Temperature dependency of excitonic effective mass and charge carrier conduction mechanism in CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin films

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In this paper we explain the temperature dependence of excitonic effective mass and charge carrier conduction mechanism occurs in CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin films prepared by chemical dip coating (CDC), spray pyrolysis (Spray) and repeated dipping-withdrawing (Dipping). Hall Effect study confirmed that prepared CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ samples are p-type semiconductor having carrier concentration of the order of ~ $10^{16}$ cm$^{-3}$. The charge carrier mobility, mean free path and mean free life time were found to decrease with increasing temperature due to polaronic effect. The excitonic effective mass is estimated to (0.090–0.196)m$_e$ and excitonic binding energy (15–33) meV, well consistent with Wannier-Mott hydrogenic model and the nature of exciton is likely to be Mott-Wannier type. From electrical measurement, it was observed that charge carrier conduction in CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ is governed by migration of I$^-$ and CH$_3$NH$_3^+$ vacancies and vacancy-assisted diffusion processes depending on temperature.

Now-a-days, methylammonium lead halide perovskites (MLHP) are regarded worldwide as an emerging material class in the field of photovoltaic and optoelectronics. The typically chemical formula of MLHP is AMX$_3$, where A is the organic/inorganic cation (CH$_3$NH$_3$), M is a heavy metal cation (Pb) and X is halide anions (I). When X site is replaced by another halogen element such as chlorine (Cl) into AMX$_3$, it converts to mixed halide perovskites CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. This mixed halide perovskites exhibit semiconducting nature with some exciting properties for photovoltaic and optoelectronic device applications. The single-junction solar cell architecture, based on CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite, shows power conversion efficiency of 25.5%$^1$. Besides, CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin film shows multi-colored emission$^2$–$^5$, second harmonic generation or frequency doubling$^5$, bimolecular recombination$^6$, trap-assist recombination$^7$, strong tunable interband transitions$^8$, and ambipolar charge transport$^9$. However, mixed halide perovskite suffers a compositional instability due to halide (I, Br) segregation$^{10}$. But a very small addition of Cl into (I/Br) lattice restrains the halide phase segregation, improves the charge carrier mobility, carrier lifetime and stability of solar cells without changing the crystallographic domain size$^{11}$. These properties are directly correlated with the temperature dependent charge transport behavior in CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ and expected to improve device configuration compared to (I/Br) composition.

Up to now, multiple approaches such as transient terahertz (THz) spectroscopy$^{6,12}$, combination of time-resolved terahertz with optical transient reflection spectroscopy (TRTS-TR)$^{13}$, photoluminescence quenching (PLQ)$^{14}$, time resolved electro-absorption spectroscopy$^{15}$, time-of-flight (TOF) photoconductivity$^{16}$ and Hall effect measurement$^{17}$ have been carried out to explore the transport properties of lead halide perovskites. These pioneer studies reveal the presence of non-Langevin charge carriers$^6$, strong back-scattering on free carrier dynamics$^{12}$, existence of higher hole mobility compared to electron mobility$^{13}$, large electron–hole diffusion lengths (> 1 μm)$^{14}$, electric field assisted charge carrier separation$^{15}$, grain size dependent mobility$^{16}$, and influence of self-doping in carrier concentration$^{17}$. Despite the advancement in deep-seated perceptive in transport behavior, a lot of issues such as charge-carrier type, the mechanisms for restraining carrier mobility, origin of electron–hole recombination rates, donor or acceptor ionization energy, position of Fermi level, effective mass

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of charge-carriers, grain boundary barrier height, carrier mean free path-life time in CH₃NH₃PbI₃₋ₓClₓ still perplexes the researchers. It is well known that the mixed halide perovskite undergoes a phase transition from orthorhombic-tetragonal-cubic at 160 K and in between (315–330) K, respectively. However, the study of charge carrier dynamics is limited to tetragonal phase while it is also important to explore such properties for cubic phase above room temperature (RT).

