Effect of tertiary butylpyridine in stability of methylammonium lead iodide perovskite thin films

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Abstract. Perovskite material is a great visible light absorber in perovskite solar cells (PSCs). PSC has reported power conversion efficiency (PCE) of 22.1%. However, performance instability of the solar device base on this material hampers its commercialization. One of the factors responsible for performance instability in the cell is temperature. In this work, we carried out stability study of perovskite film treated with tertiary butylpyridine (tBP) as a surface modifier. Concentrations of tBP added in perovskite material film were varied and the samples were subjected to temperature degradation test in a temperature-controlled chamber for 120 h. Ultraviolet–visible (UV–Vis) spectrophotometers, Fourier-transform infrared (FT-IR) spectrometers and X-ray diffractometers (XRD) were used to characterize the properties of the temperature-stability-tested samples. The results show that the sample treated with $100\,\mu l$ of tBP has the best resistance to temperature degradation after the duration of the test. The surface-modified perovskite films, with $100\,\mu l$ of tBP, may reduce the degradation of PSCs.

Keywords. Degradation; perovskite material; surface modification; temperature; thin film.

1. Introduction

The chemical formula ABX_3 describes the perovskite material where the A, B and X sites are occupied by an organic cation ($CH_3NH_3^+$), metal cation (Pb^{2+}) and halide anion (I^-), respectively [1–3]. Perovskite is an active layer in perovskite solar cells (PSCs). PSC is one of the third-generation solar cells. The third generation of solar cells reduces the cost of the solar cells using Earth-abundant elements, inexpensive fabrication (low temperature, solution processing and a roll-to-roll manufacturing) and easy installation (lightweight and flexibility) [4]. Among the third-generation solar cells, PSC has the highest power conversion efficiency (PCE) of 22.1% [5]. One of the striking challenges in PSC is the performance instability of the cells due to degradation of the component(s) in the device. Salado *et al* [6] reported that perovskite layer causes degradation in the PSCs. Despite high quantum efficiency in hybrid PSCs, the performance instability of the device due to temperature and ambient moisture limits the actual application of PSCs [7]. One of the external factors responsible for the degradation of PSCs is temperature. Most semiconducting materials exhibit photo-oxidation in the presence of light [8] as solar panels are placed directly in the sun. In most cases, perovskite films processed in an inert atmosphere degrade, hampering the mass production

and real applications of the PSCs [9]. Several techniques have been deployed in tackling the performance instability of hybrid PSCs. Han's group used the lead (II) dioxide–dimethyl sulphoxide (PbI_2(DMSO)) complex to increase the transformation process, leading to high-performance solar cells [10].

Liu *et al* [11] reported efficient and stable PSCs prepared in ambient air based on surface-modified perovskite layer. They added 4-tertiary-butylpyridine (tBP) into PbI_2 to form a mixed solution before introducing methylammonium iodide for perovskite film formation. The tBP changed the surface of PbI_2 and enhanced the performance and stability of the hybrid PSCs fabricated in ambient air. However, optimization of the concentrations of tBP was not reported in the research. Li *et al* [12] used anti-solvent materials to modify the surface of PbI_2 layer to create voids before dropping methylammonium iodide to form the perovskite layer. They discovered that the anti-solvent extracted dimethylformamide (DMF) used as a solvent in the film before annealing, leading to PbI_2 crystallization and film-volume reduction. The reduction of film volume helps in the proper formation of perovskite on the addition of methylammonium iodide and the reduction of unreacted PbI_2, which is unwanted during film formation.

In this work, we report the optimization of concentration of tBP as a surface modifier towards the stability of perovskite layer. Before addition of methylammonium iodide, tBP of

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different concentrations (0–250 μl) was added to the surface of PbI$_2$ and the samples were subjected to temperature stability test in a temperature-controlled chamber for 120 h. The characterized samples of as-prepared and aged films revealed the volume of tBP required for temperature-stable films for real application in photovoltaic technology.

2. Materials and methods

2.1 *Perovskite thin films deposition*

Glass substrates were ultrasonically cleaned with detergent, distilled water, acetone, ethanol and isopropyl alcohol (IPA), for 15 min at 27°C and blow-dried with nitrogen gas. A two-step method of deposition of perovskite films was used. PbI$_2$ (Aldrich, 99.9985%; 460 mg) was dissolved in 1 ml DMF and then different volumes (0–250 μl in a step size of 50 μl) of tBP were added in the PbI$_2$ solutions and warmed at 70°C for 20 min with magnetic stirring. The mixture was then spin-coated on the substrate at 4000 rpm for 30 s. We dropped a solution of methylammonium iodide in 2-propanol (30 mg ml^{-1}) on the films and spin-coated at 2500 rpm for 30 s in ambient condition. Afterwards, the as-prepared films were annealed at 100°C for 30 min and the colour changed to dark brown.

