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Thermochimica Acta 326 (1999) 183–186

thermochimica acta

Study of solid–solid phase change of $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ for thermal energy storage

Weiping Li[a,*], Daosheng Zhang[a], Taiping Zhang[a], Tianzhi Wang[a], Deshui Ruan[a], Dengqing Xing[b], Houbin Li[b]

[a] *Department of Chemistry, Central China Normal University Wuhan, Hubei 430079, China*
[b] *Tibet Autonomous Region Solar Energy Research Institute, Lhasa, 850001, China*

Received 14 April 1998; received in revised form 7 July 1998; accepted 22 July 1998

Abstract

A series of *bis*(*n*-alkylammonium) tetrachlorometallates (II) $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ (C_nM, where n=10, 12, 16 and M=Cu, Zn, Hg, Mn, Co, Ni) were synthesized and elementary analysis carried out. Their solid–solid phase transitions were studied using DSC and IR. Transition temperatures of C_nMn, C_nCo, C_nZn and C_nCu lie between 28 and 86 kJ mol^{-1}. They are potential thermal-energy storage materials. C_nNi, C_nCd, C_nHg are unsuitable for thermal storage use, because C_nNi has poor thermal stability; moreover, C_nCd and C_nHg in the low temperature has lower latent heat for these application.

Keywords: Alkylammonium tetrachlorometallates (II); Phase diagram; Solid–solid phase transition; Thermal-energy storage; Transition enthalpy

1. Introduction

Materials for thermal-energy storage are, typically, salt hydrates or paraffins which absorb large amounts of heat as they exhibit a phase change. Certain molecular crystals undergo a solid-state crystal transformation in which sufficient heat is absorbed, such that they may also be used for practical heat storage applications. The advantages of solid-state phase-change material(s) (PCM) are that a liquid phase need not be contained, segregation of components is less likely, and stable composites may be fabricated in which the solid-state PCM is dispersed.

Many solids undergo reversible phase changes 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.

The *bis*(*n*-alkylammonium) tetrahalometallates (II) (C_nM) are organometallic compounds of the general formula $(n\text{-}C_nH_{2n+1}NH_3)_2)MX_4$, where M is a divalent metal atom, X a halogen and n varies between 8 and 18. These compounds are characterized by high enthalpic, reversible solid–solid phase transitions between two polymorphic forms in the 273–393 K range [1,2].

*Corresponding author.

0040-6031/99/$ – see front matter
PII: S0040-6031(98)00497-3

We have reported measurements of the relevant thermal properties of selected C_nMs in order to evaluate their usefulness in thermal-energy storage systems.

2. Experimental

M(II)Cl_2 (M=Cu, Zn, Hg, Mn, Co, Ni), HCl alkylamine and absolute ethanol used here were analytical reagents.

In this paper, all the concentrations of the samples in the phase diagrams were expressed in wt%.

Compounds of the type $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ were obtained as platelets by mixing hot ethanolic solutions of MCl_2 (M=Cu, Cd, Hg, Mn, Co, Ni), HCl and alkylamine in a 1 : 2 : 2 molar ratio. The solutions were concentrated by boiling, then allowed to cool to room temperature and filtered. The products were recrystallized twice from absolute ethanol. The results of elementary analysis of C_nM with a Perkin–Elmer 2400 elemental analyzer are given in Table 1.

Infrared spectra were registered with a Nicolet Magna IR 750 FT-IR spectrometer equipped with a variable temperature sample cell. DSC curves were registered between 273 and 473 K in a flow of nitrogen on a Perkin–Elmer DSC-7 differential scanning calorimeter at a scanning rate of 5 K min^{-1}. The temperature scale was calibrated by means of measurements on pure reference compounds. Transition enthalpies were obtained by using a sample of pure indium as reference standard [ΔH_m=3.26 kJ mol^{-1}].

Table 1
Calculated and found mass compositions of various $(RNH_2)_2MCl_4$ compounds

	C%		H%		N%	
	calc.	found	calc.	found	calc.	found
$C_{10}Cu$	45.86	46.19	9.24	9.43	5.35	5.03
$C_{10}Zn$	36.45	36.25	7.34	7.40	4.25	4.16
$C_{10}Mn$	46.81	46.04	8.19	8.38	5.46	5.13
$C_{10}Co$	46.45	45.43	8.13	8.51	5.42	5.01
$C_{12}Cu$	49.88	48.30	9.70	9.66	4.85	4.20
$C_{12}Zn$	49.72	48.27	9.67	9.68	4.83	4.48
$C_{12}Mn$	50.61	49.81	9.91	9.91	4.8111	4.68
$C_{12}Co$	50.29	49.99	9.78	10.14	4.89	4.31
$C_{16}Cu$	55.69	54.93	10.44	10.47	4.06	3.55
$C_{16}Co$	56.08	55.88	9.64	11.12	4.09	3.87
$C_{16}Zn$	55.56	55.25	10.49	10.36	4.05	4.13
$C_{16}Mn$	56.39	56.17	10.57	11.21	4.11	3.64

