Affordable and sustainable new generation of solar cells: calcium titanate (CaTiO₃) – based perovskite solar cells

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Abstract. Indonesia is located along the equator lines with the high intensity of solar radiation averaging about 4.5 kWh of electrical energy/day. This potential leads to the self-sustaining energy possibility fulfilling the electricity needs. Due to their unique electronic structures and high-cost merit over the existing commercial PV technologies, perovskite solar cells (PSCs) have emerged as the next-generation photovoltaic candidate. Their highest power efficiency can be achieved of up to 22.1% in the last 5-6 years. However, this high efficiency came from CH₃NH₃PbI₃ materials which contain lead, a toxic material. Herein calcium titanate (CT) as a lead-free perovskite material were synthesized through sintering of calcium carbonate (CaCO₃) and titanium oxide (TiO₂) by the sol-gel method. CT powders were characterized by SEM, XRF, FTIR and XRD then applied it onto the mesoporous hetero junction PSCs, with a device architecture ITO/TiO₂/CaTiO3/C/ITO. By manipulating the raw material stoichiometry and heating temperature in the synthesis of CaTiO₃, the device shows the highest power conversion efficiency (PCE) of 2.12%, short-circuit current density (J_SC) of 0.027 mA cm⁻², open circuit voltage (V_OC) of 0.212 V and fill factor (FF) of 53.90%. This sample can be an alternative way to create lead-free, large-scale, and low-cost perovskite solar cells.

1 Introduction

Indonesia is a tropical country located along the equator line which receives a lot of solar energy every year. Most of Indonesian areas get a quite intense of solar radiation with the average daily radiation about around 4 kWh/m² [1]. For Indonesia which has a lot of small and isolated islands where electricity demand is quite low, photovoltaic solar energy system is one of solutions to meet Indonesia electricity needs [2].

The current generation of photovoltaics is perovskite solar cells (PSCs) that developed very rapidly in the past few years due to the outstanding semiconductor photoelectric properties of organic-inorganic perovskite materials and exceptional efforts in perovskite material and device investigation [3]. In 2009, research conducted by Miyasaka et al. employed the lead perovskite, CH₃NH₃PbI₃ (MAPbI₃), as light absorbers in the solar cells and demonstrated a power efficiency (PCE) of 3.8% [4]. Then, in just 7 years, the maximum PCE of PSCs has rapidly improved from 3.8% to 22.1%, now rivalling the efficiency of silicon solar cells [5]. However, compared to its high efficiency, material stability issue and toxicity of lead have remarkably limited its further step toward commercialization [6].

Calcium titanate (CaTiO₃) is one of the perovskite materials with the general formula of ABX₃, the cation A is occupied in a cube-octahedral site and the cation of B is occupied in an octahedral site where X is halide [7]. CaTiO₃ also shows dielectric properties with a relative permittivity value of up to 186 and the band gap of 3.8 – 4.00 eV which can be used as a optoelectronic device [8]. Depend on the phase transition temperatures, CaTiO₃ can be divided in four space groups: orthorhombic (Pbnm), orthorhombic (Cmcm), tetragonal (I₄/mcm) and cubic (Pm3 m) [9]. Among them, cubic phase formed in the high temperature (T > 1300°C), tetragonal phase is a transient compound which formed in very limited temperature (1250 °C < T < 1349°C), while the orthorhombic phase (Pbnm) is stable at room temperature [9–11].

The raw material sources of titanium in the synthesis of calcium titanate are minerals rutile, ilmenite and anatase and its main features are: rutile is a scarce mineral, it crystallizes in the tetragonal system and a density of 4.18 to 4.25 g/cm³. Ilmenite presented hexagonal crystallization and rhombohedra, and a density of 4.10 to 4.80 g/cm³ [9]. While anatase showed tetragonal system and a density of 3.79 to 3.97 g/cm³ [12]. Luttrell et al.[13] showed that anatase has a larger band gap than rutile TiO₂ due to the different surface orientation, thus it is generally accepted that anatase exhibits a higher photoactivity than those of rutile.
CaTiO$_3$ perovskite structure can be obtained by several synthesis methods such as solid state reaction method [14], co-precipitation method [15], wet-chemical method (sol-gel) [16] and hydrothermal technique [17]. Sol-gel method provides important benefits over the other techniques due to the low cost, easy preparation route, tuneable composition control, high crystal homogeneity and lower temperature of crystallization [18]. However, undesired phase due to unreacted precursors are the drawbacks beside the loss of stoichiometry and wide particle size problems [19]. Hence, some process modifications are needed to ensure their reproducibility for mass production.

