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Temperature dependences of electric properties of tetramethylammonium mono- and pentaiodide

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The dielectric properties of tetramethylammonium monoiodide and pentaiodide were investigated in broad temperature range (−150°C till +50°C). It was demonstrated that the structural organization of the polyiodide chain containing I...I charge-assisted halogen bonds influenced the parameters and the mechanism of electric conductivity of considered compound. The impedance spectroscopic measurements revealed that the direct current electric conductivity of pentaiodide salt is around four orders of magnitude higher than that of corresponding monoiodide. Moreover, pentaiodide demonstrates the hopping mechanism of conductivity.

Keywords: Impedance spectroscopy; electric conductivity; tetramethylammonium salts; polyiodides; halogen bonding.

1. Introduction

Polyiodides with organic cations are widely used as components of dye-sensitized solar cells (DSSC).^{1–3} Long-chain tetraalkylammonium cations with polyiodide anions of various stoichiometry are widely spread as components of such devices due to low melting point so that they can be treated as ionic liquids.^{4,5} Moreover, they demonstrate clear dependency between the melting point and polyiodide ratio: the more iodine atoms are located in the anion the lower is the melting point. Furthermore, this row tends to form various crystal structures with different polyiodide anions leading to convenient functionalization of materials suitable for solar cells production. Finally, simple synthetic procedure and crystallization of the corresponding polyiodides together with easily obtained and stable source the monoiodides⁶ turn tetraalkylammonium salts into perfect model compounds in the studies of polyiodide structural features and conductive properties. Structural study of polyiodides cannot be performed without touching the topics of noncovalent interactions in the solid state, especially halogen bonding.^{7,8} Halogen bond is defined as an attractive interaction in which the halogen atom acts as an acceptor of electron density and provides its electrophilic site for bonding.⁹

Recent study of structural features, anion transformations and electrical conductivity of polyiodides under hydrostatic pressure shows that even polyiodides that are dielectrics at

ambient conditions can perform conductive properties under the change of external conditions: temperature, pressure, mechanical stress due to small structural transformation in the anionic part.^{10,11} The existence of switchable properties that appears only under controlled change of experimental procedure can be prominent in the design of molecular switches. Latest experimental and theoretic structural and conductive studies summarize the list of possible undergoing processes in polyiodide anions including reverse interconversion of triiodide to iodine and iodide anion.¹² Impedance spectroscopy was previously used for the characterization of 3-thiophenemethylamine polyiodide revealing high photoconductivity and short response time.¹³ Quantum-chemical calculations of alkylammonium polyiodide have been previously performed in attempt to understand the undergoing processes inside DSSC in terms of HOMO–LUMO.¹⁴

Finally, the analysis of polarization effects of tetramethylammonium pentaiodide (TMAPI) is highly important due to the known fact of dependency of observed vibration bands in Raman spectrum on the wavelength of laser which is used for spectrum excitation.¹⁵ Thus, following above-mentioned trends, the processes undergoing in the pentaiodide structure under cooling and alternating current in comparison to those with corresponding tetramethylammonium monoiodide (TMAMI) are in the center of attention in this paper.

2. Materials and Methods

To investigate the dielectric properties of TMAMI and TMAPI, initial single crystals were milled into the powder and, then, pressed (five tons) in pellets. The thickness and diameter of these pellets were around $d_{cr} = 850 \mu\text{m}$ and $d = 5 \text{ mm}$, respectively.

2.1. Sample characterization

TMAPI was initially obtained in a single crystal form by the interaction of TMAMI and iodine in 1:2 ratio in ethanol solution. Pentaiodide crystals were grown during slow solvent evaporation at room temperature. TMAMI was recrystallized from ethanol in order to obtain white thin needle-like crystals.

Crystal structure of TMAMI (CSD refcode QQQCVG02¹⁶) is characterized by rather isolated iodide ions (Fig. 1(a)), while TMAPI (refcode DULZOZ01¹⁷ at room temperature, CCDC Number: 1958945 at 100 K¹⁸) tend to form a cage-like net structure with organic cation inside due to multiple I...I contacts (Fig. 1(b)).

