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Thermal And Structural Study Of A Perovskite Layer $[NH_3^{\sim} (CH_2)_3 - COOH] CdCl_4$

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Abstract

In this paper we present a study of a Phase Change Material type Perovskite Layer which have solid-solid transitions and thermal properties suitable for Thermal Energy Storage. Structural study shows that organic chain in this organic-inorganic compound presents “trans” and “gauche” conformations due to the acid function. DSC study shows three transitions with the increasing of temperature due to the change of conformations in the organic chain.

Introduction

Thermal energy storage (TES) is a useful tool to increase energy efficiency and energy savings. Solar thermal energy can be stored as sensible heat (water and rock), latent heat (water/ice and salthydrates) or combination of these (Koca *et al.,* 2008). The most effective way of latent thermal energy storage is by employing phase change materials (PCM) (Akgün *et al.,* 2008) due to its advantages of high energy storage density, its isothermal operating characteristics during solidification and melting processes, and nearly invariable temperature during the phase change which leads to a small size and low level of heat loss (Koca *et al.,* 2008; Zhang *et al.* 2007).

The most suitable PCMs for TES are the solid-solid transition, then the solid-liquid transition (Busico *et al*., 2007). Among the evaluated PCMs with solid-liquid transition: fatty acids, salts hydrates and paraffins. Fatty acids (carboxylic acids with number of carbon atoms ≥ 4) are promising ones because of their high latent heat storage capacity, good thermal properties and thermal reliability, and no or less volume change during phase change (Sari *et al*., 2008; Alkan and Sari, 2008; Sari and Karaipekli, 2008).

The advantages of solid-state phase change materials are that a liquid phase need not be contained, segregation of components is less likely, and stable composites may be fabricated in which the solidstate PCM is dispersed.

Many solids undergo reversible phase change in the solid-state, but very few have sufficiently energetic transformations to be of potential, practical use in thermal energy storage. There are, however, three classes of solid-state PCMs which appear to be promising: Layer Perovskite organometallics, cross linked polymers, and certain hydrocarbon molecular crystals (Li *et al*., 1999).

Perovskite Layer compounds

Several papers have been published on Perovskite Layer compounds with the general formula $(C_nH_{2n+1}NH_3)$ MX_4 (CnM for short) where M is a divalent metal atom and X represents an halogen (M = Cu, Mn, Zn, Co, Cd…) (X = Cl, Br…). This bis (n-alkylammonium tetrahelo metallates) form lamellar type structures in which the sheets of corner-shared MX_6 octahedra are sandwiched between a pair of layer of n-alkylammonium chains. The cavities between the octahedra are occupied by the NH_3 groups which are attracted to the MX_6 by hydrogen bonds N-H….X (Kang *et al*., 1993; Prasad *et al*., 1989). So, the Perovskite Layers are typical “Sandwich” system because of the regular alternation of inorganic and hydrocarbon regions that consist of long chain

alkylammonium groups ionically bonded to an inorganic support.

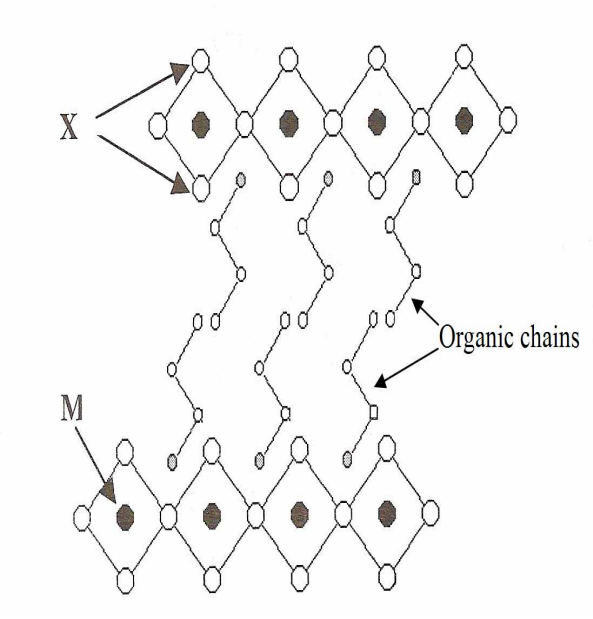

Figure 1. Organic-inorganic layers in Perovskite Layer

These linear alkyl chains are the origin of a peculiar thermal behavior of this compound (Busico *et al*., 2007). Indeed, CnM compounds undergo a variety of interesting high enthalpic and reversible solid-solid structural phase transitions (Ning *et al*., 1992) between two polymorphic forms in the temperature range (273-393 K) (Li *et al*., 1999).

