Microstructure, Optical, and Electrical Properties of Barium Titanate ($BaTiO_3$) and $Ba_{1-x}Nd_xTiO_3$ Thin Films Deposited by Chemical Solution Deposition (CSD) Method

R. P. Rini, A. U. L. S. Setyadi, F. Nurosyid, and Y. Iriani

Abstract Barium titanate ($BaTiO_3$) and $Ba_{1-x}Nd_xTiO_3$ thin films used by chemical solution deposition method and prepared with spin-coating technique. The thin films of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ were grown on a quartz and silicon (Si) substrate. The research aim is to get the best of mole variation of Nd doping to ferroelectric material properties. Doping Nd was varied at 5, 10% in $BaTiO_3$. The thin films were annealed at 850 °C with one hour holding time. The crystal structure, optical and electrical properties of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ have been investigated. The microstructure of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ were analyzed using XRD equipment, which showed that $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ crystal had a perovskite shape. The addition mole dopant (x) neodymium (Nd^{3+}), the diffraction angle of the XRD results were seen shifting to the right. As the mole dopant (x) Nd increased, so crystallinity from the $Ba_{1-x}Nd_xTiO_3$ thin films decreased. The crystallite size of $BaTiO_3$, $Ba_{0.95}Nd_{0.05}TiO_3$, and $Ba_{0.9}Nd_{0.1}TiO_3$ were 70; 21; 28 nm. The addition mole dopant (x) Nd^{3+} resulted in smaller grain sizes but it did not significantly affect thickness. The greater the addition mole dopant (x) Nd, the smaller the band-gap produced. The results of the IV characterization showed that the $Ba_{1-x}Nd_xTiO_3$ thin films had a response to light and photovoltaic effects.

Keywords $BaTiO_3$ · Neodymium · Microstructure · Optical properties · CSD

1 Introduction

The development of science and technology is increasingly advanced, particularly in Physics in the area of electronics. The growth of thin films is mostly done and applied in the electronics field such as solar cells. Solar cells are the use of solar energy as

R. P. Rini · A. U. L. S. Setyadi · F. Nurosyid · Y. Iriani (✉)
Physics Department, Graduate Program, Universitas Sebelas Maret, Jl. Ir. Sutami 36A Kentingan, Surakarta 57126, Indonesia
e-mail: yofent_iriani@staff.uns.ac.id

F. Nurosyid · Y. Iriani
Physics Department, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, JL. Ir. Sutami 36A Kentingan, Surakarta 57126, Indonesia

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an alternative energy that is made by converting solar energy into electrical energy. Ferroelectric is a dielectric material that is able to change the electric polarization spontaneously due to the application of an external electric field [1]. The development of ferroelectric thin film research is increasingly becoming a great potential issue since it can be applied to solar cells [2]. The electric field in the ferroelectric solar cells can control and regulate the response of solar cells [3]. When ferroelectric material is applied to solar cells under ultraviolet lighting, this ferroelectric material will have a high output voltage i.e., above 1 kV [2].

$BaTiO_3$ is one of the materials that attract the attention of many researchers because its ferroelectric nature has a high dielectric constant and a large electro-optical coefficient [4]. The $BaTiO_3$ thin film has an ABO_3 perovskite structure, where A is located at the corner of the cube, B is located on the diagonal of the cube space, and O is located at the diagonal plane of the cube [5]. Perovskite $BaTiO_3$ has five types of crystal structure including hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral. Each of which depends on the temperature of the phase [6]. $BaTiO_3$ can be made in the form of thin films using several deposition methods such as vacuum and non-vacuum methods. The vacuum method consists of Laser Ablation, Chemical Vapor Deposition (CVD), PVD, Ion Plating [7]. The non-vacuum method consists of Screen Printing, Dip Coating, Electrophoresis, Electrodeposited, Spray Pyrolysis, and Spin Coating [5], sol-gel or Chemical Solution Deposition (CSD) [6]. CSD is a thin-film manufacturing method that combines physical and chemical methods. The steps of making thin films by using CSD method include making solutions, conducting spin coating process with a certain rotational speed, then conducting annealing process [8].

