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EPR and ^{13}C NMR study of the [TMA]$_2$Cu$_{0.5}$Zn$_{0.5}$Cl$_4$ compound

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ABSTRACT

The [TMA]$_2$Cu$_{0.5}$Zn$_{0.5}$Cl$_4$ compound was obtained by slow evaporation at room temperature. The sample was characterized by differential scanning calorimetry, electron paramagnetic resonance (EPR) and ^{13}C NMR spectroscopy at different temperatures. The calorimetric study showed five endothermic peaks at 248, 271.7, 278, 286, and 293.7K. The phase transitions at 248 and 271 were detected by EPR analyses and that at 286 was observed by ^{13}C NMR study.   © 2012 Trade Science Inc. - INDIA

INTRODUCTION

Organic–inorganic hybrid materials represent a new class of materials that may combine desirable physical properties characteristic of both organic and inorganic components within a single molecular-scale composite. Inorganic materials offer the potential for a wide range of electronic properties (enabling the design of insulators, semiconductors, and metals), magnetic and dielectric transitions, substantial mechanical hardness and thermal stability. Organic molecules, on the other hand, can provide high fluorescence efficiency, large polarizability, plastic mechanical properties, ease of processing and structural diversity. The phase transitions in tetramethylammonium tetrahalogenometallic compounds [TMA]$_2$MX$_4$,where M represents divalent metals (TMA = N(CH)$_4$)$_,$ (M = Zn, Co, Cu, Mn…) and X halogens (X = Cl, Br, or I), have been well investigated. Their highest-temperature phase (the normal phase) commonly belongs to the K$_2$SO$_4$-II type structure. As temperature decreases, they undergo various series of phase transitions. Interest in these compounds has been growing as some of them exhibit interesting structural and physical properties like ferro-electricity, ferro-elasticity and low dimensional magnetism[1-10]. At room temperature, the [TMA]$_2$Zn$_{0.5}$Cu$_{0.5}$Cl$_4$ compound crystallizes in an orthorhombic system (*P*21*cn* space group) with *Z* = 4 and the following unit cell dimensions: *a* = 8.988 (3), *b*= 15.527 (2) and *c* = 12.269 (4) Å. The crystal structure consists of alternating organic–inorganic [(TMA)$^+$/(Cu)Zn ZnCl$_4$$^{2-}$] layers and organic sheets (TMA)$^{2+}$[11]. All Organic groups and (Cu)ZnCl$_4$$^{2-}$ are not disordered. Their main geometrical features are those commonly observed in the atomic arrangements of (TMA)$_2$ZnCl$_4$ and (TMA)$_2$CuCl$_4$[12, 13]. The dielectric permittivity study in the temperature interval from 200K to 305K shows that this compound exhibits a ferro-electric–paraelectric phase transition at 293K[14].

Indeed, in this work, we report the differential thermal analysis, EPR, ^{13}C NMR spectroscopy and dielectrical proprieties at different temperatures for [TMA]$_2$Zn$_{0.5}$Cu$_{0.5}$Cl$_4$ compound.

EXPERIMENTAL

The synthesis of the title compound,

$[TMA]_2Zn_{0.5}Cu_{0.5}Cl_4$, was performed by a mixture of $(CH_3)_4NCl$, $CuCl_2$ and $ZnCl_2$ (molar ratio 4 : 1 : 1) in distilled water. The mixture was stored at room temperature. After a few days, square yellow crystals appeared.

Schematically, the reaction can be written:

$$4(TMA)Cl + CuCl_2 + ZnCl_2 \xrightarrow{\;H_2O\;}$$
$$2[TMA]_2\,Cu_{0},Zn_{0},_5Cl_4$$
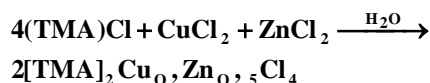
Differential scanning calorimetry measurements were performed by heating the sample from 200 to 400 K using a Netzsch-DSC 204 calorimeter. EPR experiments were carried out using Brukerspectrometer working at the X-band frequency. Typical microwave powers in the range 20–200 mW and a modulation magnetic field about 5 G were commonly used for all the reported experiments. An Oxford instrument cryostat was used for variable temperature measurements in the 110– 300 K range. The NMR experiments were performed on powdered samples at different temperatures (233 = T = 323 K) on a Bruker MSL 300 spectrometer working at 5KHz.