2.2 *Films degradation measurement*

Stability test of the perovskite samples against temperature was carried out in a fabricated temperature-controlled chamber. Treated and untreated samples were inserted in the temperature-controlled chamber as reported elsewhere [13] and left for 24–120 h at intervals of 24 h. Then, the temperature-conditioned samples were characterized.

2.3 *Characterization of perovskite films*

The as-prepared and aged samples were characterized using a UV–Vis spectrophotometer (Lambda 35 Perkin-Elmer), X-ray diffractometer (PANalytical Empyrean) and Fourier-transform infrared (FT-IR) spectrometer (Thermo Scientific, iS5 Nicolet). The FT-IR measurement was carried out using KBr pellets as substrate. We performed the X-ray diffraction using fixed CuKα radiation, in ambient condition.

3. Results

3.1 *Optical properties of as-prepared and aged perovskite films*

The stability test of as-prepared perovskite films prepared in ambient condition was carried out in the temperature-controlled environment. The absorption of the films kept at a temperature of 55 and 85°C and an average relative humidity
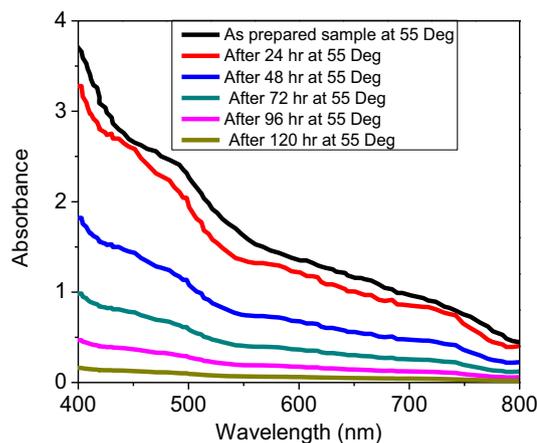

Figure 1. Absorbance spectra of perovskite films at 55°C aged without tBP.

of 38±3% was measured. The perovskite films were exposed to light of 360 ± 10 mW cm^{-2} and monitored for 5 days at two different temperatures of 55 and 85°C.

Figure 1 shows tBP-untreated films; room temperature was between 27 and 29°C. The samples were aged for 0, 24, 48, 72, 96 and 120 h at 55 and 85°C. The samples were aged under continuous illumination of light at the temperature of 55°C for 120 h. A small effect of temperature was noticed on the samples treated at the temperature of 55°C for 24 h.

The samples at the temperature of 55°C aged for 120 h were visibly degraded. The peaks of absorption occurred at 491 and 748.75 nm corresponding to the absorption values of 2.4085 and 0.7561, respectively. There was visible degradation of the samples after 24 h. This shows that the samples degrade after 24 h to form PbI$_2$ and the degradation is proportional to the duration and amount of light illumination on the samples. Also, the offset absorption of the samples occurs at 780 nm and it is in agreement with the report of Abdelmageed *et al* [14]. In 120 h, 95.09% of the sample was degraded. This shows that using such films in fabrication of PSCs involves degradation risk, which can affect the efficiency of the cell.

Also, perovskite films without tBP treatment were aged under illumination of light at 85°C (figure 2). The absorption spectra of samples tested at temperature of 85°C show exponential decay with time. The perovskite film stored at 85°C decayed faster than the film stored at 55°C as shown in figures 1 and 2. The films at temperatures of 55 and 85°C show different absorption features upon aging. The film stored at 85°C shows very low absorption across the visible spectrum upon degradation and a weak absorption peak at 500 nm.

