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Anisotropic Thermoelectric Devices Made from Single-Crystal Semimetal Microwires in Glass Coating

L.A. KONOPKO,[1,3] A.A. NIKOLAEVA,[1] A.K. KOBYLIANSKAYA,[1] and T.E. HUBER[2]

1.—Ghitu Institute of Electronic Engineering and Nanotechnology, Academy of Sciences of Moldova, Chisinau, Republic of Moldova. 2.—Department of Chemistry, Howard University, Washington, DC 20059, USA. 3.—e-mail: l.konopko@nano.asm.md

Thermoelectric heat conversion based on the Seebeck and Peltier effects generated at the junction between two materials of type-*n* and type-*p* is well known. Here, we present a demonstration of an unconventional thermoelectric energy conversion that is based on a single element made of an anisotropic material. In such materials, a heat flow generates a transverse thermoelectric electric field lying across the heat flow. Potentially, in applications involving miniature devices, the anisotropic thermoelectric (AT) effect has the advantage over traditional thermoelectrics that it simplifies the thermoelectric generator architecture. This is because the generator can be made of a single thermoelectric material without the complexity of a series of contacts forming a pile. A feature of anisotropic thermoelectrics is that the thermoelectric voltage is proportional to the element length and inversely proportional to the effective thickness. The AT effect has been demonstrated with artificial anisotropic thin film consisting of layers of alternating thermoelectric type, but there has been no demonstration of this effect in a long single-crystal. Electronic transport measurements have shown that the semimetal bismuth is highly anisotropic. We have prepared an experimental sample consisting of a 10-m-long glass-insulated single-crystal tin-doped bismuth microwire (d = 4 μm). Crucial for this experiment is the ability to grow the microwire as a single-crystal using a technique of recrystallization with laser heating and under a strong electric field. The sample was wound as a spiral, bonded to a copper disk, and used in various experiments. The sensitivity of the sample to heat flow is as high as 10^{-2} V/W with a time constant τ of about 0.5 s.

Key words: Thermoelectric device, anisotropic thermoelement, bismuth, glass-insulated single-crystal microwire, flat spiral

INTRODUCTION

There is much interest on thermoelectric generators because they can be used in the field of alternative energy sources. Thermoelectric generators are solid-state devices that convert thermal energy into electric energy using thermoelectric (TE) materials such as Bi_2Te_3 and bismuth. Thermoelectric effects of electronic materials appear because, at the atomic scale, a temperature gradient causes charge carriers to diffuse from the hot side to the cold side, accompanied by a thermoelectric voltage. The large TE voltage that appears at the junction between two different thermoelectric materials, or the Seebeck effect, is the basis of most practical thermoelectric devices such as coolers and generators. One of the attractive properties of TE generators is that they can be used with a wide range of thermal energy sources including solar, radioactive decay thermal sources, and even body temperature.[1,2] Typical commercial thermoelectric

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devices, called modules, are made of a battery with a large number of thermoelectric elements of alternating type-*n* and type-*p*. The working principle is the Seebeck effect. The feasibility of the manufacture of a miniature thermoelectric device consisting of 102 elements with a cross-section of about 0.1 mm × 0.1 mm was demonstrated by Kishi et al.[3,4] Kishi was motivated by the problem of powering wristwatches without batteries. The Kishi TE device can harvest enough energy for the watch, tens of microwatts, from the user‘s skin in contact with the wristwatch. The device consisted of elements that were bonded into silicon substrates via solder bumps, cut with a dicing saw, and assembled into modules. Although this fabrication method was successfully demonstrated, this TE device has not received wide utilization maybe because it is not cost-effective due to the complex manufacturing. It would be very interesting to be able to achieve a high level of miniaturization in a simpler thermoelectric architecture. We have investigated a different approach, a method based on anisotropic thermoelectric materials. Snarsky et al.[5,6] and Anatychuk et al.[7] studied this problem theoretically, and it is called the transverse thermoelectric effect. In a crystal with anisotropic thermal conductivity, electrical conductivity, and Seebeck coefficient, a transverse component of the electric field appears if the heat flux passes in a direction that does not coincide with the principal axes of the crystal. The anisotropic thermoelectric (AT) effect has several advantages for miniature devices. In ATs, the thermopower is proportional to the temperature gradient, $(T_1 - T_2)l/h$, where $(T_1 - T_2)$ is the available temperature difference, h is the device transverse dimension (thickness t of a film) and l is the length. Thus, one can increase the thermoelectric voltage by simply decreasing h or increasing l.

