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Photoelectrochemical cell performance of chemically deposited $MoBi_2Te_5$ thin films

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ABSTRACT

Molybdenum bismuth telluride thin films have been prepared on clean glass substrate using Arrested Precipitation Technique (APT) which is based on self organized growth process. As deposited $MoBi_2Te_5$ thin films were dried in constant temperature oven at 110°C and further characterized for their optical, structural, morphological, compositional and electrical analysis. Optical absorption spectra recorded in the wavelength range 300-800 nm showed band gap (Eg) 1.44 eV. X-ray diffraction pattern and scanning electron microscopic images showed that $MoBi_2Te_5$ thin films were nanocrystalline having rhombohedral structure. The energy dispersive spectroscopic analysis of as deposited thin films showed close agreements in theoretical and experimental atomic percentages of Mo^{4+}, Bi^{3+} and Te^{2-} and suggest that the chemical formula $MoBi_2Te_5$ assigned to molybdenum bismuth telluride thin film material is confirm. The resistivity and thermoelectric power measurement studies showed that the films were semiconducting with n-type conduction. The fill factor and conversion efficiency (η) are determined by fabricating PEC cell using $MoBi_2Te_5$ thin film electrode. In this article we report the optostructural, morphological, compositional and thermoelectric characteristics of nanocrystalline $MoBi_2Te_5$ thin films to check its suitability as photoelectrode in PEC Cell. Copyright © 2012 VBRI Press.

Keywords: Arrested precipitation technique, PEC cell, X-ray diffraction, microstructure, transport properties.

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Introduction

During recent years, thermoelectric materials aiming at thermoelectric devices applications have attracted much attention because the applications of thermoelectric microcooling devices are very promising for thermal management of microelectronics and optoelectronics [**1**]. Transition metal chalcogenide represent an important family of materials that have been proven useful as thermoelectric materials in optoelectronic devices [**2**], ferromagnetic semiconductors [**3**], supercapacitors [**4**], quantumdots [**5**], sensors [**6**] and photovoltaic's [**7**]. Bismuth chalcogenide compounds are considered to be the best candidates for thin film thermoelectric coolers due to their excellent **fig.** of merit and thermoelectric properties near room temperature region [**8**]. Since last decades, efforts are in progress to enhance the properties of these materials using different approaches is to synthesis it in nanoscale [**9-12**]. The bismuth chalcogenides are applicable in optical and photosensitive devices in photoelectrochemical cells (PEC) in solar selective decorative coatings and in the fabrication of an ideal Hall Effect magnetometer [**13**] Molybdenum dichalcogenides are indirect semiconductors with their optical band gap comparable to solar spectrum. Thus molybdenum dichalcogenide hold promise in photovoltaic applications such as photoelectrode in high efficiency photoelectrochemical solar cells. The main advantage of molybdenum dichalcogenide semiconductor is the prevention of electrolyte corrosion because of photo transition involving non bonding d-d orbital of Mo atoms [14]. Because of these characteristics of binary chalcogenides we have attempted to prepare ternary molybdenum bismuth telluride thin film.

Until now, different fabrication techniques such as spray pyrolysis [**15**], reflux method [**16**] including liquid phase epitaxy, bulk powder synthesis, thermal evaporation [**17**] and pulsed electrochemical deposition [**18**] has been employed for chalcogenide compounds. These commonly used methods are either costly or difficult to realize. APT provides an attractive alternative route to the fabrication of high quality thin film with promising properties offering several advantages over other methods. These include low cost, high controllability with silicon microfabrication processes as well as room temperature fabrication.

To the best of our knowledge this is the first reported synthesis of ternary nanocrystalline $MoBi_2Te_5$ thin film using self organized growth process popularly known as arrested precipitation technique [**19-21**]. The APT process based on Ostwald ripening law [**22**]. The purpose of present work is to establish and optimize the growth condition to produce nanocrystalline $MoBi_2Te_5$ thin films. As grown films were then used for characterization study such as optostructural, optoelectronic, compositional and surface morphology. All these characteristic properties of nanocrystalline $MoBi_2Te_5$ thin films are used to check, its suitability as photoelectrode in PEC solar cell.

