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# Thermoelectric performance enhancement of copper iodide pellets through potassium iodide doping



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# HIGHLIGHTS

• P-type CuI is identified as a non-toxic, eco-friendly thermoelectric material.

• KI doping (0-9 %) significantly enhanced the electrical and thermal properties of CuI.

 $\bullet$  Electrical conductivity of CuI pellets reached 5.08 S  $m^{-1}$  at 373 K with 9 % KI doping.

 $\bullet$  Maximum Seebeck coefficient of 7.3 mV  $K^{-1}$  achieved by 7 % KI doped pellets.

 $\bullet$  ZT improved from 0.035  $\times$   $10^{-3}$  to 26.95  $\times$   $10^{-3}$  exhibiting strong thermoelectric potential.

# ARTICLE INFO

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# ABSTRACT

The search for efficient and eco-friendly thermoelectric materials has garnered significant attention to meeting energy demands and address waste heat recovery challenges. Copper iodide (CuI), a p-type semiconductor with non-toxic properties, shows promise for thermoelectric applications, although it has not been extensively studied. This study investigates the thermoelectric performance of CuI doped with varying concentrations (0–9 %) of potassium iodide (KI). This doping significantly modified the electrical and thermal properties of CuI pellets. The electrical conductivity exhibited a notable increase, peaking at 5.08 S m<sup>-1</sup> at 373 K with 9 % KI doping, which can be attributed to enhanced charge carrier density and bandgap reduction. The thermal conductivity also increased due to improved electron mobility, whereas the Seebeck coefficient reached a maximum of 7.3 mV K<sup>-1</sup> at 7 % KI doping, demonstrating optimal thermoelectric performance at this concentration. The figure of merit (ZT) was maximized at 7 % KI doping, recording a remarkable increase from 0.035 × 10<sup>-3</sup> (undoped) to 26.95 × 10<sup>-3</sup> at 373 K. These findings underscore the potential of KI-doped CuI as an efficient thermoelectric material and pave the way for further optimization in advanced energy applications.

#### 1. Introduction

With a growing population and increasingly sophisticated lifestyles, global energy demand is rising dramatically, leading to rapid depletion of non-renewable resources such as fossil fuels, which may be exhausted within 100 years [1]. Many conventional non-renewable energy sources destroy the environment by emitting pollutants that drive global warming and other issues. As a result, there's growing interest in developing and enhancing renewable energy solutions. Further, more

than two-thirds of global energy is lost as waste heat, prompting scientists to explore its reuse. Thermoelectric energy generation, a clean energy conversion technology, can convert waste heat into electricity. Recent research has uncovered many new materials for thermoelectric energy conversion [2–4]. In addition, thermoelectric energy recovery has gained significant interest due to its potential to harness solar energy and capture waste heat from cooking and industrial waste heat [5–7]. Thermoelectric generators convert heat directly into electricity, and they do not have any moving parts or fluids, ensuring durability and

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environmental benefits [8].

The performance of thermoelectric devices is depicted by their dimensionless figure of merit,  $ZT = \alpha^2 \sigma T/\kappa$ , where  $\alpha$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity and *T* is the absolute temperature [6,9]. A high Seebeck coefficient, low thermal conductivity, and high electrical conductivity should all be properties of a good TE material. Metals have high electrical and thermal conductivities and thus, their power factor is rather low. On the other hand, insulators are poor thermal and electrical conductors. Hence, the overall *ZT* of both the metals and insulators is low. The semiconductors and semi-metals have significant Seebeck coefficients, comparatively high electrical conductivity, and lower thermal conductivity, which could result in higher *ZT* values [10]. It is important to investigate promising thermoelectric generators is based on their *ZT* and power factor values.