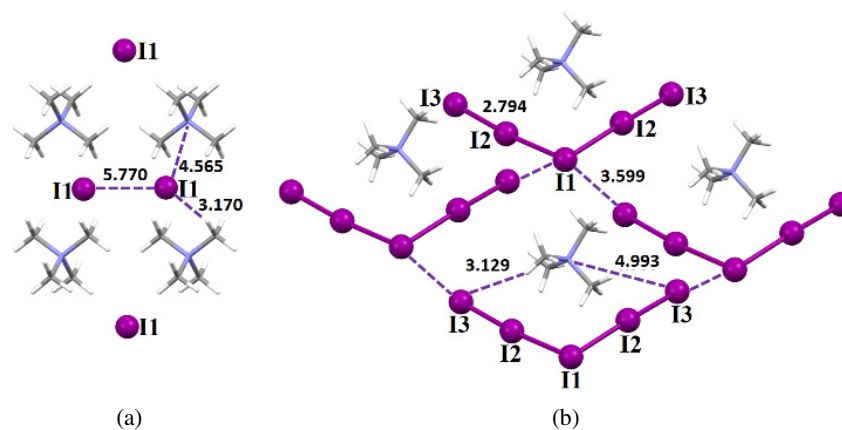


Fig. 1. The fragments of TMAMI (a) and TMAPI (b) crystal structures with selected short contacts distances (Å).

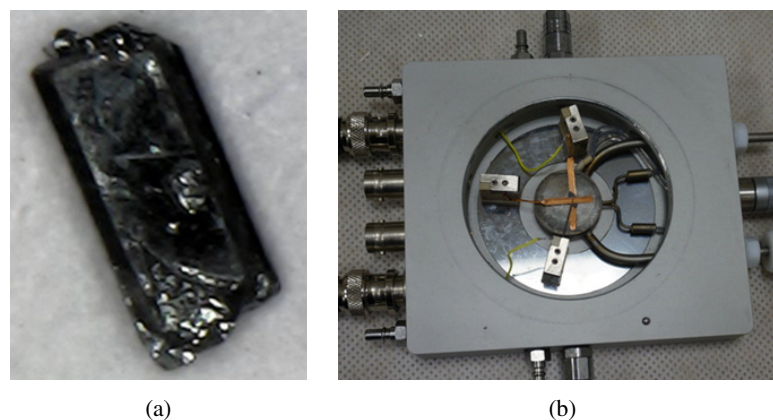


Fig. 2. The appearance of: (a) TMAPI crystal under $4\times$ microscope magnification; (b) temperature-controlled chamber with copper electrodes.

TMAPI crystallizes as large prismatic crystals of dark color with green refruent surface (Fig. 2(a)). Its structure has been proved by single-crystal X-ray diffraction; obtained crystallographic model coincides with Cambridge Structural Databank structure (CSD refcode DULZOZ01). Crystal packing in this structure is formed by pentaiodide 3D organization via the symmetric motif of I...I halogen bonds with 3.5986 Å distance (100 K) (Fig. 1(b)). Tetraalkylammonium cations are located inside such pentaiodide squares.

Comparison of selected interatomic distances (Table 1) shows that the most notable change with temperature is observed for I1...I3 charge-assisted halogen bond ($\Delta = 0.044 \text{ \AA}$) which is responsible for the formation of continuum anionic net and cationic cage (Fig. 1(b)). Thus, further discussed changes in dielectric properties can be more likely associated with tiny structural rearrangements in this particular fragment of TMAPI crystal structure.

2.2. Impedance spectroscopy methodology

The complex impedance spectra ($Z = Z' - iZ''$) of the prepared TMAMI and TMAPI tablets were measured in the

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Table 1. Comparison of the geometric parameters for the crystal structure of Tetramethylammonium penta- and monoiodide at 273 K and 100 K.