Experimental

$MoBi_2Te_5$ thin films were deposited using APT on microglass slide substrates from aqueous bath. The deposition bath consisted of an aqueous solution of Mo-TEA, Bi-TEA complexes and sodium tellurosulphite for $MoBi_2Te_5$ thin film growth. Initially high purity precursors of Ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$, 99 % pure, s-d fine-chem.], Bismuth nitrate [AR gread, $Bi(NO_3)_3.5H_2O$, 99 % pure, s-d fine-chem.] triturated separately in triethanolamine [$C_6H_{15}NO_3$, 99 % pure, Merck] complexing agent to form clear solution of Mo-TEA, Bi-TEA complex. Sodium tellurosulphite was prepared by refluxing tellurium metal power [AR gread, 99 % pure, s-d fine-chem.] separately with anhydrous sodium sulphide [Na_2SO_3, 99 % pure, s-d fine-chem.] at 90°C for 8 hours. The concentrations of precursors, pH of bath solution, temperature of bath and rate of substrate rotation were finalized at the initial stages of the thin film formation. By obtaining proper conditions good quality and uniform film was obtained on substrate support. The film growth involves reaction of Mo^{4+}, Bi^{3+} and Te^{2-} ions in aqueous medium. At alkaline pH 10 and temperature 55^0 C. Mo-TEA, Bi-TEA arrested metal ions slowly dissociate from complex and reacts with chalcogen ion Te^{-2}. Ion by ion condensation took place which results in thin film formation on substrate surface. Ionic product K exceed the solubility product Ksp at pH 10 which results in condensation of metal ions and chalcogen ions [23] into quasi binary thin film formation $MoTe_2$, Bi_2Te_3 to ternary $MoBi_2Te_5$ thin film layer.

Characterization of sample

The thickness of the film was determined by surface profiler [AMBIOS XP-1]. The optical transmittance was measured using UV-Visible NIR- Spectrophotometer [Hitachi model 330 Japan] in wavelength range 300 to 800 nm. The structure of thin film was determined by X-ray Diffraction (XRD) analysis [Philips PW-1710 X-ray diffractrometer] with Cu Kα target having wavelength 1.540A^o for the 2θ ranging from 20^o to 80^o. The surface morphology and compositional analysis of as deposited thin films were determined by using Scanning Electron Microscopy (SEM) attached with Energy Dispersive Spectroscopy (EDS) model [JEOL- JSM-6360 A]. DC electrical conductivity was measured by two probe method in the temperature range 300K to 500K. Thermoelectric power measurement was carried out under the condition of maximum temperature difference and minimum contact resistance. Silver paste was applied to films to ensure good ohmic contacts.

Results and discussion

Growth kinetics and reaction mechanism for thin film formation

Molybdenum bismuth telluride thin films were deposited from an aqueous alkaline medium containing Mo-TEA, Bi-TEA complexes and sodium tellurosulphite solution. The deposited process based on simple ion by ion mechanism it involves three steps i) Dissociation of complex to free Mo^{+4} and Bi^{+3} ions. ii) Formation of Te^{2-} ions. iii) Formation of $MoBi_2Te_5$ by ion by ion condensation.

In the beginning the Mo-TEA and Bi-TEA complex dissociates and release Mo^{+4} and Bi^{+3} ions at pH 10and temperature 55^o C.

$$(NH_4)_3[Bi2N(CH_2\text{-}CH_2\text{-}O)_3] + 6H_2O \xrightarrow{pH\ 10} Bi^{3+} + 3NH_4OH + 3OH^- + 2[N(CH_2\text{-}CH_2\text{-}OH)_3] \quad (1)$$

$$(NH_4)_3[Mo2N(CH_2\text{-}CH_2\text{-}O)_3] + 6H_2O \xrightarrow{pH\ 10} Mo^{4+} + 2NH_4OH + 4OH^- + 2[N(CH_2\text{-}CH_2\text{-}OH)_3] \quad (2)$$