This study was thoroughly investigated the structural and physicochemical properties of CaTiO$_3$ powders which were synthesized using sol-gel method. Later, the paste form of the synthesized CaTiO$_3$ are deposited in an active perovskite layer for the lead-free PSCs application. The effect of the heat treatment temperature and CaCO$_3$:TiO$_2$ stoichiometric ratio in the synthesis of lead-free CaTiO$_3$ perovskite material were examined in order to improve PSCs device performance.

2 Experimental Methods

2.1. Materials

CaTiO$_3$ powder were synthesized by reacting the commercial CaCO$_3$ powder and TiO$_2$ anatase powder obtained from MTI Corporation (99%) with the solvent of ethanol purchased from (96%) Merck Millipore Corporation. Potassium iodide (KI) (0.5 M) and iodine solution (I$_2$) (0.05 M) as an electrolyte solution was purchased from Nirwana Abadi Surabaya and Fadjar Kimia Bogor trading business, respectively. All the chemicals mentioned above, except for CaTiO$_3$, were directly used without further purification. Graphite was used as a source of carbon from candle soot as the counter electrode. Indium Tin Oxide (ITO) glass (ITO-P008-1, Zhuhai Kaivo Optoelectronic Technology Co. Ltd., Guangdong, China) were used as a substrate with the resistivity of 18 – 24 Ω sq$^{-1}$.

2.2 Synthesis of CaTiO$_3$ Powder

Each CaCO$_3$ powder and TiO$_2$ powder (1:7 molar fraction) were dissolved in ethanol and stirred for 2 h at room temperature. The slurries were then dried in a $100^\circ$C oven for 1 h. The mixed powders were crushed then sintered by furin air at $900^\circ$C for 2 h, with the ramp rate of $3^\circ$/min to obtain fine powder of CaTiO$_3$.

2.3 Device Fabrication

PSCs devices based on CaTiO$_3$ were fabricated in the ITO/TiO$_2$/CaTiO$_3$/C/ITO mesoporous heterojunction configuration. An ITO glass were sequentially cleaned with a mild detergent, distilled water and ethanol in ultrasonic bath. In addition, the CaTiO$_3$ paste was prepared by dissolving CaTiO$_3$ into ethanol and stirred until completely dissolved at room temperature. The TiO$_2$ and CaTiO$_3$ paste were deposited onto the cleaned ITO substrate by dip-coating technique, sequentially. Then, carbon was coated as a counter electrode. KI and I$_2$ solution were dropped onto the surface of active area of the PSCs. The device active area was 11.1 cm$^2$.

2.4 Characterization

X-Ray Diffraction (XRD) patterns were obtained using a PANalytical type X’Pert Pro diffractometer with Cu-Kα as the radiation source. Samples were scanned between 10 and $100^\circ$ in 20 with a resolution of 0.05°, 40 kV, and 40 mA. Crystal size was measured by Scherrer equation. SEM image of CaTiO$_3$ powder were measured by scanning electron microscopy (SEM, FEI type Inspect 21). The measurement conditions were 100 kV at various magnifications, as shown on scale bar of the images. The elemental analysis was performed using NEX QC+QuantEZ type of Rigaku X-Ray Fluorescence (XRF) and Fourier-transform infrared (FTIR) spectroscopy (PerkinElmer Spectrum version 10.5.1). PSCs devices performance was carried out under illumination of incandescent lamps with a power of 40 Watt at a distance of 5 cm. The PSCs object is subjected to light with a certain intensity on the top electrode (anode). The digital multimeter is connected to both electrodes with positive pole at the cathode and negative pole at the anode.

3 Results and Discussion

3.1 Structural and Physicochemical Properties of CaTiO$_3$ Powder

1.1.1 Morphologies of CaTiO$_3$ powder

Figure 1 a-d show SEM micrographs of well-defined raw material (CaCO$_3$ and TiO$_2$) and synthesized perovskite CaTiO$_3$ particles with the different molar ratio. It can be
seen that all the samples have spherical morphologies, except for CaCO₃ (Fig. 1a) which has a non-spherical morphology. The non-spherical shape may come from hygroscopic nature of CaCO₃ which is very sensitive to react with the water content from the environment humidity. This reason is in line with the Zhao et al. [20] study explaining that small variations in water content can cause the significant shape changes. As shown in Fig. 1c-d, all of the CaTiO₃ powders exhibit an ultra-agglomeration powder with the size of roughly 100 ± 25 nm. They are robustly agglomerated due to the highly chemically active particles [21]. It is worth noting that the synthesized CaTiO₃ powders are spreading more evenly and uniformly than those of CaCO₃ and TiO₂ powders, which gives an exceptional uniform morphology of perovskite crystal formation.