The solid-solid transition temperatures and enthalpies are strongly dependent on the length of the chains (Busico *et al*., 1980), they increase with the number of carbon atom (Li *et al*., 1999). In fact, many thermal and structural studies showed that the phase change involve the hydrocarbon regions only, leaving the inorganic layers quite unchanged, and consist mainly in the order-disorder transition of the linear alkyl chains from a conformationally ordered state to a disordered one in which the chains gain a conformational freedom compared with that they would have in melt (Busico *et al*., 1980), this disorder state is resulting from the reorientational and conformational dynamics of the alkylammonium groups. As the chain length increases, structural phase transitions due to the formation of chain conformers become more important (Kang *et al*., 1993)**.** For all these reasons, CnMs may be one of the most promising candidates as an energy storage material. (CnNi are unsuitable for thermal storage use because it has poor thermal stability (Li *et al*., 1999).

In this paper we study a new perovskite layer compound $[NH_3\text{-}(CH_2)\text{-}COOH]_2\ CdCl_4$. where the organic layer is an amino acid. This compound could involve both thermal properties of the Perovskite Layer compounds and of the butyric acid as the short fatty acid.

Structural study of [NH3-(CH2)3-COOH]2CdCl4 at 293 K

Single crystals of the composite were studied by "diffractometre" Enraf-Nonious CAD4. The resolution of the structure was done by the heavy atom method and SHELX97 program. Patterson function help to situate Cadmium and Chlor atoms when difference Fourier sections determined the coordinates of the other atoms of both organic chains.

The principal results and crystallographic characteristics of the crystallographic cell of the studied compound are presented in table1, and figure2 present an Oretp view of the structure according to the c axis. It shows the CdCl6 octahedra and hydrogen bonds between NH_3^+ and Cl. Figure3 present an Ortep view of the organic chains according to the a axis.

a (Å)	b (Å)	c (Å)	β (°)	System	Z	Group
7.409 (3)	7.489 (2)	15.479 (9)	107.49 (4)	Monoclinic	2	P21

Table 1. Parameters of the crystalline cell.