ε' and ε'' dielectric measurement were performed over a broad frequency window, $10^{-1} < f\,(Hz) < 10^6$ in a temperature range $220 < T\,(K) < 320$ using a NOVOCONTROL system integrating ALFA dielectric interface.

CALORIMETRIC STUDY
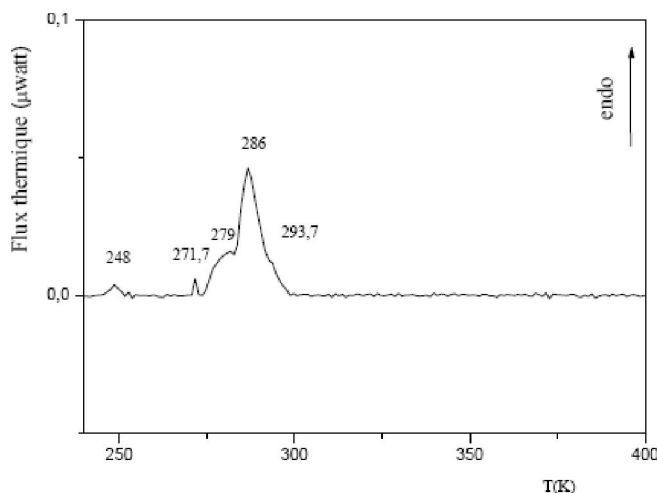
Calorimetric study showed five endothermic peaks

Figure 1 : differential scanning calorimetry of $[TMA]_2Zn_{0.5}Cu_{0.5}Cl_4$ compound

at 248, 271.7, 279, 286, and 293.7 K, indicating the availability of six phases (Figure 1). The derivative compounds $[TMA]_2CuCl_4$ and $[TMA]_2ZnCl_4$ single crystals underwent phase transitions at 265, 293, and 298 K, and at 161, 181, 276.3, 278, and 293 K, respectively[12, 13].

EPR STUDY

$3d^9$-Cu^{2+} ions are characterized by an electronic S = 1/2 and nuclear spin I = 3/2. The EPR spectra of the $[TMA]_2Zn_{0.5}Cu_{0.5}Cl_4$ samples exhibit common features and consist in two more or less anisotropic signals whatever the location of the metal ions inside in the matrix pores. Typical EPR spectra are summarized in Figure 2 for the compound at different temperatures. The EPR spectra are generally composed of two signals.
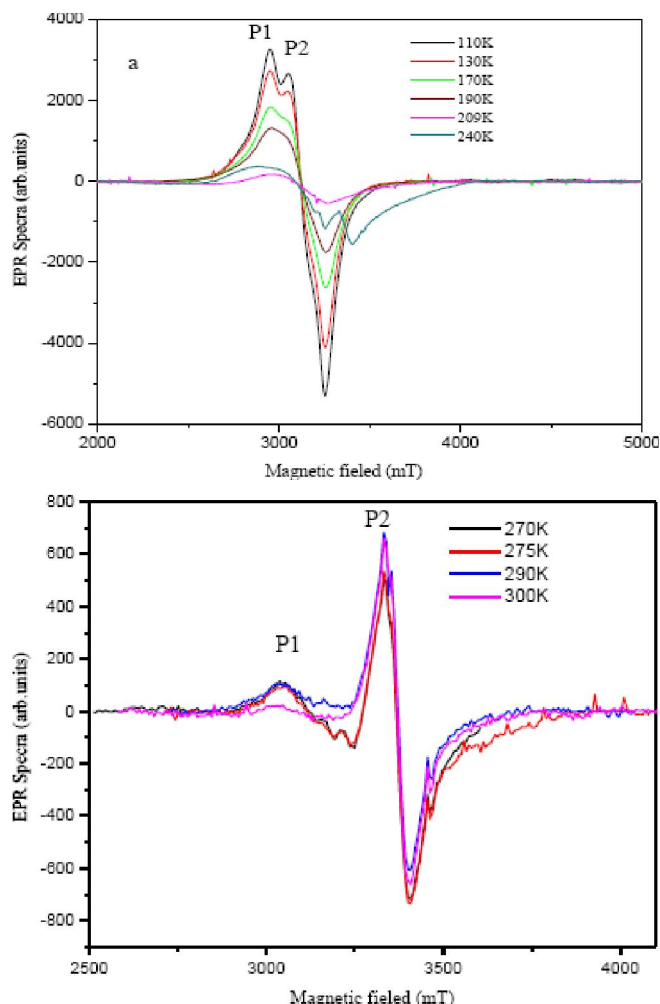