$BaTiO_3$ has a wide gap energy ($Eg > 3$ eV) [3]. To use the $BaTiO_3$ as solar cell material, it is necessary to reduce the energy gap by giving doping. Materials that can be used for doping administration such as Ni^{2+}, Er^{3+}, Mn^{4+}, Zn^{2+}, Hf^{4+}, Fe^{2+}, Ce^{4+}, W^{6+}, Gd^{3+}, Nd^{3+}, Sr^{2+} and Co^{2+} [3]. Atoms in perovskite materials can be doped using other atoms provided in which the radius of the atom is almost the same with the radius of the atom replaced [8]. The addition of neodymium (Nd^{3+}) can replace Ba^{2+} in the position of *perovskite* A. This happens since the atomic radius Nd^{3+} (0.995 Å) is smaller than Ba^{2+} (1.35 Å) and the radius of Ti^{4+} (0.68 Å) [8]. The addition mol dopan neodymium (Nd^{3+}) in the making process of $BaTiO_3$ is ion donor (donor doping) that donates excess valence electrons to ion Ba^{2+} [8]. The doping material given can affect the crystal structure, microstructure, and optical properties of a material [3]. In this paper presented $BaTiO_3$ substituted ionic Nd^{3+} [8].

In this research, $BaTiO_3$ thin film is doped with (Nd^{3+}) use the chemical solution deposition (CSD) method with the spin coating technique. The solution $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ was grown on quartz and silicon (Si) substrates deposited using spin coating with a rotational speed of 5000 rpm. The samples annealing process used 850°C with a holding time of 1 h. Samples were characterized using X-Ray Diffraction (XRD) equipment used to determine the microstructure, Scanning Electron Microscopy (SEM) used to determine the grain size and the thickness of the film, UV-Vis used to determine the amount of absorbance and transmittance of thin films, and a Keithley I–V Meter used to determine the amount of current and voltage of thin films.

2 Experiment

The thin films of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ used by chemical solution deposition method (CSD). Doping Nd was varied at 5, 10 in $BaTiO_3$. The material used in this research was *Barium Acetate* [$Ba(CH_3COO)_2$] 99.00%, *Neodymium Acetate* [$Nd(CH_3COO)_3$] 99.9%, *Acetic Acid* [(CH_3COOH)] 100%, *Titanium Isopropoxide* [$Ti(OC_3H_7)_4$] 97%, *Ethylene Glycol* [($HOCH_2CH_2OH$)] 100%. There were several steps of making $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ solutions including preparing tools and materials and weighing ingredients to mixing materials. The solution was deposited on the Quartz and silicon (Si) substrate, prepared with spin-coating technique at a rotational speed of 5000 rpm. The samples were annealed at 850 °C with a holding time of 1 h. The material properties of the samples were identified using XRD equipment for microstructure testing. The XRD equipment had a Lamda Cu (1.5406 Å). Samples were characterized using SEM to determine the morphology and the thickness of the samples. In addition, samples were characterized using UV-Vis spectrophotometer to determine the amount of absorbance and transmittance of thin films. Ultimately, samples were characterized using a Keithley I–V Meter to determine the amount of current and voltage of thin films.

3 Result and Discussion

3.1 Characterization of Microstructure

The XRD characterization results was show on Fig. 1. Based on Fig. 1, it can be seen that there are almost no other phases that affect the crystal structure of $BaTiO_3$ thin film and $Ba_{1-x}Nd_xTiO_3$. In this experiment, increasing mole dopant Nd succeeded in replacing Ba, therefore the diffraction pattern produced by $Ba_{1-x}Nd_xTiO_3$ was similar to $BaTiO_3$ pattern.

Based on the XRD results, with the addition mole dopant Nd, the diffraction angle is seen shifting to the right. These results are consistent with what has been done by Sandi et al. [9]. The ionic Nd^{3+} can replace Ba^{2+} in the perovskite structure. Along with the addition mole dopant Nd, it was also seen that the intensity value produced from XRD was getting higher. In accordance with the research of Iriani et al. the additional mole dopant Nd^{3+} on the $BaTiO_3$ thin films can increase the intensity of value formed [8].