Recently, it is reported that charge carriers generate self-induced rotation of the organic part (CH₃NH₃⁺), which polarizes lead halide perovskite lattice to form quasi-particle polarons. The conception of polaron is used to explain intrinsic electrical properties because it describes the interaction between charge carriers and phonons. The interaction of charge carriers with the organic part has significant influence on the effective mass, temperature and magnetic field dependent carrier transport and electrical conductivity of the mixed halide perovskite material.

In our previous work we report the characterization of nano-crystalline CH₃NH₃PbI₃₋ₓClₓ thin films prepared on glass substrate by chemical dipping-withdrawing (CDC), spray pyrolysis (Spray) and repeated dipping-withdrawing (Dipping) techniques in an ambient atmosphere. Our study confirmed the presence of tetragonal and mixed cubic-tetragonal phase in CH₃NH₃PbI₃₋ₓClₓ thin film. The film morphology was composed with spherical, rod, cuboid and polyhedral like crystal grains of sizes 100 nm to 2 μm. However, this article concentrates on the charge carrier transport of CH₃NH₃PbI₃₋ₓClₓ thin films using Hall Effect and dc-electrical conductivity measurement as a function of temperature, ranging from RT to 378 K. The carrier concentration, mobility, excitonic effective mass, excitonic binding energy, Fermi level, grain boundary barrier height and mean free life time of charge carriers are calculated from Hall Effect study. Furthermore, activation energies in CH₃NH₃PbI₃₋ₓClₓ thin films are exposed from electrical study. The effect of polarons on charge carrier dynamics and possible carrier conduction mechanism in CH₃NH₃PbI₃₋ₓClₓ thin films has been discussed. Therefore, in-depth study of charge carrier transport and conduction mechanism above RT for CH₃NH₃PbI₃₋ₓClₓ may provide a broader impact in the arena of perovskite research.

**Results**

**Temperature dependent Hall effect study.** Temperature dependent Hall voltage measurement is done at a constant magnetic field of 9.815 KG and the variation of Hall voltage is shown in Fig. 1. From the Hall Effect study Hall mobility (µH) and carrier concentration (nₑ) have also been calculated.

From Fig. 1 it is seen that the Hall voltage is positive and increased up to a certain temperature after which it decreases all through the measured temperature range for all samples. The positive sign of Hall voltage indicates that CH₃NH₃PbI₃₋ₓClₓ is a p-type material. It is reported that a lot of Pb, CH₃NH₃, I and Cl vacancies present in the films as because precursor solution was prepared by dissolving CH₃NH₃I and PbCl₂ at a molar ratio 3:1. However, Pb and CH₃NH₃ vacancies play the vital role for p-type conductivity of prepared CH₃NH₃PbI₃₋ₓClₓ thin films because of the lower formation energy of Pb and CH₃NH₃ compared to halogen vacancies.

The temperature dependent carrier concentration (left scale) and mobility (right scale) for (a) CDC, (b) spray and (c) dipping deposited CH₃NH₃PbI₃₋ₓClₓ thin films are shown in Fig. 2. The carrier concentration and mobility of dipping deposited sample is found almost half of the CDC and spray deposited samples. However, RT mobilities are found higher for all our samples than previously reported works. Table 1 shows a comparison of RT mobilities for perovskite CH₃NH₃PbI₃₋ₓClₓ obtained in different studies. It is reported that the breaking of inversion symmetry generates Rashba effect which enhance longitudinal optical phonon scattering by displacing the organic part or Pb-halogen bending or stretching and limits the increase of charge-carrier mobility at room temperature.

The carrier concentration and mobility can be affected by both magnetic field and temperature but the effect of temperature is dominant. In this study, the carrier concentration of all CH₃NH₃PbI₃₋ₓClₓ samples is found to increase exponentially (Fig. 2) with increasing temperature but mobility shows completely an opposite trend. Such behavior can be explained as: the presence of Pb, CH₃NH₃ and halogen vacancies in mixed halide perovskite creates free dipolar polarons by inducing a rotational re-organization of organic CH₃NH₃ dipoles; such polarons...
can migrate between the inorganic site of perovskite structure and lower the electron–hole recombination. Furthermore, sub-lattice thermal vibrations of inorganic octahedral have also an effect on carrier concentration and mobility in perovskite samples. Both the reorientation of organic site and sub-lattice thermal vibration enhance