3. Results and discussion

Fig. 1(a) depicts the low-frequency region of the IR spectra of $C_{10}Zn$ at room temperature [3]. This is characterized by the 725 cm^{-1} band (methylene rocking mode), which is a doublet, because there are two chains in each crystallographic unit cell, and by the methylene twisting absorption, which is split into several peaks in the 1200–1300 cm^{-1} region, due to the regular interaction of the CH_2 groups of the same chain. Fig. 1(b) shows the IR spectra of the high-temperature solid polymorphs of $C_{10}Zn$. The 725-cm^{-1} band, in this case, is broad, with no obvious splitting observed. The methylene twisting absorption is very broad and unsplit, because of the lack of regular interactions between the CH_2 groups in the same chain. The transition temperature and enthalpies measured from the DSC curves for pure C_nM are given in Table 2.

The DSC data for C_nM show the solid–solid transition temperature of the C_nCu, C_nZn, C_nMn and C_nCo

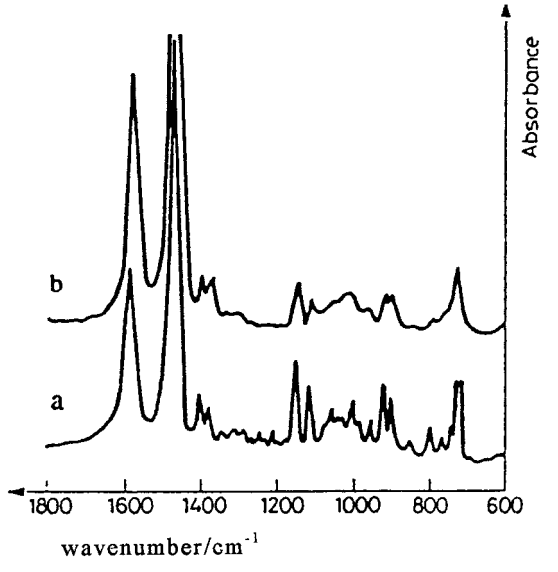

Fig. 1. The 1800–600 cm^{-1} region of the IR spectrum of $C_{10}Zn$. (a) Room-temperature ordered phase; and (b) high-temperature disordered phase (T=363 K).

Table 2
Solid–solid transition temperature, enthalpies of the C_nM

Substance	T/K			ΔH/(kJ mol^{-1})		
$C_{10}Cu$	306.92		310.06	28.74		3.92
$C_{10}Zn$	353.29		435.94	43.37		9.49
$C_{10}Mn$	305.95			36.11		
$C_{10}Co$	350.86			38.43		
$C_{12}Cu$	325.69		332.22	34.16		6.39
$C_{12}Zn$	361.38		429.10	60.82		8.90
$C_{12}Mn$	327.20		329.57	42.26		3.75
$C_{12}Co$	333.86		361.12	19.31		33.96
$C_{16}Cu$	345.95	354.74	369.17	39.41	5.56	10.09
$C_{16}Zn$	372.28		433.64	86.76		8.42
$C_{16}Mn$	346.28		364.11	59.72		11.50
$C_{16}Co$	366.57	372.85	437.26	7.26	71.47	9.46

between 305 and 373 K, transition enthalpy between 28–86 kJ mol^{-1}. The thermal-storage behavior of the $C_{10}Co$–$C_{16}Co$ system. Transition temperatures and enthalpies, measured from the DSC curves for the mixed materials, and their pure components are in presented in Table 2. Fig. 2 presents an approximate phase diagram derived from the data in Table 3.

In our discussion, we shall use the phase diagram of the $C_{10}Co$–$C_{16}Co$ system as an example. For $C_{16}Co$ (=57%, wt%) the product is a mixed compound, (n-$C_{10}H_{21}NH_3)_2CoCl_4$-($n$-$C_{16}H_{33}NH_3)_2CoCl_4$. The crystallization products obtained with $C_{16}Co$<57% are crystal mixtures of this mixed salt and the pure α-phase decylammonium salt, while the products obtained with $C_{16}Co$>57% are mixtures of the mixed salt and the pure α-phase hexadecylammonium salt. At temperatures lower than the eutectic points, the system contains the pure decylammonium salt and the mixed salt in the α-phase. At temperatures intermediate between the eutectic point and the transition of the mixed salt, the system contains a β-phase. At temperatures higher than the transition point of the mixed salt, the system contains two β-phases of different compositions in the stable β-phase region. At temperatures higher than the melting point of the mixed salt, the system is in a liquid state. By means of cooling curves and DSC methods, the phase diagram of the solid–solid transition systems $C_{10}Co$–$C_{16}Co$, $C_{12}Co$–$C_{16}Co$, $C_{10}Zn$–$C_{16}Zn$ and $C_{12}Zn$–$C_{16}Zn$ have been determined [4]. Compounds C_nM and their binary mixtures have solid–solid transition temperatures between 343 and 382 K, and transition enthalpies in the 38–78 kJ mol^{-1} region. Compounds C_nM and their binary mixtures are potential thermal-energy storage materials. C_nNi, C_nCd and C_nHg are unsuitable for thermal storage use because C_nNi has poor

