RP Current Trends In Engineering And Technology (e-ISSN: 2583-5491)
Vol. 4, No. 1 (January – March 2025) pp. 1–6

Cite this article: Study the effects of surface passivation using PMMA on hole transport layer of CuO, *RP Cur. Tr. Eng. Tech.* **4** (2025) 1–6.

Original Research Article

Study the effects of surface passivation using PMMA on hole transport layer of CuO

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ARTICLE HISTORY
Received: 02 March 2025
Revised: 30 April 2025
Accepted: 01 May 2025
Published: 02 May 2025

KEYWORDS
Perovskite Solar Cell (PSC);
Hole transport layer (HTL);
Cupric oxide (CuO);
Surface passivation;
Polymethylmethacrylate (PMMA).

ABSTRACT
This study reports a comparative analysis of hole transport layer with and without surface passivation. Hole Transport Layer (HTL) of copper oxide (CuO) was fabricated using copper oxide powder of high purity, by Doctor Blade method on Indium tin oxide (ITO) substrate. The HTL was passivated using Polymethylmethacrylate (PMMA) solution by Spin coating method, so that the interface provide enhancement in the performance of Perovskite Solar Cells (PSCs). Surface passivation was done to enhance mobility and stability in semiconductor films, as PMMA is chemically stable and enduring polymer. Characterizations for analyzing morphology, structure, optical and electrical properties were done using analytical tools that includes X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX), UV-VIS-NIR Spectroscopy and Current Voltage (I-V) measurements. Surface Passivation properties were also analyzed with these characterization tools to ascertain the effect on morphology, and optical-electrical properties. SEM images of copper oxide (CuO) and PMMA passivated copper oxide (CuO/PM) hole transport layers confirmed rough and porous morphology with distinguished particles, which facilities the movement of holes through the active layer of high conductivity. More compact layer was formed after passivation which was due to significant reduction in the surface roughness of the CuO film. The EDX studies supported the chemical composition of the HTL layer and confirmed the presence of PMMA in CuO film on ITO substrate. XRD spectra indicated the presence of predominantly monoclinic CuO phase along with less intense peaks corresponding to cubic Cu_2O phase in the grown CuO HTL. UV-Vis. absorption spectra showed that the absorbance for CuO film was more than CuO/PM film, possibly some light has been scattered that was reaching to the interface of CuO/PM as PMMA being insulating polymer by nature. A step was also observed in absorbance spectra of CuO film at high wavelength side as there can be a band gap transition of charge carriers within the CuO, when light energy equal to or greater than the band gap energy absorbed causing sharp decrease in absorbance. Presence of some defects also influences the absorbance spectra which can also be verified with few unidentifiable peaks observed in XRD spectra of CuO film. I-V characterization curves give linear relation between current and voltage due to ohmic behavior shown by conducting nature of the fabricated CuO HTL. It was observed that surface passivation layer has not significantly changed the conductivity of the film but provides high mobility for holes and good stability hat can facilitate future applicable PSC devices. This study shows our attempt to passivate CuO thin film using PMMA and analyze its effects on properties of synthesized film that may contribute towards the development of HTLs for potential PSCs.