The absorption of the films at the two temperatures closely matches the absorbance of PbI$_2$ with a strong absorption peak at 500 nm, which is similar to the report of Christians *et al* [15]. Crystallographic data, reported earlier from methylammonium lead iodide films degraded in light, confirmed that the perovskite films stored in light do degrade to form PbI$_2$ [16]. The as-prepared film was compared to the aged films, and
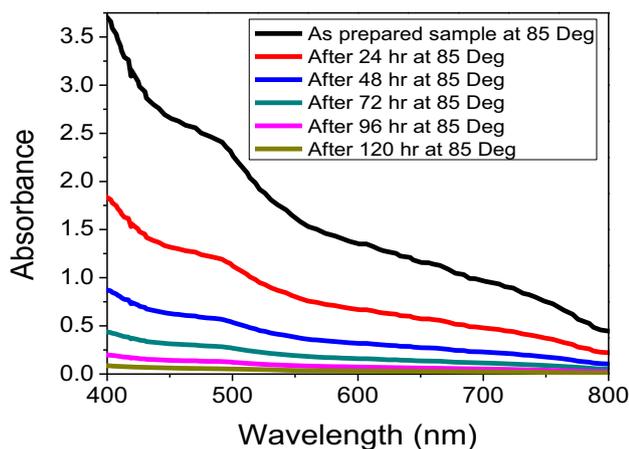
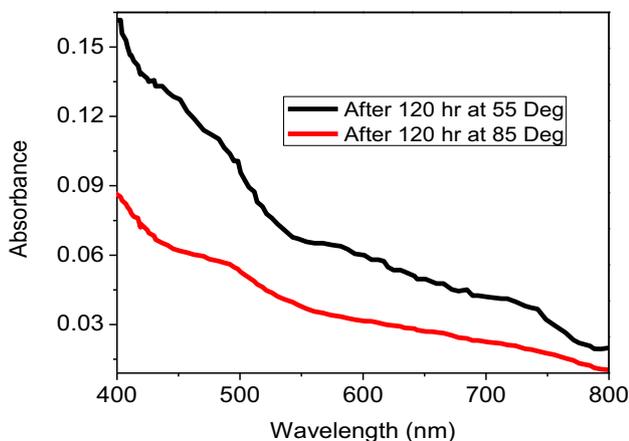**Figure 2.** Absorbance spectra of perovskite films at 85°C aged without tBP.

Figure 3. Comparison of absorbance spectra of perovskite films at 55 and 85°C aged for 120 h without tBP.

Figure 4. Absorption spectra of treated $CH_3NH_3PbI_3$ films with concentration variation of tBP.

Table 1. Concentration of tBP in $CH_3NH_3PbI_3$ films and their respective absorbance.

Sl. no.	tBP concentration (µl)	Average absorbance (a.u.)
1	0	1.9732 ± 0.71
2	50	1.8737 ± 0.70
3	100	1.9381 ± 0.70
4	150	1.8381 ± 0.70
5	200	1.7422 ± 0.70
6	250	1.84551 ± 0.70

they showed adverse visible degradation. About fifty percent (50%) of the pristine sample degraded within 24 h. The rate of degradation of the sample was higher when subjected to light illumination at temperature of 85°C, than at 55°C. After five hours (5 h), about 2.3% of the pristine sample remained. There is blue-shift in absorption by the samples as they degrade as shown in figure 2. In addition, at different temperatures, blue-shift in absorption offset of the samples was observed. The perovskite films could have been transformed to another material as they reacted at these temperatures. Results of samples degraded at both temperatures for 120 h (figure 3) show the extent of samples' degradation with respect to the temperature. The sample subjected to temperature of 85°C at 120 h degraded more than the sample tested at 55°C for the same duration.

The result clearly demonstrates that subjecting perovskite film to temperature of 85°C adversely degrades the sample. After 24 h, it was seen vividly that the perovskite was very sli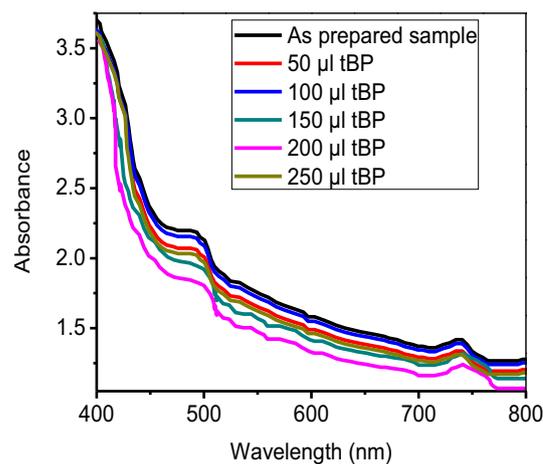ghtly degraded at 55°C, and showed more degradation at 85°C. This result is in agreement with previous report made by Juarez-Perez *et al* [17] and Conings *et al* [18]. Figure 4 shows the effect of tBP treatment on the ultraviolet–visible (UV–Vis) absorption spectra. The perovskite thin films were synthesized in ambient condition. Various concentrations of tBP on perovskite film and their respective samples absorption behaviours are shown in figure 4. All the samples were freshly prepared with various concentrations of surface modifier (tBP). The samples were treated with 0, 50, 100, 150, 200 and 250 µl of tBP. The sample treated with 100 µl tBP has the highest absorbance among the samples treated with tBP. The offset absorption of the sample treated with 50 µl tBP occurred at 780 nm, which is in agreement with reported value [19]. Figure 4 shows that tBP treatment causes a slight red-shift in the offset absorption, which could be attributed to tuning behaviour of the film due to incorporation of tBP in lattices of perovskite. Significant difference in absorption intensities of the treated films was observed between the as-prepared film and the tBP-treated films.

