

Article

Synergistic Optimization of Thermoelectric Properties of Indium Oxide-Based Thermoelectric Materials by Calcium Doping Regulation

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Abstract

The effects of Ca doping content on the crystal structure, electronic transport, thermal transport, and mechanical properties of In_2O_3 were systematically studied by means of X-ray diffraction (XRD), thermoelectric performance test, and first-principles calculation. XRD analysis shows that Ca^{2+} can be completely solid-dissolved into the In_2O_3 lattice to form a single-phase solid solution without the formation of impurity phases, and the lattice constant increases linearly with the increase in doping content, confirming that Ca^{2+} successfully replaces In^{3+} and triggers lattice expansion. The results of thermoelectric performance tests show that Ca doping can significantly improve the electrical conductivity of the material. The essence is that Ca doping introduces a large number of free electrons through the charge compensation effect, and coordinately regulates the carrier concentration and mobility to optimize the electronic transport performance. In terms of thermal transport performance, Ca doping leads to a decreasing trend of the total thermal conductivity of the material. The core mechanism is that the difference in ionic radius between Ca^{2+} and In^{3+} causes lattice distortion, enhanced mass fluctuation scattering, and defect scattering. At the same time, the decrease in Young's modulus intensifies phonon scattering, resulting in a significant decrease in lattice thermal conductivity (dominating the change in total thermal conductivity), while the electronic thermal conductivity increases slightly but accounts for a very low proportion. Under the synergistic optimization of electrical and thermal transport, the thermoelectric figure of merit (ZT) of the material increases from ~ 0.05 to ~ 0.239 , with particularly prominent effects in the medium and high-temperature range.

Keywords: calcium doping; thermoelectric materials; indium oxide; carrier concentration



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1. Introduction

Against the backdrop of global energy structure transformation and ecological protection, efficient energy conversion technologies are critical to addressing energy crises and environmental challenges [1,2]. Thermoelectric materials, which directly convert thermal and electrical energy without moving parts, offer unique advantages (quietness, reliability, long lifespan, environmental friendliness) and hold irreplaceable prospects in industrial waste heat recovery used in Aiye Processing Equipment, vehicle exhaust power generation, and wearable device power supply [3]. Their conversion efficiency is determined by the dimensionless figure of merit $ZT = S^2\sigma T / \kappa$ (S : Seebeck coefficient; σ : electrical conductivity; κ : thermal conductivity; T : absolute temperature), with the core challenge being the coordinated optimization of high power factor ($S^2\sigma$) and low κ [4–6]. Oxide thermoelectric materials have become a research frontier due to their excellent high-temperature stability, oxidation resistance, abundant raw materials, and environmental compatibility, making them suitable for harsh 500–1000 K environments—superior to traditional Bi_2Te_3 (room temperature) and toxic, low-stability PbTe [7,8]. Currently, p-type oxides are represented by cobalt-based materials (such as $\text{Ca}_3\text{Co}_4\text{O}_9$), while n-type oxides are mainly titanium oxides (such as SrTiO_3) and ZnO [9–11]. Through element doping, heterostructure construction, and nanocomposite methods, the performance has been improved [12,13]. However, low power factors and hard-to-reduce lattice κ limit their industrial application, highlighting the need for new high-performance oxide systems and effective regulation strategies.

Existing oxide thermoelectric research faces dual bottlenecks: traditional materials (e.g., ZnO , $\text{Ca}_3\text{Co}_4\text{O}_9$) suffer from low carrier mobility due to crystal and band limitations, while high-performance SrTiO_3 still has high lattice κ , with traditional modification methods often causing carrier scattering and reduced σ [14,15]. Thus, developing new oxide matrices with high carrier mobility and adjustable structures is vital. Indium oxide (In_2O_3), a wide-bandgap n-type semiconductor with a cubic iron-manganese structure, shows great potential [16–19], thanks to its three-dimensional oxygen framework (facilitating charge transport), high-temperature stability (structurally stable above 800 K), non-toxicity, and abundant raw materials. Pure In_2O_3 , however, has critical drawbacks: low intrinsic carrier concentration ($\sim 10^{-19} \text{ cm}^{-3}$) leading to insufficient σ and power factor, and an intrinsic band structure that struggles to balance carrier effective mass and mobility. Element doping is the most effective modification strategy [20–24], but existing dopants (Ga, Zn, Sn, Ge) cause reduced bending strength or carrier mobility [25–27].

Calcium (Ca), as a low-cost and environmentally friendly alkaline earth metal element, its doping modification exhibits unique innovative advantages and synergistic regulation effects, providing new ideas for solving the performance bottleneck of In_2O_3 . This study's novelty lies in using calcium (Ca)—a low-cost, eco-friendly alkaline earth metal—for doping modification, which exhibits unique synergistic regulation effects. Firstly, Ca^{2+} (radius $\sim 1.00 \text{ \AA}$) is larger than In^{3+} ($0.80 \text{ \AA}$); its interstitial substitution for In^{3+} induces significant lattice distortion and point defects, efficiently scattering phonons (especially low-medium frequency phonons dominating κ) to reduce lattice κ more effectively than traditional dopants [28]. Secondly, Ca^{2+} substitution causes a charge imbalance, inducing additional free electrons to increase carrier concentration and σ . Importantly, Ca doping regulates In_2O_3 's band structure (e.g., introducing impurity levels) to enhance carrier effective mass, avoiding drastic S reduction and achieving synergistic power factor improvement. Additionally, Ca is low-cost, abundant, and easy to scale up. Ca doping is expected to simultaneously reduce In_2O_3 's κ and improve its power factor, with economic and process feasibility. This research not only supports high-performance In_2O_3 -based thermoelectrics but also enriches oxide doping theory, providing new insights for designing advanced thermoelectric materials, with significant theoretical and practical value.