**Figure 2.** Charge carrier transport of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. Variation of carrier concentration (left scale) and mobility (right scale) with temperature at a constant magnetic field of 9.815 KG for (a) CDC, (b) spray and (c) dipping deposited CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin films.

| Perovskites                | Measurement | $n_c$ (cm$^{-3}$) | $\mu_H$ (cm$^2$/V-s) | Ref.    |
|----------------------------|-------------|-------------------|-----------------------|---------|
| CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin films | Hall        | 7.1 × 10$^{16}$   | 46                    | CDC, This work |
|                            | Hall        | 6.8 × 10$^{16}$   | 49                    | Spray, This work |
|                            | Hall        | 2.6 × 10$^{16}$   | 20                    | Dipping, This work |
|                            | PLQ         | –                 | 2.1                   | $^{14}$ |
|                            | THz         | –                 | 11.6                  | $^{6}$  |
|                            | THz         | 1.0 × 10$^{15}$   | 33                    | $^{28}$ |
|                            | THz         | –                 | 27                    | $^{33}$ |
|                            | Microwave   | –                 | 27                    | $^{29}$ |
| CH$_3$NH$_3$PbI$_3$ single crystals | Hall | (9 ± 2) × 10$^9$ | 105                   | $^{54}$ |
|                            | Hall        | (1.0–1.2) × 10$^{11}$ | 80–95             | $^{25}$ |
| CH$_3$NH$_3$PbI$_3$ thin films | THz        | –                 | 8                     | $^{5}$  |
|                            | THz         | –                 | 35                    | $^{28}$ |
|                            | THz         | –                 | 20                    | $^{30}$ |
|                            | TOF         | –                 | 0.25                  | $^{30}$ |
|                            | Microwave   | –                 | 30                    | $^{30}$ |
|                            | Microwave   | –                 | 29                    | $^{30}$ |

Table 1. The RT Hall carrier concentration ($n_c$) and mobility ($\mu_H$) of CDC, spray and dipping deposited CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin films.
the localized charge carriers which introduce a dynamic force for the movement of charges with increasing temperature. Therefore, a polarization potential of polaron originated by enhanced localization suppresses carrier velocity and reduces the mobility of CH₃NH₃PbI₃₋ₓClₓ samples. Such a decrease of mobility with increasing temperature is measured by ultrafast spectroscopic method at temperature range -200 °C to 100 °C. 

Effective mass, excitonic binding energy and Fermi level calculation. The acceptor ionization energy, Fermi level and effective mass of charge carriers have been calculated from the temperature dependent Hall voltage measurement. The temperature dependent carrier concentration in the presence of a constant magnetic field can be represented by following equations,

\[ n_c = (p_0 N_a)^{\frac{1}{2}} \exp \left( -\frac{E_a}{2K_BT} \right) \]  \hspace{1cm} (1)

and

\[ p_0 = 2 \left( \frac{2\pi m^*_h K_B T}{\hbar^2} \right)^{\frac{3}{2}} \]  \hspace{1cm} (2)

where \( E_a \) is the acceptor ionization energy, \( N_a \) is the acceptor density, \( m^*_h \) is the effective mass of hole, \( T \) is the absolute temperature, \( K_B \) is the Boltzmann constant and \( \hbar \) is the reduced Planck constant. The value of \( E_a \) can be obtained from the slope of \( \ln(n_c T^{-3/4}) \) vs. \( 1/T \) graph (Fig. 3). From figure it is clear that the variation of carrier concentration with temperature can be defined by two discrete temperature regions (TR): TR-I (298–343) K and TR-II (344–378) K. In TR-II, the values of \( \ln(n_c T^{-3/4}) \) decrease linearly with inverse temperature, whereas, in TR-I, it decreases monotonically with lower slope compared to TR-II. The effective mass of hole \( m^*_h \) can be found out using \( E_a \) as,