Recently introduced $p \times n$-type transverse thermoeletrics,[8–10] in which the Seebeck coefficient changes sign depending on mutually perpendicular crystallographic directions, have a large transverse Seebeck coefficient. Thus, a quasi-one-dimensional metal, $Li_{0.9}Mo_6O_{17}$ (lithium purple bronze), has an extreme thermopower anisotropy along mutually perpendicular crystallographic axes (200 μV/K).[10] $p \times n$-type materials will allow the development of new types of thermoelectric applications on the microscale and at cryogenic temperatures. A laser-induced transverse Seebeck component was observed in *c*-axis-inclined thin film samples of manganite oxide $La_{1-x}Ca_xMnO_3$,[11,12] layered cobaltite Ca_xCoO_2,[13,14] high-temperature superconductors $YBa_2Cu_3O_{7-\delta}$,[15] $Bi_2Sr_2CaCu_2O_8$,[16] and oxyselenide BiCuSeO.[17] These samples have potential applications in fast response and highly sensitive photodetectors. The AT effect has been demonstrated with artificial anisotropic thin film consisting of layers of alternating thermoelectric type,[18] but there has been no demonstration of this effect in a long single-crystal. We have conducted experiments with bismuth which is an example that has good thermoelectric properties as indicated by a thermoelectric figure-of-merit, ZT, of 0.3,[19] is highly anisotropic and can be made into long single-crystal small-diameter wires. In this approach, rather than TE junctions, a single TE element is used. TE conversion is based on the anisotropy of thermopower.

SAMPLES AND EXPERIMENT

We studied the possibility of using glass-insulated Bi and Bi-Sn microwires to design an anisotropic thermoelectric generator (ATG) and a heat flux sensor (HFS). Glass-insulated microwires of pure and Sn-doped Bi were prepared by the Ulitovsky method[20] (see inset in Fig. 1a). The microwires were cylindrical single-crystals with the $(10\bar{1}1)$ orientation along the wire axis; the C_3 axis was inclined at an angle of 70° to the wire axis. This technique described in[21,22] makes it possible to prepare single-crystal wires with diameters d of 50 μm to 40 nm. We prepared continuous glass-insulated single-crystal microwires of Bi and Bi-Sn alloys with a length of up to a few tens of meters and with a given diameter of 0.5–50 μm. A scanning electron microscope image of a 1.3-μm glass-insulated Bi microwire is shown in Fig. 1a.

Transverse thermopower is defined as $S_{\text{trans}} = U/\Delta T$, where U is the voltage across the sample and ΔT is the transverse temperature gradient. We constructed a special setup consisting of two Al plates with different temperatures, which was used to measure transverse thermoelectric power in a 4.5-cm-long microwire.[23] Displacements of the plates relative to each other cause the rotation of the microwire; therefore, it is possible to record dependence of the transverse thermopower on the direction of the temperature gradient. Contacts to the microwires were made using liquid eutectic InGa, which prevented the microwire from twisting during rotation. This setup allows recording the dependence of microwire magnetoresistance (TMR) on the direction of the transverse magnetic field, and thus determining the orientation of the main crystallographic axes of the microwire. For this purpose, aside from the plates, two neodymium permanent magnets, which generate a transverse magnetic field of ~ 0.5 T, were used. The detailed arrangement of a Bi microwire in the special setup, and the necessary orientation of the main crystallographic axes in the microwire to provide the maximum output voltage of the anisotropic thermoelement (ATE) obtained by winding the single-crystal microwire into a flat spiral, are described in Ref. 23. All measurements of the transverse thermopower of the microwires were performed at room temperature. For measurements of the temperature dependence of the thermopower, a Leybold 4.2 GM cryocooler was employed.