Bond distances	$C_4H_{12}N^+I_5^-$, 273 K	$C_4H_{12}N^+I_5^-$, 100 K	$C_4H_{12}N^+I^-$, 273 K
I(2)–I(3)	2.7924	2.7939	—
I(1)–I(2)	3.1486	3.1396	—
I(1), . . . , I(3)	3.6422	3.5986	—
I(3), . . . , I(2)	4.3587	4.2488	—
I(3), . . . , N(1)	4.9110	4.9930	4.5650
I(3), . . . , H(2)	3.2687	3.1290	3.1705

spectral range from 10^{-2} Hz to 5×10^6 Hz with a Novocontrol Beta System impedance spectrometer. The amplitude of the probing oscillating voltage was 0.1 V. The pellets were mounted in temperature-controlled chamber Linkam (Fig. 2(b)). The measurements of impedance spectra were carried out in the temperature range from -150°C till $+50^\circ\text{C}$.

The spectra of the dielectric permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ were evaluated from the impedance spectra using the relations

$$\varepsilon' = Z''d_{\text{cr}}/2\pi f\varepsilon_0S(Z'^2 + Z''^2), \quad (1)$$

$$\varepsilon'' = Z'd_{\text{cr}}/2\pi f\varepsilon_0S(Z'^2 + Z''^2), \quad (2)$$

where ε_0 is the dielectric permittivity of vacuum, S is the electrode area.

The dielectric spectra of TMAMI could be measured only at temperatures above 0°C , as at lower temperatures the electric current flowing through this sample was out of the measuring range of the impedance spectrometer.

For a more detailed investigation of dielectric properties, the complex dielectric spectra were transformed into the complex modulus spectra: $M = 1/\varepsilon$.

The electric properties (direct current conductivity and mechanism of electric conductivity) were investigated using complex conductivity spectrum representation

$$\sigma = i2\pi\varepsilon_0\varepsilon. \quad (3)$$

To analyze the electric properties of the samples following from these spectra, the real and imaginary parts of Eq. (3) could be written in explicit forms as

$$\sigma' = 2\pi f\varepsilon_0\varepsilon'' + \sigma'_{\text{hop}} + \sigma_{\text{DC}}, \quad (4)$$

$$\sigma'' = 2\pi f\varepsilon_0\varepsilon' + \sigma''_{\text{hop}}. \quad (5)$$