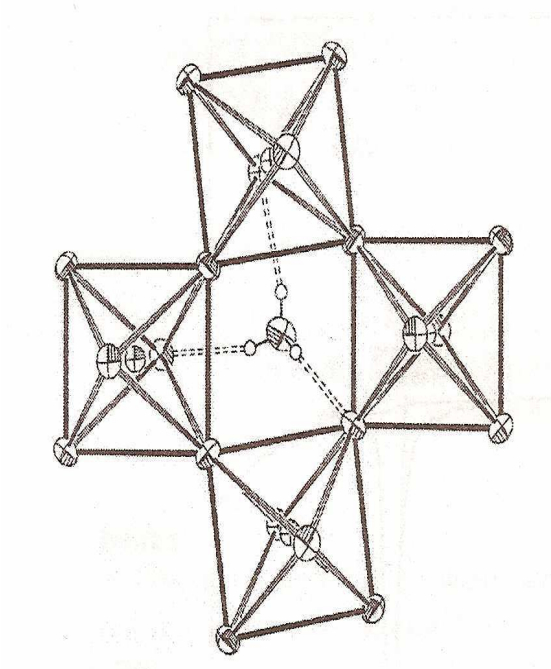

Figure 2. Structural arrangement of the inorganic part

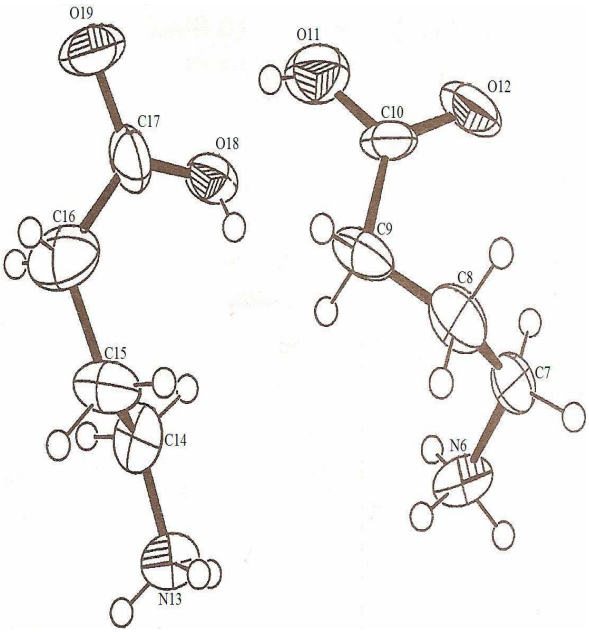

Figure 3. Projection of the organic chain according to the a axis

The values of dihedral angles and their conformations "trans" or "gauche" are shown in table2. Let recall that "trans" conformation involving four successive atoms in the alkylene chain corresponds to a dihedral angle close to 180° (or -180°) and "gauche" conformation to the case where the dihedral angle is close to 70° (or -70°) (Khechoubi *et al*., 1994)

	Dihedral angles (°)	Conformation
N6C7C8C9	- 61.6	gauche
C7C8C9C10	-71.7	gauche
C8C9C10O11	-176.4	trans
C8C9C10O12	1.2	trans
N13C14C15C16	-175.0	trans
C14C15C16C17	-69.8	gauche
C15C16C17O18	3.3	trans
C15C16C17O19	-172.3	trans

Table 2. Dihedral angles in both organic chains of the cell

It has been shown that in the Cadmium series, "gauche" conformations are present for even values of n (n=4 in particular). However table2 shows that this compound has both conformations "gauche" and "trans". We think that the existence of both configurations is due to the "encombrement" caused by the acid function which can be remarkable in figure 3.

Thermal study

To understand thermal properties and transition behavior of the compound, calorimetric measurement was taken by a DSC "Universal V 2.5 TA Instruments" in a range of temperature (293K – 523K). The results of heating are reported in figure 4. It shows three transitions, the first is exothermic and the others are endothermic. The principal characteristics of the three transitions are shown in table3.

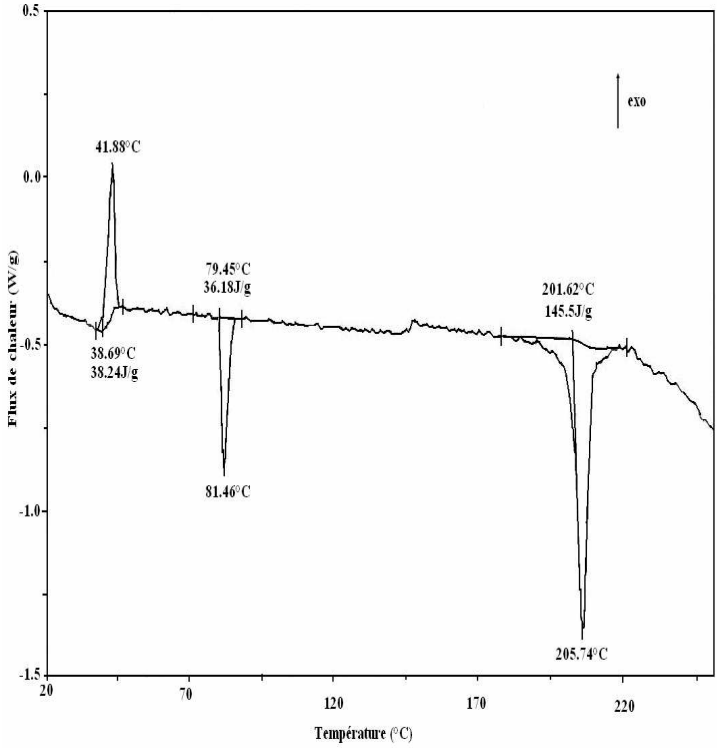

Figure 4. DSC analysis of phase transitions in the compound $[NH_3\text{-}(CH_2)\text{-}COOH]_2CdCl_4$

Signal	T0(K)	TS(K)	DH (j/g)
1st	311.69	314.88	-38.24
2nd	352.45	354.46	36.18
3rd	474.62	478.74	145.5

Table 3. Thermodynamic characteristics of the transitions

Discussion

As mentioned before, the transitions in Perovskite Layers are due to the change of conformations in the organic chains, and since the "gauche" conformation is the one known for Cadmium series, we think that with the increasing of temperature, "trans" dihedral angles tend to be "gauche" but the acid function block this reorientation or push the "gauche" ones to change in "trans" in order to make more space between the function acid and the other atoms in the organic chain limiting the interactions.

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Appendix: At the end of the paper

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