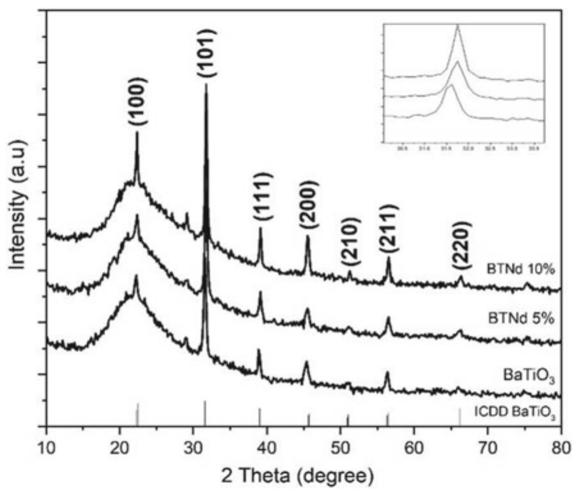

Fig. 1 Diffraction pattern of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$

Table 1 Crystallinity and crystallite size of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin films

Sample	Crystallinity (%)	Crystallite size (nm)
$BaTiO_3$	83.33	70
$Ba_{0.95}Nd_{0.05}TiO_3$	80.31	21
$Ba_{0.90}Nd_{0.10}TiO_3$	80.27	28

The calculation of the crystallinity samples can be seen in Table 1. The addition mole dopant Nd causes the crystallinity of the thin film decrease. The crystallinity of the samples is calculated from the magnitude of the intensity of the diffraction peaks formed. The crystallinity of the samples is a picture of the level of regularity of the crystals that are formed in each film.

The crystallite size of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin films can be calculated using the following Scherrer equation [3]:

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

Table 2 Lattice parameters of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin films from the calculation result

Sample	Lattice parameters (Å)		Tetragonality
	a = b	c	
$BaTiO_3$	4.003	4.020	1.004
$Ba_{0.95}Nd_{0.05}TiO_3$	4.003	4.020	1.004
$Ba_{0.90}Nd_{0.10}TiO_3$	4.016	4.030	1.003

where the value of β is the value of FWHM, θ is the diffraction angle, k is the constant of Scherrer which is at 0.9, and λ is the wavelength of X-ray. The calculation of the crystallite size samples can be seen in Table 1.

Based on the additional mole dopant Nd, the result of crystallite size dwindled. In accordance with studies that have been carried out by Gaur et al. that the crystallite size decreases with the additional mole dopant Nd [8]. The result of the crystallite size ranges from 70 to 28 nm.

The refined XRD results using the GSAS software can be seen in Fig. 2. This software processes with a refinement process so that the crystal structure and lattice parameters a, b, and c of the thin film can be identified.

The lattice parameter values from the GSAS software refinement results can be seen in Table 3. The result shows that thin film $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ has a tetragonal structure since it has a lattice parameter value $a = b \neq c$ and the angle $\alpha = \beta = \gamma = 90°$. The results of refinement $Ba_{1-x}Nd_xTiO_3$ thin film diffraction pattern with