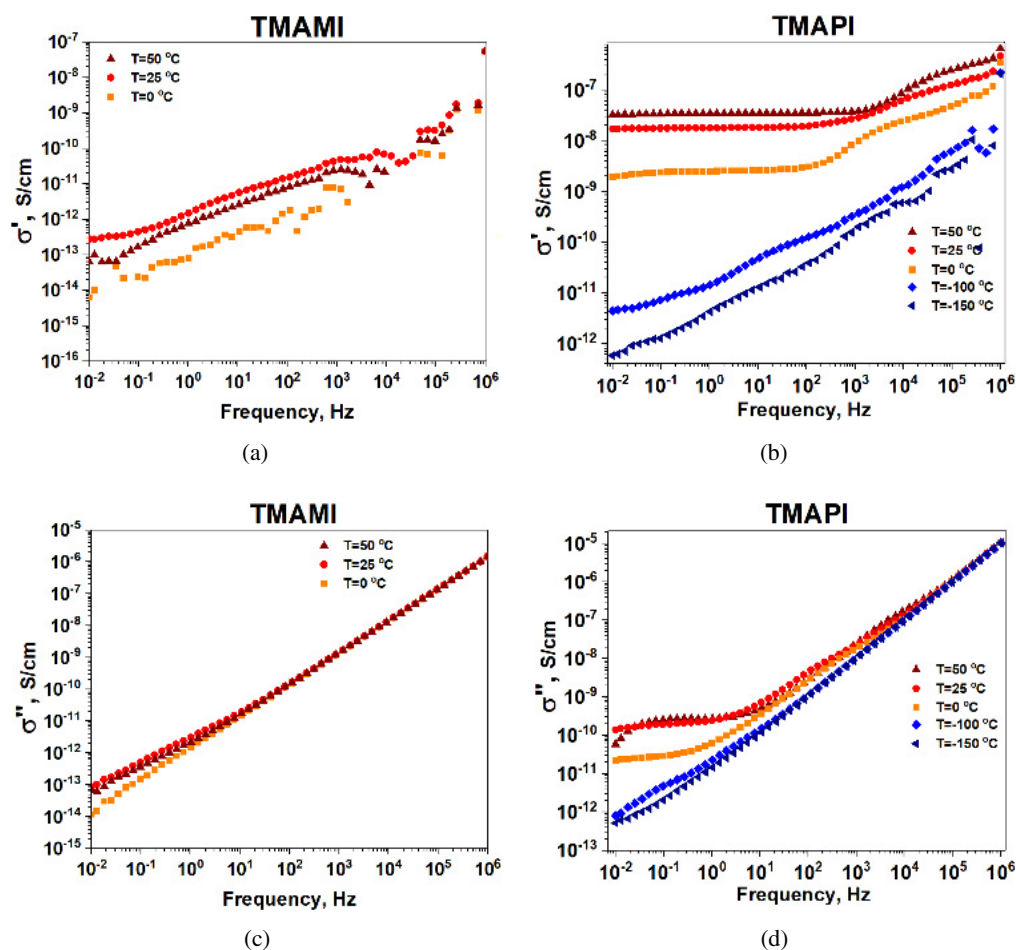


Fig. 3. Real and imaginary parts of electric conductivity spectra for TMAMI (a, c) and TMAPI (b, d) at different temperatures.

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Here, $\sigma_{\text{hop}} = \sigma'_{\text{hop}} - i\sigma''_{\text{hop}}$ is the complex hopping conductivity, σ_{DC} is the real value electronic DC conductivity.

In the limiting case, $f \rightarrow 0$ Hz, these following formulae are reduced:

$$\sigma' \approx \sigma'_{\text{hop}} + \sigma_{\text{DC}}, \quad (6)$$

$$\sigma'' \approx \sigma''_{\text{hop}}. \quad (7)$$

Therefore, σ_{DC} could be found estimated from the horizontal asymptote ($\sigma'(f) \rightarrow \sigma_{\text{DC}}$ at $f \rightarrow 0$ Hz) and the parameters of hopping conductivity from the functional dependence of the σ' and σ'' in this frequency limit.

3. Results and Discussion

As follows from Fig. 3, the conductivity spectra of TMAMI and TMAPI samples are remarkably different. The real part of conductivity spectra of TMAPI (Figs. 3(b) and 3(d)) has pronounced horizontal asymptote at almost all temperatures

and its σ_{DC} varies in the range from 5.8×10^{-13} S/cm ($T = -150^\circ\text{C}$) till 3.3×10^{-8} S/cm ($T = 50^\circ\text{C}$).

In case of TMAMI, it was impossible to correctly estimate σ_{DC} at $T = -150^\circ\text{C}$ owing to insufficient sensitivity of the impedance spectrometer. However, at $T = 25^\circ\text{C}$, it is equal to around 4.6×10^{-12} S/cm. Hence, the DC conductivity of TMAMI is around four orders of magnitude higher than that of TMAPI.

In comparison with TMAMI, TMAPI demonstrates the pronounced hopping mechanism of electric conductivity. As follows of imaginary parts of both samples, σ'' spectra of TMAMI tends to zero at $f \rightarrow 0$ Hz which means that the contribution of the hopping mechanism of conductivity is infinitesimal (Fig. 4).

The situation changes dramatically for TMAPI. Pentaoidide anion induces the hopping conductivity. As one can clearly see from σ'' spectra of TMAPI, they have nonzero asymptotic behavior at low frequency limit. Hence, one can estimate the imaginary part of the hopping conductivity as