Freshly prepared sodium tellurosulphite hydrolyses in aqueous alkaline medium to generate Te^{2-} ions

$$Na_2TeSO_3 + OH^- \xrightarrow{pH10} Na_2SO_4 + HTe^- \quad (3)$$

$$HTe^- + OH^- \longrightarrow H_2O + Te^{2-} \quad (4)$$

when the reaction (1), (2), (4) is slow enough, the heterogeneous nucleation of $MoBi_2Te_5$ would occur slowly on the immersed substrate surface. Deposition of thin film material can be expected as per ion by ion condensation reaction,

$$Mo^{4+} + 2Bi^{3+} + 5Te^{2-} \longrightarrow MoBi_2Te_5 \quad (5)$$

The absorbance measurements have been taken by using an UV-Vis NIR spectrophotometer in order to determine the band gap value of the material. The absorption coefficient (α) of the deposited film is calculated from the observed absorbance and transmittance values using the following equation [**24**].

$$\alpha = \frac{1}{t} \ln \left(\frac{A}{T}\right) \quad (6)$$

where, α is absorption coefficient in Cm^{-1}, t is film thickness, A is absorbance and T is transmittance. The nature of transmission is determined using the following equation 7 [**25**].

$$\alpha h\nu = A\,(h\nu - Eg)^n \quad (7)$$

where, A is Energy dependant constant, Eg is band gap energy of material, hυ is photon energy and n is index number (1/2, 3/2…..) depending upon mode of transition. The optical absorption spectra of $MoBi_2Te_5$ thin film have been recorded as a function of wavelength in the range between 300 to 800 nm. The value of absorption coefficient (α) rises sharply owing to band to band transition.

Fig. 1 represents the plot of wavelength Vs absorption of $MoBi_2Te_5$ thin film. The plot of (hυ) Vs $(\alpha h\upsilon)^2$ was shown in inset image which is linear at absorption edge, indicating a direct allowed transition. The straight line portion was extrapolated to the energy axis and when $(\alpha h\upsilon)^2$ =0, the intercept gives the band gap energy (Eg). It is observed that the band gap of $MoBi_2Te_5$ thin film was 1.44 eV.

The surface morphology of $MoBi_2Te_5$ thin films was investigated by using Scanning electron micrograph technique. SEM has been proved to be a unique, convenient and versatile method to analyze surface morphology of thin film and to determine the grain size. Scanning electron micrograph of $MoBi_2Te_5$ thin film in the as grown condition is as shown in **Fig. 2** represents an image at magnification (× 6,000). The microstructure of the film observed by SEM shown that, on the surface of $MoBi_2Te_5$ film the agglomerate particles composed of spherical grains were distributed on the substrate homogeneously, but many voids existed between particles in the film. The smooth and uniform, adherent film surface without cracks feature observed in low magnification, so it has shown high mechanical stability of the film. The inset image represents the higher magnification (× 20,000) of the same sample. The spherical nature of the particle with average grain size in order to 400 nm is discernable from the image.

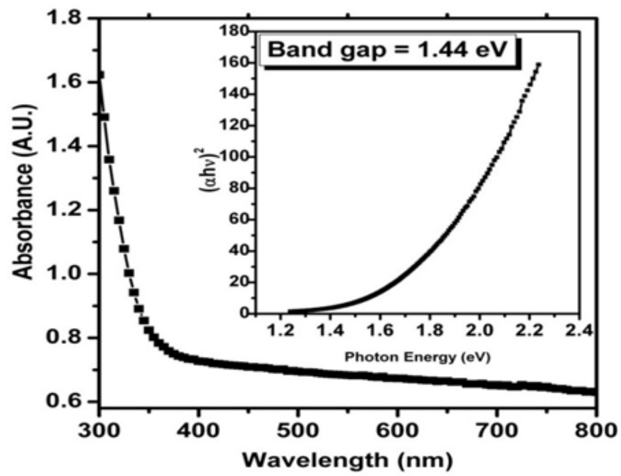

Fig. 1. Determination of band gap $MoBi_2Te_5$ thin film.