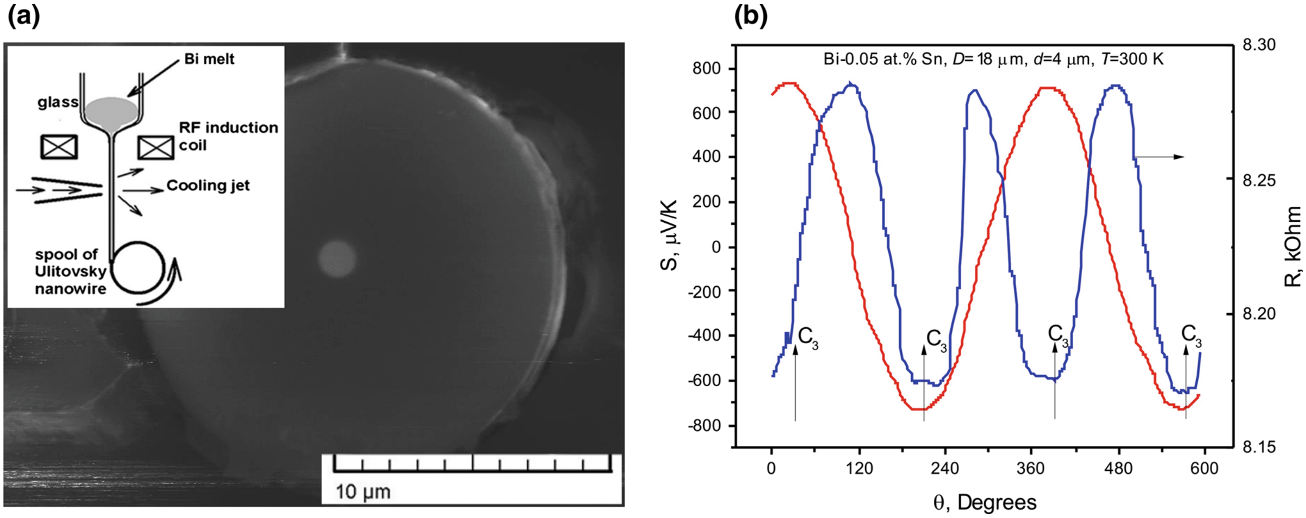

Fig. 1. (a) Scanning electron microscope image of a 1.3-μm glass-insulated Bi microwire. Inset the Ulitovsky method for preparation of long glass-insulated wires with small diameters. (b) Dependences of (left axis) the transverse thermopower on the direction of the temperature gradient and (right axis) transverse magnetoresistance (TMR) on the direction of magnetic field for a Bi-0.05at.%Sn microwire (D = 18 μm, d = 4 μm) after pooling of the wire through a zone-melting recrystallization setup in a strong inclined (β = 54°) electric field.

RESULTS AND DISCUSSION

To determine the optimum geometric parameters of a microwire and the optimum orientation of the main crystallographic axes of a single-crystal microwire relative to the transverse temperature gradient, transverse thermopower in thin glass-insulated single-crystal Bi and Bi-Sn microwires with various diameters d was studied. The measurement results for the Bi-0.05at.%Sn microwire sample with D = 18 μm and d = 4 μm are shown in Fig. 1b. The rotation diagrams of TMR of large single-crystal samples of bismuth, doped bismuth, and bismuth antimony were studied experimentally and theoretically.[24] The observed anisotropy of TMR in Fig. 1b can be accounted for by the shape of the Fermi surface, where the Fermi surface in the microwire is almost the same as in the bulk conductor. It is evident from the rotation diagrams of TMR that the transverse thermopower is maximal if the temperature gradient is directed towards the C_3 axis. Thus, we confirmed the previously obtained result[23] about the preferred orientation of the main crystallographic axes in bismuth microwires to obtain the maximum transverse thermopower. Moreover, we measured the transverse thermopower in the same nanowires before and after the use of recrystallization in a strong inclined electric field. We observed that the transverse thermopower increases by 15% after that heat treatment.