TE materials have been thoroughly researched since the 20th century and enhancing ZT values is the main goal of TE research. Bi<sub>2</sub>Te<sub>3</sub> and PbTe are the most widely used thermoelectric materials [1]. All bismuth and antimony chalcogenide-based materials, including Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>, and Sb<sub>2</sub>Te<sub>3</sub>, have good thermoelectric properties, but these materials are toxic, rare and expensive [11]. There is a vital need of low-cost, non-toxic, and abundant thermoelectric materials. Few studies have focused on optimizing CuI and their blends and functionalizing them to enhance their thermoelectric performance, such as controlling nanostructure size and morphology. While CuI shows promise, its efficiency and practical applicability still require further exploration compared to established materials [12,13]. CuI is one of the promising p-type non-toxic thermoelectric materials. It is a wide bandgap semiconductor with three crystalline phases which are rock salt ( $\alpha$ ), wurtzite ( $\beta$ ), and zinc blende phase ( $\gamma$ ). CuI shows a stable  $\gamma$ -CuI phase below 350 °C, which has a wide bandgap of 3.1 eV and the electrical conductivity is  $\sim 10^{-5}$  S cm<sup>-1</sup> at room temperature [14,15].

A study showed that Sn-doped CuI can achieve a Seebeck coefficient of 1260  $\mu$ V K<sup>-1</sup> at room temperature [16], showcasing its potential for efficient thermoelectric applications. Additionally, undoped CuI thin films have demonstrated Seebeck coefficients around 600  $\mu$ V K<sup>-1</sup> [17]. Klochko et al. synthesized semi-transparent copper iodide thin films on flexible poly(ethylene terephthalate) substrates as p-type thermos-legs for a wearable thermoelectric generator. The best obtained flexible p-CuI thin film single thermos-leg demonstrated output power 17.1  $\mu$ W/m<sup>2</sup> at the temperature gradient  $\Delta$ T = 35 K at near-room temperatures [18]. Fully transparent p type CuI thin films were fabricated by Yang et al. [19], which showed a good mechanical flexibility with a higher power density of 2.4 mW cm<sup>-2</sup> at  $\Delta T = 50$  K and a ZT value of 0.23. Schmidl et al. [20] fabricated copper iodide on Spacer Fabrics as Textile thermoelectric device for energy generation. The Seebeck coefficient of these fabrics were observed between 112 and 153  $\mu$ V K<sup>-1</sup> in a temperature range between 30 °C and 90 °C and the maximum output power reached 99 nW at temperature difference of 65.5 K with respect to room temperature for a single textile element [21,36]. Extensive amount of research has been done on transparent CuI thin films. However, only one report has been published so far on bulk CuI. Mulla et al. [37,38], reported that as prepared bulk CuI possesses a Seebeck coefficient of ~431  $\mu$ V K<sup>-1</sup> with a resistivity ~ 0.26  $\Omega$ -cm, resulting in the room temperature thermoelectric power factor  $\sim 70~\mu W~m^{-1}~\breve{K}^{-2}.$  Annealing at moderate temperatures (~400 K) improved thermoelectric power factor, that is  ${\sim}142~\mu\text{W}~\text{m}^{-1}~\text{K}^{-2}$  at room temperature, which reaches to  ${\sim}160~\mu W~m^{-1}~K^{-2}$  at 353 K.

In this study an attempt has been made to enhance the thermoelectric properties of CuI through doping. The temperature dependent electrical conductivity, Seebeck coefficient and thermal conductivity of pellets made out of CuI and KI doped CuI powder have been measured and the temperature dependent power factor and Figure of merit have been calculated for both commercial and KI doped CuI. The power generated from CuI and KI doped CuI has also been measured.

# 2. Experimental details

All chemicals used for preparation were sourced from Sigma Aldrich®, having purity levels above 98 %. CuI and KI were vacuumdried for 2 h at ~50 °C prior to the use. In the process of preparing CuI paste, CuI was mixed with anhydrous acetonitrile and subjected to hand grinding using a mortar and pestle for 15 min, resulting in a finely powdered substance after evaporating the acetonitrile. To fabricate KI-doped CuI pellets, various KI concentrations (0 %, 1 %, 3 %, 5 %, 7 %, and 9 %) were mixed with CuI in specific weight ratios using anhydrous acetonitrile. CuI sample pellets were then formed using a pellet press system with a consistent force of 40 kN (equivalent to 301 MPa) applied for 5–7 min.