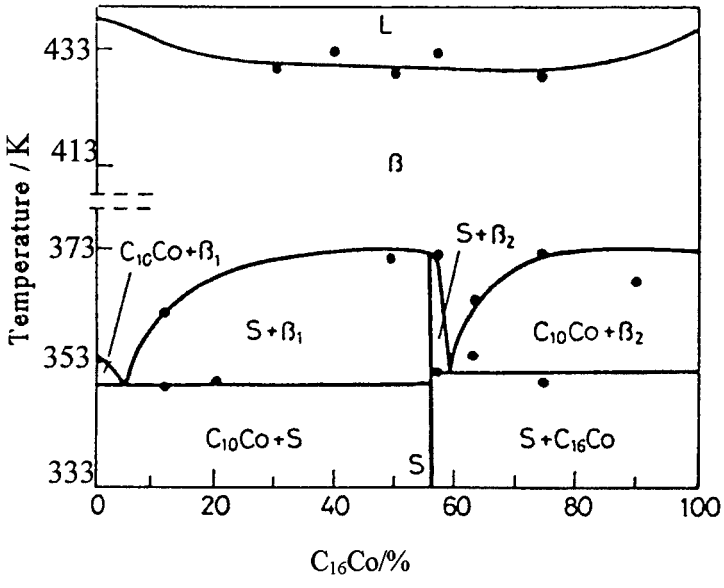

Fig. 2. Phase diagram of the $C_{10}Co$–$C_{16}Co$ system.

Table 3
Solid–solid transition temperatures, enthalpies of the $(C_{10})_x(C_{16})_{1-x}Co$ system

$C_{16}Co$/wt%	T/K				ΔH/(kJ mol^{-1})
0		355.15		438.15 [a]	38.43
11.41	349.65		362.65		
30.00	350.70		371.93	430.96 [a]	43.59
40.00	353.47		372.83	433.22 [a]	49.63
50.00	350.49		372.17	429.86 [a]	44.96
56.95	352.67		373.02	432.91 [a]	49.46
62.95	354.95		364.65		
74.05	353.17		372.56	429.72 [a]	46.52
82.00	359.15		372.95		
90.00	362.10		368.15		
100		372.85		437.26 [a]	78.73

[a] Melting temperatures.

thermal stability; moreover, C_nCd and C_nHg in the low-temperature region has lower latent heat for this application.

Solid–solid transition temperatures and transition enthalpies of C_nM increase with the number of carbon atom in the chains.

	$C_{10}Zn$	$C_{12}Zn$	$C_{16}Zn$	
T_{tr}/K	353.29	361.38	372.28	
				increasing
ΔH_{tr}/ kJ·mol^{-1}	43.37	60.82	86.76	

The different types of thermal behavior can be observed for compounds with different metals, but with the same n. The different thermal behaviors depend on different metal atoms. We studied metal atoms of C_nM of groups IB, IIB, VIB, VIII which belong to

	$C_{12}Zn$	$C_{12}Cd$	$C_{12}Hg$	
T_{tr}/K	361.38	327.31	329.03	
				decreasing
ΔH_{tr}/ kJ·mol^{-1}	60.82	28.30	25.68	

References

[1] V. Busico, C. Carfagna, V. Salerno, The layer perovskites as thermal energy storage systems, Solar Energy 24 (1980) 575.
[2] E. Landi, M. Vacatello, Metal dependent thermal behavior in $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$, Thermochim. Acta 13 (1975) 441.
[3] Xu Ruiyun, Kong Dejun, Cia Xian-E, Zhu Jing, Studies of solid–solid phase transitions for $(n\text{-}C_{18}H_{37}NH_3)_2MCl_4$, Thermochim. Acta 164 (1990) 207.
[4] Ruan Deshui, Li Weiping, Hu Qizhu, Phase diagrams of binary systems of alkylammonium tetrachlorometallates (II), J. Thermal Analysis 45 (1995) 235.