Further observation shows that the particle size grows up as the ratio of TiO₂ increase (Fig. 2d) which is in a good agreement with XRF and XRD results (vide infra). CaTiO₃ powders with CaCO₃:TiO₂ ratio of 1:7 (Fig. 2d) have slightly larger diameter particle than the ratio of 1:1 due to the high percentage of TiO₂ composition exist in CaTiO₃ powders (Table 1, Fig. 1, Fig. 5). It can be noted that TiO₂ has larger diameter particles than those of CaCO₃ in its pure form (Fig. 2a-b), contributing to the increasing bulk particle size of CaTiO₃ in the agglomeration process.

1.1.2 Chemical composition of CaTiO₃

The chemical composition of CaTiO₃ powder were measured using two methods, that are XRF (Table 1, Figure 3) and FTIR (Figure 4). As shown in Table 1, the main composition in the CaTiO₃ is calcium and titanium which more than 16% and more than 53%, respectively. As increasing TiO₂ molar ratio from 1 to 7 (Table 1, Figure 3) and FTIR (Figure 4). As shown in Table 1, the main composition in the CaTiO₃ is calcium and titanium which more than 16% and more than 53%, respectively. As increasing TiO₂ molar ratio from 1 to 7 respect to 1

| Elements (weight %) | Variable CaCO₃:TiO₂ |
|---------------------|---------------------|
| Ca                  | 43.11               | 16.22               |
| Ti                  | 53.37               | 78.46               |
| V                   | 1.24                | 1.53                |
| Fe                  | 1.49                | 2.89                |
| Ni                  | 0.35                | 0.41                |
| Cu                  | 0.16                | 0.20                |
| Zn                  | 0.09                | 0.11                |
molar CaCO₃, the composition of titanium increases fifty percent. This sharp increase due to the raw material sources of titanium in the synthesis of calcium titanate are anatase phase which has the highest percentage of TiO₂ (98%) among the other phase of TiO₂ [9].

The FTIR spectra of CaTiO₃ with different CaCO₃:TiO₂ molar ratio synthesized at 900°C by sol-gel method are shown in Figure 4. As shown in molar ratio of 1:1 and 1:5 FTIR graph, some peaks in the range of 3600 - 3000 cm⁻¹ band are exist. It has been assigned to the O – H stretching modes of surface absorbed water corresponding to the symmetric and asymmetric stretching vibration of weakly bound water interacting with its environment via hydrogen bonding and to stretching vibrations of hydrogen-bonded OH groups [22]. As molar ratio increase to 1:7, there was no peak found indicating that absence of moisture and water molecular in this system [23]. Hence, molar ratio of 1:7 is the best condition to form a water free content of CaTiO₃ perovskite powders.

The band at ~1423 cm⁻¹ (for molar ratio of 1:3 and 1:7) is due to a weaker, symmetrical stretching band v(C–O) [24]. In addition, the band of CaTiO₃ (with molar ratio of 1:1) at 1415 cm⁻¹ is assigned to carboxylic group [19]. The broad bands observed in the sample with molar ratio of 1.3 and 1.7 are at 1338 – 931 cm⁻¹ are contributed to O – H bonded to titanium [25]. The interesting part in FTIR spectra (Fig. 4) is as molar ratio of TiO₂ decrease, the peak become slightly shifted into the smaller wavelength (886.75 cm⁻¹, 877.96 cm⁻¹, 875.19 cm⁻¹ for molar ratio of 1:7, 1:3, 1:1, respectively). It is known first that the peaks between 1200 – 700 cm⁻¹ indicate the Ti-O bonds vibration [26]. Hence, the shifting to the smaller wavenumber gives less energy required by titanium and oxygen atoms to vibrate with their certain number [27]. As a result, it can be seen that the peak of molar ratio 1:1 corresponding to the bonding of Ti-O bond length becomes increasingly elongated in the cell size.

![Fig. 3. XRF images of CaTiO₃ powder with the CaCO₃:TiO₂ molar ratio of (a) 1:1 and (d) 1:7 at 900°C.](image)

The broad peaks of all samples are observed at the range of 700–400 cm⁻¹ which is due to the Ti – O stretching vibration [19]. The most intense peaks is found in a range 573 – 420 cm⁻¹, indicating the presence of calcium titanate in all samples [28]. It clearly indicates that sol-gel method is a well-established synthetic routes to prepare calcium titanate perovskite materials.

1.1.3 XRD analysis of CaTiO₃

Figure 5 shows X-Ray diffraction patterns for CaTiO₃ powders heat treated at 600°C and 900°C with different precursor molar ratio. All the produced powders have similar XRD patterns and exhibit highly pure crystalline CaTiO₃ with the growth orientation along (1 2 1) direction. Their diffraction peaks match well with JCPDS card No. 22-0153 having orthorhombic structure with space group Pbnm and lattice parameter a = 5.441 Å, b = 7.643 Å and c = 5.381 Å [15,20]. It implies that the pure high crystallinity of CaTiO₃ powders with Pbnm orthorhombic crystal structure can be prepared from the sol-gel method with above mentioned molar ratio.