For the crystallographic characterization, prepared KI doped CuI samples prepared in this study were analyzed using X-ray diffraction (XRD). The experiment was performed using the RIGAKU Ultima IV X-ray diffractometer instrument that utilizes Cu K $\alpha$  radiation with  $\lambda = 1.54184$  Å to investigate the crystalline structure. The surface morphology and microstructural structure of the samples were analyzed by means of field emission scanning electron microscopy (FE-SEM, Hitachi SU6600) at a voltage of 15 kV. All samples were subjected to a gold-sputtering procedure before analysis. The elemental composition was determined by Oxford instrument energy-dispersive X-ray spectroscopy (EDX) with Aztec software integrated with SEM, with a spectral acquisition power of 15 kV and a scanning time of 60 s.

To determine electrical conductivity, *I-V* curves were obtained with a Metrohm® Autolab PGSTAT128N potentiostat/galvanostat by placing sample pellets between stainless steel electrodes. Silver paste was applied to ensure reliable electrical contact. 'Linear sweep voltammetry' was conducted within voltage range of 0.1 V–1.0 V using the 'Nova 1.11' program. Measurements were occurred at controlled temperatures (300 K–400 K) using digital thermometers with K-type thermocouples.

For Seebeck coefficient measurement, a pellet was positioned between upper and lower steel electrodes with a controlled temperature gradient. The potential difference was measured using a Keithley 2000 Source meter. *I-V* curves were generated with the 'Peccell' software while varying voltage (-0.5 V-0.5 V), and temperature readings were recorded. The generated power was calculated using these obtained *I-V* curves for different temperatures.

Thermal conductivity was determined using the absolute steadystate axial flow method. The sample was sandwiched between electrodes in a Teflon holder. Then, the bottom electrode was placed on the nichrome coil placed inside the sample holder. The heat produced is what causes the coil's temperature to change, and the power supply adjusts it appropriately. The constant power supplied to the nichrome coil was measured using Extech® multimeter. After the steady state was reached, the two temperatures were measured using two digital thermometers. The thermal and electrical conductivity and seebeck coefficient measurements were repeated five times, and the average values are given in the graphs, along with respective standard deviation values.

# 3. Result and discussion

# 3.1. XRD analysis

The powder X-ray diffraction (PXRD) pattern of the undoped CuI and KI doped CuI is shown in Fig. 1. The peaks identified were labeled using the Miller index. The observed XRD peaks confirm the successful KI doping and CuI is in the zinc blende phase ( $\gamma$ ) [22,23]. The XRD patterns of KI doped CuI do not show any significant changes compared to that of undoped CuI, depicting the successful doping nature of KI into CuI lattice structure.

The *d* spacing, crystallite size (*D*), strain ( $\varepsilon$ ), and dislocation density ( $\delta$ ) related to the significant peaks in Fig. 1 were determined using Debye Scherrer relations.



Fig. 1. XRD spectra of Ki doped CuI pellets [24].

$$D = \frac{0.94\lambda}{W\cos\theta} \tag{1}$$

$$\varepsilon = \frac{W \cos \theta}{4} \tag{2}$$

$$\delta = \frac{1}{D^2} \tag{3}$$

Here *D* is the crystallite size,  $\lambda$  is the X-ray wavelength,  $\theta$  is Bragg's angle, and *w* is the full width at half maximum (FWHM) of the peak in radians. The calculated parameters are given in Table 1, while the weighted average values are given in Table 2.

In the CuI semiconductor doped with KI, the relationship among the average crystallite size (D), strain ( $\epsilon$ ), and dislocation density ( $\delta$ ) exhibits an inverse correlation between crystallite size and both strain and dislocation density. As the KI doping concentration increases, the average strain and average dislocation density also increase, while the average crystallite size decreases until a certain limit (7 %) as shown in Table 3 [25,26].

This trend can be attributed to the introduction of lattice distortions

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#### Table 2

Calculated weighted	l average values	s of crystallite	size (D), st	rain ( $\varepsilon$ ), an	d dislo-
cation density ( $\delta$ ).					