The results of as-prepared methylammonium lead iodide films treated with tBP of various concentrations and various concentrations of tBP used are presented in table 1.

Supplementary figure 1 (S1) shows the absorption spectra of aged methylammonium lead iodide films treated with 50 µl of tBP. The spectra show that absorption of the films
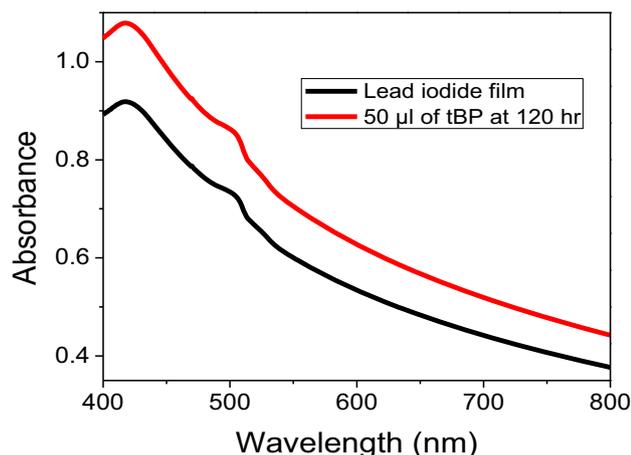
Figure 5. Comparison of absorption spectra of aged $CH_3NH_3PbI_3$ and lead iodide films.

Figure 6. Absorption spectra of $CH_3NH_3PbI_3$ films modified with 100 μl of tBP and aged for 5 days at 55°C.

Table 2. Mean absorbance value of samples from 24 to 120 h with their respective sample names.

Sample name	Average absorbance (%)
PA0	2.5763 ± 1.40
PA1	2.5671 ± 1.60
PA2	1.4262 ± 0.89
PA3	0.7709 ± 0.48
PA4	0.3671 ± 0.23
PA5	0.1266 ± 0.08

is inversely proportional to duration of aging. The samples maintained absorption peaks at 491 and 748 nm for 96 h, which agrees with earlier report of Liu *et al* [11]. The peaks at 748 nm disappeared as the sample aged for 120 h in sample treated with 50 μl tBP for 120 h. Figure 5 compares the absorption spectrum of lead iodide and sample treated with 50 μl tBP for 120 h. Both samples have peaks at 504 nm. This further shows that the sample aged for 120 h at 55°C degraded to lead iodide (PbI_2) material. This indicates that the perovskite materials degraded and transformed to PbI_2. The reaction that could lead to degradation of perovskite film to PbI_2 is stated in equation (1):

$$CH_3NH_3PbI_3 \xrightarrow{\text{Temperature}} CH_3NH_3I\,(g) + PbI_2\,(s) \qquad (1)$$

The volatile CH_3NH_3I vaporized and PbI_2 as left out [20]. The average absorbance values of the films are shown in table 2.

Supplementary figure 2 compares the absorption spectra of PA1 and PbI_2, which showed close match between the samples.

Figure 6 shows the spectra of the aged $CH_3NH_3PbI_3$. Negligible degradation of the perovskite sample was recorded for 5
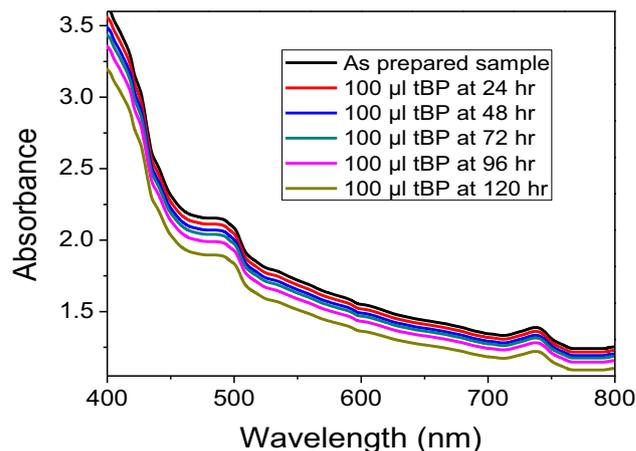
days at 55°C. Comparing figure 7a and b with Supplementary figure 1, the sample treated with 100 μl of tBP resists degradation more than the sample treated with 50 μl. This shows that surface modification of perovskite film with 100 μl stabilizes the film better. This could be attributed to modification of Pb^{2+} and or $CH_3NH_3^+$ defects on the perovskite surface with the tertiary butyl group of the tBP. Supplementary figure 2 shows the absorption spectra of $CH_3NH_3PbI_3$ films modified with 50 μl of tBP and aged for 120 h at 85°C. All the films have high onset absorption at 748 nm. The optical bandgap of the perovskite film was calculated from the onset wavelength using equation (2):