1. Introduction

Most of the energy needs are catered by fossil fuel based energies, which intern has consequences on global warming and climate change. Therefore Photovoltaic (PV) Solar Cell technology advanced significantly as a sustainable source of energy [1]. In fact, it has been suggested that PVs will account for 35 % of the additional electricity generation capacity installed globally by 2040 [2]. Their important characteristics like durability, compactness, low maintenance, generate electricity in remote environments made it possible to have various applications like electricity generators, battery chargers, daily appliances, transportations, factories, many more [3, 4]. Within few decades, perovskite solar cells (PSCs) have revolutionized the photovoltaic field with their impressive power conversion efficiency, simple fabrication process and low material costs [5, 6]. In PSCs architecture, the hole transport layer (HTL) is a critical element and hold important functional property to gather and move holes from the perovskite light-absorbing layer in order to work in tandem with the electron transport layer to facilitate the separation of the electron-hole pairs in the perovskite active layer [7, 8]. So, the key approach of our research is to develop low cost but effective thin film which has high mobility for holes. HTL can enhance the performance, stability and efficiency of PSCs to great extent, therefore it ought to be highly clear to permit the flow of photons from the emissive layer and have high hole mobility [7]. The most commonly used organic hole transport material is spiro-OMeTAD, which has wide range of properties and band energy which matches with that of perovskite but lower hole mobility than other organic hole transport materials. Also, there are difficulties in process and cost in producing Spiro-OMeTAD makes it less favorable. Other most common material used is organic polymer PEDOT:PSS, which has high price and quite difficult to be applied to large-scale fabrication of solar cells. As organic materials have several drawbacks, such as aging, lack of optical-electrical stability, difficulty in modifying the properties, cost and ambiguity in their fabrication processes, so inorganic materials especially metal oxides will be more promising in solving such problems [9,10]. Transition metal oxides are good choice to be used as HTL because of low cost, availability, high electrical-optical stability and modification in their properties. But there are metal oxides like NiO and MoO_3 which have specific requirement of deposition, low conductivity and long term stability issues [9-11]. Therefore among transition metal oxides, CuO is a potential alternative material that needs to be studied for HTL. It is a p-type semiconductor with band gap ranges from 1.2 eV to 1.9 eV with excellent hole transporting property. It is low cost, non toxic, highly stable, easy to fabricate with techniques like spin coating, sol-gel method, thermal deposition and doctor blade method; and dissolvable in wide range of solvents like ethanol, acetone, chloroform [10, 12]. Various methods are reported to deposit the CuO thin film, like spray pyrolysis, sol-gel method, hydrothermal growth, vacuum deposition techniques and few others. We have used Doctor Blade method being simple and cost effective method for obtaining desired thickness coatings on ITO substrate [13, 14]. Further to enhance mobility of holes, increase life time and stability of HTL film, surface passivation needs to be done. We used an organic polymer PMMA as a passivation material for its chemical and mechanical stability and it forms a uniform layer on various substrates [15]. The hydrophobic nature of PMMA polymer successfully reduces the CuO surface defect concentration and thus reduces resistance to the oxidation process from moisture [16]. For depositing thin films fluorine doped tin oxide (FTO) is mostly used as a substrate because of high conductivity and transparency. However, it is expensive and fluoride present in it causes environmental hazard. Therefore we used Indium tin oxide (ITO) as a favorable alternative which is widely used in many optoelectronic devices including solar cells [17]. In the present research, our attempt was to analyze the effects of passivating layer on CuO film properties and for which different characterizations were done using various analysis tools to study structural, optical and electrical properties.

2. Experimental

High quality materials and high purity chemical reagents were purchased from commercial sources and used as received. Further cleaning of ITO substrate was done and chemicals were used without further purification.

Synthesis of CuO film on ITO glass substrate by Dr Blade Method

Material used: ITO as glass substrate, Copper oxide powder (CuO), PEG (Polyethylene glycol), Polymethylmethacrylate (PMMA), acetone, ethanol, D.I. water.

Ultrasonication of ITO glass substrate: The ITO-coated glass substrates were cleaned by ethanol and deionised water, each for 20 minutes using an ultrasonic bath to avoid any contamination. The cleaned ITO substrates were dried in oven at 100°C for 30 minutes to deposit hole transport layer of CuO.

Deposition of HTL : Paste of CuO was prepared by grinding commercially available high purity 2 gm of CuO powder with 0.8 gm of PEG (keeping ratio of CuO: PEG as 3:1) using mortar pastel for 2 hours. To get a consistent paste, DI water was drop caste 3-4 times within the paste. Thin layer of CuO was deposited on ITO glass substrate by Doctor Blade Method. The deposited substrate was sintered at 250°C for 6 hours in the furnace. After that samples were cooled and further annealed in H.T.F. for 30 minutes at a rate of 2°C /minute up to 450°C of constant temperature followed by cooling at room temperature [17, 18].