\[ E_a = \frac{e^4 m^*_e}{2(4\pi \varepsilon \varepsilon_0 h)^2} \]  \hspace{1cm} (2)

where \( \varepsilon \) is the dielectric constant of the material and \( \varepsilon_0 \) is the permittivity of free space. Several research groups used dielectric constant \( \varepsilon = 5.6 \) to 25.7 (for high to low frequency) and excitonic effective mass \( \mu^* = 0.1m_e \) for calculating excitonic binding energy of perovskite. However, in this study \( \varepsilon = 9 \) has been used for calculating \( m^*_h \) according to hydrogenic model. The values of \( m^*_h \) are estimated to 0.16\( m_e \), 0.42\( m_e \), 0.38\( m_e \) (\( m_e \) is the rest mass of electron) in the TR-I and 2.16\( m_e \), 2.23\( m_e \), 3.04\( m_e \) in the TR-II for CDC, spray and dipping deposited samples, respectively. The estimated \( m^*_h \) is found in good agreement with recently reported values. Taking the effective mass of electron \( m^*_e = 0.21m_e \) from theoretical calculations, the excitonic effective mass \( \mu^* \) is estimated to (0.090–0.196)\( m_e \) using equation, \( 1/\mu^* = 1/m^*_e + 1/m^*_h \) and tabulated in Table 2. The estimated \( \mu^* \) in TR-I is close to ~0.104\( m_e \), found for tetragonal phase (≥ 145 K). However, \( \mu^* \) in TR-II is found high because of non-parabolic nature of valance bands in CH₃NH₃PbI₃₋ₓClₓ. Theoretical study suggested that lead vacancies diminish antibonding atomic orbital overlap resulting in flatten of valance bands. Moreover, polaronic effect and strong hydrogen bonding due to van-der-Waals interactions may also increase \( \mu^* \).

The excitonic binding energy, \( E_b \) of all perovskite samples has been calculated using the equation,
The excitonic binding energy is found (15–24) meV for TR-I and (32–33) meV for TR-II, which is well consistent according to Wannier–Mott hydrogenic model. This variation of \( E_b \) in TR-I and TR-II is due to temperature dependent polaronic effect of CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\). The extending radius of the lowest bound state \( r^* \) is calculated to ascertain the nature of excitons in CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\) using the equation, 
\[
 r^* = \frac{\varepsilon}{\mu^*} \frac{\hbar}{m_e} r_b,
\]
where, \( r_b \) is the Bohr radius. The \( r^* \) is estimated to 5.29 nm, 3.40 nm, 3.52 nm in TR-I and 2.49 nm, 2.48 nm, 2.43 nm in TR-II for CDC, spray and dipping deposited samples. The value of \( r^* \) is larger than the lattice constants (either cubic or tetragonal) of CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\) indicating that the exciton is weak and likely to be Mott–Wannier type.

The position of Fermi level \( E_F \) can be determined by knowing the value of \( E_a \), \( N_a \) and \( m^*_h \) of the following equation
\[
 E_F = -\frac{1}{2} E_a + \frac{1}{2} \left( k_b T \right) \ln \left[ \frac{N_a \hbar^3}{\left( 2 \pi m^*_h k_b T \right)^{3/2}} \right]
\]
(4)

The values of \( E_a \), \( N_a \) and \( E_F \) for both higher and lower temperature regions are tabulated in Table 2. The parameters \( n_c \) and \( N_a \) are not equal but vary with temperature and film processing methods as well, indicates CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\) is very sensitive to environment, chemical composition, growth parameters etc. The Fermi energy is found negative means \( E_F \) lies below the acceptor level.

### Grain boundary parameters and grain size calculations.

The transport properties of a polycrystalline semiconductor are generally influenced by grain boundary effect. According to grain boundary trapping model\(^4\), the trapping states create a depletion region in the grain and a potential barrier at the interface. In a semiconductor sample the relation between charge carrier mobility and grain boundary barrier height can be expressed as
\[
 \mu_h = \mu_0 T^{1/2} \exp \left( -\frac{\phi_b}{k_b T} \right)
\]
with
\[
 \mu_0 = \frac{e \xi}{\left( 8 \pi m^*_h k_b \right)^{1/2}}
\]
where, \( \phi_b \) is the grain boundary barrier height and \( \xi \) is the grain size. The slope of \( \ln(\mu_h T^{1/2}) \) vs 1/T graph (Fig. 4) gives the barrier height \( \phi_b \) and intercept will provide grain size \( \xi \).