$$E_g = hc/\lambda \qquad (2)$$

where E_g is optical bandgap energy, h is Planck's constant, λ is wavelength and c is speed of light. The optical bandgap energy is 1.59 eV, which corresponds to the value reported by Burschka *et al* [21]. There is noticeable decrease in sample absorption of light as the duration of sample aging increases. The adverse effect of photo-induced degradation on the sample shows that after 24 h, the sample subjected to the temperature of 85°C reduces its average absorption by 39%; 45% of the film is retained on the substrate at 120 h of the photo-illumination test. This showed that the 50 μl of tBP added to the film could not inhibit degradation of the film. Supplementary figure 3 shows the perovskite film treated with 100 μl of tBP. The average absorption value of the sample after 24 h was 1.75 ± 0.63. The percentage of the absorbance of the film that did not degrade was about 94% after 24 h. After 120 h, the sample's absorbance value retained was 1.17 ± 0.42 (63%). This shows that addition of 100 μl of tBP in the film reduced degradation of the perovskite film. Also, Supplementary figure 4a and b shows samples treated with 150 μl of tBP and subjected to photo-illumination for 5 days at 55 and 85°C, respectively. The absorbance of the
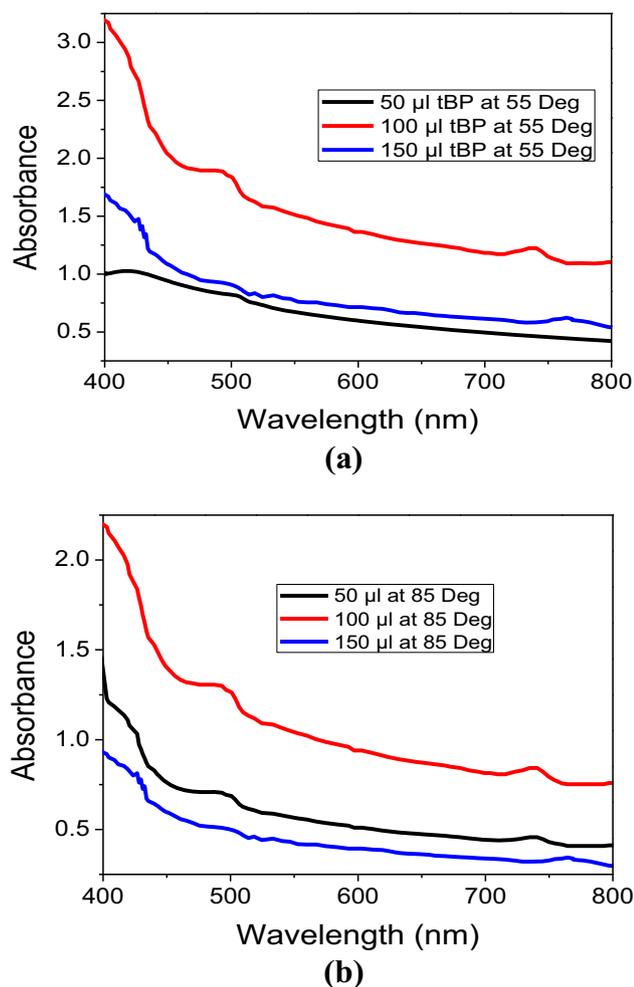
Figure 7. Absorption spectra of $CH_3NH_3PbI_3$ films modified with 50, 100 and 150 μl of tBP and aged for 5 days at (**a**) 55°C and (**b**) 85°C.

sample at 85°C reduced from 1.84 ± 0.70 to 1.15 ± 0.44 after 24 h. This implies that 63% of the absorption value of the sample is retained on the substrate. Further, exposing the sample at 85°C for 120 h showed that the sample's absorbance value reduced to 0.48 ± 0.18 (26.09%). Here, the amount of tBP in the perovskite film could not inhibit degradation in the sample. It shows that 100 μl of tBP is preferred for inhibiting degradation of the sample. The extents of stabilization of 50, 100 and 150 μl of tBP aged for 5 days at 55 and 85°C are shown in figure 7a and b. The sample treated with 100 μl of tBP inhibited degradation at both temperatures for 120 h.

