

Room temperature optical properties of organic–inorganic lead halide perovskites



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ABSTRACT

Past two years have seen the rapid emergence of a new class of solar cell based on mixed organic–inorganic halide perovskites. The optical and optical frequency dielectric properties of these perovskites at ambient temperatures are important both to the design of optimised solar cells and in other areas such as the refinement of electronic band structure calculations. Limited previous information has been published. The experimental optical and related dielectric constants of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films are reported at 297 K as determined by detailed analysis of reflectance and transmittance data. Absorption coefficients are also extracted from these data and compared with a range of previously reported values.

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1. Introduction

Mixed organic–inorganic halide perovskites hold considerable promise for future low cost, high efficiency photovoltaic solar cells [1]. Beside application as thin-film cells in their own right [1–3]; this flexibility and high radiative efficiency makes these perovskites of interest as top cells for both silicon and CIGS tandem cell technology [4]. Accurate determination of perovskite optical constants and dielectric properties are of particular importance for informed optical design [5] for such tandem cell technology with only approximate values of the refractive index being used in recent perovskite–silicon tandem cell optical design studies [6,7]. The limited published information on the optical and dielectric properties motivates this work. Findings are also relevant to other applications, such as in fine tuning and accuracy assessment of electronic structure calculations [8,9].

Temperature dependent dielectric constants of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X=\text{I}, \text{Br}, \text{Cl}$) at microwave frequencies (50–150 GHz) were reported in 1987 [10] and also in 1992 at frequencies below 1 MHz [11]. A widely cited optical frequency dielectric constant of 6.5 for $\text{CH}_3\text{NH}_3\text{PbI}_3$ was reported in 1994 [10] calculated from diffuse powder reflection, with a value of 4.8 deduced for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ from reflectance from a crystalline sample [12]. The frequency dependency of $\text{CH}_3\text{NH}_3\text{PbI}_3$ dielectric constant conforms to expectations [1] with a value of 60.9 at low frequencies resulting

from a combination of dipolar, ionic and electronic contributions. As frequency increases, the dipolar contribution due to CH_3NH_3 cation motion drops out, by attaining a new plateau value of 29.7. Finally, the ionic contribution disappears with only the electronic contribution remaining at optical frequencies. A giant dielectric constant for the iodide recently has been reported [13], although the measurement approach captures what may be a device rather than an intrinsic material property. Several groups [8,9,14,15] reported theoretical calculations of dielectric functions of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X=\text{I}, \text{Br}, \text{Cl}$). Xing et al. [16] report the experimental refractive index of spin coated 65 nm thick $\text{CH}_3\text{NH}_3\text{PbI}_3$ film although no measurement details were given and the data have obvious drawbacks.

Since the present paper was submitted, several other papers have also addressed this issue. The complex refractive index of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ was recently reported via ellipsometric analysis [17]. Two effective medium approximation (EMA) layers consisting of perovskite and a certain percentage of voids (air) were used in the associated modelling although the layers were not physically characterised. An apparently anomalous peak in the reported extinction coefficient (k) at around 730 nm is not seen in other works [18–21]. The optical constants of $\text{CH}_3\text{NH}_3\text{PbI}_3$ were also reported by fitting ellipsometric data [22] although comparison between experimental and fitted data is not provided. The absorption coefficient derived from the extinction coefficient in the sub-bandgap region is also much higher (around $4 \times 10^4 \text{ cm}^{-1}$ at 1.5 eV) than other published values [18–21]. The complex refractive index of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the visible wavelength range has also been reported [23] although experimental details regarding the fit, including how the baseline

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correction was applied to account for scattering losses, were not given. A more detailed work on the complex refractive index of $\text{CH}_3\text{NH}_3\text{PbI}_3$ has been reported by combining reflection, transmission and ellipsometric measurements [24].

This work reports the real and imaginary parts of the dielectric function ϵ at optical frequencies, as well as the refractive index n , extinction coefficient k and absorption coefficients α , of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin-film perovskites as deduced from measured values of reflectance (R) and transmittance (T).

2. Methods

2.1. Material preparation and optical measurement

The $\text{CH}_3\text{NH}_3\text{PbI}_3$ film was deposited onto a borosilicate glass substrate coated with 45 nm thick compact TiO_2 layer using a relatively standard sequential solution processing technique as previously reported [25]. More details are given in Ref. [26].

Reflectance (R) and transmittance (T) of this $\text{CH}_3\text{NH}_3\text{PbI}_3$ film were measured using a Varian Cary UV–vis–NIR spectrophotometer at close to normal incidence with a measurement light spot of around 5 mm in diameter. For $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, similar R , T data reported by Wehrenfennig et al. [18] for vapour-deposited films were interpreted using identical procedures.