As comparison, JCPDS card No. 21-1272 and No. 37-1497 for TiO₂ anatase phase and CaO are presented to check if there any undesired phases such as TiO₂ and...
CaTiO₃ perovskite powders. As TiO₂ ratio increase, the mean value of crystalize size or particle size is increasing, which shows a good agreement with the measured particle size distribution from SEM analysis (Fig. 2). This behaviour can be ascribed to the aggregates production and nuclei formation [31].

Table 2. Degree of crystallinity and crystal size of CaTiO₃ powder with the different preparing conditions.

| Variable | CaCO₃:TiO₂ | FWHM | Crystallinity (%) | Crystal size (nm) |
|----------|------------|------|-------------------|-------------------|
| 1:1 (600°C) | 0.19 | 88.56 | 25.30 |
| 1:1 (900°C) | 0.18 | 96.68 | 17.70 |
| 1:3 (900°C) | 0.17 | 97.19 | 22.93 |
| 1:5 (900°C) | 0.15 | 97.43 | 34.07 |
| 1:7 (900°C) | 0.13 | 97.61 | 40.27 |

3.2 Device Performance

The successfully synthesized CaTiO₃ perovskite powder is applied onto the active layer of perovskite solar cells device, as can be seen in Figure 6. The schematic illustration of mesoporous heterojunction n-i-p architecture of PSCs with the configuration of ITO/TiO₂/CaTiO₃/C/ITO are shown in Fig. 6a. According to Zhou et al. [32] work, mesoporous architecture was better used for providing high surface area for appropriate perovskite loading. Fig. 6b shows the photograph of lead-free PSCs devices using synthesized CaTiO₃ powders as an active perovskite layer.

The photovoltaic output parameters of PSCs with the different variable conditions are listed in Table 3. The highest efficiency is achieved by CaTiO₃ perovskite material with the condition of highest TiO₂ ratio (1:7) at 900°C. The more Ti content (XRF, Fig. 3) reinforced by the more Ti – O bonding (FTIR, Fig. 4) and TiO₂ intensity peaks in XRD (Fig. 5) at that condition (1:7, 900°C), suggesting that the high TiO₂ content of perovskite polycrystals can infiltrate into the pores of TiO₂ (act as electron transport material, ETM) improving the PCEs [33]. As shown in Table 3, the cells made from CaTiO₃ perovskite powders exhibited higher V₉₃ than those of TiO₂. The V₉₃ Values depend on the difference between the Fermi level of the oxide and the redox potential of electrolyte, resulting in higher V₉₃ [34].
4 Conclusion

The CaTiO$_3$ perovskite material have been successfully synthesized by sol-gel method. From the investigation of structural and physicochemical properties of the synthesized CaTiO$_3$, the CaCO$_3$:TiO$_2$ molar ratio of 1:7 and heating temperature of 900°C give the best condition to form orthorhombic CaTiO$_3$ crystal structure and applied it onto the active area of lead-free PSCs application. The highest PCE obtained of up to 2.12% with JSC value of 0.212 mA cm$^{-2}$, VOC of 0.212 V and FF of 53.9%. This sample can be an alternative way to create lead-free, large-scale, and low-cost perovskite solar cells.

We acknowledge Central Laboratory of Malang State University for several samples characterization device. This work was supported by Lembaga Penelitian dan Pengabdian Masyarakan (LPPM) Institut Teknologi Kalimantan, Indonesia.

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Table 3. Photovoltaic output parameters of PSCs with different TiO$_2$ molar fraction and different annealing temperature.

| Variable | CaCO$_3$:TiO$_2$ | J$_{SC}$ (mA/cm$^2$) | V$_{OC}$ (V) | FF | PCE (%) |
|----------|------------------|---------------------|-------------|-----|--------|
| 1:1 (600°C) | 0.024 | 0.198 | 0.226 | 0.549 |
| 1:3 (600°C) | 0.016 | 0.102 | 0.437 | 0.607 |
| 1:5 (600°C) | 0.018 | 0.156 | 0.455 | 0.738 |
| 0:1 (900°C) | 0.007 | 0.083 | 0.606 | 0.245 |
| 1:1 (900°C) | 0.013 | 0.126 | 0.471 | 0.635 |
| 1:3 (900°C) | 0.012 | 0.110 | 0.687 | 0.706 |
| 1:5 (900°C) | 0.023 | 0.185 | 0.415 | 1.386 |
| 1:7 (900°C) | 0.027 | 0.212 | 0.539 | 2.031 |