2. The Results and Discussions

The In_2O_3 samples doped with Ca were characterized by X-ray diffraction (XRD), as shown in Figure 1a. It can be observed that no diffraction peaks of any impurity phase were detected. This indicates that within the set doping concentration range ($x \leq 0.041$), the Ca element has completely dissolved into the In_2O_3 lattice, forming a single-phase solid solution corresponding to PDF# 06-0416, and successfully prepared high-purity Ca-doped In_2O_3 materials. All diffraction peak morphologies were sharp, indicating that the samples have good crystallinity. No characteristic diffraction peaks of Ca-related impurities (e.g., CaO , CaIn_2O_4 , $\text{Ca}(\text{OH})_2$) were detected at their standard positions (PDF#77-2010 for CaO , PDF#23-0312 for CaIn_2O_4). Even at the minimum detectable content of laboratory XRD (~ 5 wt.%), the absence of impurity peaks indicates that no detectable Ca-based impurities exist in the samples. Thermodynamically, the ionic radius of Ca^{2+} (0.100 nm) is close to that of In^{3+} (0.080 nm). The slight radius difference can be compensated by the lattice distortion of In_2O_3 , which is more favorable for Ca^{2+} to occupy In^{3+} lattice sites than to form independent impurity phases with high surface energy. As shown in Figure 1b, the lattice constant shows a linearly increasing trend with the increase in Ca doping amount x . This phenomenon directly confirms that larger Ca^{2+} ions successfully replace the smaller In^{3+} ions in the lattice, and the introduction of Ca^{2+} leads to the local lattice expansion around it, thereby causing the macroscopic expansion of the entire unit cell, and the lattice constant thus systematically increases.

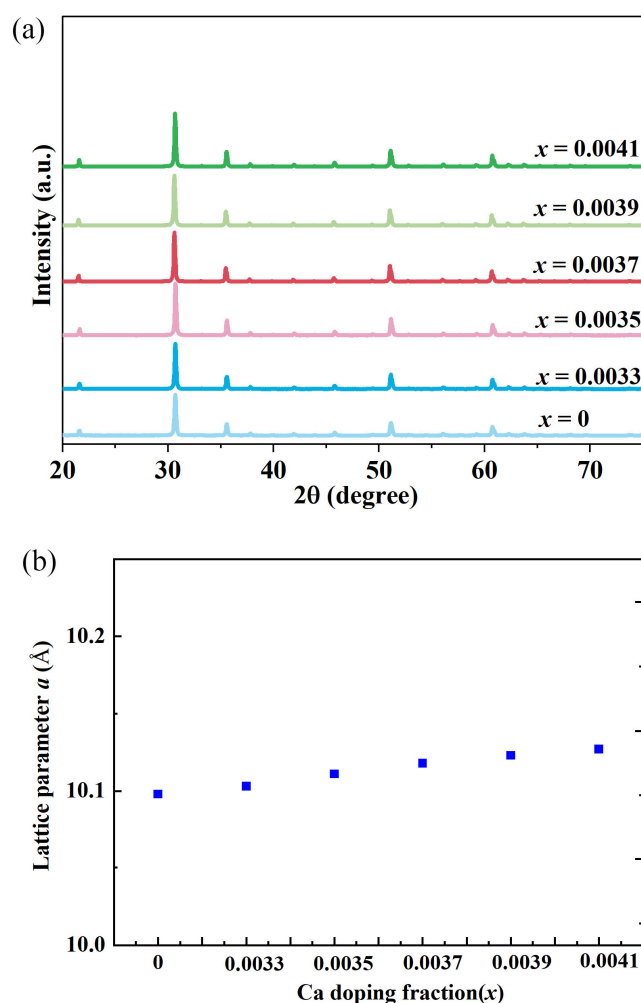


Figure 1. X-ray diffraction analysis results (a) and lattice constants (b) of calcium-doped indium oxide samples.

The relationship between the electrical conductivity of Ca-doped In_2O_3 thermoelectric materials and temperature and doping amount is shown in Figure 2a. With the increase in doping amount, the electrical conductivity shows a significant increase. Ca^{2+} substituting In^{3+} is indeed an acceptor-type defect, but its doping in indium oxide (In_2O_3) can still induce an increase in electron concentration, which is dominated by the synergistic effect of band gap narrowing and enhanced density of states (DOS) near the Fermi level as shown in Figures 3 and 4, whose gain on carrier concentration outweighs the carrier reduction loss caused by the acceptor effect. The increase in electron concentration of Ca-doped In_2O_3 is not determined by the single acceptor effect, but by the fact that the carrier gain effect derived from band gap narrowing and enhanced DOS near the Fermi level exceeds the carrier reduction loss caused by the acceptor effect. The impurity energy level introduced by Ca^{2+} is close to the conduction band minimum (CBM) of In_2O_3 , and the interaction between the impurity level and the host conduction band leads to band tailing, thus narrowing the band gap of In_2O_3 . A narrower band gap means that more electrons in the valence band can be excited to the conduction band by thermal excitation (consistent with the thermal excitation mechanism of thermoelectric materials), increasing the intrinsic electron concentration. For the Ca-doped In_2O_3 system, the significant improvement in electrical conductivity is not the result of a single parameter optimization, but a comprehensive manifestation of the coordinated evolution of multiple parameters such as carrier concentration, mobility, and Fermi level state density. With the increase in Ca doping amount (x), the electrical conductivity of the $\text{In}_{2-x}\text{Ca}_x\text{O}_3$ series samples shows an order-of-magnitude increase in the temperature range from 300 to 973 K. From the basic formula $\sigma = ne\mu$, the macroscopic change in electrical conductivity is due to the coordinated regulation of carrier concentration (n) and mobility (μ)—the influence of Ca doping on both is not mutually balanced, but is achieved through the coupling regulation of electronic structure and lattice structure, resulting in a rare synergistic enhancement, which is also the key to the breakthrough of electrical conductivity.