The barrier height and grain size of all samples have been estimated for two different temperature regions (TR-I, TR-II) and tabulated in Table 3. From table it is clearly seen that the formation of bigger grain size is favorable at low temperature (TR-I) for mixed halide perovskites.

### Mean free path and mean free time calculations.

According to conventional Drude-Sommerfeld model, the carrier mean free path (\( L_m \)) and mean free time (\( \tau_m \)) in CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\) thin films can be calculated from the following equations
\[
 L_m = \frac{\mu H (3m^*_h k_b T)^{3/2}}{e}
\]
(6)
\[
 \tau_m = \frac{\mu H m^*_h}{e}
\]
(7)

The variation of \( L_m \) and \( \tau_m \) with temperature for CDC, spray and dipping deposited CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\) thin films are given in Fig. 5.

### Table 2.

| Samples   | \( E_a \) (eV) | \( N_a \times 10^{16} \) (cm\(^{-3}\)) | \( E_F \) (eV) | \( m^*_h/m_e \) | \( E_b \) (meV) |
|-----------|-----------|------------------|------------|------------|---------|
| TR-I      | TR-II     | TR-I            | TR-II     | TR-I      | TR-II   | TR-I   | TR-II   | TR-I      | TR-II |
| CDC       | 0.028     | 0.364           | 2.00      | 6.34      | 0.14    | 0.19   | 0.090   | 0.191     | 15    | 32    |
| Spray     | 0.071     | 0.378           | 3.80      | 11.3      | 0.035   | 0.189  | 0.140   | 0.192     | 24    | 32    |
| Dipping   | 0.065     | 0.512           | 0.19      | 96.7      | 0.032   | 0.256  | 0.135   | 0.196     | 23    | 33    |

The excitonic binding energy is found (15–24) meV for TR-I and (32–33) meV for TR-II, which is well consistent according to Wannier–Mott hydrogenic model. This variation of \( E_b \) in TR-I and TR-II is due to temperature dependent polaronic effect of CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\). The extending radius of the lowest bound state \( r^* \) is calculated to ascertain the nature of excitons in CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\) using the equation, 
\[
 r^* = \frac{\varepsilon}{\mu^*} \frac{\hbar}{m_e} r_b,
\]
where, \( r_b \) is the Bohr radius. The \( r^* \) is estimated to 5.29 nm, 3.40 nm, 3.52 nm in TR-I and 2.49 nm, 2.48 nm, 2.43 nm in TR-II for CDC, spray and dipping deposited samples. The value of \( r^* \) is larger than the lattice constants (either cubic or tetragonal) of CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\) indicating that the exciton is weak and likely to be Mott–Wannier type.
From figures it is seen that both $L_m$ and $\tau_m$ are lower at TR-I compared to TR-II. The magnitudes of $L_m$ and $\tau_m$ decrease with the increase of temperature except a sudden jump at around 340 K. The polaronic effect originated from rotational re-organization of $\text{CH}_3\text{NH}_3$ dipoles enhances trap assisted recombination with increasing temperature which reduces the carrier mean free path and mean free life time.

In the mixed halide perovskite, the transition from tetragonal to cubic phase occurs at temperature ~ 330 K\cite{19,42} due to the tilted inorganic $\text{PbI}_6$ octahedral and disparity of organic $\text{CH}_3\text{NH}_3^+$ rotation. Such phase transition can modify the physical properties of mixed halide perovskites, though it does not cause remarkable change in optical and photovoltaic properties\cite{43}. Recently, tetragonal to cubic phase transition is associated with the relative strength of the metal-halogen and hydrogen bonds as reported\cite{44}. In our study, during the temperature dependent Hall measurement we have applied a magnetic field of ~ 1 T. This magnetic energy shifted the tetragonal to cubic phase transition at slightly higher temperature at (340–344) K.

