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# Nanoscaled $In_2O_3$:Sn films as material for thermoelectric conversion: achievements and limitations

**G KOROTCENKOV[1,*], V BRINZARI[2] and B K CHO[1]**

[1]School of Material Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500712, Republic of Korea

[2]Department of Theoretical Physics, State University of Moldova, Chisinau, Republic of Moldova

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**Abstract.** **In this paper, thermoelectric properties of nanoscaled $In_2O_3$:Sn films are considered. The limitations that may appear during the usage of such materials in devices developed for the market of thermoelectric generators and refrigerators are also analysed. It is shown that nanoscaled $In_2O_3$:Sn is a promising material for thermoelectric applications. It is also established that insufficient thermal stability of nanostructured materials is the main limitation of these materials application in high-temperature thermoelectric converters. Optimization of grain boundary parameters and the usage of specific surrounding atmosphere can significantly improve the efficiency of thermoelectric conversion of nanostructured materials in the region of intermediate temperatures.**

**Keywords.** **Power factor; filtering effect; stability; doping; conductivity; grain size.**

## 1. Introduction

There is a huge amount of waste heat such as heat from the cars, different technological processes and humankind activities, which can be converted into useful energy, helping to increase the production efficiency and improve living conditions [1]. Therefore, the development of different types of energy conversion technologies, including thermoelectric energy conversion, is currently one of the most pursued directions of research. The main objective of this research was to improve the efficiency of thermoelectric conversion. Search and study of new *n*-type metal oxides, suitable for thermoelectric converters, is considered as a promising way to improve the efficiency of thermoelectric conversion [2–6]. As it is known, the conversion efficiency is usually expressed through the dimensionless factor of merit ZT, which is linearly dependent on the temperature:

$$\mathrm{ZT} = \alpha^2 \cdot \sigma \cdot T/\kappa = \mathrm{PF} \cdot T/\kappa, \quad (1)$$

where $\alpha$ is the Seebeck coefficient; $\sigma$ the conductivity; $\kappa$ the coefficient of thermal conductivity; $T$ the absolute temperature and PF is a power factor, electric component of thermoelectric conversion efficiency. This means that an increase in operating temperature is the easiest method to increase ZT. As compared with conventional thermoelectric materials, such as PbTe, $Bi_2Te_3$, etc., metal oxides have considerably better chemical and thermal stabilities, and therefore they are able to operate at temperatures above 1000°C. In addition, the increase in the operating temperature is accompanied by increase in electroconductivity and decrease in thermal conductivity of metal oxides [7–9]. These changes should lead to a further increase in ZT. However, experiments have shown that devices based on *n*-type conductive metal oxides prepared using high temperature sintering, had low efficiency of thermoelectric conversion [4,6–11], which made their utilization in thermoelectric generators, economically unprofitable. It should be noted that the search of new metal oxides of *p*-type conductivity, which are also in demand for thermoelectric module production, is less relevant, since such materials with the required value of ZT (ZT $\sim$ 1) are already found [5,6]. For example, $NaCoO_2$ at 800 K has a ZT value of $\sim$1.2 [12]. Materials with a ZT value exceeding 1 are, in general, considered as acceptable for thermoelectric applications.

Experimental studies [3,8] and theoretical calculations [13–16] showed that there is another fundamental possibility to increase ZT. This possibility is associated with utilization of nanostructured materials with a characteristic size of the order of a few nanometers.

It was established that because of using the low-dimensional materials, the increase in ZT may come through a combination of two mechanisms: (1) a reduction in the lattice thermal conductivity due to the scattering [14], or the refraction [15] of phonons at the physical boundaries of the nanoscale structure, and (2) an increase in the power factor PF, or at least the avoidance of a decrease in power factor with the decrease in $\kappa$, through size quantization in the structures with lower dimensionality (1D and 2D structures) or through energy filtering of the electrons involved in the charge transport [13,16].