KI concentrations	Average Crystallite Size, D (nm)	Average Strain, $arepsilon$ ( $ imes 10^{-4}$ )	Average Dislocation Density, $\delta$ ( $\times$ $10^{-4}~\text{nm}^{-2}\text{)}$	
0 %	50.18	7.35	4.19	
1 %	49.18	7.52	4.40	
3 %	43.91	8.49	5.68	
5 %	39.68	9.15	6.41	
7 %	41.19	9.05	6.42	
9 %	41.62	8.94	6.27	

Table 3

I,	Cu	and	Κ	mass	fractions	calculated	using	EDX	analysis

KI concentrations	I/ %	Cu/ %	K/ %
0 %	$59.5\pm0.5$	$40.5\pm0.5$	0
3 %	$59.9 \pm 0.8$	$\textbf{37.9} \pm \textbf{0.8}$	$\textbf{2.1} \pm \textbf{0.2}$
7 %	$61.9 \pm 0.9$	$31.8\pm1.0$	$\textbf{6.3} \pm \textbf{0.3}$
9 %	$64.3 \pm 0.2$	$\textbf{27.4} \pm \textbf{0.3}$	$8.3\pm0.1$

and structural defects caused by the incorporation of KI into the CuI matrix. The strain ( $\varepsilon$ ) arises due to the mismatch in ionic radii between Cu<sup>+</sup> and K<sup>+</sup>, leading to lattice distortions. As strain increases, the crystal lattice becomes more distorted, hindering the growth of larger crystallites and resulting in a reduction in average crystallite size (D). Additionally, the dislocation density ( $\delta$ ), which represents the number of dislocations per unit volume, increases with strain. The increase in dislocation density is a direct consequence of the higher number of structural defects and imperfections introduced by KI doping.

Mathematically, these relationships can be expressed as:  $\delta \propto ^1_{D^2}$  and  $\varepsilon \propto ^1_{D}$ 

These equations indicate that as the crystallite size decreases, both the strain and dislocation density increase, supporting the observed experimental results. The increase in strain and dislocation density with KI content suggests that KI doping introduces more lattice imperfections, influencing the structural and electronic properties of CuI.

Further, the crystal defects significantly reduce the lattice thermal conductivity. As reported by Wang et al. [27], in some materials, this reduction can reach up to 86.7 %, thus significantly increasing the ZT

Table 1

XRD peak data analysis results of the KI doped CuI. Calculated values of the 2θ, crystal plane, d spacing, crystallite size (D), strain (ε), and dislocation density (δ).

KI mass fraction	2θ (deg.)	Crystal plane	d spacing (Å)	FWHM (deg.)	Average Crystallite Size, D (nm)	Average Strain, $\varepsilon$ ( $ imes 10^{-4}$ )	Average Dislocation density, $\delta$ ( $\times 10^{-4}\text{nm}^{-2})$
0 %	25.55	(111)	3.48	0.15	56.8	6.37	3.10
	42.25	(220)	2.14	0.19	46.2	7.84	4.68
	50.00	(311)	1.82	0.22	41.0	8.84	5.96
1 %	25.45	(111)	3.50	0.15	56.5	6.41	3.13
	42.15	(220)	2.14	0.20	44.4	8.15	5.06
	49.90	(311)	1.83	0.23	40.2	9.01	6.20
3 %	25.5	(111)	3.49	0.17	50.5	7.17	3.92
	42.2	(220)	2.14	0.22	40.8	8.88	6.01
	50	(311)	1.82	0.28	32.5	11.14	9.47
5 %	25.5	(111)	3.49	0.21	40.6	8.91	6.05
	42.3	(220)	2.13	0.24	36.5	9.91	7.49
	50	(311)	1.82	0.22	42.0	8.61	5.66
7 %	25.5	(111)	3.49	0.18	48.6	7.45	4.23
	42.2	(220)	2.14	0.25	35.3	10.27	8.04
	50	(311)	1.82	0.27	33.7	10.75	8.81
9 %	25.5	(111)	3.49	0.17	49.0	7.40	4.17
	42.2	(220)	2.14	0.25	35.0	10.33	8.14
	50	(311)	1.82	0.26	35.1	10.32	8.12

value of a thermoelectric material.

#### 3.2. SEM and EDX analysis

Fig. 2 displays the SEM images and EDX analysis data of KI-doped CuI pellets. The SEM images reveal the formation of larger, well-defined grains with an average size of approximately 500 nm, along-side smaller, fine particles distributed throughout the structure. This microstructural variation suggests the presence of multiple growth mechanisms influenced by the KI doping. The EDX analysis confirms a progressive increase in potassium (K) and iodine (I) concentrations as the amount of KI introduced into the samples is increased (Table 3). This compositional change indicates the successful incorporation of KI into the CuI matrix, potentially affecting the material's morphology and electronic properties.