**Conduction mechanisms and activation energies.** The electrical conduction process in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ is rather complex. It is strongly dependent on temperature, vacancies or interstitial defects and activation energies of the materials. In general, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ includes Pb, $\text{CH}_3\text{NH}_3$ and halogen vacancies as suggested from theoretical and experimental studies\cite{45,46}. The low energy vacancies create a rotational re-organization of organic $\text{CH}_3\text{NH}_3$ dipoles resulting in free dipolar polarons in mixed halide perovskite\cite{20}. Eames et al.\cite{45} proposed that these vacancies migrate from one site to the neighboring site due to low activation energy. They found activation energies involved 0.58 eV and 0.84 eV for migrating $\text{I}^-$ and $\text{CH}_3\text{NH}_3\text{H}_3^+$ vacancies, respectively. Futscher et al.\cite{47} also reported that the predicted activation energies for migration of $\text{I}^-$ and $\text{CH}_3\text{NH}_3\text{H}_3^+$ are (0.08–0.58) eV and (0.46–1.12) eV, respectively. Besides, grain boundary effect has an influence on carrier transport and the activation energies (0.18–0.27) eV were predicted for different grain size above 260 K\cite{48}. In Fig. 6, it is clearly seen that there are three temperature regions where carriers are conducted through different conduction mechanisms. For further clarification, the activation energy was also calculated by Arrhenius equation which contains three separate activation energy terms,

$$\sigma_{dc} = \sigma_1 \exp \left( \frac{-\Delta E_1}{k_B T} \right) + \sigma_2 \exp \left( \frac{-\Delta E_2}{k_B T} \right) + \sigma_3 \exp \left( \frac{-\Delta E_3}{k_B T} \right)$$

(8)

**Figure 4.** Figure for calculating grain boundary parameters. $\ln (\mu_n T^{1/2})$ vs $1/T$ graph for CDC, spray and dipping deposited $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin films.

**Table 3.** Grain boundary barrier height ($\phi_b$), grain size ($\zeta$), mean free path ($L_m$), mean free life time ($\tau_m$) and activation energies ($\Delta E$) for CDC, spray and dipping deposited $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin films.
where, $K_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\sigma_I$, $\sigma_{II}$ and $\sigma_{III}$ are pre-exponential factors and $\Delta E_{I}$, $\Delta E_{II}$ and $\Delta E_{III}$ are activation energies for region I, II and III, respectively. From the slope of $\ln \sigma$ vs $1000/T$ plot (inset of Fig. 6), the activation energies were calculated and tabulated in Table 3.

From Fig. 6, it is seen that dc-electrical conductivity ($\sigma_{dc}$) decreases with increasing temperature in region I (294–317) K. The initial decrease is caused by the strong interactions in between organic–inorganic part and rotational disorder of methylammonium cation within perovskite structure. In addition, longitudinal optical phonon scattering may also decrease the conductivity with temperature in region I. The activation energy $\Delta E_{I}$ (Table 3) is found negative in region I, suggesting the Fermi level is pinned to the valance band of all samples. In region II (318–357) K, the dc-electrical conductivity increase slowly with increasing temperature and $\Delta E_{II} = 0.44$, 0.51, 0.47 eV for CDC, spray and dipping deposited samples respectively, which indicates the migration of $I^-$ vacancies to PbI$_6$ octahedron edge$^{45-47}$. In region III (358–378) K, $\sigma_{dc}$ increases rapidly and $\Delta E_{III} \approx \Delta E_{II}$. The activation energies $\Delta E_{III}$ are found close to 0.84 eV for CDC and spray deposited and $\Delta E_{III} = 0.57$ eV for dipping deposited samples. The rapid increase of $\sigma_{dc}$ in region III occurs because of diffusion or migration of CH$_3$NH$^+$ in addition to $I^-$ vacancies to PbI$_6$ octahedra or neighbor central vacant site$^{45-47}$. Therefore, the conduction processes are attributed to the migration of $I^-$ and CH$_3$NH$_2^+$ suggesting the existence of ionic transport in CH$_3$NH$_3$Pb$_{1-x}$Cl$_x$. Moreover, the concentrations of charge carriers (majority holes) which are activated with acceptor ionization energy ($E_a$) favorable for the transport across grain boundaries of CH$_3$NH$_3$Pb$_{1-x}$Cl$_x$ samples.
Discussion