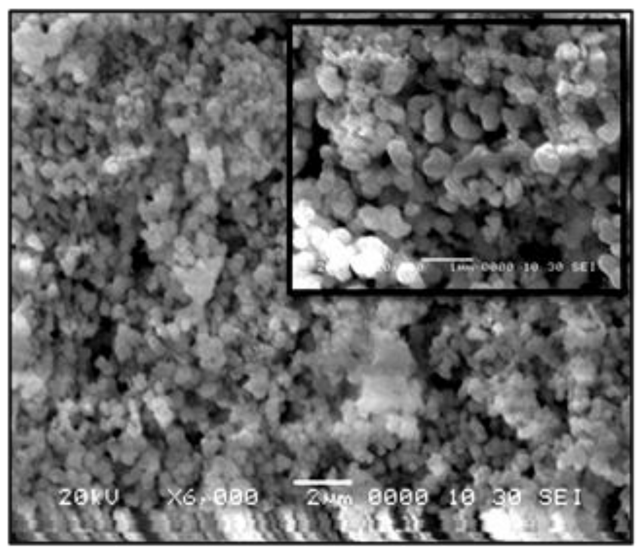

Fig. 2. SEM micrograph of $MoBi_2Te_5$ thin film.

The composition of $MoBi_2Te_5$ is a topic of main importance since PEC properties are influenced by deviations from stoichiometry. The typical EDS spectrum of synthesized material is as shown in **Fig. 3**. This analysis shows that the atomic percentage of Mo^{4+}, Bi^{3+} and Te^{2-} confirms the assigned stoichiometry to synthesized compound. The expected and actual atomic percentage of Mo, Bi and Te is as shown in inset table. The EDS data showed close agreements in theoretical and experimental values of Mo^{4+}, Bi^{3+}, Te^{2-} so atomic weight percent suggest the chemical formula $MoBi_2Te_5$ of as deposited molybdenum bismuth telluride thin film. The percentage of Mo and Bi in the film is slightly higher than expected, this is attributed to the fact that Mo^{4+} state is more stable and reactive than in Mo^{6+} state as well as bismuth is more metallic and its reactivity towards Te^{2-} is higher. Moreover molybdenum and bismuth forms antisite defects [**23**]. This is responsible for slightly variation in stoichiometry of ternary $MoBi_2Te_5$ thin film.

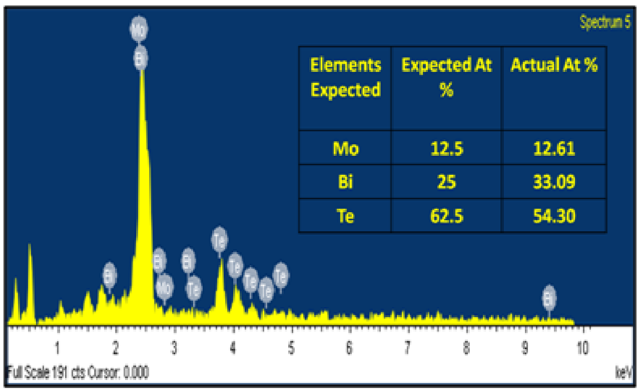

Fig. 3 EDS spectrum of $MoBi_2Te_5$ thin film.

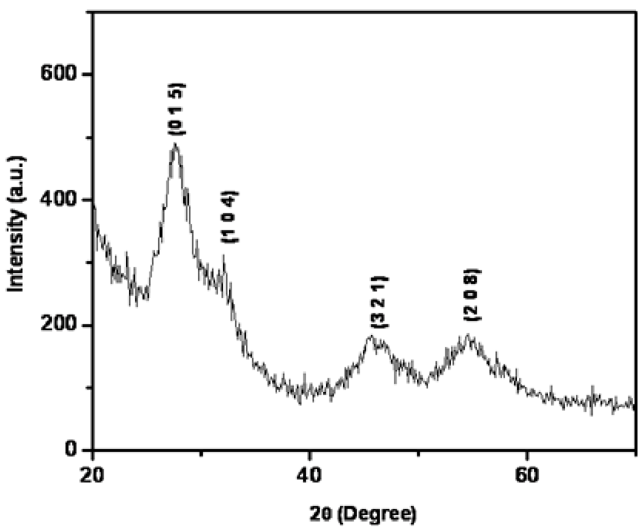

Fig. 4. X-ray diffraction of $MoBi_2Te_5$ thin film.

The crystal structure of $MoBi_2Te_5$ thin film was studied by X-ray diffraction with CuKα radiation (λ=1.540A°). **Fig. 4** shows typical X-ray diffraction of $MoBi_2Te_5$ thin film. X-ray diffraction pattern reveals that the deposited film possesses nanocrystalline nature with rhombohedral structure. The diffraction peaks of rhombohedral $MoBi_2Te_5$ are found at 2θ values of angles 32.1°, 38.2°, 45°, 53.1° corresponding to lattice planes (0 1 5), (1 0 4), (3 2 1), (2 0 8) respectively. The different peaks in difractogram are indexed and the corresponding values of interplaner spacing'd' are calculated and compared with standard values of JCPDS data (Card No. 08-0021 and 23-1257).