# 3.3. Electrical conductivity

Fig. 3 demonstrates the temperature-dependent electrical conductivity of CuI doped with varying concentrations of KI calculated using corrent voltage curves given in suplemantary materials. As expected for semiconductor materials, all samples exhibited an increase in electrical conductivity with rising temperature, as more electrons from the valence band gain sufficient energy to transit to the conduction band. The electrical conductivity of the samples ranged from 0.06 S m<sup>-1</sup> to 0.76 S m<sup>-1</sup>, further confirming their semiconducting nature.

 $K^+$  in Potassium iodide (KI) can induce lattice defects for CuI, contributing to enhancing the conductivity. In the CuI lattice, KI can dissociate into  $K^+$  and ions. Since CuI also contains I<sup>-</sup> ions, added KI increases the iodide concentration. The additional I<sup>-</sup> ions can make some Cu<sup>+</sup> ions to leave their lattice sites, creating copper vacancies. Cu vacancies act as acceptor defects, increasing p-type conductivity.

The K<sup>+</sup> ions (1.33 Å) are larger than Cu<sup>+</sup> ions (0.91 Å) [28] and thus, K<sup>+</sup> cannot easily substitute Cu<sup>+</sup>. Therefore, K<sup>+</sup> might occupy interstitial sites, which causes lattice distortion or expansion, creating strain in the crystal structure. Such defects can enhance conductivity. These mechanisms collectively lead to a significant enhancement in electrical properties of CuI [29,41].

The dislocation density (defects in the crystal structure where atoms are misaligned) calculated by XRD shows an increase with the added amout of KI, and this behavior correlates with conductivity except 9 % KI sample. 9 % KI sample has shown slightly low dislocation density and the higher conductivity in this sample may also have been contributed by the mobility of interstitial ions.

Increased structural defects with added KI reduce the activation energy required for ion hopping. In addition, stress fields surrounding these dislocations change the atomic structure, extending interstitial sites and reducing migration barriers. Disintegrated cores, which may contain excess vacancies or interstitials, further increase the availability of charge carriers. Optimal density of displacement is necessary to maximize diffusion while minimizing scattering effects, which ultimately results in the observed increase in conductivity [30,31].

The enhancement in electrical conductivity observed up to 7 % KI can be attributed to the increased lattice defects. However, the further improvement in conductivity beyond 7 % KI may be ascribed to the enhanced mobility of iodide ions along the grain boundaries. Iodine at the grain boundaries can also moves outward, and as the concentration of iodine in the interstitial medium increases, the probability of trapping I-holes on the surface also increases. The conductivity increases until all the iodine at the grain boundaries have left the system [32]. The room temperature conductivity of the undoped sample 0.06 S  $m^{-1}\ has$ increased to 0.76 S  $\mathrm{m^{-1}}$  with addition of 9 % of KI. Notably, the highest electrical conductivity was achieved in the CuI sample doped with 9 % KI, with a conductivity value of 5.08 S  $m^{-1}$  at 373 K. Although the conductivity enhanced with the increasing concentration of KI, measurements were not conducted for samples with more than 9 % KI, since the Seebeck coefficient and figure of merit decreased for the samples with higher KI concentrations.

## 3.4. Thermal conductivity

Fig. 4 displays the temperature-dependent thermal conductivity of copper iodide (CuI) doped with varying concentrations of potassium iodide (KI). Notably, as the concentration of KI increases, the thermal conductivity of CuI also exhibits a notable increase. The total thermal conductivity in this context can be a result of combined contributions from lattice vibrations and electron transport through the lattice structure. The heightened electrical conductivity, attributed to the presence of higher concentrations of KI, fosters a more substantial flow of electrons within the material. Consequently, this heightened electron mobility can leads to a pronounced increase in thermal conductivity as KI concentration within CuI is increased. These results reveal interconnected dynamics governing electrical and thermal properties within KI-doped CuI.

The room-temperature thermal conductivity of the undoped sample, initially measured at 0.10 W m<sup>-1</sup> K<sup>-1</sup>, increased to 0.45 W m<sup>-1</sup> K<sup>-1</sup> with the addition of 9 % KI. The maximum thermal conductivity recorded for the undoped sample was 1.22 W m<sup>-1</sup> K<sup>-1</sup> while the doped sample exhibited a maximum value of 3.48 W m<sup>-1</sup> K<sup>-1</sup>.