Voltage E that arises on the ATE outputs is as follows[5,6,25]:

$$E = \alpha_{12}\Delta T\frac{a}{b} = (\alpha_{33} - \alpha_{11})\sin\beta\cos\beta\,\Delta T\frac{a}{b} = (\alpha_{33} - \alpha_{11})\sin 2\beta\,\frac{1}{2b}\frac{Q_z}{\kappa_{33}\sin^2\beta + \kappa_{11}\cos^2\beta} \qquad (1)$$

where α_{11} and α_{33} are the thermopower along the C_1 and C_3 axes, respectively, $\alpha_{33} - \alpha_{11}$ is the anisotropy of the thermopower, β is the inclination angle of the C_3 crystallographic axis relative to the sample axis, ΔT is the transverse temperature gradient, a is the length of the sample, b is the thickness of the sample, Q_z is the heat flux through the ATE, and κ_{11} and κ_{33} are the thermoconductivity along the C_1 and C_3 axes, respectively.

Volt–Watt sensitivity of the ATE is as follows:

$$s = \frac{E}{Q_z} = \frac{(\alpha_{33} - \alpha_{11})\sin\beta\cos\beta}{b(\kappa_{33}\sin^2\beta + \kappa_{11}\cos^2\beta)} \qquad (2)$$

For the Bi samples, the maximum sensitivity is achieved at angle β:

$$\beta_{\text{opt}} = \pm\,\text{arctg}\sqrt{\frac{\kappa_{11}}{\kappa_{33}}} = 52.78^\circ \qquad (3)$$

To achieve the maximum efficiency of the anisotropic device based on Bi, it is necessary to provide an inclination angle β of the C_3 axis of 52.8°. We have developed a novel technology of recrystallization of glass-insulated Bi and Bi-Sn single-crystal microwires in a high electric field. This technology makes it possible to obtain single-crystal microwires and change the orientation of the main crystallographic C_3 axis along the direction of a high electric field. The resulting recrystallized glass-insulated microwires can be bent at a radius of 2 mm without breaking. This feature allowed using the developed recrystallization technology for winding the microwire into a flat spiral directly at the output of the setup; moreover, the orientation of the C_3 axis in the wire will be the same at all points of the wound