Based on this, there is a task of both reviewing the effectiveness of this approach in relation to the *n*-type metal oxides, and evaluating limitations which may appear while

*Author for correspondence (ghkoro@yahoo.com)

using nanoscaled materials in thermoelectric applications. In the present study, this problem has been solved in relation to nanoscaled $In_2O_3$:Sn films. For these purposes, specifics of the electrical and thermoelectric properties of $In_2O_3$:Sn films have been studied. According to refs [17,18], $In_2O_3$:Sn is among the most promising *n*-type metal oxides for thermoelectric applications. Doping with tin, which is a donor to $In_2O_3$, provides necessary increase in the conductivity of the films.

## 2. Experimental

ITO film deposition on polished alumina and silicon substrates was performed by spray pyrolysis method [19]. For this purpose, a mixture of 0.2 M water solution of $InCl_3$ and $SnCl_4 \cdot 5H_2O$ was used for deposition of thin films with different thicknesses (in the range of 100–400 nm) and Sn/In ratios at pyrolysis temperature of 350–520°C.

X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used for structural characterization of deposited films. XRD analysis was carried out by a Siemens D5000 diffractometer and Rigaku Rotaflex X-ray diffractometer with a rotating anode source, working with CuK$\alpha$. For structural characterization, we used $\theta/2\theta$ mode of measurements. The size of crystallites forming the film was evaluated by Scherrer's formula. For SEM measurements, we used the scanning electronic microscopes Jeol JSM840, Philips XL30 and Stereoscan JS360 Cambridge Instruments with structural resolution of ~3–4 nm. AFM images were obtained using multimode scanning probe microscope with Nanoscope IIIa Controller of Digital Instruments. These measurements have been carried out in contact scanning mode using an AS-0.5 scanner (scan rate 2 Hz; resolution 2–3 nm).

Thermoelectric properties, i.e., the conductivity and the Seebeck coefficient, were studied over a temperature range of 20–450°C. Measurements were conducted in the conditions of linear temperature gradient $\Delta T/\Delta x$ along one axis and in the mode of slow heating (~10°C min$^{-1}$). Two thermocouples in the vicinity of the each electrode were used for the measurement of sample temperatures and their difference, $\Delta T$ between electrodes. An accuracy of $\Delta T/\Delta x$ measuring was better than 5%. Temperature difference did not exceed 20°C in the whole temperature range. Electrodes of silver paste were applied to the samples with deposited films on alumina substrate (dimensions of 10 × 4 × 0.5 mm). All experimental samples were annealed for stabilization of film's parameters at $T_{an} = 550$°C for 0.5 h.

## 3. Results and discussion

Studies showed that nanostructured $In_2O_3$:Sn films ($d \sim 90$ nm) with a grain size of 25–30 nm had much higher efficiency of thermoelectric conversion (figure 1a) in comparison with $In_2O_3$ prepared using conventional approach based on synthesis and high temperature sintering. If the best $In_2O_3$:Sn samples densified during high-temperature annealing at $T = 1000$–$1500$°C and having a crystallite size of tens of micrometers had a power factor of 0.4–0.5 mW m$^{-1}$K$^{-2}$ [7,10,11], then our nanoscaled $In_2O_3$:Sn films had PF reaching 4–5 mW m$^{-1}$K$^{-2}$. At the moment, this is the best result obtained for the *n*-type metal oxides designed for thermoelectric applications (figure 1b). This demonstrates that nanoscale metal oxides are promising materials for thermoelectric convertors, because observed increase in the efficiency of converting heat into electricity makes the use of thermoelectric generators cost-effective.

The analysis of the $In_2O_3$:Sn films properties showed that such values of PF cannot be explained by specific electrophysical parameters of the films studied, since the electrical conductivity of the $In_2O_3$:Sn films did not exceed the value usually observed for $In_2O_3$-doped with different impurities (figure 2).