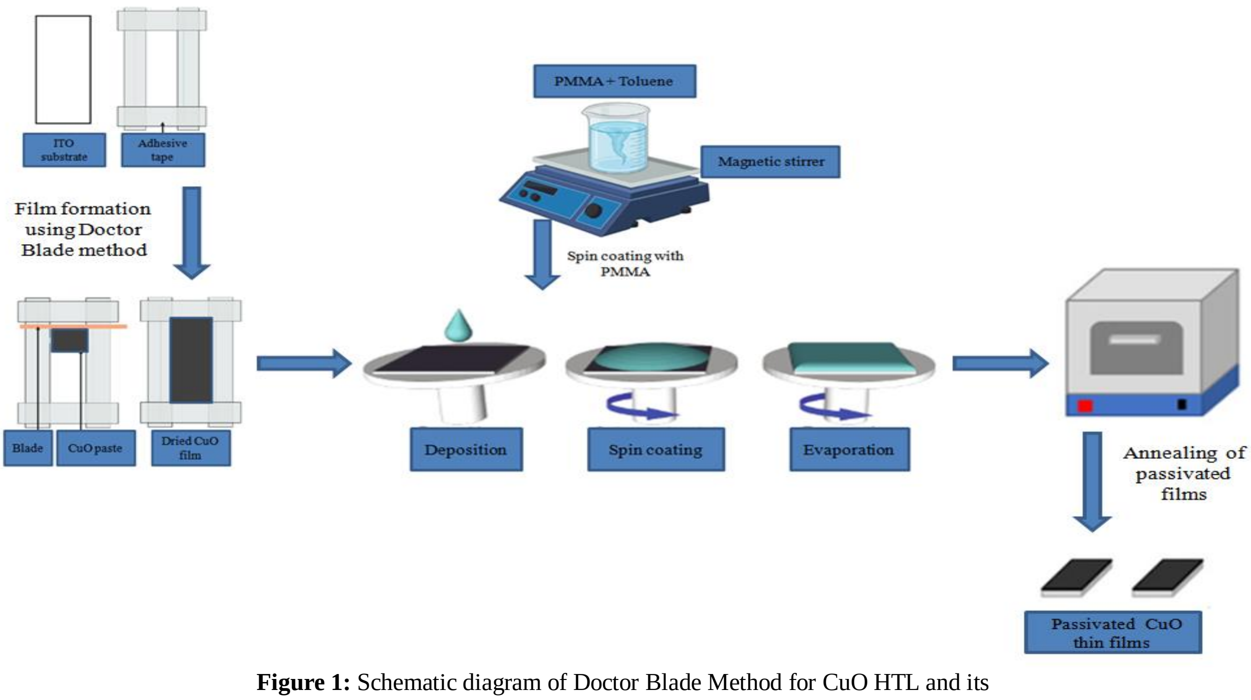

Figure 1: Schematic diagram of Doctor Blade Method for CuO HTL and its Surface Passivation using Spin Coating deposition with PMMA followed by annealing.

Preparation of Polymethylmethacrylate (PMMA) solution

For preparing the precursor solution, amount of 300 mg of PMMA was taken with 20 ml of toluene in a beaker. Stirring was done for an hour at 6o°C, first with a speed of 1500 rpm and then raised the speed to 3000 rpm. A clear solution was obtained that was covered and kept for further use.

Surface Passivation of HTL film using Polymethylmethacrylate (PMMA)

The surface passivation of HTL of CuO was done using Spin coating method. The film was kept on the rotating chunk that was at the centre of Spin coater. After optimizing the speed, the spin coater was then set at a speed of 2500 rpm. Spin coating was performed with above prepared PMMA solution on ITO glass substrate by filling the glass dropper to few drops (2-3). Dropping 1 or 2 drops on middle of the ITO glass and set the device spun and repeated this procedure. It has been observed that the material get evenly spread over the film and we obtained layered film structure. Surface passivated films were sintered at 600°C temperature in H.T.F. for 30 minutes [15, 16].

Characterization

The structural characteristics and crystalline phases of the samples were examined using a Bruker D8 Advance X-ray diffractometer, utilizing CuKα radiation with a wavelength of 0.15405 nm. XRD measurements were conducted over a 2θ range of 10º to 80º at a scan rate of 3º/min at ambient temperature. The surface morphology of the HTL layers was analyzed using Field Emission Scanning Electron Microscopes (FE-SEM), including the TESCAN MIRA II LMH and Emcrafts Genesis-1000 High Vacuum models for different resolutions. UV-Vis absorption and reflectance spectra for the HTL, spanning from 200 to 800 nm, were recorded using a Cary 5000 UV-Vis-NIR spectrophotometer. Current-voltage curves were acquired using a solar simulator. All the characterizations were performed at room temperature.

