition, three sets of six pairs of thermocouples constitute thermoelectric piles to measure the temperature differences between the sample cell and inner shield, between the inner shield and the middle shield, and between the middle shield and the outer shield, respectively. When the sample cell is heated and the temperature of the sample cell increases, the thermopiles will immediately induce such a temperature change, and the heaters wound on the inner shield, the middle shield and the outer shield will be started up and the tracking heating is performed during the whole process. Because there is no temperature difference between the calorimetric system and it's surroundings during the measurement process, so the heat radiation and heat conduction are nearly eliminated. Since the three kinds of heat transfers have been effectively eliminated and controlled, the temperature change and the corresponding energy can be accurately measured, and heat capacities can be accurately determined. When this method is used to investigate the phase transition and determine the temperature and enthalpy change of the phase transition, it has a great advantage over the DSC technique because of it's higher accuracy of the temperature, energy and heat capacity data. In addition, after the sample is added to the sample cell, the air and humidity in the cell are pumped out by a high-vacuum pump, and then the highly pure helium gas is introduced into the sample cell so as to accelerate the achievement of the thermal equilibrium state in the sample cell. Although the sample cell is sealed in the heat capacity measurements and this would influence the solid–liquid and liquid–gas phase transitions with large volume change, as for the solid–solid phase change materials it is shown in practice that atmosphere pressure has little effect on the temperature and enthalpy change of the solid–solid phase change, hence the measurement is accurate. Heat-capacity measurements are continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The liquid nitrogen is used as a coolant. The heating rate and temperature increments are generally controlled at 0.1–0.4 K/min and 1–3 K. The heating duration is 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period are always kept within $\pm10^{-3}$ K/min during the acquisition of all heat-capacity data. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with it's surroundings [15]. The reliability of the calorimeter has been confirmed by heat capacity measurements of the reference standard material (α-Al_2O_3) over the temperature range $78\le(T/\text{K})\le400$. Deviations of the experimental result from those of smoothed curve lie within $\pm0.20\%$, while the uncertainty is $\pm0.30\%$, as compared with the values given by the former National Bureau of Standards [16] over the whole temperature range.