A more detailed examination of the reasons of such behaviour of thermoelectric properties of the $In_2O_3$:Sn films led to the conclusion that the increase in the efficiency of thermoelectric conversion occurred due to nanoscaled structure of the films studied. Research results reported in refs [3,16] and our calculations for $In_2O_3$:Sn with optimal doping [20] showed that a so-called filtering effect was possible in such nanoscaled structures and at a certain ratio of

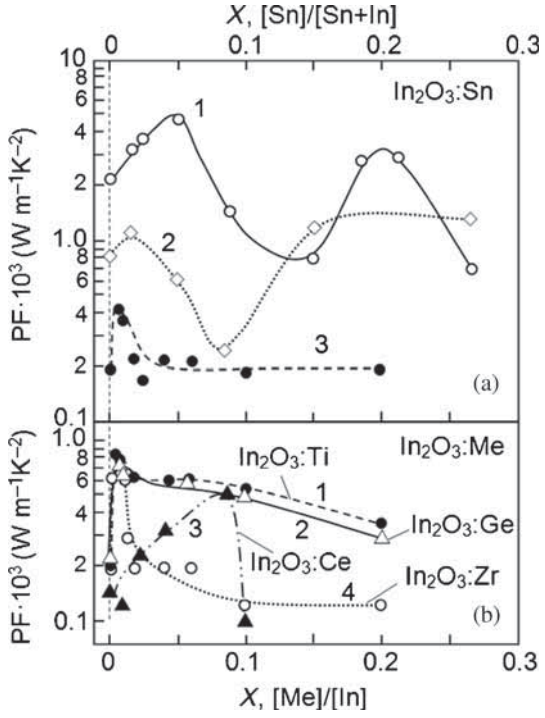


**Figure 1.** (**a**) 1, 2—$In_2O_3$:Sn deposited by spray pyrolysis: 1—$T_{pyr} = 350$°C; 2—$T_{pyr} = 450$°C; 3—$In_2O_3$:Sn prepared using solid reaction route and then sintered ($T_{sint} = 1400$°C, $t = 48$ h, air) [10]; (**b**) $In_2O_3$:Me samples were prepared using standard solid reaction route and then sintered: 1—$In_2O_3$:Ti ($T_{sint} = 1400$°C, $t = 48$ h, air) [10]; 2—$In_2O_3$:Ge ($T_{sint} = 1300$°C, $t = 48$ h in air) [11]; 3—$In_2O_3$:Ce ($T_{sint} = 973$ K for $t = 2$ h) [7]; 4—$In_2O_3$:Zr ($T_{sint} = 1400$°C, $t = 48$ h, air) [10].

the Fermi level and band bending, $U_b$, this effect could give the rise in power factor to more than five times. The calculations and their results are shown in figure 3. They indicate that this growth in the PF can be achieved in semiconductors of *n*-type conductivity if the band bends upwards and the height of potential barrier, $U_b$ exceeds only on a few kT at the position of the Fermi level in the conduction band. Band diagrams showing the change in current transport mechanism on changing $U_b$ are shown in the same figure. We believe that the formation of the surface depletion region or space charge region (SCR) in the $In_2O_3$:Sn grains is a result of combined action of the following two factors. The first one is the segregation of the tin atoms in the surface layer, which is accompanied by the accumulation of charged defects in the structurally distorted surface region, and the second one is oxygen chemisorption on the surface of the $In_2O_3$:Sn grains, which is accompanied by the capture of electrons from the conduction band. According to our estimates, the filtering effect starts affecting the thermoelectric properties when the crystallite size becomes smaller than 50–70 nm, and this influence increases with decrease in the grain size.

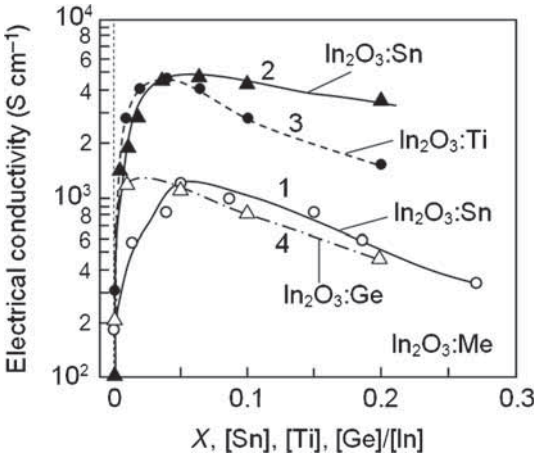


**Figure 2.** 1—$In_2O_3$:Sn deposited by spray pyrolysis ($T_{pyr}$ = 350°C); 2, 3—$In_2O_3$:Sn and $In_2O_3$:Ti prepared using solid reaction route and then sintered ($T_{sint}$ = 1400°C, $t$ = 48 h, air) [10]; 4—$In_2O_3$:Ge samples were sintered in air at $T_{sint}$ = 1300°C ($t$ = 48 h) [11].