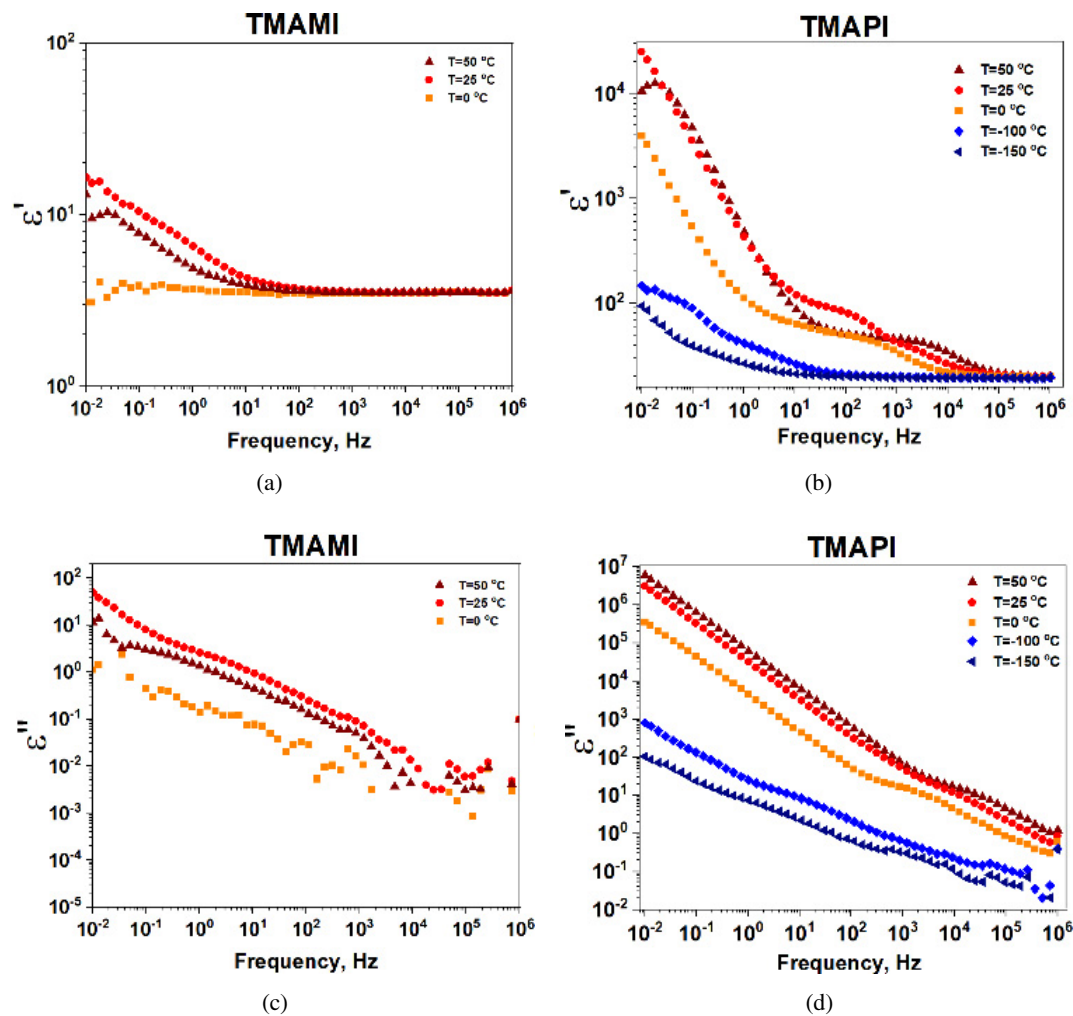


Fig. 4. Real and imaginary parts of dielectric spectra for TMAMI (a, c) and TMAPI (b, d) at different temperatures.