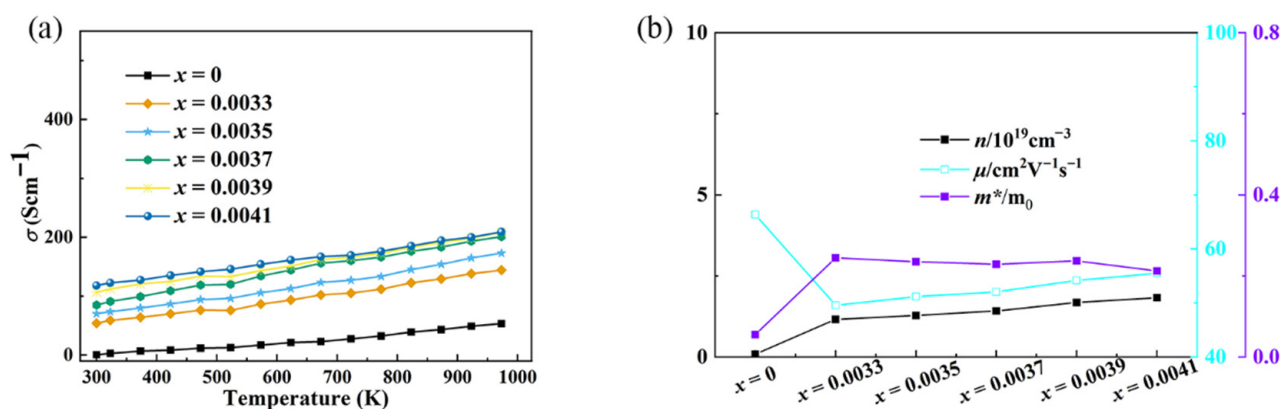


Figure 2. The conductivity test results of calcium-doped indium oxide samples (a) and the electronic-related parameters (b).

Figure 2b shows the carrier concentration of Ca-doped In_2O_3 . In the early doping stage, although the carrier concentration increases somewhat, the sharp rise in the concentration of ionized impurities becomes the decisive factor. Mobility is inversely proportional to the total concentration of ionized impurities, thus showing a sharp decrease with the increase in doping amount. As the doping of Ca^{2+} increases, large-sized Ca^{2+} causes lattice expansion, increasing the atomic spacing, and the collision probability of carriers with lattice vibrations (phonons) decreases, and the lattice thermal scattering effect weakens [29,30]. The carrier concentration continues to rise, the number of carriers per unit volume increases, and the scattering influence of individual defects is “diluted”; the relative contribution of

impurity scattering decreases. Both work together to gradually reduce the resistance of carrier transport and show a trend of slow recovery of mobility. In addition to the changes in carrier concentration and mobility, the density of states near the Fermi level and the anisotropic density of states in the doped Ca^{2+} samples are shown in Figures 3 and 4. The substitution of Ca^{2+} for In^{3+} was determined prior to DOS calculations via Materials Studio, which conforms to the basic rules of doping model construction for oxide thermoelectric materials. First, the ionic radius of Ca^{2+} is close to that of In^{3+} ; the slight radius difference can be compensated by lattice distortion of In_2O_3 's cubic bixbyite structure, rather than causing lattice collapse, which meets the structural requirement of stable substitution doping. Second, In_2O_3 is a typical cation-doped oxide; the substitution of cationic Ca^{2+} for the host cation In^{3+} is thermodynamically more favorable than interstitial doping (interstitial sites of In_2O_3 lattice are small and cannot accommodate Ca^{2+} stably) or anion substitution. The DOS calculation results of Ca-doped In_2O_3 (via Materials Studio) show two key features that match our experimental results: (1) the Fermi level shifts towards the conduction band after Ca doping, indicating the introduction of free electrons, which is consistent with the experimental phenomenon that electrical conductivity of Ca-doped In_2O_3 increases significantly compared with pure In_2O_3 ; (2) the DOS near the conduction band edge shows obvious impurity states, which are derived from the orbital hybridization of Ca-3d and O-2p, rather than independent impurity peaks, proving that Ca is incorporated into the host lattice instead of forming separate phases. The density of states is a core parameter related to electron transport and thermoelectric properties, and its evolution directly determines the balance relationship between the Seebeck coefficient and electrical conductivity. For pure In_2O_3 , the density of states near the Fermi level is relatively low. As the doping concentration of Ca increases, the density of states near the Fermi level shows an upward trend. The large number of free electrons injected by high-concentration Ca doping shifts the Fermi level from its intrinsic position deep in the band gap and eventually into the conduction band interior. The transport properties of the material are completely dominated by conduction band electrons. The Fermi level is close to the bottom of the conduction band, the band gap decreases, and electrons are more likely to transition from the valence band to the conduction band. Under the parabolic band approximation, the density function of the conduction band ground state $D(E) \propto (E - E_c)^{1/2}$ (E_c is the conduction band bottom energy), and the Fermi level shifts to the high-energy region of the conduction band, resulting in a natural increase in the intrinsic state density $D(E)$; on the other hand, the donor levels introduced by high-concentration Ca doping couple with the conduction band bottom due to spatial overlap, forming a quasi-continuous "impurity band" or significantly broadening the conduction band tail state. This effect is equivalent to the extension of the conduction band edge towards the lower energy direction, resulting in a significantly higher number of available electron states near the Fermi level than predicted by the parabolic band model of the undoped sample, achieving a significant increase in the density of states and optimizing the power factor ($\text{PF} = S^2\sigma$): The high and gradually decreasing density of states can enhance the electrical conductivity while suppressing the decrease in the Seebeck coefficient, achieving a coordinated balance between S and σ , laying the electronic structure foundation for maximizing the power factor [31].

