Raman scattering investigation of the high temperature phase transition in [N(C$_3$H$_7$)$_4$]$_2$SnCl$_6$

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HIGHLIGHTS

- The phase transition of [N(C$_3$H$_7$)$_4$]$_2$SnCl$_6$ compound has been analyzed by Raman spectroscopy.
- The analysis of the wavenumber positions and half-widths have been discussed.
- The temperature dependencies of the reduced intensity have been analyzed using order-disorder models.
- The analysis of the correlation lengths were reported and discussed.

GRAPHICAL ABSTRACT
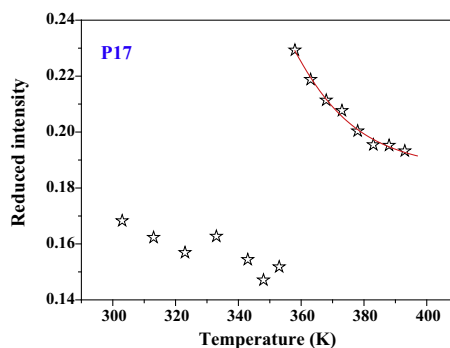
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ABSTRACT

The phase transition at high temperature of bis-tetrapropylammoniumhexachlorostannate compound has been investigated by Raman spectroscopy as a function of temperature from 303 K to 393 K. While the bands mainly associated with the internal modes of the SnCl$_6$ anions only undergo weak changes, strong evolutions of wavenumbers, widths and intensities of many lines associated with the organic cations are observed with discontinuities in the vicinity of the phase transition at 362 K. The most important changes are observed for two lines at 1137.5 cm^{-1} and 1159.4 cm^{-1} (at room temperature) issued from twisting of CH$_2$ groups and skeletal deformation of the cations. The spectral characteristics of these lines are analyzed and consistently described in the framework of an order–disorder model for the phase transition. The temperature dependency of the reduced peak intensity allowed to determine the critical exponents and evolution of the correlation length on approaching the transition.

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Introduction

Organic–inorganic compounds based on elements of groups 14 and 15 as (Sb, Sn, Bi, Pb) have been extensively investigated in recent years owing to their interesting physical properties [1–4]. These materials have demonstrated potential applications in developing of low cost electronic devices (as Thin Film Transistor or Organic–Inorganic Emitting Diode) [5–7].

On the other hand, several halogenometalates compounds with various size of alkylammonium cation exhibit numerous structural phase transitions related to reorientation motion of alkyl chains [8–12] and so are classified as "order–disorder. In fact, recent reports which focus mainly on introduction of tetrapropylammoniumchloride amin into metal halides of elements of groups 14 and 15 show that these compounds undergoes sequence of phase transitions, which makes the research of this family very attracted [13,14].

In view of this consideration and in order to explore the mechanism of phase transition in this family of compounds, we have

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successfully synthesized a new compound of formula bis- tetrapropylammonium hexachlorastannate.

X-ray diffraction studies of $N(C_3H_7)_4]_2SnCl_6$ single crystals at room temperature showed that it crystallizes in orthorhombic space group Pbca with a = 15.818 (2) Å, b = 14.913 (2) Å, c = 29.131 (4) Å and Z = 8 [15]. The crystal lattice is made of isolated distorted $SnCl_6$ anions and two conformational types of cations, linked through C–H···Cl Van der Waals and electrostatic interactions. Differential scanning calorimetry (DSC) measurements revealed that this compound undergoes two phase transitions at 244 K and 362 K prior to decomposition starting in the vicinity of 411 K.

Raman scattering investigations as a function of temperature present great interest since this indirectly brings information regarding molecular conformation and how the alkylammonium cations contribute to the mechanism of the phase transitions.

The purpose of this paper is to investigate by Raman scattering the dynamics of this compound and the mechanism of the phase transition at high temperature in relation with the conformation of the alkylammonium chains.

Experimental section

$[N(C_3H_7)_4]_2SnCl_6$ crystals were grown by slow evaporation, at room temperature. Details of the growth procedure and single crystal X-ray diffraction study were described elsewhere [15].

The Raman spectra were recorded using a Horiba-Jobin-Yvon T64000 spectrometer in the frequency range 100–3800 cm^{-1}, and using the 514.53 nm line of an argon-krypton ion laser for excitation. The measurements were performed under microscope (X50 objective with long working distance) with polarized excitation on a good quality transparent single crystal oriented with respect the birefringence axis, which actually corresponds to the crystallographic axes in this orthorhombic system. The resolution of the instrument was set at 0.2 cm^{-1}. A Linkam heating stage was used for temperature control and measurements.

Results and discussion

Vibrational characteristics

The set of Raman bands of $[N(C_3H_7)_4]_2SnCl_6$ at room temperature are reported in Table 1. The tentative assignment is proposed on the basis of calculated vibrational modes using density functional theory (DFT) method [16].

The most intense lines in the 100–350 cm^{-1} region mainly results from the three internal vibrational modes of the $SnCl_6$ anions with only weak contributions of the $[N(C_3H_7)_4]$ cations. On the other hand, the 350–3800 cm^{-1} region only arises from the internal modes of the organic cations.