3. Results and discussion

Structural Analysis- SEM images, EDX spectra and XRD spectra were analyzed for structural properties.

SEM Analysis

SEM studies: Figure 2(a-b) illustrate the SEM images of CuO and CuO/PM hole transport layers. Figure 2(a), showed rough and porous morphology with distinguished particles agglomeration which facilities the movement of holes through the active layer of high conductivity. Figure 2(b) showed morphology of compact layered structure phase for samples passivated with PMMA solution by spin coating method [19, 20].

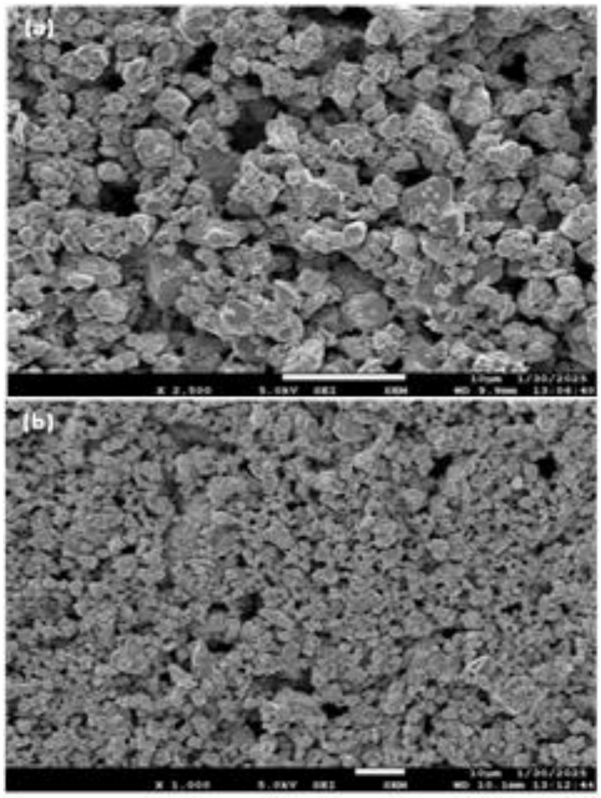

Figure 2: SEM images of (a) CuO and (b) CuO/PM HTLs.

EDX Analysis

Energy Dispersive X-ray (EDX) studies: Figure 3 shows EDX for elemental compositions of PMMA coated CuO HTL (CuO/PM). The EDX studies support the chemical composition of the HTL layer along with carbon element present in PMMA passivated layer.

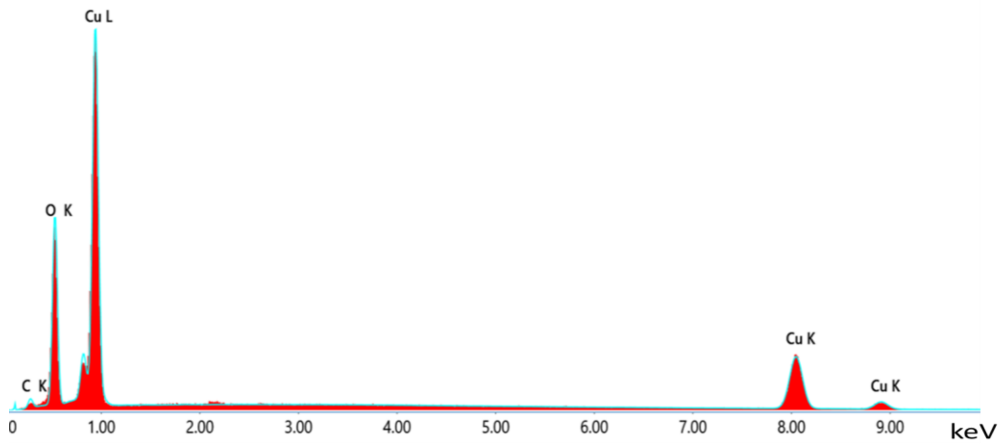

Figure 3: EDS image of CuO/PM HTL.