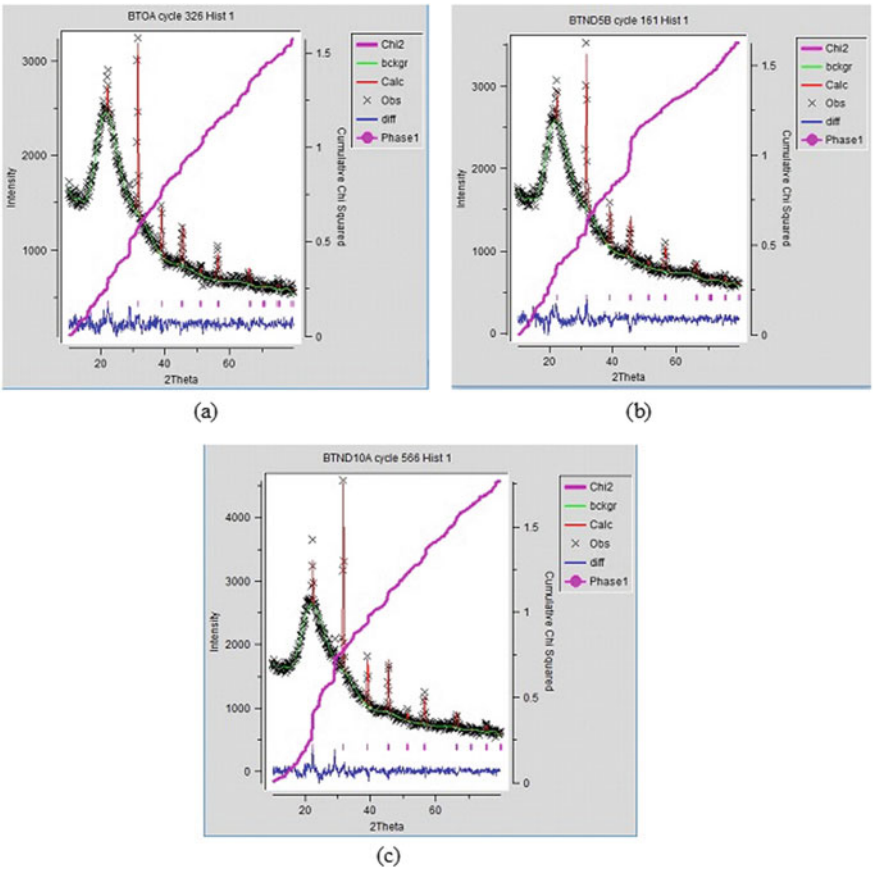

Fig. 2 The refinement of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ diffraction patterns

Table 3 Lattice parameters of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin films from the result of the refinement software GSAS

Sample	Lattice parameters (Å)		Tetragonality
	a = b	c	
$BaTiO_3$	3.992	4.018	1.006
$Ba_{0.95}Nd_{0.05}TiO_3$	3.983	4.008	1.006
$Ba_{0.90}Nd_{0.10}TiO_3$	3.984	4.002	1.004

a variation mole dopant Nd, show the alteration of lattice parameter because of dopant Nd^{3+} into $BaTiO_3$. Decrease in the $Ba_{1-x}Nd_xTiO_3$ lattice parameter with respect to the initial lattice parameter $BaTiO_3$ caused the diffraction angle of the $Ba_{1-x}Nd_xTiO_3$ thin film with a variation mole dopant Nd has shifted from the $BaTiO_3$ diffraction angle on ICDD which has a certain field orientation (*hkl*). It can affect the distance between atoms in the crystal and cause changes in parameters including grid a, b, and c. These results are in accordance with research conducted by Iriani et al. [8]. The changing in lattice parameters in the results of the refinement, thin film diffraction patterns in this study were not very significant (Table 2).

3.2 Characterization of Morphology

The morphology of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin films with magnitude 80,000× are shown in Fig. 3. Based on the addition mole dopant Nd in the $BaTiO_3$, the porosity of the thin film decreases. This happens since the granules in the thin film have experienced perfect diffusion.

Based on the result of SEM characterization, it is obtained the grain size and the thickness of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ that can be seen in Table 4. The grain size of $BaTiO_3$ thin films cannot be calculated since the granules are completely diffused. When there is an increase in the concentration of mole dopant Nd in the thin film of $BaTiO_3$, the grain size decreases. The results of this study are in accordance with the research conducted by Zhang et al. [10]. However, in the sample of $Ba_{0.90}Nd_{0.10}TiO_3$, the grain size of the sample increased. The reason for the morphological change was

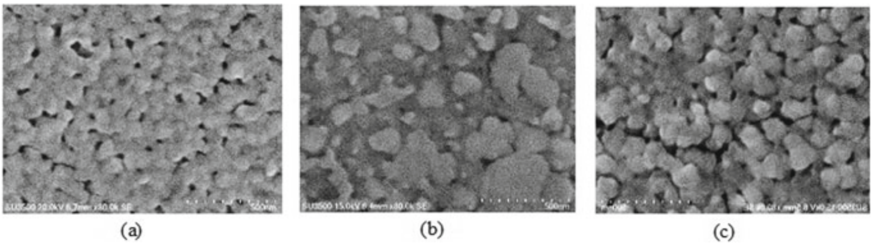

Fig. 3 SEM image of **a** $BaTiO_3$, **b** $Ba_{0.95}Nd_{0.05}TiO_3$, **c** $Ba_{0.90}Nd_{0.10}TiO_3$

Table 4 Grain size and thickness of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin films

Sample	Grain size (nm)	Thickness (nm)
$BaTiO_3$	–	633
$Ba_{0.95}Nd_{0.05}TiO_3$	103	300
$Ba_{0.90}Nd_{0.10}TiO_3$	126	335

not determined. It can only be assumed that the grain boundaries in the SEM results are clearly visible so that the number of grain size that can be calculated and the average is increasing.