The important role of the crystallite size in thermoelectric effects is confirmed by the fact that the increase in the pyrolysis temperature up to 450°C, which was accompanied by an increase in the crystallite size to 40–50 nm, resulted in a decrease in PF to 1.0–1.5 mW $m^{-1}K^{-2}$ (figure 1a, curve 2). The increase in the power factor with the grain size decreasing was also observed by Lan *et al* [8]. The grain size decrease from 600 to 50 nm in the $In_{1.92}(ZnCe)_{0.08}O_3$ samples was accompanied by an increase in PF from 0.45 to 0.8 mW $m^{-1}K^{-2}$. Importantly, the reduction in the grain size also helped to reduce the thermal conductivity of $In_{1.92}(ZnCe)_{0.08}O_3$ samples [8], another parameter whose reduction is required to increase ZT.

Our studies also showed that the real use of nanostructured films in thermoelectric generators and refrigerators might be accompanied by difficulties that could lead to limitations in their use. First of all, it concerns the stability of nanoscaled film's parameters. As it was mentioned before, to increase the efficiency of thermoelectric conversion, it is necessary to operate at high temperatures up to 1000°C and more. This means that the parameters of thermoelectric materials designed for use in such devices must be stable for a long time even at extremely high temperatures. Our study, however, showed that nanoscaled $In_2O_3$:Sn films did not possess such stability. Despite the fact that the addition of tin inhibits the growth of the $In_2O_3$ crystallites during high-temperature annealing [21], our studies showed that long-term exposure of the $In_2O_3$:Sn films already at 700°C led to a noticeable decrease in PF. The results of these tests are shown in figure 4.

Analysis of possible reasons for power factor decrease during long-term thermal annealing of the $In_2O_3$:Sn films revealed that these changes could be so big due to an increase

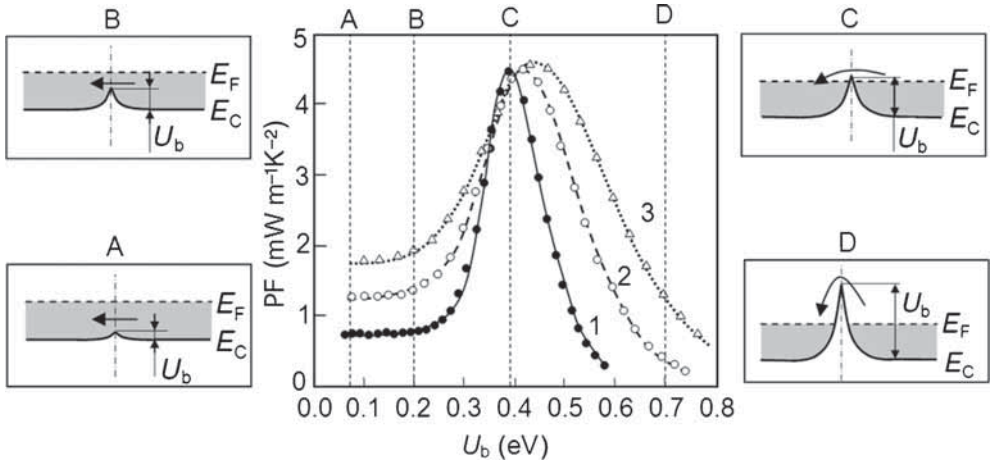


**Figure 3.** Modelled power factor of ITO as function of potential barriers at the intergrain interface at various temperatures (1—$T$ = 100°C, 2—300°C, 3—500°C). Fermi level position $E_F$ = 0.35 eV.

in the crystallites size caused by their coalescence. The effect of annealing on the crystallite size in the $In_2O_3$ films is shown in figure 5. It is seen that significant changes in the crystallite size are observed after annealing already at $T = 500$–$600$°C. With increase in the film thickness, these changes increase. This is an important result because the increase of the thermoelectric generator power will require significant increase in the thickness of the metal oxides used in these devices. In the nanocrystalline $In_2O_3$ pellets from the powder synthesized by sol–gel method, the process of solid state sintering (densification) starts in the same temperature range [21]. According to ref. [21], the grain size in the $In_2O_3$ pellets prepared from synthesized powders increased from 25 to 180 nm, when the annealing temperature increased from 600 to 1000°C.