One driving factor behind this observed increase in thermal conductivity with escalating KI concentration is the donor dopant nature of KI. Essentially, KI acts as a donor by providing additional electrons to the CuI crystal lattice. These surplus electrons serve to augment the population of charge carriers within the material. As a result, the thermal conductivity increases as a consequence of the increased charge carrier density in the CuI lattice. This fundamental understanding of the donor dopant effect offers valuable insights into the mechanisms governing the enhancement of thermal conductivity in CuI solutions with varying KI concentrations [33].

Dislocations in CuI can contribute to increased thermal conductivity



Fig. 2. SEM and EDX analysis of 0, 3, 7, and 9 % KI containing CuI pellets.



Fig. 3. (a) Temperature-dependent electrical conductivity and (b) Arrhenius plots as a function of KI amounts added to CuI pellets.



**Fig. 4.** The temperature dependent thermal conductivity with added amount of KI in the CuI pellets.

through enhanced electronic transport, particularly in systems exhibiting mixed ionic and electronic conduction. In such cases, dislocations reduce electron scattering, facilitating more efficient charge transport. Additionally, when dislocations align to form low-dimensional pathways, they can promote anisotropic phonon transport, overriding conventional scattering effects. The unique phonon dynamics in the CuI superionic lattice may further enable displacement-assisted thermal flux, distinguishing it from conventional oxide materials. These mechanisms collectively highlight the intricate interplay between structural defects and thermal transport in KI-doped CuI [34,35].

#### 3.5. Seebeck coefficient

In Fig. 5, the temperature-dependent Seebeck coefficient of CuI doped with KI is presented, depicting variations in conductivity with differing concentrations. Throughout the temperature range under investigation, positive values of the Seebeck coefficient for the CuI samples were consistently observed, thereby confirming p-type semiconductor behaviour of CuI. As the temperature was raised, concurrent increases in the Seebeck coefficient values were noted. Likewise, as the concentration of KI was progressively elevated, a corresponding increase in the Seebeck coefficient was observed, peaking at 7 % KI doping and subsequently decreasing at 9 %. Notably, at an average temperature of 374 K, the Seebeck coefficient reached its maximum, recording a remarkable value of 7.3 mV K<sup>-1</sup> when 7 % KI was doped into CuI. This behaviour of electrical conductivity and thermal conuctivity while former gave the highest values at 7 % while latter gave the highest



Fig. 5. Temperature-dependent Seebeck coefficient of CuI pellets with varying amounts of added KI.

values at 9 %.

At the same time, the generated voltage showed a positive correlation with temperature, although the highest ratio of generated voltage to temperature difference was obtained at the above critical temperature. The observed increase in the Seebeck coefficient of CuI caused by the incorporation of KI dopants indicates an order of magnitude increase. This remarkable increase can possibly be attributed to the increased number of charge carriers generated by the introduction of KI in the CuI material, thereby enabling their effective diffusion in response to temperature gradients.

The highest dislocation density and the Seebeck coefficient are shown for the 7 % KI doped CuI, indicating a direct correlation between dislocation density and Seebeck coefficient. Watling et al. studied the impact of dislocation density on Seebeck coefficient of quantum wells in the Si/SiGe system and reported a similar correlation, indicating that the higher dislocation scattering leads to a higher Seebeck coefficient [36]. Similar to that report, the higher dislocation density in 7 % KI doped CuI may increase the randomness of charge carrier flow in the system, leading to a higher Seebeck coefficient. Further, Martin et al. also have reported an enhancement of Seebeck coefficient through energy barrier scattering in PbTe nanocomposites [37].