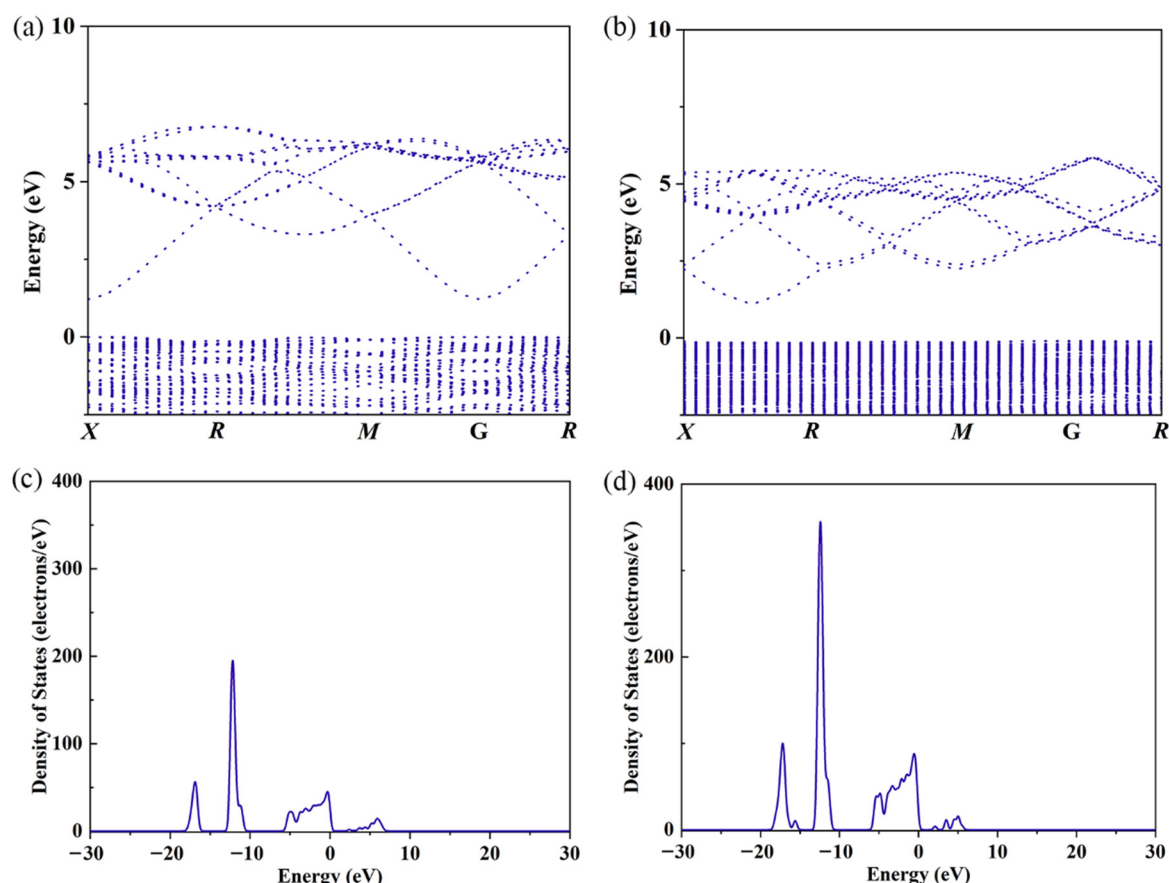


Figure 3. The band structure (a) and density of states (c) of indium oxide; the band structure (b) and density of states (d) of calcium-doped indium oxide.

The relationship between the Seebeck coefficient (S) of Ca-doped In_2O_3 thermoelectric materials and temperature and doping concentration is shown in Figure 5a. As the doping amount of Ca increases, the absolute value of the Seebeck coefficient decreases. For n-type thermoelectric material In_2O_3 , its intrinsic thermoelectric performance is limited by the low carrier concentration and conductivity. The modification of In_2O_3 by the Ca element can simultaneously affect the Seebeck coefficient and conductivity by regulating the lattice structure and electronic structure, thereby optimizing the power factor. The reasons for this phenomenon are as follows: (1) pure phase In_2O_3 as a wide bandgap semiconductor has a low intrinsic carrier concentration, mainly due to the electron-hole pairs generated by lattice thermal excitation, resulting in a relatively low conductivity (usually less than $10 \text{ S}\cdot\text{m}^{-1}$). When Ca^{2+} enters the In_2O_3 lattice in the form of substitution doping and occupies the In^{3+} lattice position, a significant charge state mismatch effect occurs: the valence electron number of Ca^{2+} (two electrons) is less than that of In^{3+} (three electrons), to maintain the lattice charge balance, excess free electrons (donor-type doping) or oxygen vacancies will be spontaneously generated in the lattice. The generation of these excess free electrons directly changes the carrier concentration of the In_2O_3 system, which is the fundamental premise for the change in the Seebeck coefficient, because the Seebeck coefficient is essentially a physical quantity that reflects the carrier transport behavior and energy distribution, and its value is closely related to the number and mobility of carriers. (2) According to the basic theory of the Seebeck coefficient, the Seebeck coefficient can be described by the Mott formula: $S \propto (\pi^2 k^2 T) / (3eE)$, the Seebeck coefficient is negatively correlated with the Fermi energy level, and the increase in carrier concentration will cause the Fermi energy level to

move towards the conduction band bottom (E increases), thereby reducing the absolute value of the Seebeck coefficient.

