Transport properties of Mg$^{2+}$ ion doped Cu(HCOO)$_2$
organic molecular single crystals

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Thermally stimulated discharge current (TSDC) of Mg$_x$ Cu(HCOO)$_2$ organic molecular single crystals has been studied in the low temperature (77-300K) region. The pure ($x = 0$) single crystals show only one TSDC peak at 183 K with the maximum current of 5.5 nA, which is attributed to ‘detrapping of charge carriers’. But three peaks were observed in impurity doped ($x = 1$ and 2 mole %) Cu(HCOO)$_2$ single crystals. The maximum current in these crystals was in the order of few microamps. The two new peaks have been assigned to ‘Trap-limited band transport model’ and ‘Maxwell-Wagner effect’. Relaxation parameters and activation energies of these crystals have been calculated.

1 Introduction

Transport properties of homo- and hetero-molecular single crystals have been drawing considerable attention of scientists and technologists from many disciplines. Because the square planar Heisenberg ferromagnetic organic molecular single crystals with tetragonal symmetry are known to display a large number of distinct phases under appropriate conditions of temperature and magnetic fields. At the same time the low dimensional physics of mobile charge carriers with strong coulomb interactions between oxygen ligand and copper (II) transition metal ion has attracted an enormous amount of theoretical and experimental interests since the discovery of layered high $T_c$ superconductors.

In this paper, the transport properties of pure and Mg$^{2+}$ ion doped Cu(HCOO)$_2$ organic molecular single crystals by using ‘Thermally Stimulated Discharge Current’ (TSDC) technique are described. This technique was originally proposed by Bucci et al., and it is a sensitive method for the investigation of transport properties of single crystals. Hence an attempt has been made to study the transport properties of the fore-mentioned single crystals. These crystals are built up of dimeric entities formed by two edge sharing Cu$_2$O$_4$ polyhedra, giving rise to bis(μ-Oxo) [Cu$_2$O$_4$] entities. In these crystals the copper(II) ions are in a 4+1 oxygen environment of formate ligand in square pyramidal geometry with Cu-O distance 1.9 Å and Cu-O’ distance is 2.79 Å similar to a high $T_c$ superconductor.

2 Experimental Details

The blue prismatic pure single crystals of Cu(HCOO)$_2$ have been grown by slow evaporation of a stoichiometric saturated solution of CuO and formic acid (90%)—water (20.80) at ambient temperature. 1 and 2 mole % of Mg$^{2+}$ ion doped Cu(HCOO)$_2$ crystals have been grown by adding MgO (Fluka) as impurity to the pure saturated solution.

TSDC measurements have been carried out on these crystals by making ohmic electrical contacts using silver paint (1228 G Eltecks Corporation, Bangalore). The sample was first cooled to the required temperature ($T_i$), and polarised by an externally applied electric field ($E_p$) of strength 2 kV/cm for about 15 min and cooled to 77K. Then after the electric field was switched off. The sample thus prepared was heated thereafter at a constant heating rate ($β$) of 3°C/min, and the discharge current was measured by Keithly 616 electrometer.

3 Theory

The relaxation parameter at a temperature $T$ is given by:

$$\tau = \tau_0 \exp \left( \frac{U}{kT} \right)$$  \hspace{1cm} (1)

where $U$ is activation energy and $k$ is Boltzmann constant. The expression for the discharge current in the sample at a heating rate of $β$ is given by:

$$i(T) = A \exp \left[ \frac{-U}{kT} - \frac{1}{\beta \tau_0} \int \exp \left( \frac{-U}{kT'} \right) dT' \right]$$ \hspace{1cm} (2)

Differentiating Eq. (2) and putting it to zero one can get the temperature $T_m$ at which a maximum current occurs.
The low temperature tail of Eq. 2 can be written as:

$$\log i(T) = \text{constant} - \frac{U}{kT} \quad \ldots (4)$$

From Eq. (4), the activation energy \( U \) can be determined from a plot of \( \log i(T) \) versus \( 1/T \) and \( \tau_0 \) can be calculated from Eq. (3). Using Eq. (1) \( \tau \) can be calculated at \( T_m \) and at 300 K.