Numerous studies have shown that the stability of the properties of polycrystalline materials depends on the crystallite size. The larger the grain size is, the higher is the temperature at which the transformation of the structural properties of the materials begins. In this regard, it is quite obvious that when working with nanoscaled materials, it will be necessary to make a choice, either to increase the crystallite size to improve the stability at high temperature or to reduce the operating temperature. Only future study will show which approach is more effective.

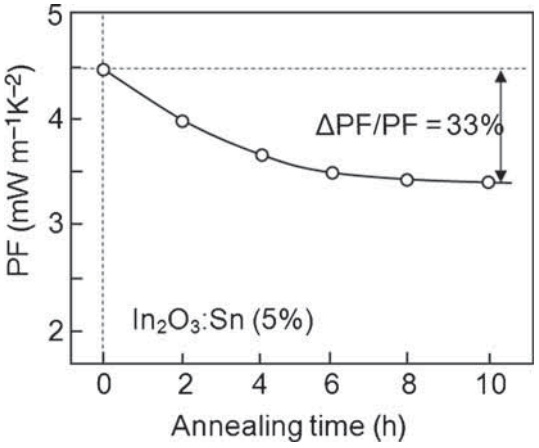


**Figure 4.** Instability of the power factor measured for $In_2O_3$:Sn (5% Sn) during thermal treatment in air at $T_{an} = 700$°C. $In_2O_3$:Sn films were deposited at $T_{pyr} = 350$°C.

Generally, an improvement in the structural stability of the metal oxide is being solved by introducing a second component in the metal oxide, which is due to segregation at the surface of the crystallites that prevents interaction between crystallites and their coalescence. However, the experiment showed that the introduction of the second component cannot completely prevent the growth of crystallites during high temperature annealing. Doping only reduces the possible structural changes in metal oxides.

Furthermore, the range of impurities which may be used in thermoelectric materials is very limited. First, these impurities must be donor or isoelectronic, i.e., electrically inactive. Second, the second metal oxide phase, which is formed during doping by these impurities, must be highly conductive. Third, the oxides formed by these elements must have a high melting temperature and these doping impurities should not form liquid phases due to eutectic reactions. Otherwise, the introduction of these elements will be accompanied by strong decrease in the conductivity or will stimulate structural changes in the film during the heat treatment. According to the available experimental results, the impurities that are contraindicated for use in thermoelectric $In_2O_3$ include Mg, Nb, Y, Mn, Si, Al, Lu and Fe.

In addition, the effect of crystallite size stabilization is usually observed at concentrations exceeding the solubility limit of these additives in the main metal oxide. Unfortunately, these concentrations are unacceptable for thermoelectric materials, since at these concentrations, there is an increase in resistance due to the increase in the concentration of structural defects [22] and a decrease in electron mobility.

Another factor that must be considered when choosing additives is the impact of these additions on the height of

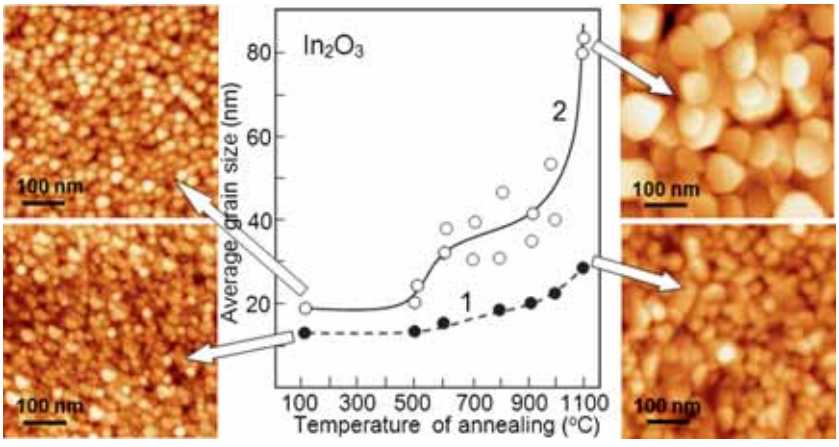


**Figure 5.** Dependences illustrating the influence of annealing on the average crystallite size in the $In_2O_3$ films deposited by spray pyrolysis at $T = 520$°C, and AFM images of these films after deposition and after annealing at 1100°C: 1—$d \sim 50$ nm, 2—$d \sim 200$ nm.