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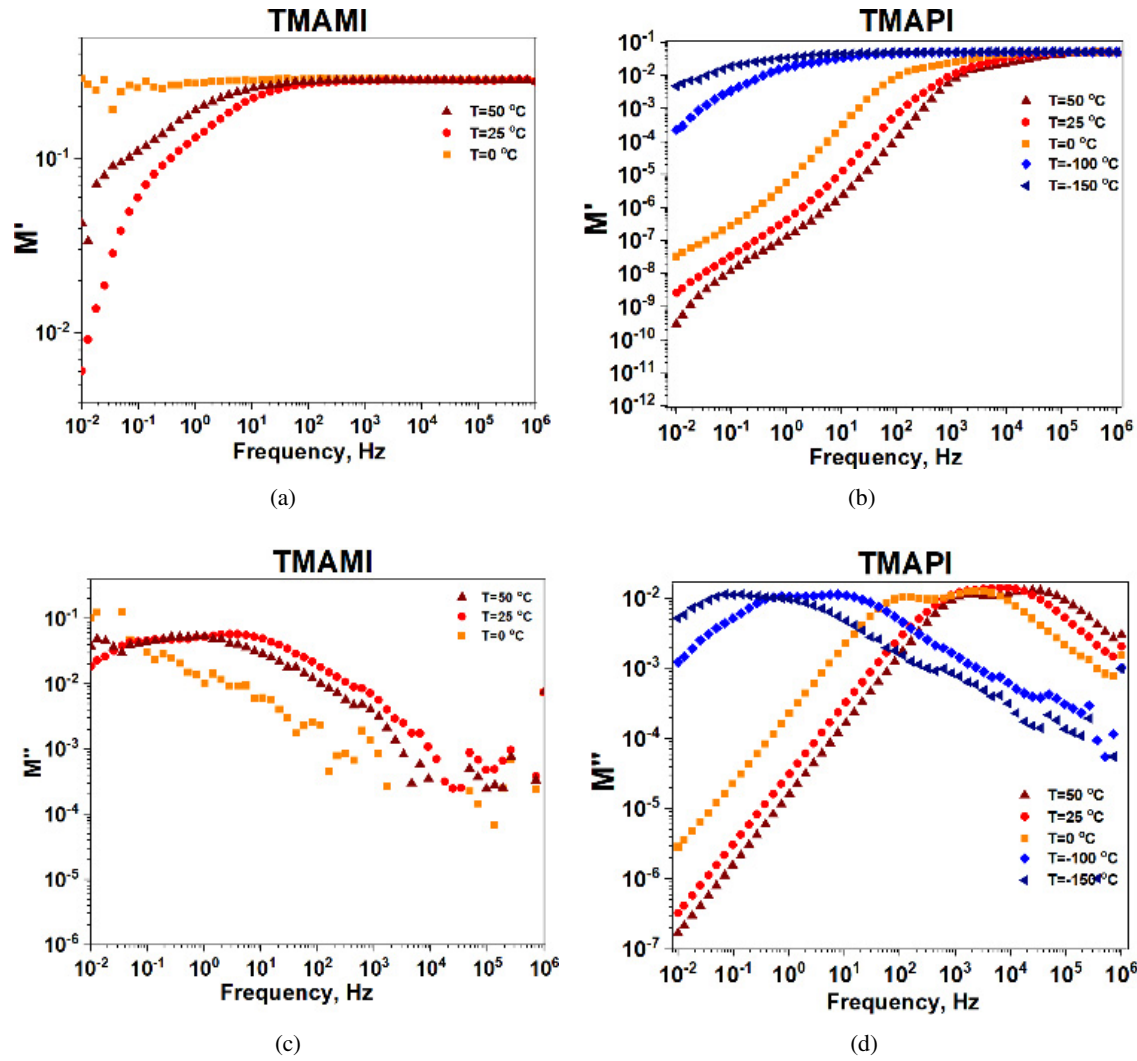


Fig. 5. Real and imaginary parts of electric modulus spectra for TMAMI (a, c) and TMAPI (b, d) at different temperatures.