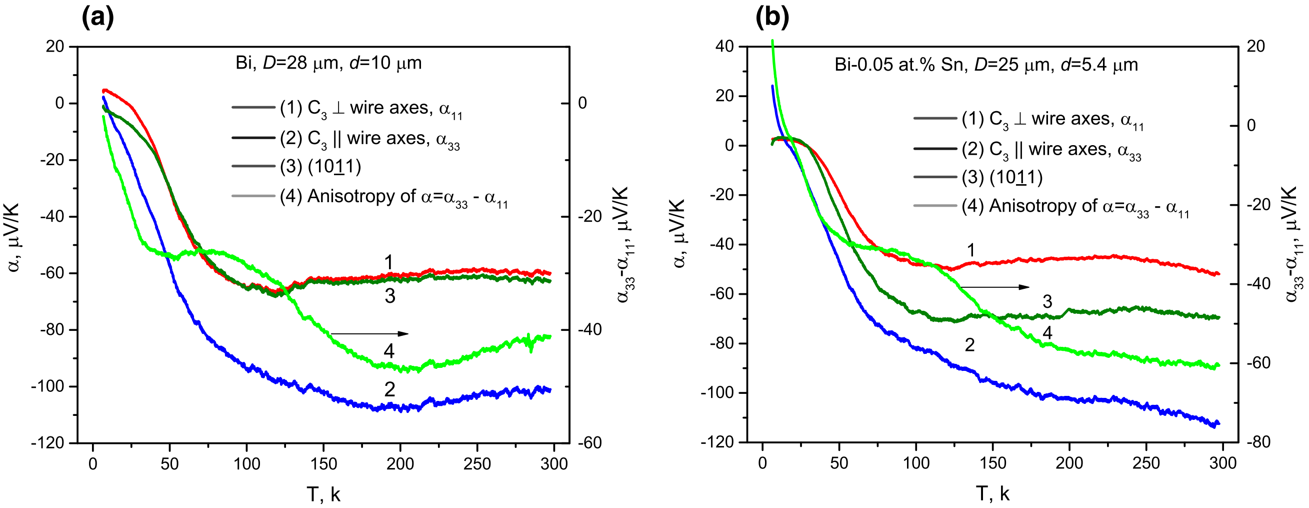

Fig. 2. (a) Temperature dependences of thermopower for Bi microwires samples ($D = 28$ μm, $d = 10$ μm) after high voltage recrystallization: (1) the microwire aligned along the C_1 axis; (2) the microwire aligned along the C_3 axis; (3) without recrystallization, the C_3 axis inclined to the microwire axis at an angle of 70°; and (4) anisotropy of thermopower, $\Delta\alpha = \alpha_{33} - \alpha_{11}$. At room temperature $\Delta\alpha \approx 40$ μV/K. (b) Temperature dependences of thermopower for Bi-0.05at.%Sn microwires samples ($D = 25$ μm, $d = 5.4$ μm) after high voltage recrystallization: (1) the microwire aligned along the C_1 axis; (2) the microwire aligned along the C_3 axis; (3) without recrystallization, the C_3 axis inclined to the microwires axis at an angle of 70°; and (4) anisotropy of thermopower, $\Delta\alpha = \alpha_{33} - \alpha_{11}$. At room temperature, $\Delta\alpha = 60$ μV/K.

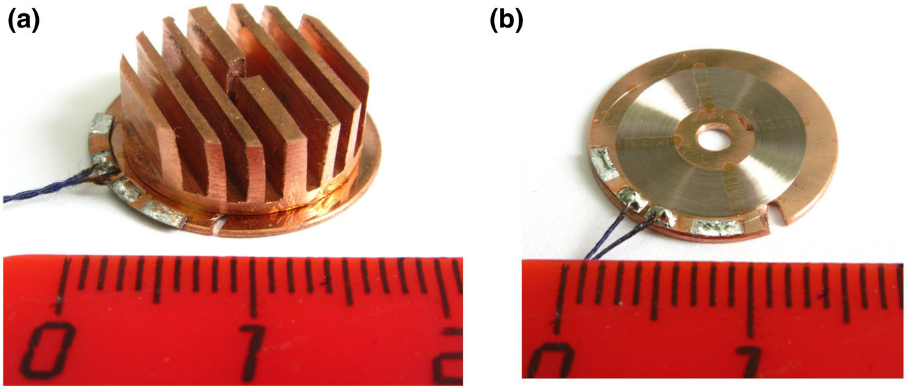

Fig. 3. Experimental samples of the anisotropic thermoelectric devices. (a) An ATG made of a long ($l \approx 10$ m) glass-insulated single-crystal Bi-0.05at.%Sn microwire ($D = 20$ μm, $d = 4$ μm) wound into a flat spiral. In the last stage of preparation of the ATG, a copper radiator was glued onto the flat spiral. (b) A HFS made of a long ($l = 9.9$ m) glass-insulated single-crystal Bi-0.05at.%Sn microwire ($D = 18$ μm, $d = 4$ μm) wound into a flat spiral.

spiral; this feature will provide high thermoelectric efficiency of the designed ATE. The schematic of the ATE prepared of a long Bi microwire wound into a flat spiral[26] is described in Ref. [23].

Thermoelectric efficiency Z_a of the ATE depends on the anisotropy of thermopower $\Delta\alpha = \alpha_{33} - \alpha_{11}$, as follows[5,6,9,10]:

$$Z_a = \frac{(\alpha_{33} - \alpha_{11})^2 \sin^2\beta \cos^2\beta}{(\kappa_{33}\sin^2\beta + \kappa_{11}\cos^2\beta)(\rho_{33}\cos^2\beta + \rho_{11}\sin^2\beta)} \tag{4}$$

