Article

A Novel Method to Significantly Improve the Mechanical Properties of n -Type $\text{Bi}_{(1-x)}\text{Sb}_x$ Thermoelectrics Due to Plastic Deformation

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Abstract: A unique method was developed to significantly improve the strength of $\text{Bi}_{(1-x)}\text{Sb}_x$ single crystals, the most effective thermoelectric (TE) materials in the temperature range from 100 to 200 K due to their plastic deformation by extrusion. After plastic deformation at room temperature under all-round hydrostatic compression in a liquid medium, n -type Bi–Sb polycrystalline solid solutions show a significant increase in mechanical strength compared to Bi–Sb single crystals in the temperature range from 300 to 80 K. The significantly higher strength of extruded alloys in comparison with Bi–Sb single crystals is associated with the development of numerous grains with a high boundary surface as well as structural defects, such as dislocations, that accumulate at grain boundaries. Significant stability of the structure of extruded samples is achieved due to the uniformity of crystal plastic deformation under all-round hydrostatic compression and the formation of the polycrystalline structure consisting of grains with the orientation of the main crystallographic directions close to the original single crystal. The strengthening of Bi–Sb single crystals after plastic deformation allows for the first time to create workable TE devices that cannot be created on the basis of single crystals that have excellent TE properties, but low strength.

Keywords: Bi–Sb crystals; plastic deformation; room temperature extrusion; hydrostatic pressure; liquid medium

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1. Introduction

A significant increase in the efficiency of thermoelectric (TE) cooling at temperatures below 200 K is currently one of the urgent problems of thermoelectricity. $(\text{Bi,Sb})_2(\text{Te,Se})_3$ solid solutions have remained the preferred thermoelectric materials for cooling purposes for many decades [1]. However, at cold temperatures of $T_c \leq 200$ K, thermoelectric materials based on Bi_2Te_3 compounds are not effective for refrigeration due to low thermoelectric efficiency at these temperatures [1–3]. Their figure of merit Z for both n - and p -type legs does not exceed $2.5 \times 10^{-3} \text{ K}^{-1}$ at $T = 200$ K, restricting their practical application at cold temperatures of $T_c \leq 200$ K [2–5].

An effective way to increase the efficiency of the TE device at cold temperatures is to maximize Z values. The most effective known thermoelectric (TE) materials at temperatures of $T \leq 180$ K are single crystals of n -type Bi–Sb solid solutions with Sb content from 7 to 15 at.% [2–5]. Below this temperature, the Z value of these crystals is two to three times higher than that of the best n -type TE materials based on $\text{Bi}_2(\text{Te,Se})_3$ solid solutions in a transverse magnetic field of $B \leq 1$ T [3,5]. The thermoelectric properties of these TEs were first measured more than 100 years ago by G. Gehlhoff and F. Neumeier, as indicated by Smith and Wolfe [6], but in all of the early works on these materials, polycrystalline specimens of unknown purity were used. The ultimate bending strength σ_b of these Bi–Sb single crystals can reach 40 MPa at room temperature when the loading force is

perpendicular to the trigonal axis [3,7–9]. To improve the bending strength of Czochralski-grown ingots, the effect of the growth parameters and the size and surface quality of the samples on σ_b has been investigated in detail by Belaya et al. [3,7]. At 77 K, the bending strength σ_b is relatively low (10–20 MPa); for example, when the bending force in a three-point test is orientated along the $\langle 10\bar{1} \rangle$ and $\langle 1\bar{2}1 \rangle$ axes, the σ_b values of $\text{Bi}_{0.91}\text{Sb}_{0.09}$ single crystals were about 18–28 MPa [8]. At $T < 200$ K, it is promising to use n -type branches from Bi–Sb single crystals together with superconducting branches from high-temperature superconductors instead of p -type branches [8,9].

However, single crystals of Bi–Sb solid solutions have not received practical application as a material for TE legs. This is mainly due to the ease of cleavage of single-crystal branches along the (111) plane perpendicular to the direction of the maximum values of Z [2,5,7,10]. In other words, Bi–Sb single crystals cannot withstand any bending along their trigonal axis, although it is in this direction that the figure of merit is the best. Therefore, the decisive condition for the successful use of TE-legs from Bi–Sb solid solutions is the development of methods for increasing the strength properties of these TE materials.