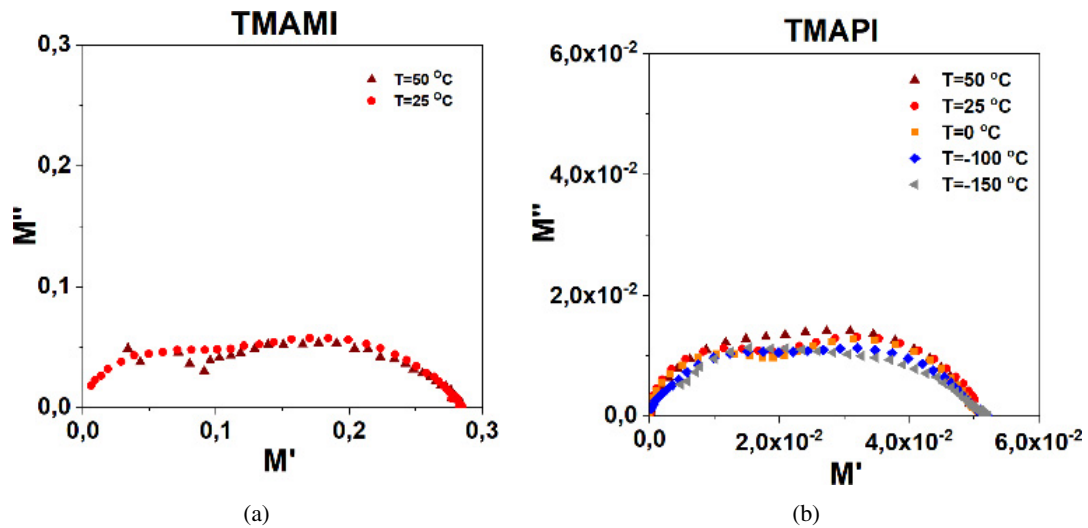


Fig. 6. Cole-Cole plots for TMAMI (a) and TMAPI (b).

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1 varying from $\sigma''_{\text{hop}} \approx 8.0 \times 10^{-13}$ S/cm ($T = -150^\circ\text{C}$)
 2 $\sigma''_{\text{hop}} \approx 1.1 \times 10^{-10}$ S/cm ($T = 50^\circ\text{C}$).

3 At the same time, at $T = 50^\circ\text{C}$, σ''_{hop} of TMAPI is
 4 falling down which could be assigned to the thermally in-
 5 duced changes of its structure. Pentaiodide anion also sig-
 6 nificantly influences the dielectric properties of TMAPI
 7 crystal (Fig. 4). The high frequency dielectric permittivity of
 8 TMAPI is around 10, whereas that of TMAMI is around 5
 9 ($T = 50^\circ\text{C}$).

10 As one can see from the complex dielectric spectra
 11 (Fig. 4) for TMAPI and TMAMI, the pentaiodide affects
 12 the relaxation processes. In case of TMAMI, imaginary
 13 parts of dielectric spectra demonstrate significantly low di-
 14 electric losses (five orders of magnitude) in comparison
 15 with TMAPI. TMAPI has also thermoactivated dielectric
 16 relaxation process in frequency range 10^{-1} Hz– 10^4 Hz
 17 (Fig. 4).

18 This process could be explained by the change of the
 19 length of halogen bonds resulting in thermally depended re-
 20 laxation of the electric polarization due to change the shape
 21 and parameters of the potential energy profile. These results
 22 correlate with the above-mentioned conclusion about hop-
 23 ping mechanism of the electric conductivity. Employing the
 24 electric modulus representation (M -representation) allowed
 25 us to confirm this hypothesis. Moreover, this formalism
 26 makes possible to separate closely located dielectric relaxa-
 27 tion modes in low frequency range. As one can clearly notice
 28 from the complex M -spectra of TMAMI and TMAPI (Fig. 5)
 29 and Cole-Cole plots (Fig. 6), there are two low frequency
 30 processes in TMAPI. This could be explained by the tem-
 31 perature driven, asymmetric double-well potential appearing
 32 in TMAPI.

35 4. Conclusions

36 The dielectric properties of TMAMI and TMAPI were
 37 investigated in temperature range from -150°C till
 38 $+50^\circ\text{C}$. The impedance spectroscopic measurements showed
 39 that the direct current electric conductivity of TMAPI is
 40 around four orders of magnitude higher than that of
 41 TMAMI. Moreover, TMAPI demonstrates the hopping
 42 mechanism of electric conductivity. We attribute this phe-
 43 nomenon as a consequence of polyiodide chains in crystals,
 44 in the formation of which the charge-assisted I...I halogen
 45 bonds play a key role.

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