# 3.6. Figure of merit

The figure of merit (ZT) for copper iodide (CuI) doped with varying concentrations of potassium iodide (KI) is presented in Fig. 6. Notably,



Fig. 6. The temperature dependent Figure of merit of CuI pellets with varying amounts of added KI.

the ZT values exhibit a general trend of increasing with higher KI concentrations, with one exception at 9 %. When comparing KI-doped CuI to undoped CuI, a significant enhancement in ZT is evident, primarily attributed to the impact of KI doping. This doping mechanism leads to a notable enhancement in both electrical conductivity and Seebeck coefficient. Although the thermal conductivity also increases with KI concentration, its effect on the overall ZT is relatively small. The highest ZT value is observed for the 7 % KI-doped CuI pellets, primarily driven by the superior Seebeck coefficient of this sample, underscoring the critical role of the Seebeck coefficient in determining ZT performance. These findings underscore the potential for optimizing the thermoelectric performance of CuI through controlled KI doping. Notably, the ZT value escalates from 0.035  $\times$   $10^{-3}$  to 26.95  $\times$   $10^{-3}$  with increasing KI concentration from 0 % to 7 % but subsequently declines to 7.678  $\times$  10<sup>-3</sup> as the concentration reaches 9 % at 373K. These findings underscore the intricate relationship between KI concentration and thermoelectric performance, revealing the potential for optimized KI doping levels in CuI for enhanced thermoelectric applications.

Since the Seebeck coefficient has the highest contribution to the Figure of merit ( $ZT \propto a^2$ ), the sample with the highest dislocation density (7 % KI doped CuI) shows the highest Figure of merit, indicating a direct correlation between dislocation density and Figure of merit.

Table 4 presents the maximum merit value (ZTmax) for various potential n-type and p-type materials, along with their corresponding temperatures. Notably, at lower temperatures, KI-doped CuI outperforms currently available materials, showing the highest ZTmax. Most of the materials exhibit a ZT on the order of -6, as shown in Table 4. However, SnSe, Cu<sub>2</sub>Se, and KI-doped CuI (present study) demonstrate exceptionally high ZT values, highlighting the potential of these materials for thermoelectric generation. Further KI-doped CuI outstanding since it gives higher ZT at temperature as loas 373 K.

#### 3.7. Power and current

Fig. 7 shows the thermoelectric properties of copper iodide (CuI) doped with different concentrations of potassium iodide (KI) based on temperature-dependent power generation. This parameter is closely linked to the thermoelectric figure of merit (ZT), as shown in Fig. 6, demonstrating a compelling parallel between the two graphs. In both cases, a remarkable observation emerges: the maximum power generation occurs in CuI samples doped with 7 % KI. This alignment highlights the central role of the Seebeck coefficient, which determines the

# Table 4

Peak values of $ZT_{max}$ for selected <i>n</i> and <i>p</i> type materials along with the con-	rre-
sponding temperatures.	