The processing (hot and cold pressing, extrusion, etc.) of polycrystalline TE materials may significantly affect the microstructure and improve their properties. A number of works indicate that extruded Bi–Sb solid solutions are promising as n -type TE material at temperatures of $T \leq 180$ K [2,5,8–10]. Extrusion of Bi–Sb materials may introduce a preferential orientation of the grains. From a thermoelectric point of view, the presence of a strong texture in this material would be favorable. Actually, if all the grains could be orientated so that their trigonal axes are nearly parallel, then their thermoelectric properties should approach those of the single crystals [2–4]. Annealing the extruded Bi–Sb alloys restores high mobility of electrons but destroys the preferred grain orientation in the $\langle 111 \rangle$ direction along the extrusion axis. As a result of high deformation during extrusion and subsequent annealing of Bi–Sb alloys, a textured polycrystal structure is formed with a characteristic grain size of 0.02–0.05 mm and high-angle grain boundaries [5,8].

Mechanical alloying of the elemental materials as reported by Martin-Lopez et al. [10] is also a powerful method for the synthesis of homogeneous powders of the $\text{Bi}_{(1-x)}\text{Sb}_x$ alloy at $x = 0.07, 0.1, 0.12, 0.15, 0.22$, with grain sizes about 10 μm , using relatively short milling times (4–15 h). The mechanical properties of the $\text{Bi}_{0.85}\text{Sb}_{0.15}$ alloy prepared by mechanical alloying and consolidated by hot extrusion were investigated at two fixed temperatures (77 and 293 K). The modulus of rupture of the polycrystalline material was roughly the same at these temperatures, with a value of about 100 MPa compared to 10 and 20 MPa for a $\text{Bi}_{0.85}\text{Sb}_{0.15}$ single crystal [10]. However, sintering methods offer the advantage of improving the mechanical strength of alloys but, unfortunately, degrade the thermoelectric performance as a result of random orientation. Moreover, impurities such as oxygen during power elaboration could be factors hindering improvement of the figure of merit [2].

However, the application of known extrusion methods [11] to Bi–Sb solid solutions does not make it possible to obtain a material possessing high strength and thermoelectric characteristics simultaneously. The effect of plastic deformation during extrusion on the structural, mechanical, and TE properties of Bi–Sb solid solutions has been little studied. This work is devoted to the development of a method for cold deformation of Bi–Sb single crystals at high hydrostatic pressure, which will improve the strength characteristics of the material without substantial decrease in the TE efficiency. A detailed study of the structure, texture, and mechanical properties of deformed Bi–Sb alloy was carried out in the temperature range from 300 to 80 K.

2. Materials and Methods

2.1. Growth of Single Crystals

The initial $\text{Bi}_{0.91}\text{Sb}_{0.09}$ single crystals were obtained using the Czochralski method [3,5,9,12–14], which is currently used in the production of more than half of the technically important crystals grown from the melt; at the same time, about 60% of all single crystals are used to obtain semiconductors [13]. The single crystal was grown on a single crystal

seed, and the melt was fed with solid antimony during the growth without additional alloying. The purity of the starting materials was 99.9999%. The single crystals 25–35 mm in diameter and 40–50 mm in length were grown in an atmosphere of high-purity helium at 140–150 kPa at the crystal pulling speed of $1.7 \times 10^{-6} \text{ m s}^{-1}$.

2.2. Extrusion of Single Crystals

To increase the strength of $\text{Bi}_{0.91}\text{Sb}_{0.09}$ single crystals, the method for their plastic deformation in a liquid medium at high hydrostatic pressure was used [5,8,9], for which the scheme and view of the extruder are shown in Figure 1. Here, castor oil used as a working fluid was first compressed to a pressure P , and the TE material was then extruded. Bi-Sb single-crystal samples for plastic deformation 12 mm in diameter and length of 25–30 mm were cut on an electric discharge machine and etched in concentrated HNO_3 to remove the damaged layer of 40–50 μm depth. The cylindrical axis was oriented along the trigonal axis [111] of the single crystal.

Figure 1. Schematic diagram of plastic deformation of Bi-Sb crystals at high hydrostatic pressure (a) and the view of the extruder (b). 1—hydrostat plunger, 2—high pressure chamber, 3—working fluid, 4—extruder plunger, 5—Bi-Sb single crystal, 6—die, 7—as extruded polycrystalline TE material, 8—lower support ring.

For extrusion, blanks with a smooth surface without visible cracks were used. Quality control of the workpiece surfaces was carried out using an MBS-9 binocular microscope. The pressure of the working fluid P required for the extrusion was selected based on the microhardness HV of $\text{Bi}_{0.91}\text{Sb}_{0.09}$ single crystals, which was measured using a PMT-3 microhardness tester on the cleavage plane (111) at room temperature and ranged from 460 to 500 MPa. Considering the plastic deformation of a crystal with an internal crack placed in a medium with a high hydrostatic pressure P , a criterion $P > \text{HV}$ was developed for preventing crystal cracking during plastic deformation, where HV is the microhardness of the crystalline material. To perform plastic deformation of $\text{Bi}_{0.91}\text{Sb}_{0.09}$ single crystals at room temperature ($T = 300 \text{ K}$), the pressure P of the surrounding liquid was chosen as 600–1100 MPa.