3.2 *Structural properties of as-prepared and aged perovskite films*

Figure 8a shows the features of $CH_3NH_3PbI_3$ film subjected to 55°C for 120 h in the temperature-controlled chamber. The freshly prepared perovskite film has perovskite signatures

crystallized at $2\theta = 14, 24, 28, 31$ and $37°$, which correspond to perovskite signatures reported by Abdelmageed *et al* [14]; the 2θ corresponds to reflection from (110), (202), (220), (310) and (240), respectively. This confirmed tetragonal phase of methylammonium lead iodide [22]. The sample subjected to temperature of 55°C for 120 h has perovskite signatures with $2\theta = 14, 24, 28, 31$ and $37°$. Both fresh and 55°C-treated samples showed the phase of metallic Pb ($2\theta = 31°$) [23]. Also, a new peak at $2\theta = 12°$ is present, which corresponds to the peak assigned to lead (II) iodide (PbI_2) film signature with $2\theta = 12, 25, 38$ and $53°$ corresponding to (001), (011), (110) and (202), respectively [24]. The intensity of the peaks subjected to 55°C reduced to nearly one-third of the freshly prepared sample value. This could be due to degradation of the material, which was revealed by the PbI_2 peak ($2\theta = 12°$) present in XRD peaks of the degraded sample. The sample subjected to 55°C degraded but retained the peaks of perovskite material. The sample subjected to temperature of 85°C for 120 h, as shown in figure 8b, has visible degradation of the perovskite material. Nearly all the peaks assigned to perovskite in freshly prepared sample vanished in the sample subjected to temperature of 85°C. The perovskite signatures existing in the film occurred at $2\theta = 14°$ and $2\theta = 28°$ with diminished intensities. PbI_2 peaks occur at $2\theta = 12, 38$ and $53°$. The effect of 85°C test on the sample is more adverse than that of 55°C test. The intensities of the perovskite peaks in the film reduced to about one-fifth of the freshly prepared sample value. The intensity of PbI_2 peaks in the sample (85°C) dominates that of perovskite peaks. Figure 9 compares the films subjected to temperatures of 55 and 85°C for 120 h.

It is clear from figure 9 that perovskite peaks that exist in the sample subjected to 55°C are more intense than the perovskite peaks in the sample subjected to 85°C. However, the PbI_2 peaks in the sample subjected to temperature of 85°C are more intense than that of the sample subjected to 55°C. This shows that perovskite film subjected to 85°C degrades more than the sample subjected to 55°C. Figure 10 shows freshly prepared perovskite films with their surfaces modified by varying tBP concentrations (in μl). Concentrations of 0–250 μl of tBP with step size of 50 μl of tBP were used. Six samples were prepared with various concentrations. The sample without tBP additive has the highest intensity of peaks. All the samples crystallize in perovskite phase, with some having non-perovskite peaks. Among all the samples treated with tBP, the sample with 100 μl of tBP has the highest intensity of peaks with perovskite signatures and preferred orientation of (110). There were no non-perovskite peaks in the sample treated with 100 μl of tBP. Samples treated with 150–250 μl have non-perovskite peaks at $2\theta = 13°$, which is assigned to PbI_2 phase. Also, sample PA5 has PbI_2 peak at $2\theta = 26°$. This shows that the optimized concentration for surface modification of perovskite film is 100 μl. This agrees with the result obtained in optical property.