Figure 2 : EPR spectra of copper at various temperatures for $[TMA]_2Zn_{0.5}Cu_{0.5}Cl_4$ samples.
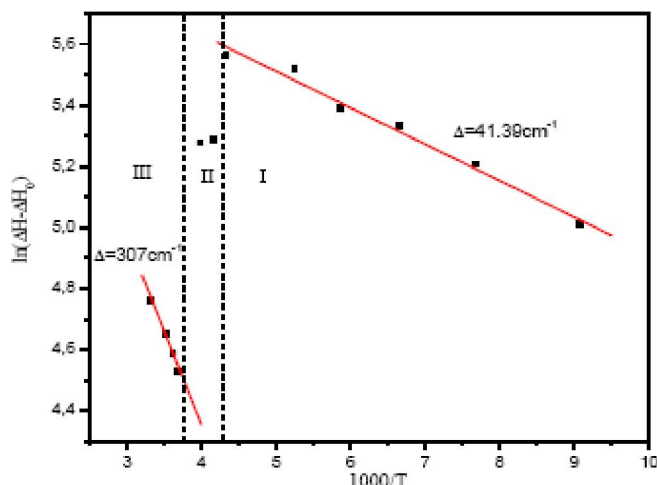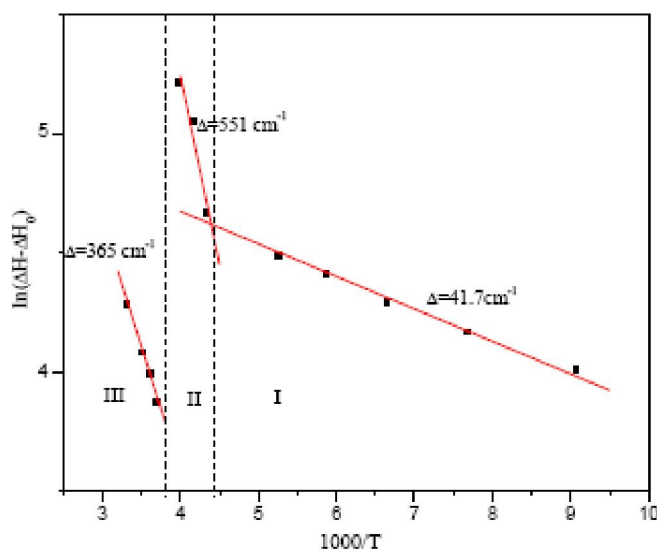
Figure 3 : Temperature dependence of ln(□□□□) vs 1000/*T* of P1

Figure 4 : Temperature dependence of ln(□□□□) vs 1000/*T* of P2

TABLE 1 : Experimental energy gaps for the two peaks at different phases.

Temperature (K)		248		271
Phase		**Phase(I)**	**Phase(II)**	**Phase(III)**
Energy gap (cm^{-1})	Peak 1	41,70	551	365
	Peak 2	41,39	----------	347

The thermal variation of the EPR line width is satisfactory accounted by an activated relaxation by phonons following the simple law □□□□□□ exp(-2□/T)[15].

In this expression, □H$_0$ represents a background line width and the exponential factor is related to the occurrence of an Orbach relaxation mechanism[15]. The above EPR line features are currently involved in the case of a dynamic Jahn Teller effect[16] as reported also

in copper based compounds. Within this framework, the relaxation law is monitored by phonons whose frequency defines the A parameter and □ represents the energy gap between the vibronic states of the metal ligands field.