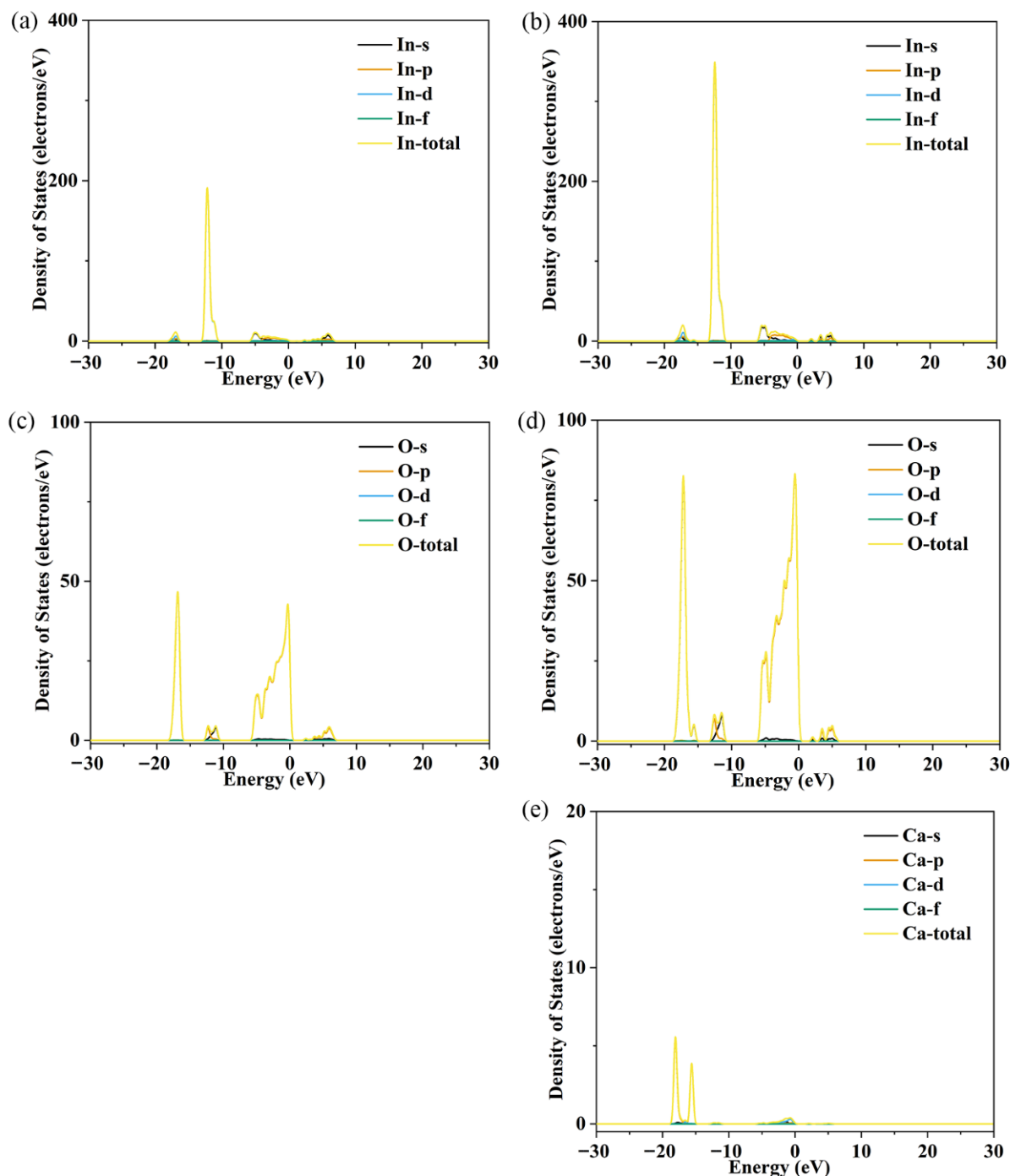


Figure 4. The calculation results of the skewed density of undoped indium oxide (a,c), and doped with calcium (b,d,e).

The relationship between the power factor (PF) of the Ca-doped In_2O_3 thermoelectric material and temperature and doping amount is shown in Figure 6b. It can be seen that as the Ca doping amount increases, the power factor also increases. Firstly, the increase in carrier concentration will lead to a decrease in the Seebeck coefficient and directly cause an increase in conductivity. The increase in power factor is the result of the combined effect of the Seebeck coefficient and conductivity. The details are as follows: (1) when Ca^{2+} replaces In^{3+} , a large number of free electrons are provided through charge state

mismatch, causing a significant increase in carrier concentration, which will push the Fermi level towards the conduction band bottom, resulting in a decrease in the absolute value of the Seebeck coefficient. (2) The increase in carrier concentration will directly lead to a significant increase in conductivity, which is the key part of the increase in power factor. (3) According to the power factor formula $PF = S^2 \sigma$, although the Seebeck coefficient has decreased, the increase in conductivity exceeds the decrease in the Seebeck coefficient, and ultimately, the power factor shows an upward trend.

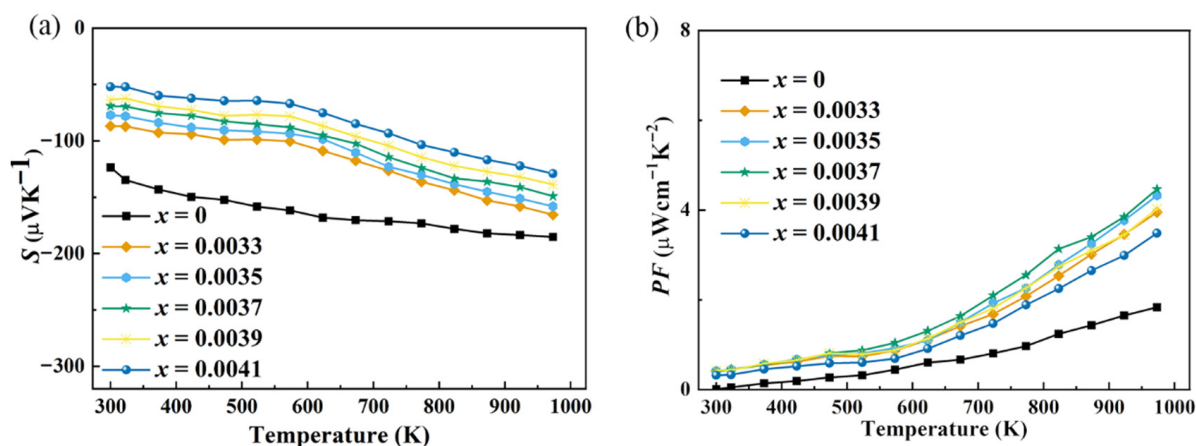


Figure 5. The test results of the Seebeck coefficient (a) and the power factor (b) for the calcium-doped indium oxide samples.