2.2. Optical modelling

The optical properties, in particular the imaginary part of the dielectric constant (ϵ_2), were determined by modelling with the computer software WVASE[®] [27], using two Psemi-Triangle (PSTRI) oscillators [27], as these were found to be important to allow accurate modelling of fundamental absorption peaks around 1.6 eV and 2.8 eV. Gaussian oscillators were used to model the remaining regions (see Ref. [26]).

The Psemi-Triangle (PSTRI) oscillator is a Herzinger–Johs Parameterized Semiconductor (PSEMI) Oscillator. This oscillator model describes analytically the dielectric functions of semiconductor materials as a sum of Gaussian-broadened polynomials. The model is flexible enough to describe the complicated critical point structure of semiconductors, and permits limited extrapolation outside the measured range. The complex dielectric function is defined as a function of photon energy E as

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) = 1 + i \sum_{j=1}^m \int_{E_{\min}}^{E_{\max}} W_j(E) \Phi(\hbar\omega, E, \sigma_j) dE + \sum_{j=m+1}^{m+p+1} \frac{A_j}{(\hbar\omega)^2 - E_j^2} \quad (1)$$

where $W(E)$ is the broadened absorption spectrum which includes joint density of states and Φ is the broadening function. Detailed

explanations of the expression can be found in Refs. [27–29].

The Gaussian oscillator is a common oscillator model based on the expression [27]

$$\epsilon_2(\omega) = A e^{-((E-E_n)/\sigma)} - A e^{-((E+E_n)/\sigma)} \quad (2)$$

The real part of the dielectric constant (ϵ_1) was extracted from ϵ_2 using the Kramers–Kronig (KK) method [30]. The real and imaginary parts of the refractive index (n and k respectively) were determined from the following relationships:

$$\epsilon_1 = n^2 - k^2; \quad \epsilon_2 = 2nk \quad (3)$$

The absorption coefficient α of the film was then calculated:

$$\alpha = \frac{4\pi k}{\lambda} \quad (4)$$

where λ is free space wavelength. For the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film, the compact TiO_2 layer and glass substrate were modelled using in-built models that gave good results for samples prepared with only those layers.

3. Results and discussion

3.1. Dielectric functions

The measured and modelled reflectance and transmission data for the perovskite films are shown in Fig. 1(a) and (b), respectively. The film thicknesses have been determined to be 172 nm and 271 nm for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films, respectively. Below 1.55 eV ($\lambda > 800$ nm), the films are transparent with the observed spectral variations in R and T largely due to interference between light reflected from front and rear interfaces. Above 2.5 eV ($\lambda < 500$ nm), the films are essentially completely absorbing with R determined solely by reflection from the top surface of the perovskite.

These dependencies allow estimation of measurement errors. Note that the modelled results underestimate both R and T in the low energy transparent region. This is due to inconsistencies in the experimental data, largely due to measurements not corresponding to exactly the same location on the sample. Since R and T independently contain nominally identical information on the optical parameters, this inconsistency provides a method for estimating the uncertainty in parameter extraction.

The optical constants n and k deduced from this modelling are shown in Fig. 2(a) and (b), respectively. Also shown (dashed line) is the only previously published data of Xing et al. [16], showing similar features but appearing to systematically overestimate k (including in the transparent region), while systematically underestimating n . The uncertainty estimates for n for the present data in

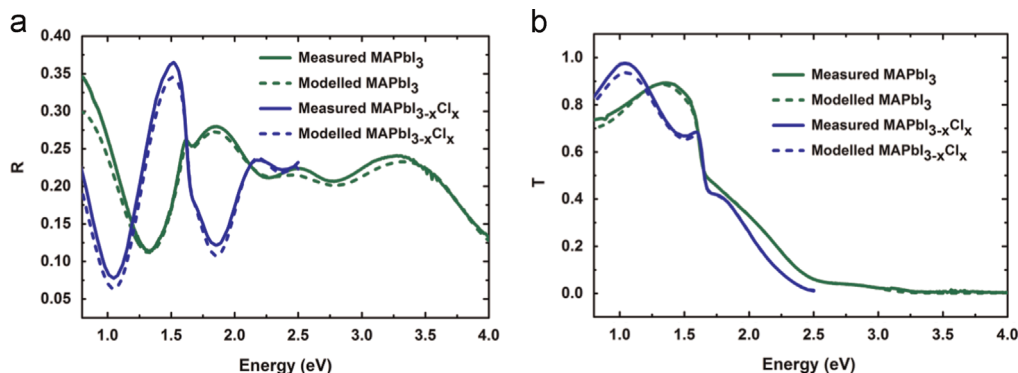


Fig. 1. Measured and modelled (a) reflectance R and (b) transmittance T spectra for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films (MA = CH_3NH_3). Below 1.55 eV, films are transparent with spectral variations largely due to interference effect. Above 2.5 eV, films are non-transmissive with reflection being from the top interface.

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