Figure 11 shows increase in intensity as the sample exposure temperature value decreases. Stronger intensity of peaks
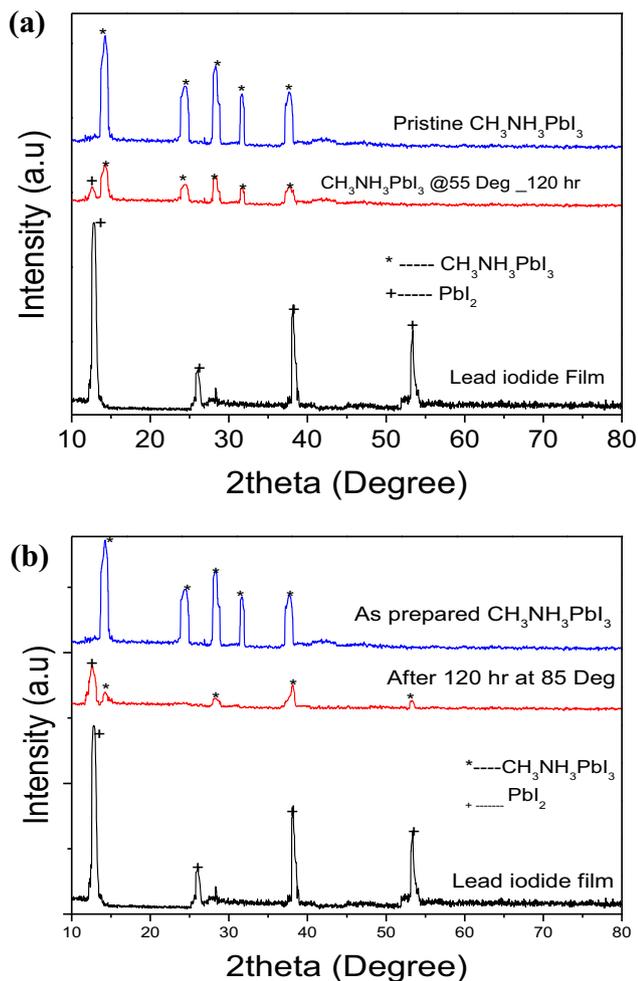
(a)

(b)

Figure 8. Comparison of perovskite film degraded at temperature of (**a**) 55°C and (**b**) 85°C with freshly prepared perovskite film for 120 h without tBP treatment.
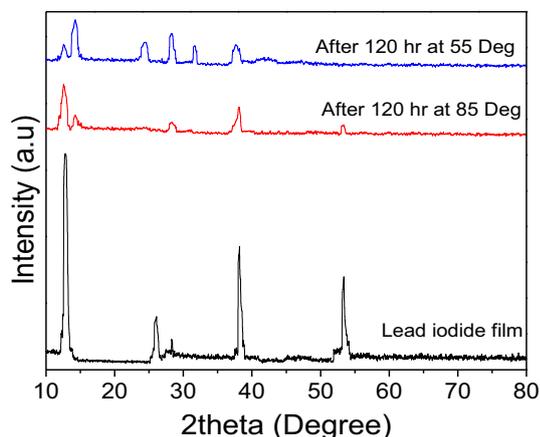

Figure 9. Comparison of perovskite film degraded at 85°C with perovskite degraded at 55°C for 120 h without tBP treatment.
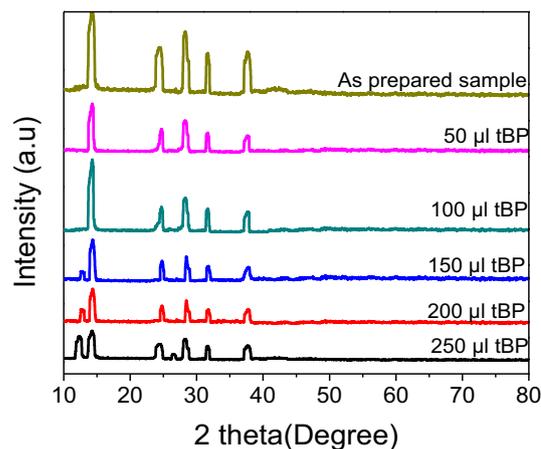

Figure 10. Freshly prepared perovskite films with surfaces modified by tBP of varying concentrations with step size of 50 μl.
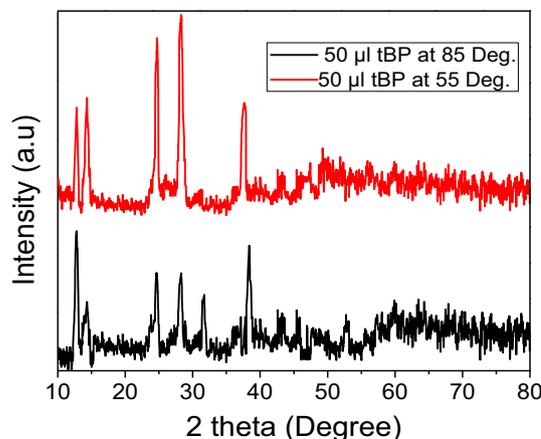

Figure 11. Perovskite films degraded for 120 h with 50 μl concentration tBP additive at 85 and 55°C.

was observed for the sample at 55°C exposed for 120 h. Figure 12 shows the sample film treated with 100 μl tBP exposed at 55 and 85°C for 120 h. The intensity of peaks of the sample exposed at 85°C is compared with intensity of peaks of the sample exposed at 55°C. It is evident that the sample peaks are reduced slightly. It shows that the surface of the films, modified with 100 μl tBP, is stable when exposed to the conditions.