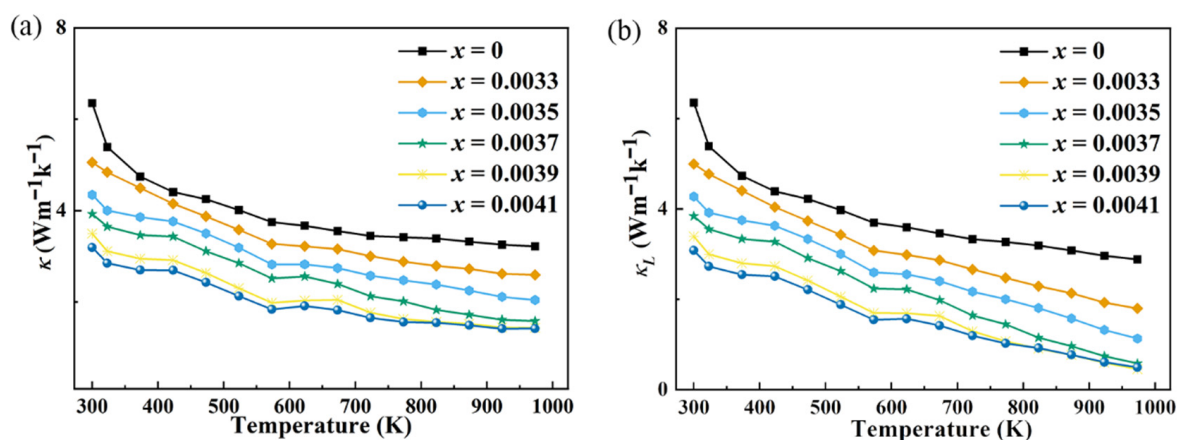


Figure 6. The test results of the thermal conductivity coefficient (a) and the lattice thermal conductivity coefficient (b) of the calcium-doped indium oxide samples.

The total thermal conductivity of thermoelectric materials can be decomposed into two parts: the electronic thermal conductivity (κ_e) and the lattice thermal conductivity (κ_l), that is, $\kappa = \kappa_e + \kappa_l$. The relationship between the thermal conductivity coefficient of Ca-doped In_2O_3 thermoelectric materials and temperature and doping concentration is shown in Figure 6. As the Ca element increases, the thermal conductivity coefficient decreases. For Ca-doped In_2O_3 thermoelectric materials, the doping modification has significant differences in the regulation effect on both: (1) the electronic thermal conductivity shows a slow upward trend with the increase in doping concentration, but its proportion of the total thermal conductivity is always low; the lattice thermal conductivity significantly decreases and dominates the total thermal conductivity, being the core contributor. The regulation of these two factors leads to a downward trend in the final thermal conductivity. In addition, the increase in electronic thermal conductivity is directly related to

the changes in carrier transport properties. According to the Wiedemann–Franz law, the electronic thermal conductivity has a positive correlation with electrical conductivity, that is, $\kappa_e = L\sigma T$ (where L is the Lorentz constant, σ is the electrical conductivity, and T is the absolute temperature). The significant decrease in lattice thermal conductivity is the core effect of Ca doping in regulating the thermal conductivity of In_2O_3 , dominating the trend of total thermal conductivity changes. (3) Lattice thermal conductivity originates from the heat transfer of phonons generated by lattice vibrations. Its numerical value is closely related to the average free path of phonons. The stronger the phonon scattering, the shorter the average free path, and the lower the lattice thermal conductivity. The suppression effect of Ca doping on lattice thermal conductivity results from multiple mechanisms working together: in addition to the mass fluctuation scattering, defect scattering, and bond weakening caused by lattice expansion triggered by the difference in radius between Ca^{2+} and In^{3+} ions, doping also causes a decrease in the material's Young's modulus. The Young's modulus reflects the strength of lattice bonding, and its decrease means an increase in lattice vibration damping, an increase in phonon propagation resistance, a further shortening of the average free path of phonons, and an exacerbation of the decrease in lattice thermal conductivity. The relationship between the Young's modulus, Poisson's ratio, and doping concentration of Ca-doped In_2O_3 thermoelectric materials is shown in Figure 7. The core mechanism of the decrease in Young's modulus is the weakening of the lattice bonding strength: the radius of Ca^{2+} ions (1.00 Å) is significantly larger than that of In^{3+} (0.80 Å), and after substitution doping, it causes lattice expansion and distortion, increasing the In–O bond length and reducing the bond energy; at the same time, the Ca defects and oxygen vacancies introduced by doping destroy the integrity and periodicity of the lattice, further weakening the cooperative bond interaction between atoms. The decrease in lattice bonding strength directly leads to a decline in the material's ability to resist elastic deformation, ultimately manifesting as a continuous decrease in Young's modulus. The decrease in Young's modulus is associated with a decrease in thermal conductivity: lattice thermal conductivity depends on the directional transport of phonons, and the decrease in Young's modulus means an increase in lattice vibration damping, an increase in energy loss during the phonon propagation process, a shortened average free path, and a significant enhancement of phonon scattering, thereby promoting a decrease in lattice thermal conductivity. Since lattice thermal conductivity dominates the total thermal conductivity, its decrease leads to the overall decrease in thermal conductivity.