XRD Analysis

XRD studies: Figure 4(a, b) indicates the XRD patterns of CuO and CuO/PM hole transport layers respectively. The appearance of sharp crystalline peaks at 2θ values of 32.6°, 37°, 38.8° corresponds to respective crystallographic planes (110), (-111), (200) of monoclinic CuO phase thin film along with other less intense peaks for corresponding planes (-202), (020), (202), (-113), (022). While crystalline peaks at 2θ values of 39.04°, 62° corresponds to respective crystal planes (111), (220) for cubic Cu_2O phase of thin film. Figure 4(b) have almost same XRD spectra with an unidentified very less intense peak at 2θ just greater than 20°.

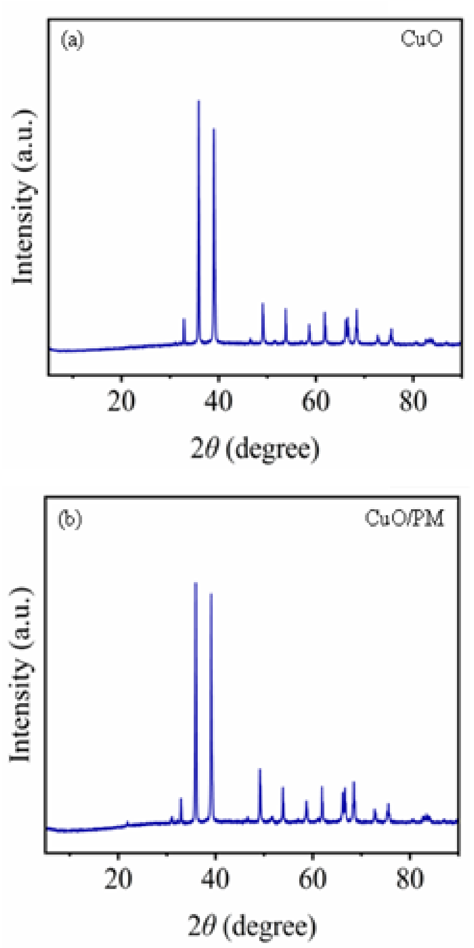

Figure 4: XRD pattern of (a) CuO and (b) CuO/PM HTLs.

Optical Analysis- UV-VIS. Absorbance graph was analyzed for optical properties.

Absorption spectral studies: Figure 5 showed the UV visible absorbance spectra of CuO and CuO/PM HTLs. The absorbance for CuO more than CuO/PM as PMMA being insulating polymer, scatter some light and reduce light intensity reaching the CuO film interface. In Figure 5 absorbance spectra of CuO film has a step near 720 nm of wavelength possibly due to band gap transition of charge carriers within the CuO, when light energy equal to or greater than the band gap energy get absorbed causing sharp decrease in absorbance[14,20-22]. Presence of some defects also influences the absorbance spectra which can also be verified with few unidentifiable peaks observed in XRD spectra of CuO film in figure.

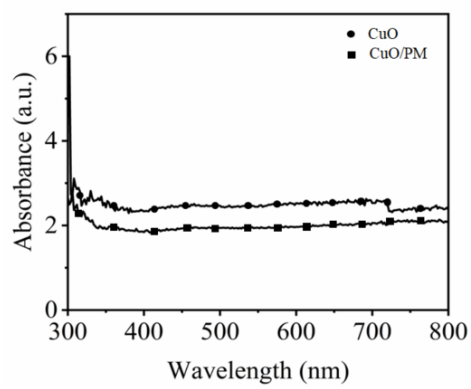

Figure 5: UV-Vis. spectra image of absorbance of CuO and CuO/PM.

Electrical Analysis- I-V measurements for analyzing electrical properties

Electrical studies: The current and voltage measurements were observed using I-V characterization curves given in Figure 6(a, b).