### 4 Results and Discussion

The TSDC spectra of \( \text{Mg}_x \text{Cu(HCOO)}_2 \) single crystals where \( x = 0 \) mole % (Fig. 1) and \( x = 1,2 \) mole % (Fig. 2) with polarisation temperature \( (T_p) \) of 200K show that the peak current increases by three orders of magnitude due to \( \text{Mg}^{2+} \) ion doping. Similarly there is a shift in the peak temperature towards lower value with increasing in \( \text{Mg}^{2+} \) ion respectively. Two new peaks were observed in \( \text{Mg}^{2+} \) ion doped crystals they were at 160, 243 K in 1 mole % doped and at 156, 230K in 2 mole % doped crystals.

The peak temperature, peak current and the activation energies, characteristic relaxation time \( \tau_m \) (relaxation time corresponding to peak temperature) and \( \tau_0 \) (relaxation time corresponding to infinite temperature) associated with the discharge processes have also been calculated and are presented in Table 1.

Several processes contribute to the discharge of electrets, but the driving force of them is the restoration of charge neutrality. The dipolar relaxation and space

### Table 1 — TSDC parameters of \( \text{Mg}_x \text{Cu(HCOO)}_2 \) single crystals

<table>
<thead>
<tr>
<th>Doping concentration (x) mole %</th>
<th>Peak temperature ( T (K) )</th>
<th>Peak current ( (A) )</th>
<th>Relaxation Parameters</th>
<th>Activation Energy ( U ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = 0 )</td>
<td>183</td>
<td>5.5 nA</td>
<td>( 1.26 \times 10^{-14} )</td>
<td>( 6.07 \times 10^1 )</td>
</tr>
<tr>
<td>( x = 1 )</td>
<td>138</td>
<td>1.5 μA</td>
<td>( 1.25 \times 10^{-13} )</td>
<td>( 4.92 \times 10^1 )</td>
</tr>
<tr>
<td>( x = 2 )</td>
<td>128</td>
<td>1.8 μA</td>
<td>( 5.36 \times 10^{-12} )</td>
<td>( 5.1 \times 10^1 )</td>
</tr>
</tbody>
</table>
charge depolarisation play a prominent role. In electrets made from polar materials, the disorientation of dipoles contributes for the TSDC, while the space charge depolarisation of the charge carriers or ions, they generally considered to move with thermally activated mobility. However if the charge carriers are electrons or hole, the depolarisation takes place due to diffusion of these carriers to electrodes.

The earlier transport properties of these crystals reveal that the charge carriers are holes, hence the TSDC peaks at 183, 148 and 128K of x=0 (pure), 1 and 2 mole % doped crystals are attributed to the diffusion of holes with thermal energy, and detrapping of charge carriers which are present as defects. The peak current in x = 0 mole % (pure) crystal is very less (5.5 nA) because of small number of free charge carriers due to strong covalent nature of Cu⁺⁺ ion with the organic (HCOO)⁻ ligand. A sudden change in peak current and peak temperature values are observed in 1 and 2 mole % doped crystals, because this Cu(HCOO)₂ single crystal is a low dimensional crystal. The occurrence of chemical or structural defects in this low dimensional single crystal shows drastic consequences on electrical and magnetic properties comparatively three dimensional crystal. Hence the sudden change in peak current and peak temperature are taking place due to low dimensional nature of this crystal.

The second peak in the low temperature region (i.e. at 160K for 1 mole % and 155K for 2 mole %) of TSDC spectrum (Fig. 2) of these doped crystals is attributed to a redistribution of the possible positions of cation vacancy that jumps around the impurity ion. The redistribution process generally contains only one peak with a narrow temperature interval. This is comparable with most of the I-V (Impurity-vacancy) pair formed with divalent impurity ions and the accompanying cation vacancies in organic single crystals.

A new third peak is observed in the relatively high temperature region in doped crystals (i.e. at 243K in 1 mole % and 230K in 2 mole %). This peak may be assigned to the Maxwell-Wagner (MW) effect. According to Maxwell-Wagner effect, a TSDC peak would exist in a heterogeneous sample consisting of different phases around the transition temperature. Mg₆Cu(HCOO)₂ crystal (x=1.2 mole %) are heterogeneous samples which are showing peierls transition at 208K. Hence this TSDC peak around 230K is attributed to the Maxwell-Wagner peak. Due to homogeneous nature of pure (x = 0 mole %) Cu(HCOO)₂ single crystal this MW peak is not observed.

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References