Material	Туре	ZTmax [ $\times$	T [K]	Ref.
		10 []		
(Bi <sub>0.25</sub> Sb <sub>0.75</sub> ) <sub>2</sub> Te <sub>3</sub>	р	1.05	323	[38]
FeNb <sub>0.8</sub> Ti <sub>0.2</sub> Sb	р	1.10	973	[39]
(Bi <sub>0.25</sub> Sb <sub>0.75</sub> ) <sub>2</sub> Te <sub>3</sub> (8 wt % Te)	р	1.27	298	[38]
Nano (Bi <sub>0.25</sub> Sb <sub>0.75</sub> ) <sub>2</sub> Te <sub>3</sub>	р	1.40	373	[40]
ZrCoBi <sub>0.65</sub> Sb <sub>0.15</sub> Sn <sub>0.2</sub>	р	1.42	973	[41]
FeNb <sub>0-88</sub> Hf <sub>0-12</sub> Sb	р	1.45	1200	[38]
Bi <sub>0.88</sub> Ca <sub>0.06</sub> Pb <sub>0.06</sub> CuSeO	р	1.50	873	[38]
β-Cu <sub>2-x</sub> Se	р	1.50	1000	[42]
La-doped BaCo <sub>4</sub> Sb <sub>12</sub>	р	1.50	850	[43]
AgSbTe <sub>2</sub>	р	1.40	800	[44]
Ba <sub>0.08</sub> La <sub>0.05</sub> Yb <sub>0.04</sub> Co <sub>4</sub> Sb <sub>12</sub>	р	1.70	850	[45]
B-doped Si <sub>0.8</sub> Ge <sub>0.20</sub> + YSi <sub>2</sub>	р	1.81	1073	[38]
AgPb <sub>m</sub> SbTe <sub>2+m</sub>	р	2.20	800	[46]
PbTe <sub>0.7</sub> Sn <sub>0.3</sub> -2.5 %K	р	2.20	923	[38]
PbTe-4 %SrTe-2 %Na	р	2.20	915	[38]
Ge <sub>0.89</sub> Sb <sub>0.1</sub> In <sub>0.01</sub> Te	р	2.30	650	[47]
PbTe-8 %SrTe	р	2.50	923	[48]
SnSe single crystal's b-axis	р	2.60	923	[49]
$\beta$ -Cu <sub>2</sub> Se/CuInSe <sub>2</sub> (1 % In)	р	2.60	850	[38]
Hf <sub>0.6</sub> Zr <sub>0.4</sub> Hf <sub>0.25</sub> NiSn <sub>0.995</sub> Sb <sub>0.005</sub>	n	1.20	900	[38]
Ti <sub>0.5</sub> Zr <sub>0.25</sub> Hf <sub>0.25</sub> NiSn <sub>0.998</sub> Sb <sub>0.002</sub> Se	n	1.50	700	[38]
Mg <sub>3</sub> Sb <sub>1.48</sub> Bi <sub>0.4</sub> Te <sub>0.04</sub>	n	1.65	725	[50]
Mg <sub>3.175</sub> Mn <sub>0.025</sub> Sb <sub>1.5</sub> Bi <sub>0.49</sub> Te <sub>0.01</sub>	n	1.71	700	[38]
Cu <sub>2</sub> .yS <sub>1</sub> / <sub>3</sub> Se <sub>1</sub> / <sub>3</sub> Te <sub>1</sub> / <sub>3</sub>	n	1.90	800	[51]
SnSe <sub>0.97</sub> Br <sub>0.03</sub> single crystal's a-axis	n	2.80	773	[52]
SnSe	р	$3.1 imes10^6$	783	[53]
Cu <sub>2</sub> Se	р	$2.0 imes10^6$	400	[54]
KI doped CuI	р	$26\times 10^3$	373	Present
				study



Fig. 7. The temperature-dependent thermoelectric power and of CuI pellets with varying amounts of added KI.

generated voltage in thermoelectric materials. In our study, we found that 7 % KI doping resulted in the highest Seebeck coefficient values within CuI, resulting in the maximum voltage generated.

The result implies that the concentration of 7 % KI represents an optimal point for power generation in CuI-based thermoelectric materials. By exploiting the synergy between electrical conductivity, thermal conductivity and the Seebeck coefficient as demonstrated in our previous results, this research provides valuable insights into the design and optimization of thermoelectric materials for efficient power generation applications. The temperature-dependent performance data presented in Fig. 7 further supports the potential of controlled KI doping to

improve the thermoelectric performance of CuI and highlights the practical significance of these findings for the development of advanced thermoelectric devices.

#### 4. Conclusions

CuI doped with KI exhibited temperature-dependent electrical conductivity, confirming its semiconducting nature. The introduction of KI significantly improved electrical conductivity, with the highest conductivity achieved at 9 % KI doping (5.08 S m<sup>-1</sup> at 373 K) out of the sample investigated. The thermal conductivity of CuI increased with higher KI concentrations due to enhanced electrical conductivity, promoting electron mobility within the lattice. CuI exhibited p-type conduction, with positive values of the Seebeck coefficient. The Seebeck coefficient increased with rising temperature and KI concentration, reaching its peak at 7 % KI doping. The highest ZT value also was observed at 7 % KI doping, indicating the potential for optimizing CuI's thermoelectric performance through controlled KI doping. The ZT value ranged from  $0.035 \times 10^{-3}$  to  $26.95 \times 10^{-3}$  with increasing KI concentration from 0 % to 7 % but subsequently declined to  $7.678 \times 10^{-3}$  at 9 % KI doping at 373 K.

#### CRediT authorship contribution statement

K.G.D.T.B. Kahawaththa: Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. L.K. Narangammana: Writing – review & editing, Supervision, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. N.D. Subasinghe: Writing – review & editing, Formal analysis, Data curation, Conceptualization. T.M.W.J. Bandara: Writing – review & editing, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2025.237043.

# Data availability

Data will be made available on request.

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