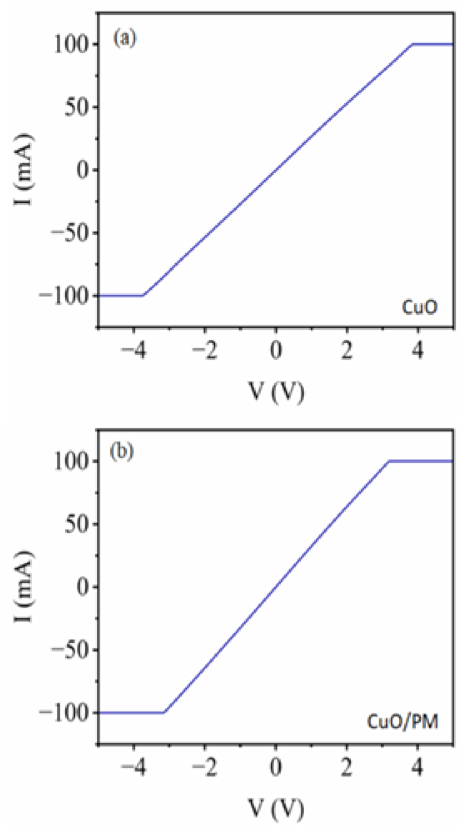

Figure 6: I-V images of (a) CuO (b) CuO/PM.

The graphs show linear relation between current and voltage for ohmic behavior of conducting film of CuO. There exists no considerable difference in the electronic properties of PMMA coated and non PMMA coated CuO which shows that surface passivation layer has not changed the conductivity of the film but provides high mobility for holes and good stability of the device. From Figure 6(b), small current value range can be observed in PMMA coated CuO film and also high value of cut in voltage as compared to CuO film without PMMA again because of PMMA nature, being organic insulator that forms a protective layer which restricts easy flow of electric current. But the surface passivation leads to protection of CuO film from contamination and hence improves stability of HTL [14, 21-22].

4. Conclusions

This approach has the potential to provide easy and economical way for HTL fabrication for stable and efficient Perovskite Solar Cells (PSCs). We have used a simple and cost-effective method, Doctor Blade method for thin film deposition of CuO on ITO substrate. To modify the surface, we passivated the film of CuO with PMMA using Spin coating method. SEM images of CuO and CuO/PM hole transport layers showed rough and porous morphology with particles agglomeration; which facilities the movement of holes through the conductive HTL to perovskite active layer. The compact layered structure phase for sample passivated with PMMA solution also observed in SEM images which reduce surface roughness of the CuO thin film. In XRD spectra, the appearance of sharp crystalline peaks at 2θ values of respective crystallographic planes showed that there existed dominating monoclinic CuO phase thin film along with less intense peaks which correspond to cubic Cu_2O phase in the grown CuO HTL. UV-Vis. absorbance spectra showed higher value of absorbance for CuO than CuO/PM; as PMMA being insulating in nature scatter some light and reduce light intensity reaching the CuO film. Also the absorbance spectra of CuO film has a step near 720 nm of wavelength possibly due to band gap transition of charge carriers within the CuO causing sharp decrease in absorbance. Presence of some defects also influences the absorbance spectra which can also be verified with few unidentifiable peaks observed in XRD spectra of HTL film. Further, a good HTL should exhibit ohmic behavior with linear characteristics and high slope. The linear relation between current and voltage in I-V graphs show ohmic behavior of conducting nature of CuO film. No considerable difference in the electronic properties of both PMMA coated and non PMMA coated CuO which showed that surface passivation layer has not modified the conductivity of HTL layer to large extent but provide high mobility for charge carriers and good stability for the PSC devices. High slope in CuO/PM film along with high value of cut in voltage as compared to CuO film due to the fact that PMMA is an organic insulator that forms a protective layer which restricts easy flow of electric current. However, the surface passivation leads to protection of CuO film from contamination and hence improves stability of HTL. From all the characterizations studied in our present research, we have concluded that the surface passivation with PMMA leads to the formation of depletion region at the interface which limits the flow of current; but it gives higher stability and carrier mobility with this surface modification by reducing chances of oxidation and moisture contamination of hole transport film surface. Thus CuO film enhance properties like electrical conductivity; while to improve carrier mobility and hence increasing overall stability of PSCs by eliminating inhomogenity within the layer, we performed surface passivation. This approach may contribute good support for future development of the PSC devices.

Acknowledgements

Authors acknowledge their appreciation to The North Cap University (C.R.F. Lab), Gurgaon and B.M. University, Rohtak for providing sample preparation and characterization facilities.

Authors' contributions

Priyanka Sangwan has done all the sample preparation related experimental work, data analysis and paper writing. Dr. Sunita Sharma did the proof reading of the research paper. Dr. Sonia did reading of the manuscript. The author read and approved the final manuscript.

Conflicts of interest

The author declares no conflict of interest.

Funding

This research received no external funding.

Data availability

No new data were created.

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