Figures 3 and 4 show the variation of ln(□□□□) with the inverse of absolute temperature (10^3/T) of P1 and P2 peaks. The change of the EPR line width with absolute temperature shows threes regions associated with three activation energies separated by two temperatures 248 and 271 K. These experimental energy gaps for the two peaks are grouped in TABLE 1.
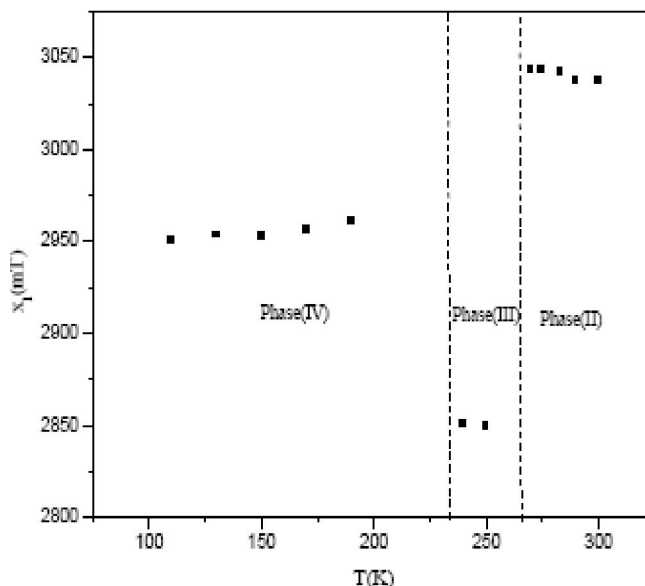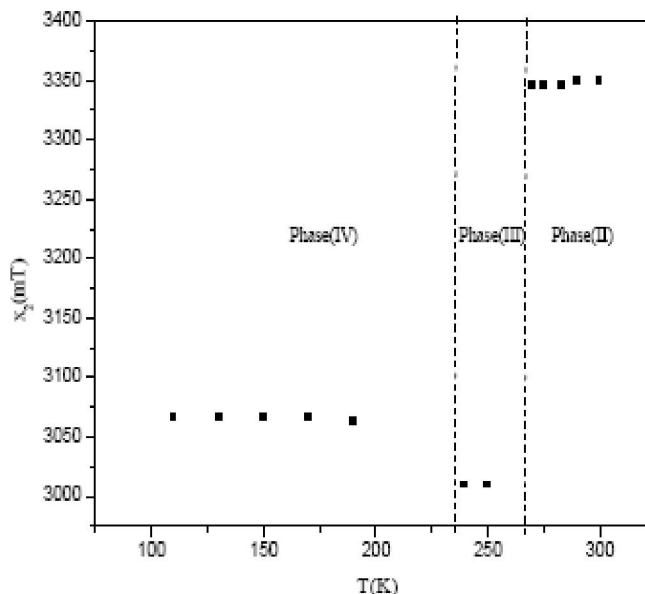

Figure 5 : Temperature dependence of the positions x1

Figure 6 : Temperature dependence of the positions x2

The changes in the width line H and the positions x1 and x2 (Figures 5 and 6) of the two peaks P1 and P2 versus temperature confirm the presence of two phase transitions at 248 and 271K detected by DSC which are related to the distortion of the $CuCl_4$ groups.

NMR STUDY

The ^{13}C NMR spectra of the $[TMA]_2Zn_{0.5}Cu_{0.5}Cl_4$ compound are showed in Figure 7. At high temperatures there is only one tetramethylammonium signal at the expected position, about 58 ppm. Below 386K, the signal splits into two with not completely equal intensities. The variation of the ^{13}C chemical shift displacement at various temperatures (Figure 8) confirms the occurrence of the phase transition at 383K detected by differential scanning calorimetry and RX measurements[11].
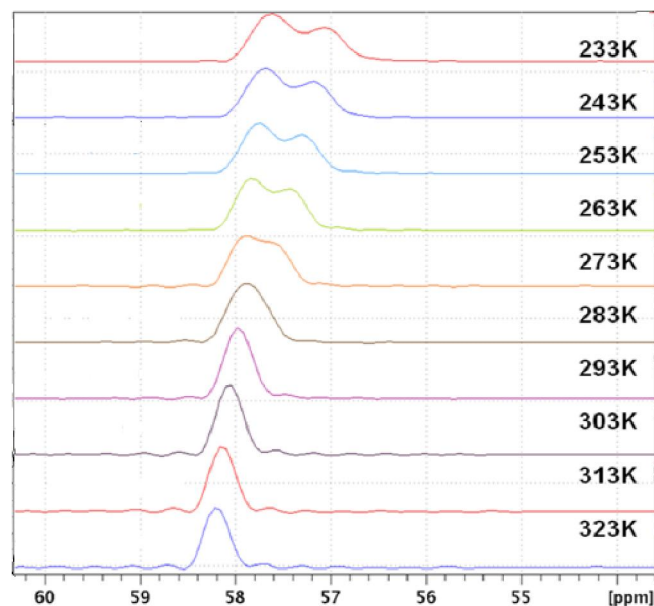