The thickness was got from the results of cross-section measurements on the $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin film, as presented in Table 4. The thickness of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ films affects the addition mole dopant Nd. When $BaTiO_3$ was given an additional mole dopant Nd, the thickness of the film got thinner. However, the more mole concentrations dopant Nd was added, the thickness of the film got thicker. As the results of research from Iriani et al. [8]. The thickness of $Ba_{0.95}Nd_{0.05}TiO_3$ is 300 nm, $Ba_{0.90}Nd_{0.10}TiO_3$ is 335 nm, and the thickness of $BaTiO_3$ pure is 633 nm.

3.3 Characterization of Optical Properties

The calculation of band-gap is using the method of *tauch-plot* with the following equation:

$$(\alpha h\upsilon)^2 = A\left(h\upsilon - E_g\right) \quad (2)$$

where $h\upsilon$ is the photon energy, A is a constant, α is the coefficient of absorption, and E_g is the optical band-gap [3].

The transmittance spectrum of quartz substrate grown by $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ is presented in Fig. 4. It can be seen that the higher the concentration mole dopant Nd is given, the lower the peak transmittance value. Based on Fig. 4, it is found that the thin film of $BaTiO_3$ reaches the highest transmittance value. The amount of this transmittance value is inversely proportional to the value of the absorbance value.

The transmittance value of $BaTiO_3$ thin film in the visible light area is greater if mole dopant Nd is increased. The addition mole dopant Nd can increase the absorption of visible light in the thin film of $BaTiO_3$. The transmittance of the $Ba_{1-x}Nd_xTiO_3$ film decreases with the decreasing wavelengths to a certain extent. Waves of absorption from thin films $Ba_{1-x}Nd_xTiO_3$ are bigger if it is compared to $BaTiO_3$. This result is in accordance with the research by Fu et al. [11].

Based on UV-Vis and cross-section test results, the band-gap value is obtained. The band-gap values of the $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin films are presented in Table 5. The results show that the band-gap of $BaTiO_3$ thin films is greater than

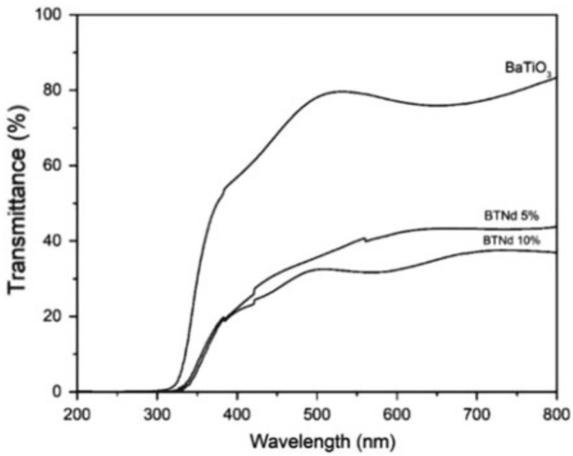

Fig. 4 Transmittance of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin films

Table 5 Energy gap of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin films

Sample	Energy gap (eV)
$BaTiO_3$	3.64
$Ba_{0.95}Nd_{0.05}TiO_3$	3.00
$Ba_{0.90}Nd_{0.10}TiO_3$	3.00

$Ba_{1-x}Nd_xTiO_3$. This happens since the addition mole dopant Nd can reduce the band-gap of the thin film. In this study, the Nd^{3+} ionic replaces the Ba^{2+} ion on the A-side so that it can cause the narrowing of the conduction band-gap. This is in accordance with the research of Jiang et al. [3]. In this study, the value of the band-gap of the thin film of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ is around 3.00–3.64 eV for the overall concentration of mole.

3.4 Characterization of Electrical Properties

The characterization of electrical properties (current–voltage) from $BaTiO_3$ and ($Ba_{1-x}Nd_xTiO_3$) thin films was got by varying mole dopant Nd^{3+} using Keithley I–V meters. Figure 5 shows the current and voltage relationship curves of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ films in dark and light conditions which indicate that the thin film has diode characteristics. The curve shows that in the $Ba_{1-x}Nd_xTiO_3$ film with Si substrate (p-type semiconductor), a connection has occurred. This curve shows that there is an induced current flow (photocurrent) so that the $Ba_{1-x}Nd_xTiO_3$ film shows the response to the light. The $Ba_{1-x}Nd_xTiO_3$ film when it is irradiated (in light conditions) has more conductive properties if it is compared to that when it is in dark conditions due to the absorption of photon energy. The result of the photon energy charge can be separated and collected by the cathode and anode. The results