The crystallite size of the deposited film was calculated using FWHM data and Debye Scherer formula given below [**8**].

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (8)$$

where, λ is wavelength of X-ray, θ is Bragg's diffraction angle at peak position in degrees and β is Full Width at Half Maximum (FWHM) of peak in radians. The crystallite size estimated for (0 1 5) peak was 38.4 nm.

The measurements of electrical resistivity of $MoBi_2Te_5$ thin film was carried out in temperature range 300 - 500 K using standard DC two point probe method under dark. A plot of 1000/T Vs log ρ for cooling cycle was shown in **Fig. 5**. The resistivity decreases with increase in temperature which is the indication of typical semiconductor characteristics [**15**]. The activation energy for conduction in low temperature region is the energy required to take place between the defect level and valence band or conduction band. At sufficiently high temperature intrinsic conductivity starts and electron conduction from valence band to conduction band takes place.

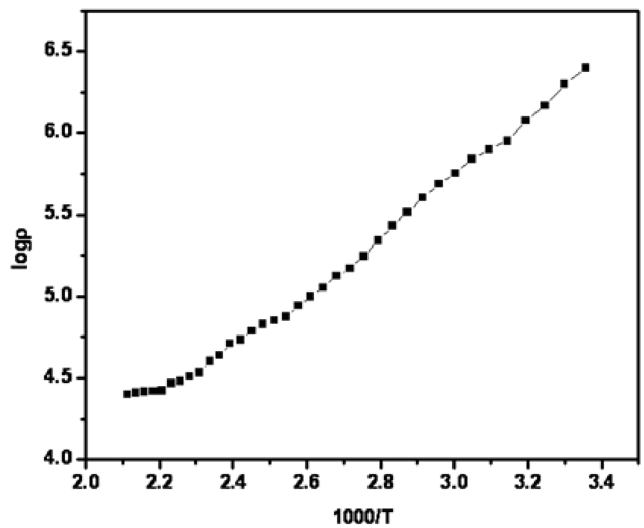

Fig. 5 Plot of 1000/T Vs log ρ for $MoBi_2Te_5$ thin film.

The activation energy Ea can be estimated according to equation:

$$\sigma = \sigma_0 e^{(-Ea/kT)} \qquad (9)$$

where Ea is activation energy for electrical conduction, k is Boltzmann constant and σ is the temperature independent part of the conductivity and σ_o represents the pre-exponential factor. Conductivity is the reciprocal of resistivity; from the graph it indicates that in high temperature σ exhibits activated behavior. In low temperature region the slope of curve continuously decreases with increasing temperature indicates that σ in this region exhibits non-activated behavior. The activation energy for high temperature region was 0.03214 eV and activation energy for low temperature region was 0.01532 eV.

The TEP is most sensitive to any change or distortion of the Fermi level in the material. The temperature difference between the ends of sample causes transport of carriers from hot to cold end and thus creates electrical field which give rise to thermal voltage. This thermally generated voltage is directly proportional to the temperature difference created across the semiconductor. The type of conductivity of $MoBi_2Te_5$ thin film was determined from TEP measurement. **Fig. 6** shows variation of thermo emf Vs temperature for $MoBi_2Te_5$ thin film. The negative sign steams from dominance of n-type behavior of the $MoBi_2Te_5$ thin films [**23**].

Optimization of preparative parameters of photoactive semiconducting electrodes by PEC method is a new, reliable and unique technique in thin film research [**26, 27**]. Photodiodes or solar cells operate without an externally applied voltage and the collection carries result from the internal field at the junction. The FTO coated glass substrates are used for the deposition of $MoBi_2Te_5$ thin films for the PEC measurements. **Fig. 7** shows plot of voltage (mV) versus current density (mA/cm^2).