where κ_{11} and κ_{33} are the components of the tensor of thermal conductivity, and ρ_{11} and ρ_{33} are the components of the tensor of resistivity. To study the anisotropy of the thermopower, samples of Bi and Bi-Sn microwires with various orientations of the C_3 axis were prepared by microwire recrystallization in a high electric field. Temperature dependences of thermopower for Bi ($D = 28$ μm, $d = 10$ μm) and Bi-0.05at.%Sn ($D = 25$ μm, $d = 5.4$ μm) microwires are shown in Fig. 2. The $\Delta\alpha$ value at room temperature in the 10-μm Bi microwire is 40 μV/K, while the anisotropy of the thermopower in the 5.4-μm Bi-0.05at.%Sn microwire is 60 μV/K. Therefore, the Bi-0.05at.%Sn microwire ($D = 18$ μm, $d = 4.2$ μm) was used to prepare an ATG and a heat flux sensor (HFS). The transverse thermopower for this microwire prepared by recrystallization in a strong inclined ($\beta = 54°$) electric field is 730 μV/K at room temperature and an effective length of the wire is $L = 4.5$ cm (see Fig. 1b). In this case, the specific transverse thermopower is $S_{\mathrm{special}} = S_{\mathrm{trans}}/4.5 = 162\ \mu$V/(K cm). To obtain a voltage of 1 V at a transverse temperature gradient ΔT of 5 K, it is necessary to use a microwire with a length of 12 m. The resistance of the microwire will be $R = 1$ MΩ, and the maximum current of that generator $I_{\max}$will be 1×10^{-6} A. We prepared an experimental sample of an ATG consisting of a 10-m-long glass-insulated single-crystal Bi-0.05at.%Sn microwire ($D = 20\ \mu$m, $d = 4\ \mu$m). In the last stage of preparation of the ATG, a copper radiator was glued onto the flat spiral. The experimental ATG sample is shown in Fig. 3a. Tests of the sample by bringing the ATG in contact with a surface at 36°C (the temperature of the human hand) showed a peak output of a fraction of a volt (210 mV) and an output power of as low as 2 nW. The output voltage is suitable for interfacing with harvesting circuits. Since the power is low, one of the objectives of optimization is to increase the power by an order of magnitude. In addition, we prepared an experimental sample of a HFS consisting of a 9.9-m-long single-crystal Bi-0.05at.%Sn microwire ($D = 18\ \mu$m, $d = 4\ \mu$m). The experimental HFS sample is shown in Fig. 3b. The sensitivity of the HFS is high ($s \sim 10^{-2}$ V/W); however, the time constant is $\tau \approx 0.5$ s. Our devices have slow responses, which can be possibly attributed to the use of microwires coated with a thick glass layer ($t \approx 7\ \mu$m). Our plan of optimization involves the development of methods for thinning the glass insulation of the wire. The prepared experimental samples show that it is possible to use a single-crystal Bi-0.05at.%Sn microwire in anisotropic thermoelectric devices.

CONCLUSIONS

The transverse thermopower in thin single-crystal Bi and Bi-Sn microwires at room temperature has been studied. The maximum transverse thermopower has been found for the temperature gradient directed toward the C_3 axis. A new material—Bi-0.05at.%Sn—has been found; at room temperature, it has high thermopower anisotropy of $\sim 60\ \mu$V/K, which is 1.5 times higher than the thermopower anisotropy in the pure bismuth microwire. A technology of zone-melting recrystallization of microwires in a high electric field, which allows controlling the direction of the C_3 axis during the preparation of ATEs, has been developed. The use of this technology made it possible to increase the transverse thermopower of Bi-0.05at.%Sn microwires in comparison with microwires of $(10\bar{1}1)$ standard orientation by more than 15%. An experimental sample of an ATG has been prepared of a long ($l \approx 10$ m) glass-insulated single-crystal Bi-0.05at.%Sn microwire ($D = 20\ \mu$m, $d = 4\ \mu$m) wound into a flat spiral. If the ATG is in contact with a surface at 36°C (the temperature of the human hand), then the peak output is a fraction of a volt (210 mV). In addition, an experimental sample of a HFS consisting of a 9.9-m-long glass-insulated single-crystal Bi-0.05at.%Sn microwire ($D = 18\ \mu$m, $d = 4\ \mu$m) has been prepared. The sensitivity of the HFS is high ($s \sim 10^{-2}$ V/W); however, the time constant is $\tau \approx 0.5$ s. Our devices have slow responses, which can be possibly attributed to the use of microwires coated with a thick glass layer ($t \approx 7\ \mu$m).