3.3 *FT-IR properties of as-prepared and aged perovskite films*

FT-IR spectroscopy was conducted for fresh and degraded samples treated with 100 μl of tBP and subjected to temperature of 85°C for 120 h to understand the molecular structure of the organic component of the film as shown in figure 13. Two functional groups from methylammonium were identified as methyl and ammonium functional groups. The methyl vibration bands were assigned to CH_3 rocking at 910 cm^{-1}
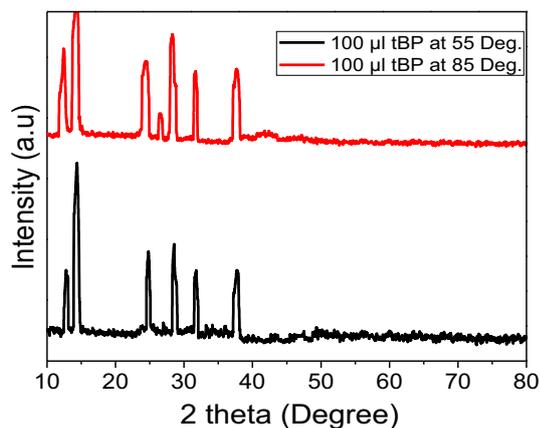
Figure 12. Perovskite films degraded for 120 h with 100 μl concentration tBP additive at 85 and 55°C.

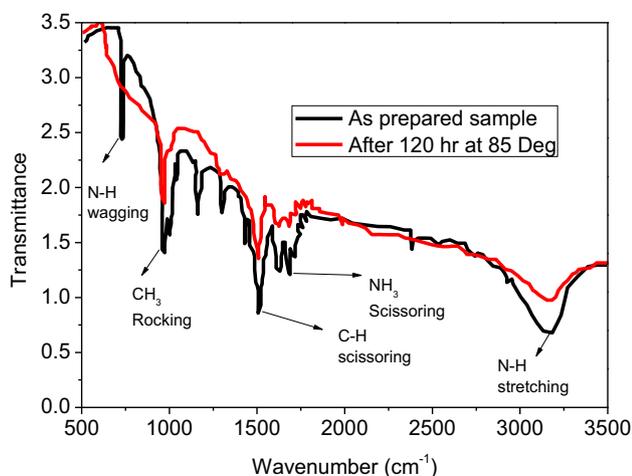**Figure 13.** FT-IR spectra of $CH_3NH_3PbI_3$ film before and after degradation at 85°C for 120 h.

and C–H scissoring at 1470 cm^{-1}. The ammonium vibration bands were also assigned to N–H wagging at 660 cm^{-1}, NH_3 rocking at 947, 961 and 1252 cm^{-1}, NH_3 scissoring at 1654 cm^{-1} and N–H stretching at 3208 cm^{-1} [16,25,26]. The intensities of ammonium bands in the degraded sample decreased at 660, 947 and 1654 cm^{-1} when compared with the methyl bands. This shows that the concentration of NH_3 functional groups in the sample decreases in magnitude at a higher rate than that of methyl functional groups. This could be due to conversion of ammonium molecules to amines that leads to deprotonation process. The decrease in the concentration of NH_3 shows that N–H bonds are weakest connections in perovskite structure. Also, NH_3 and CH_3I have boiling points of –33.34 and 42.43°C, respectively. The ammonium bond brakes faster than methyl iodide [27] and leads to decrease in N–H bonds. The sample degraded for 120 h shows no significant decrease in the peaks when compared to freshly prepared sample. This supports that the sample treated with 100 μl of

tBP resists degradation of the film when exposed to temperature of 85°C for 120 h.

4. Conclusions

Due to impediment of performance instability in PSCs, they have not been practically deployed in PV applications. Encapsulation and surface passivation of the films using hydrophobic molecules have been used as methods of stabilizing the films but the challenge remains. In this work, perovskite films prepared through spin-coating technique were synthesized and the degradation of the as-prepared and aged films treated with tBP was studied for 120 h against temperature in a temperature-controlled chamber. The surface-modified films resisted temperature degradation more than the as-prepared film at 85°C than at 55°C. It shows that the films have more adverse effect of degradation with temperature at 85°C than at 55°C. Based on the findings from the research, 100 μl of tBP reduced the rapid degradation of the perovskite films for 120 h. This shows that incorporation of tBP on the surface of PbI_2 and then CH_3NHI helps reduce degradation of perovskite films. This low-cost method could be deployed in real PV commercial application.

Acknowledgements

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