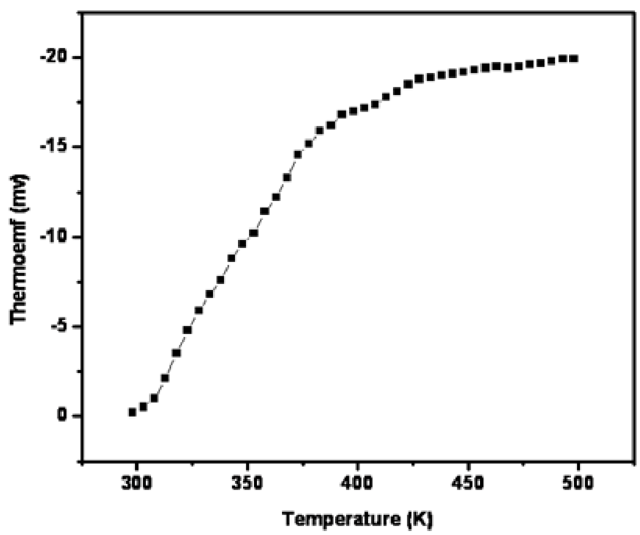

Fig. 6. Plot of Thermoemf Vs Temperature for the $MoBi_2Te_5$ thin film.

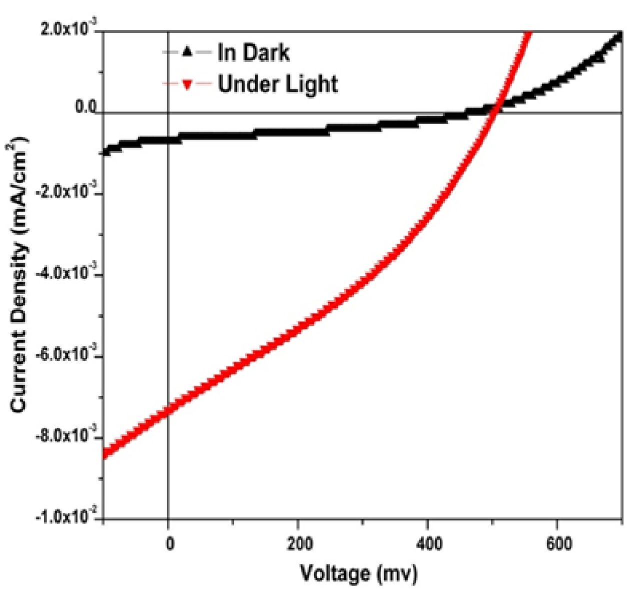

Fig. 7. Plot of voltage (mV) versus current density (mA/cm^2).

A Fill Factor (FF) which shows how closely the product Vm**.**Im approaches the product Voc**.**Isc and acts as a useful **Fig. 7** of merit for the solar cell or photodiode design, is often defined by,

$$FF = \frac{(Vm\ Im)}{(Voc\ Isc)} \qquad (10)$$

The conversion efficiency η is the most important and defined as the percentage of the total power in light that is converted in to electrical power. It can be expressed as [**28**],

$$\eta = \frac{(Im\ Vm)}{Pi} = \frac{(FF)(Isc\ Voc)}{Pi} \qquad (11)$$

where Im and Vm are the output current and voltage respectively, for the photodiode operating under maximum power conditions, Pi indicates the incident power density under illumination. Isc is the short circuit current and Voc is the open-circuit current.

From **Fig. 7** determined values of FF of $MoBi_2Te_5$ thin film was 0.295 and the conversion efficiency 0.115 % respectively. Our next attempt will be the improvement in conversion efficiency by optimizing preparative parameters of the $MoBi_2Te_5$ thin films.

Conclusion

Arrested precipitation technique is applied successfully to deposit stoichiometric, adherent and uniform deposition of $MoBi_2Te_5$ material in thin film form. Optostructural and morphological results obtained shows material can be useful for device application such as a photo electrode in solar cell and thermo cooling properties. X-ray diffraction confirms the proper phase formation of material. $MoBi_2Te_5$ exhibits an n-type semiconducting behavior with high electrical conductivity which is strongly suitable for fabricating a thin film solar cell. From the PEC it is observed that conversion efficiency 0.115%. Our future plan is to increase the efficiency of $MoBi_2Te_5$ thin film. As well as we will check the thermo cooling properties of $MoBi_2Te_5$ thin film.

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