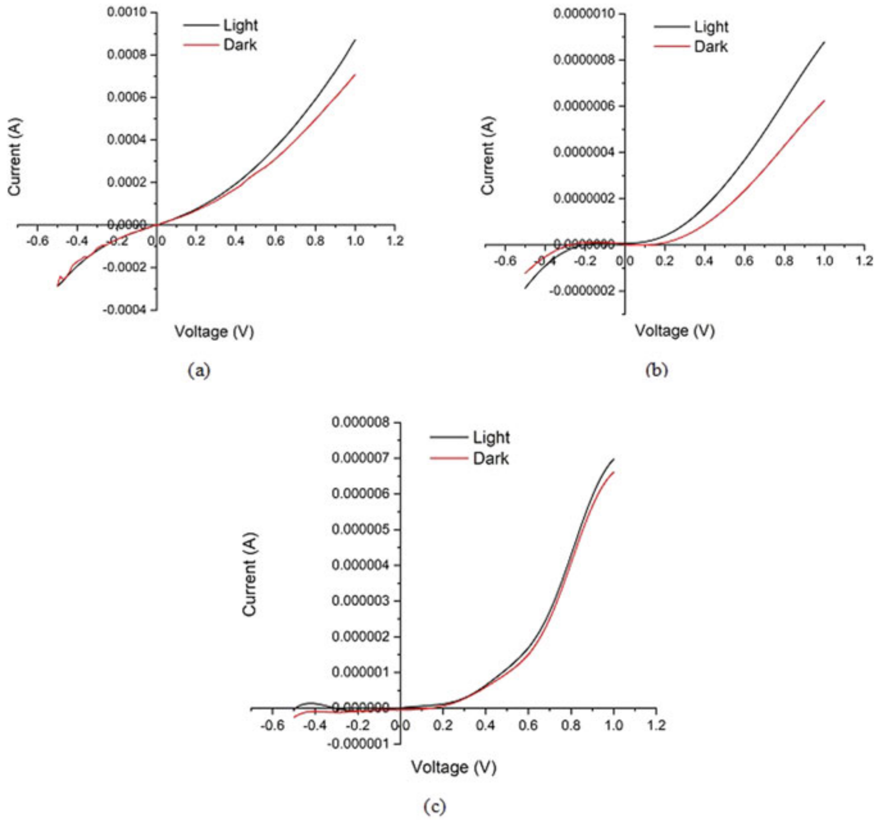

Fig. 5 Characterization curve I–V of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin films

of this study are in accordance with the research conducted by Wang et al. [12]. The amount of I_{sc} and V_{oc} value from $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ film are shown in Table 6. Based on Table 6, it can be seen that the additional mole dopant Nd^{3+} can increase the value of I_{sc} and V_{oc}. The results are in accordance with the research conducted by Jiang et al. [3].

Table 6 I_{sc} and V_{oc} value of $BaTiO_3$ and $Ba_{1-x}Nd_xTiO_3$ thin films

Sample	I_{sc} (mA)	V_{oc} (V)
$BaTiO_3$	2.14×10^{-9}	1.78×10^{-5}
$Ba_{0.95}Nd_{0.05}TiO_3$	6.88×10^{-9}	2.12×10^{-1}
$Ba_{0.90}Nd_{0.10}TiO_3$	1.09×10^{-8}	1.52×10^{-2}

4 Conclusions

The addition of mole dopant Nd^{3+} on $BaTiO_3$ caused the change of angel diffraction. The diffraction angle were seen shifting to the right. As the mole dopant Nd increased, so crystallinity from the $Ba_{1-x}Nd_xTiO_3$ thin films decreased. The crystallite size of $BaTiO_3$, $Ba_{0.95}Nd_{0.05}TiO_3$, and $Ba_{0.9}Nd_{0.1}TiO_3$ were 70; 21; 28 nm. Result of refine with GSAS software show the dopan Nd have been included in the structure $BaTiO_3$. The addition mole dopant Nd^{3+} resulted in smaller grain sizes but it did not significantly affect the thickness. The greater the addition mole dopant Nd, the smaller the band-gap produced. Moreover, the results of the IV characterization show that the $Ba_{1-x}Nd_xTiO_3$ thin films have a response to the light and the photovoltaic effects.

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