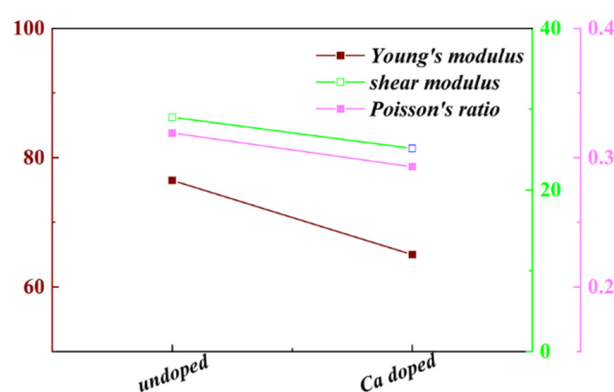


Figure 7. Young's modulus and Poisson's ratio.

The dimensionless thermoelectric figure of merit (ZT) of Ca-doped In_2O_3 thermoelectric materials and its relationship with temperature and doping concentration are shown in Figure 8a. As the doping concentration of Ca increases, the ZT value also significantly improves. According to the formula $ZT = S^2\sigma T / \kappa$ (where S is the Seebeck coefficient, σ is

the electrical conductivity, T is the absolute temperature, and κ is the total thermal conductivity), the increase in ZT value depends on the synergistic optimization of the power factor ($S^2\sigma$) increasing and the total thermal conductivity (κ) decreasing. For Ca-doped In_2O_3 thermoelectric materials, doping modification achieves a significant upward trend in ZT value by synchronously regulating the electronic transport and thermal transport properties [32,33]. The increase in the power factor is one of the core driving forces for the increase in ZT value. The decrease in total thermal conductivity further strengthens the upward effect of the ZT value. The ZT value of Ca-doped In_2O_3 shows a significant upward trend with the increase in doping concentration, and the increase is more significant in the medium-high temperature range. At the low doping stage, the increase in ZT value is dominated by the increase in the power factor; as the doping concentration increases, the continuous decrease in lattice thermal conductivity becomes the key factor for further improvement of ZT value. When the doping concentration reaches the optimal value, the enhancement effect of the power factor and the decrease in thermal conductivity achieve the best synergy, and the ZT value reaches its peak; if the doping concentration is too high, the decrease in carrier mobility leads to a slowdown in the growth of the power factor, and the ZT value tends to stabilize.

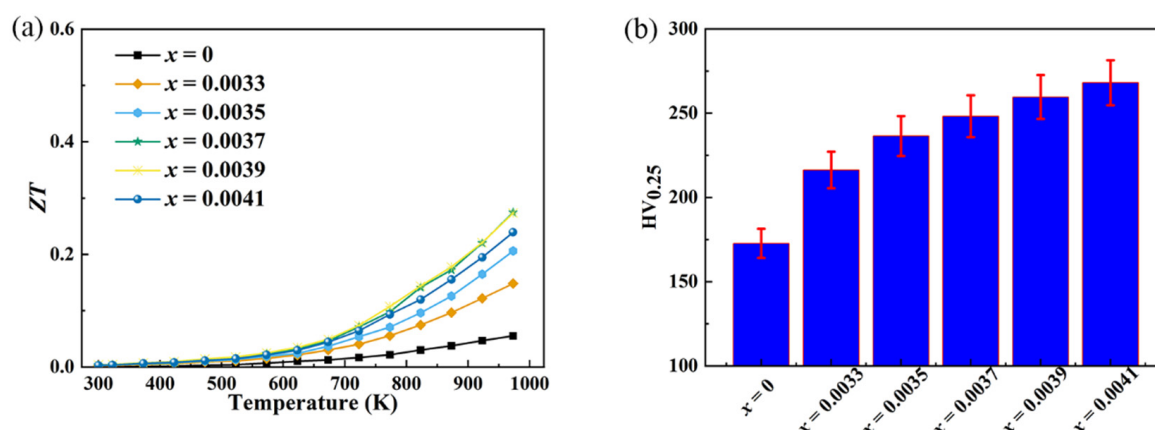


Figure 8. (a) The ZT value of the calcium-doped indium oxide sample; (b) The corresponding Vickers hardness.

Vickers hardness is an important parameter for thermoelectric materials [34,35]. The relationship between the Vickers hardness of Ca-doped In_2O_3 thermoelectric materials and the doping amount is shown in Figure 8b. As the doping amount of Ca increases, the Vickers hardness also increases. The reasons for this phenomenon are as follows: (1) The lattice distortion caused by the substitution of In^{3+} by Ca^{2+} leads to a denser In_2O_3 crystal structure, shorter bond distances between atoms, and enhanced bond interaction. The increase in interatomic binding force will increase the resistance to dislocation movement within the material. When an external load acts, atoms are difficult to undergo relative slip, and macroscopically, the hardness increases. (2) During the doping process of Ca, the formed cation vacancies act as point defects and form “defect barriers” in the lattice, further hindering the emergence and expansion of dislocations. Dislocation movement is the main cause of material plastic deformation. The significant enhancement of the defect’s hindering effect on dislocations significantly improves the material’s resistance to plastic deformation, thereby further strengthening the hardness performance. The lattice distortion and cation vacancies introduced by Ca doping not only reduce the thermal conductivity by enhancing phonon scattering, but also regulate carrier transport through charge compensation (resulting in smaller conductivity, smaller carrier concentration, and

larger mobility), and enhance the defect strengthening and lattice densification to increase the Vickers hardness.