The whole Raman spectra of $[N(C_3H_7)_4]_2SnCl_6$ in the temperature range 303–393 K are shown in Fig. 1

The detailed analysis clearly indicates that all the Raman bands remain unaffected in the temperature range 303–358 K. Then below this range, in the vicinity of the order–disorder phase transition detected by DSC measurements, several bands exhibit changes in their position, intensity and half-width. These observations can be explained by a decrease of C–H···Cl Van der Waals and electrostatic interactions between the organic and inorganic parts with increasing temperature [17], and the change of the structure of the crystal.

In order to quantitatively analyze the evolution of Raman bands versus temperature, the Raman spectra have been deconvoluted by means Labspec software using a combination of Gaussian and Lorentzian functions. Fig. 2 (in Supplementary data) show the

Table 1
Tentative assignments of the bands observed in the Raman spectrum of $[N(C_3H_7)_4]_2SnCl_6$ compound.

Wavenumber (cm^{-1}) / Labeling	Assignments
158.9 (P1)	$\nu_5(SnCl_6)$
232.5 (P2)	$\nu_2(SnCl_6)$
307.3 (P3)	$\nu_1(SnCl_6)$
330.6 (P4)	$\delta(NC4) + \delta(C–C–C)$
372.9 (P5)	$\delta(NC4) + \delta(C–C–C)$
467.8 (P6)	$\delta(NC4) + \delta(C–C–C)$
749.6 (P7)	$\delta(C–C–C) + \delta(C–N–C) + \rho_r(CH_2) + \nu(NC_4) + \nu(C–N–C) + \nu(NC)$
785.5 (P8)	$\delta(C–C–C) + \delta(C–N–C) + \rho_r(CH_2) + \nu(NC_4) + \nu(C–N–C) + \nu(NC)$
846.5 (P9)	$\nu(NC) + \delta(C–C–C) + \nu(NC_4) + \nu(C–N–C)$
910.1 (P10)	$\delta(C–N–C) + \delta(C–C–C)$
939.3 (P11)	$\nu(C–C)$
969.7 (P12)	$\nu(NC) + \delta(C–N–C)$
1006.5 (P13)	$\delta(C–N–C) + \nu(C–C)$
1034.5 (P14)	$\delta(C–C–C) + \delta(C–N–C) + \nu(C–C) + \delta(N–C–C)$
1056.1 (P15)	$\delta(C–N–C) + \delta(C–C–C)$
1101.6 (P16)	$\delta(C–C–C)$
1137.5 (P17)	$t(CH_2) + \delta(skeletal)$
1159.4 (P18)	$t(CH_2) + \delta(skeletal)$
1185.3 (P19)	$\delta(skeletal)$
1317.8 (P20)	$\omega(CH_2) + t(CH_2)$
1351.5 (P21)	$\delta(skeletal)$
1380.4 (P22)	$\omega(CH_2)$
1457.7 (P23)	$\delta_s(CH_3)$
1480.7 (P24)	$sciss(CH_2) + \delta_{as}(CH_3)$
1524.4 (P25)	$sciss(CH_2)$
2877.8 (P26)	$\nu_s(CH_3) + \nu_s(CH_2)$
2913.3 (P27)	$\nu_s(CH_2)$
2938.7 (P28)	$\nu_s(CH_2)$
2955.4 (P29)	$\nu as(CH_3) + \nu as(CH_2)$
2966.2 (P30)	$\nu as(CH_3) + \nu as(CH_2)$
2980.3 (P31)	$\nu as(CH_3) + \nu as(CH_2)$
2998.7 (P32)	$\nu as(CH_3) + \nu as(CH_2)$
3047.2 (P33)	$\nu as(CH_3) + \nu as(CH_2)$

ν_s: symmetric stretching; ν_{as}: asymmetric stretching; δ_s: symmetric bending; ω: wagging; sciss: scissoring; t: twisting; δ: bending.
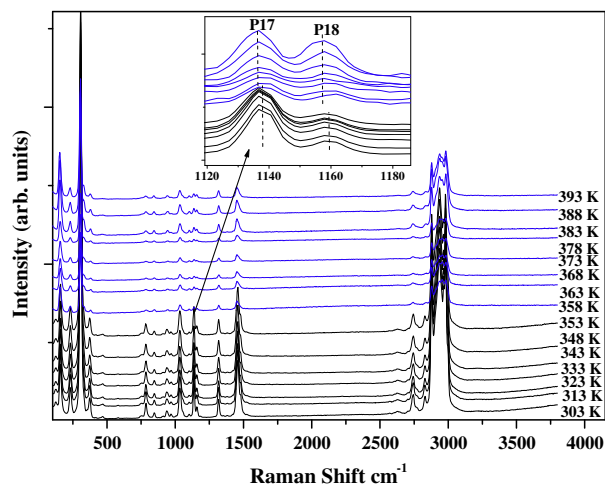
Fig. 1. Temperature evolution of the Raman spectra in the 100–3800 cm^{-1} frequency range.

deconvolutions of the room temperature spectra in the 100–600 cm^{-1}, 600–2000 cm^{-1} and 2000–3600 cm^{-1} spectral ranges. Fig. 3 (in Supplementary data) reports the temperature dependence of position and half-width of selected lines.

The lines issued from the internal modes of the $SnCl_6$ anions do not show significant changes: the wavenumber and line width