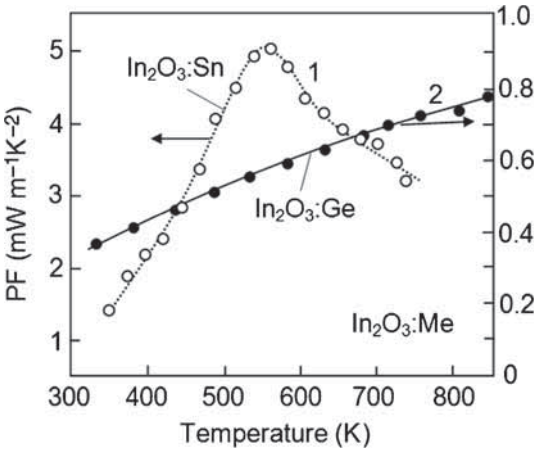


**Figure 6.** Experimental values of power factor as a function of temperature for (1) $In_2O_3$:Sn (5%) and (2) $In_2O_3$:Ge (5%) films. $In_2O_3$:Sn (5%) were deposited at $T_{pyr} = 350°C$. $In_2O_3$:Ge samples were prepared using standard solid reaction route ($T_{sint} = 1300°C$, $t = 48$ h in air) [12].

the potential barrier at the interface between crystallites. As shown earlier, exactly this parameter determines how effectively the filtration effect influences power factor. It seems that the $In_2O_3$ doping with tin allows the implementing of optimal parameters of the intergrain interface, providing maximum optimizing influence of the filtration effect on the power factor. The behaviour of the interface of crystallites after introduction of new additives is not known.

In the nanoscaled materials, it is also necessary to take into account the height of the potential barrier at the intergrain interface, which controls the conductivity of the film, depends on the concentrations of oxygen and water chemisorbed on the surface of the crystallites. As is known, the concentration of oxygen and water chemisorbed on the metal oxide surface is controlled by the surface processes and is dependent on both temperature and surrounding atmosphere including air humidity [23,24]. As a result, power factor of nanoscaled materials can have fundamentally different temperature dependences compared to sintered materials, where the influence of the surface effects on the value of PF is minimized (figure 6). Unlike a monotonic increase in power factor with increasing temperature observed for the sintered $In_2O_3$ films (figure 6, curve 2) [4,11], for nanoscaled $In_2O_3$ films, the appearance of a maximum at $T \sim 250°C$ is observed in $PF = f(T)$ dependences (figure 6, curve 1). This means that when using the nanoscaled materials, there are additional factors that require control. On the other hand, in this case, there are additional opportunities to influence the efficiency of thermoelectric conversion. In particular, through changes in temperature and the surrounding atmosphere, we see the possibility to influence the height of the potential barrier between the crystallites and thereby achieve maximum impact of the filtration effect on the thermoelectric conversion. For example, according to refs [23,24], at $\sim$250°C temperature, a maximum power factor is observed, which corresponds to the temperatures at which desorption of water from the surface of $In_2O_3$ and a slight decrease in $U_b$ take place. Considering the strong optimizing influence of filtration effect on the efficiency of thermoelectric conversion (figure 3), one can suggest that by controlling the surface state of the $In_2O_3$ crystallites, values of PF and ZT, acceptable for practical use, may be achieved at temperatures which are significantly below 1000°C. This will allow exploiting nanoscaled materials in thermoelectric convertors without the threat of degradation of their structural and electrophysical properties. It should be noted that the achievement of acceptable values of PF and ZT at decreased temperature gradient significantly reduces the requirements for materials and designs used in thermoelectric generators and greatly expands opportunities for their applications. Typically, thermal sources have a temperature, not exceeding 500–600°C.