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. D.M. Rowe, *Modules, Systems, and Applications in Thermoelectrics* (Boca Raton: CRC Press, 2012).
2. M. Ki, M.S. Kim, S. Kim, C.Kim. Lee, and Y.J. Kim, *Smart Mater. Struct.* 23, 105002 (2014).
3. Thermic, Seiko Watches, THE SEIKO MUSEUM, http://museum.seiko.co.jp/en/collections/clock_watch/category3/collect041.html.
4. M. Kishi, Y. Yoshida, H. Okano, H. Nemoto, Y. Funanami, M. Yamamoto, and H. Kanazawa, in *Proceedings ICT'97*, pp. 653–656 (1997).
5. A.A. Snarskii, A.M. Palti, and A.A. Ascheulov, *Fiz. Tekh. Poluprovod.* 31, 1281 (1997).
6. A.A. Snarskii and L.P. Bulat, in *Thermoelectrics Handbook: Macro to Nano,* ed. by D.M. Rowe (CRC Press, New York, 2006), Ch. 45.
7. L.I. Anatychuk and A.V. Prybyla, *J. Electron. Mater.* 40, 1304 (2011).
8. C. Zhou, Y. Tang, K. Heinselman, S. Birner, and M. Grayson, *Phys. Rev. Lett.* 110, 227701 (2013).
9. Y. Tang, B. Cui, C. Zhou, and M. Grayson, *J. Electron. Mater.* 44, 2095 (2015).
10. J.L. Cohn, S. Moshfeghyeganeh, C.A.M. dos Santos, and J.J. Neumeier, *Phys. Rev. Lett.* 112, 186602 (2014).
11. X.H. Li, H.-U. Habermeier, and P.X. Zhang, *J. Magn. Magn. Mater.* 211, 232 (2000).
12. K. Zhao, K.-J. Jin, Y.-H. Huang, H.-B. Lu, M. He, Z.-H. Chen, Y.-L. Zhou, and G.-Z. Yang, *Phys. B* 373, 72 (2006).
13. T. Kanno, S. Yotsuhashi, and H. Adachi, *Appl. Phys. Lett.* 85, 739 (2004).
14. T. Kanno, K. Takahashi, A. Sakai, H. Tamaki, H. Kusada, and Y. Yamada, *J. Electron. Mater.* 43, 2072 (2014).
15. Z.H. He, Z.G. Ma, Q.Y. Li, Y.Y. Luo, J.X. Zhang, R.L. Meng, and C.W. Chu, *Appl. Phys. Lett.* 69, 3587 (1996).
16. Th. Zahner, R. Schreiner, R. Stierstorfer, O. Kus, S.T. Li, R. Roessler, J.D. Pedarunig, D. Baüerle, and H. Lengfellner, *Europhys. Lett.* 40, 673 (1997).
17. G. Yan, L. Wang, S. Qiao, X. Wu, S. Wang, and G. Fu, *Opt. Mater. Express* 6, 558 (2016).
18. Th. Zahner, R. Forg, and H. Lengfellner, *Appl. Phys. Lett.* 73, 1364 (1998).
19. H.J. Goldsmid, *Introduction to Thermoelectricity* (Berlin: Springer, 2010).
20. V.S. Larin, A.V. Torcunov, A. Zhukov, J. González, M. Vazquez, and L. Panina, *J. Magn. Magn. Mater.* 249, 39 (2002).
21. N. Brand, D. Gitsu, A. Nikolaeva, and Ya. Ponomarev, *Sov. Phys. JETP* 45, 1226 (1977).

22. D. Gitsu, L. Konopko, A. Nikolaeva, and T. Huber, *Appl. Phys. Lett.* 86, 102105 (2005).
23. L. Konopko, A. Nikolaeva, T. Huber, and A. Tsurkan, in *IFMBE Proceedings, vol 55*, pp. 119–122 (2016).
24. D.M. Jacobson, *Phys. Status Solidi B* 58, 243 (1973).
25. A. Mityakova, S. Sapozhnikov, V. Mityakov, A. Snarskii, M. Zhenirovsky, and J. Pyrhonena, *Sensors Actuators A* 176, 1 (2012).
26. L. Konopko, A. Nikolaeva, P. Bodiul and A. Tsurkan, *MD Patent No.* 4333 (2015).