In summary, the charge carrier conduction mechanism of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin films have been evaluated as a function of temperature ranging from room temperature to 378 K. Hall measurement study confirms that the prepared CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ films are p-type semiconductor with carrier concentration of the order of ~ 10$^{16}$ cm$^{-3}$. The carrier mobility found to decrease with increasing temperature due to polaronic effect. At RT, the mobilities for CDC, spray and dipping deposited samples are 46, 49 and 20 cm$^2$V$^{-1}$ s$^{-1}$, respectively. The excitonic effective mass ($\mu^*$) is estimated to be (0.090–0.196)m$_e$, and excitonic binding energy ($E_b$) varies from (15–33) meV, suggesting Mott-Wannier type exciton. Additionally, the grain boundary barrier height, mean free path and mean free life time of charge carriers have also been evaluated. Electrical study reveals that multi-conduction processes are involved in CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$, which is governed by the migration of vacancies, vacancy-assisted diffusion of mobile ions and accumulation of holes across grain boundaries.

Methods

Synthesis. Lead halide perovskite solution for fabricating CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin films was prepared using the following procedure. Methylamine (CH$_3$NH$_2$) solution was mixed with hydroiodic acid and ethanol at room temperature. The solution was perturbed continuously by stirring with a magnetic stirrer at a constant speed in an ice bath for 2 h. The color of CH$_3$NH$_3$I solution transforms from red to transparent and heated at 100 °C for 4 h in a furnace to achieve white-colored CH$_3$NH$_3$I powder. Finally, CH$_3$NH$_3$I and lead(II) chloride powders were dissolved in anhydrous N,N-dimethylformamide at a molar ratio 3:1 to achieve a mixed halide perovskite precursor solution.

CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin films have been fabricated at ambient atmosphere by three different methods. These methods are (a) Chemical dip-coating (CDC) (b) Spray pyrolysis (spray) and (c) Repeated dipping-withdrawing (dipping). The details of preparing CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solution and different steps which have been made in these methods to deposit CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin films have been reported elsewhere$^{2,3,5}$.

Characterization. Temperature dependent Hall voltage was measured at constant magnetic field of 9.815 KG using the conventional van-der-Pauw method. The magnetic field used for the study of Hall Effect was provided by electromagnets designed and produced by Newport instruments Ltd. England. The circuit arrangement for temperature dependent Hall Effect measurement is shown in Fig. 1S. A dc voltage from the power supply unit was applied in order to flow the sample current through the specimen. Current and voltages were measured by a digital electrometer and a digital multi-meter. A voltage stabilizer was used so that a steady supply of current without fluctuation was maintained through the magnet. A special designed heater was used to vary temperature. The variation of temperature is controlled by a variac and measured by a chromel–alumel thermocouple connected with a digital multi-meter.

The resistivity of all samples was measured by van-der-Pauw method. Experimental setup of the van-dar-Pauw's specimen to measure the resistivity with varying temperature is shown in Fig. 2S. The details of preparing CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ solution and different steps which have been made in these methods to deposit CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin films have been reported elsewhere$^{2,3,5}$.

Figure 6. Electrical properties of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. Temperature dependent dc-electrical conductivity of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ thin films showing three distinct regions. Inset shows the variation of ln$\sigma$ with 1000/T graph for calculating activation energy.
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A.M.M.T.K. designed the project, conducted all measurements, analyzed the data and wrote the manuscript. M.K.R.K. conceives and designed the project, analyzed the data, wrote the manuscript and supervised the whole work. M.S.H. designed and supervised the project. All authors reviewed the manuscript.

**Competing interests**
The authors declare no competing interests.

**Additional information**

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