## 4. Conclusions

The studies have shown that the use of nanoscaled $In_2O_3$:Sn films for thermoelectric conversion is promising direction. However, for successful commercial application of these materials, it is necessary to solve the problems associated with improving either stability of nanoscaled material's parameters at high temperatures or efficiency of thermoelectric conversion at intermediate temperatures. This means that it is necessary either to find impurities, which could stabilize the structure of nanoscaled materials, while maintaining their thermoelectric characteristics, or to create conditions to ensure maximum influence of the filtering effect on the efficiency of thermoelectric conversion. Taking into account that the chemisorption mechanism controls the formation of a potential barrier on the surface of metal oxides in the temperature range of 200–550°C, it is clear that the band-structure engineering becomes of particular importance for thermoelectric materials designed to operate at higher temperatures. In this context, clarification of the role of 'segregation mechanism' in the formation of a potential barrier on the surface of metal oxides at high temperatures is of considerable interest.

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## References

[1] Date A, Date A, Dixon C and Akbarzadeh A 2014 *Renew. Sust. Energ. Rev.* **33** 371

[2] Macklin W J and Moseley P T 1990 *Mater. Sci. Eng. B* **7** 111

[3] Koumoto K, Wang Y, Zhang Z, Kosuga A and Funahashi R 2010 *Annu. Rev. Mater. Res.* **40** 363

[4] Ohtaki M, Ogura D, Eguchi K and Arai H 1994 *J. Mater. Chem.* **4** 653

[5] Koumoto K, Funahashi R, Guilmeau E, Miyazaki Y, Weidenkaff A, Wang Y and Wa C 2013 *J. Am. Ceram. Soc.* **96** 1

[6] Zhu Q, Hopper E M, Ingram B J and Mason T O 2011 *J. Am. Ceram. Soc.* **94** 187

[7] Liu Y, Lin Y-H, Xu W, Cheng B, Lan J, Chen D, Zhu H and Nan C-W 2012 *J. Am. Ceram. Soc.* **95** 2568

[8] Lan J, Lin Y-H, Liu Y, Xu S and Nan C-W 2012 *J. Am. Ceram. Soc.* **95** 2465

[9] Liu Y, Xu W, Liu D-B, Yu M, Lin Y-H and Nan C-W 2015 *Phys. Chem. Chem. Phys.* **17** 11229

[10] Guilmeau E, Bérardan D, Simon Ch, Maignan A, Raveau B, Ovono D and Delorme F 2009 *J. Appl. Phys.* **106** 053715

[11] Berardan D, Guilmeau E, Maignan A and Raveau B 2008 *Solid State Commun.* **146** 97

[12] Fujita K, Mochida T and Nakamura K 2001 *Jpn. J. Appl. Phys.* **40** 4644

[13] Hicks L D and Dresselhaus M S 1993 *Phys. Rev. B* **47** 12727

[14] Simkin N V and Mahan G D 2000 *Phys. Rev. Lett.* **84** 927

[15] Dames C, Dresselhaus M S and Chen G 2003 *MRS Proc.* **793** 15

[16] Vashaee D and Shakouri A 2004 *Phys. Rev. Lett.* **92** 106103

[17] Brinzari V, Damaskin I, Trakhtenberg L, Cho B K and Korotcenkov G 2014 *Thin Solid Films* **552** 225

[18] Korotcenkov G, Brinzari V and Cho B K 2016 *Solid State Sci.* **52** 141

[19] Korotcenkov G, Cho B K and Brinzari V 2013 *Adv. Mater. Res.* **748** 22

[20] Brinzari V, Nika D L, Damaskin I, Cho B K and Korotcenkov G 2016 *Physica E* **81** 49

[21] Olav Løveng, Sunde T, Einarsrud M-A and Grande T 2013 *J. Eur. Ceram. Soc.* **33** 565

[22] Korotcenkov G and Cho B K 2014 *Sensor Actuat. B* **196** 80

[23] Korotcenkov G, Brinzari V, Stetter J R, Blinov I and Blaja V 2007 *Sensor Actuat. B* **128** 51

[24] Korotcenkov G, Blinov I, Ivanov M and Stetter J R 2007 *Sensor Actuat. B* **120** 679