Figure 7 : Temperature variation of the ^{13}C NMR spectrum of $[TMA]_2Zn_{0.5}Cu_{0.5}Cl_4$ compound.

When the temperature decreases, the unit cell (the asymmetry unit also) is multiplied along b direction. A polytipisme comportment is observed. In this case, Cu^{2+} and Zn^{2+} donot occupy the same site and we can differentiate two types of inorganic tetrahedra $CuCl_4$ and $ZnCl_4$. In the organic-inorganic sheets, we deduce the sequence: $CuCl_4$-TMA^+-$ZnCl_4$. Each organic layer is rounded by three $CuCl_4$ and three $ZnCl_4$ anions. Anion-cation distance in the first type (in the inorganic-organic layer) is shorter than the second type (between

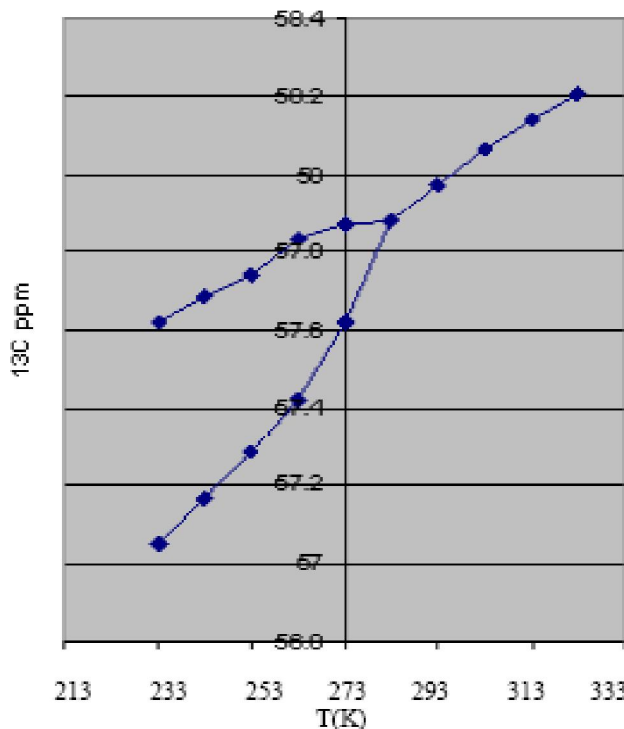**Figure 8 : Temperature variation of ^{13}C chemical shift displacement.**

the layers). Indeed, when comparing of $CuCl_4$-TMA^+ distances, one deduces two types of cations:

- TMA^+ in the organic-inorganic layer
- TMA^+ in the organic layer

CONCLUSION

The Organic–inorganic Compound $[TMA]_2Zn_{0.5}Cu_{0.5}Cl_4$ is characterized by many phase transition. DSC measurements between 200 and 400K for this mixed matrix system revealed five phase transitions at 248, 271.7, 278, 286, and 293.7K. The variation of ε' and ε'' versus temperature at different frequencies shows that the presence of a peak at 293K corresponds to the ferroelectric-paraelectric phase transition which is second order type[14]. The transitions at 248 and 271 are detected by EPR analyses which are related to the distortion of the $CuCl_4$ group. The phase transition at 286 is observed by ^{13}C NMR study which is related to the motion of the organic group (TMA).

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