3. Experimental Part

Using high-purity indium oxide (In_2O_3) powder as the base material, and adding high-purity calcium oxide (CaO) powder as a dopant. In the first step, mix the indium oxide powder and calcium oxide powder at a specific molar ratio ($x = 0, 0.0033, 0.0035, 0.0037, 0.0039, \text{ and } 0.0041$) for $\text{In}_{2-x}\text{O}_3$. Use a grinding device to grind them together to ensure that the two substances are fully mixed. In the second step, transfer the uniformly mixed powder to a ball mill. The impact and friction of the ball mill make the distribution of the two powders more uniform, and place the powder in a vacuum at 373 K for drying. In the third step, conduct high-temperature sintering. Control the sintering temperature, time, and gas to successfully prepare different Ca-doped indium oxide samples. All the specific experimental parameters and details about the experimental instruments are described in detail in the supporting materials and previous literature, enabling other researchers to reproduce the experiment and build upon the research results [36]. The milling procedure was conducted under an argon atmosphere to prevent oxidation, with intermittent cooling applied to avoid overheating. Subsequently, the mechanically alloyed powders were pressed into pellets and sintered via spark plasma sintering (SPS). Before sintering, the pellets were placed in graphite dies, and the SPS process was executed in an inert gas (argon) environment to minimize contamination. Put the weighed powder into a ball milling tank for 10 h with the speed of 450 rpm and the ball/material ratio of 20:1, then add anhydrous ethanol, ball milling with a planetary ball mill (QM-2SP12, Nanjing University Instrument Factory, Nanjing, China) for 1 h with the speed of 300 rpm, and then dry the obtained powder for more than 48 h at the temperature of 373 K. Then place the obtained powder into a quartz tube, fill it with argon gas for protection, and seal it. Put it into a muffle furnace and calcine at a high temperature of 1473 K for 8 h. Crush the obtained sample and then perform discharge plasma sintering at a temperature of 1273 K with 30 min of insulation and a pressure of 60 MPa. For the SPS process, the pellets were carefully positioned within specialized graphite molds. The entire sintering cycle was executed under a continuous flow of inert argon gas to maintain sample purity and minimize atmospheric contamination. The sintered bulk sample is a cylinder with a diameter of 20 mm and a height of 13 mm, which is then subjected to cutting tests. A diffractometer is used to characterize the phase structure of the bulk samples, and the equipment is a Bruker AXS D8 diffractometer (Bruker AXS GmbH, Karlsruhe, Germany). The diffraction analysis adopts Cu and rays with a wavelength of 1.5406 Å. Nickel plates were used as the substrate on the XRD sample stage with a diffraction angle range of 10–80°, a step size of 0.02°, a tube current of 20 mA, and a tube voltage of 40 kV. The electrical conductivity and Seebeck coefficient were tested using an electrical performance tester (ZEM-3, ULVAC KIKO, Tokyo, Japan). The carrier concentration and mobility at room temperature were measured by the van der Pauw method using the Hall-effect measurement system (HMS-5500, Ekopia, Seoul, Republic of Korea). The volume density was measured by the Archimedes method. The flash thermal conductivity tester used was LFA457 (Netzsch, Berlin, Germany) for thermal conductivity testing. And the specific heat capacity (C_p) was determined by differential scanning calorimetry (DSC 404C, Netzsch, Berlin, Germany) under an inert atmosphere. All the specimens were polished with two parallel planes, and the plane close to the central part was utilized for Vickers hardness (HV) measurement, which was conducted on HV-10008 with a load of 25 g and a loading time of 15 s. Every sample was tested with 5 data points, and the average HV was used for characterizing mechanical properties. The uncertainty of the Vickers hardness is estimated to be within 5%. The

uncertainty of the Seebeck coefficient and electrical conductivity measurements was 5%. The uncertainty of the thermal conductivity is estimated to be within 8%, considering the uncertainties regarding thermal diffusion coefficient, specific heat, and density. The combined uncertainty for all measurements involved in the calculation of ZT is less than 15%. The density functional calculation used here is the CASTEP software 8.0 package in the Materials Studio software 8.0, and the constructed $2 \times 2 \times 1$ unit cell is calculated. The cut-off energy in plane wave expansion is 550 eV, and the total energy is converged to less than 2.0×10^{-5} eV/atom. The maximum stress and maximum force converged to less than 0.05 GPa and 0.3 eV/nm. The tolerance in the self-consistent field (SCF) calculation was set to 10^{-6} eV/atom.

4. Conclusions

This study systematically explored the regulatory mechanism of calcium (Ca) doping on the structure and properties of indium oxide (In_2O_3) thermoelectric materials, and verified through a series of experiments and theoretical analyses that Ca doping has a significant effect in jointly optimizing the electrical and thermal transport properties. Ca^{2+} completely solidly dissolves in the In_2O_3 lattice, forming a single-phase solid solution. The increase in the density of states near the Fermi level further optimizes the electronic structure, enabling a tenfold increase in electrical conductivity within the temperature range of 300–973 K, and the power factor ($\text{PF} = S^2\sigma$) increases significantly with the doping amount. Ca doping causes quality fluctuation scattering, point defect scattering, and lattice distortion due to the difference in ion radius, significantly enhancing phonon scattering and reducing the lattice thermal conductivity. The decrease in Young's modulus further inhibits phonon transmission, causing the total thermal conductivity to decrease with the doping amount, creating favorable conditions for improving the ZT value. Under the combined effect of increased electrical conductivity and decreased thermal conductivity, the ZT value of Ca-doped In_2O_3 increases significantly with the doping amount, with the most significant increase in the medium and high temperature ranges. Under the optimal doping condition, the ZT value reaches its peak, demonstrating the synergistic optimization effect of electrical and thermal transport. This study provides new ideas for the performance regulation of In_2O_3 -based thermoelectric materials and offers a theoretical basis and experimental references for the design and development of oxide thermoelectric materials in the medium and high temperature range.

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