The extrusion process in a hydrostat consists of two stages: preparatory and extrusion. In the preparatory phase, the working fluid is compressed as the plunger moves inside the pressure chamber, prior to extrusion of the TE material. The preparatory stage ends when the hydrostat plunger contacts the extruder plunger. Extrusion ratio, showing how many times the length increased or the cross-sectional area of the product decreased in one pass of extrusion, was 1.2, 3, 5, and 10.

2.3. Study of the Crystal Structure of Single Crystals and Extruded Specimens

The deformation of the material in the surface layer occurs under conditions that differ significantly from the conditions of deformation of the bulk of the crystal. Therefore, the crystal structure of the surface layer differs from the crystal structure of the bulk of the crystal. The 10–15 μm thick surface layer was removed by etching in 70% nitric acid; then, the sample was washed sequentially in concentrated hydrochloric acid, distilled water, and isopropyl alcohol and dried.

For structural study of the perfection of the grown crystals, a method with reflection recording was used. In this case, the cleavage plane (111) was investigated. For the topographic study, the Schultz method was used with a point source of white X-ray radiation [15,16]. The cleavage plane of the sample was located at an angle of 20–25° to the source. On radiographs, the surface protrusions are displayed as light stripes, and the depressions are dark. The width of these stripes was used to determine the angle of disorientation of the substructural components. Additionally, the divergent beam X-ray technique [17] has been used for precision measurement of the lattice period of perfect single crystals and for studying structural changes in deformed crystals. By changing the shape and width of the lines, it is possible to determine the angles of rotation of the substructural components of the crystal and the perfection of a small region with a length of 10–50 μm .

To determine the quantitative characteristics of the preferential structural orientation, we used a model in which the texture of a real crystal is considered as a combination of perfectly oriented substructures corresponding to the observable crystalline textures. In this model, a technique for magnetometric analysis was developed, which is almost independent of the state of grain boundaries, the presence of micropores at grain boundaries, as well as inevitable fluctuations in the concentration of impurities and composition [18]. This method is based on the magnetic properties of Bi–Sb crystals, which are anisotropic diamagnets at room temperature, with a weak dependence of the magnetic susceptibility on composition.

The rotating moment which acts on a textured diamagnetic sample of the mass m in a magnetic field can be determined through the free energy of the sample F as [18]

$$M(\varnothing) = -\partial F / (\partial \varnothing) = -M \sum_i w_i \partial f_i / \partial \varnothing \quad (1)$$

where i is one of the textures, $w_i = m_i/m$ is the specific content of the i th texture; f_i is the specific (per unit mass) free energy of the i th texture in the magnetic field, and $\varnothing$ is the angle between the chosen direction in the sample, which is usually the one with the highest symmetry.

The magnetic properties of single crystals of diamagnetic Bi–Sb alloys are determined by two main values of the specific magnetic susceptibility tensor, namely k_3 along the (111) trigonal axis and k_1 perpendicular to the (111) direction. If the (111) axis in the i th texture is tilted at an angle $\varnothing_i$ to the direction of the uniform magnetic field H , then

$$f_i = -\frac{1}{2} H^2 [k_3 - (k_1 - k_3) \sin^2 \varnothing_i]. \quad (2)$$

By varying the orientation of poly- and monocrystalline samples with respect to the magnetic field so that the rotating moments are maximal for the given field, we obtain the specific content of the prevailing texture

$$w_1 = m_0/m \times (H_0/H)^2 \times \overline{M}/\overline{M}_0 \quad (3)$$

where $\overline{M}$ and $\overline{M}_0$ are the maximal rotating moments for a textured polycrystal in the field H and for a single crystal of the same composition in the field H_0 , respectively.

Since Bi–Sb alloys have a predominant <111> texture at a degree of deformation over 90%, the {111} axial texture prevails, and in this case, the {111} basal planes of the grains are oriented along the extrusion axis. Using this method, which does not require direct

measurements of the magnetic susceptibility, the content of texture $\langle 111 \rangle$ ($W_{\langle 111 \rangle}$) was obtained by changing the orientation of the polycrystalline samples with respect to the magnetic field so that the torques were maximum for a given field.

2.4. Three-Point Bending Test of $\text{Bi}_{0.91}\text{Sb}_{0.09}$ Alloy

A schematic diagram of the rhombohedral and hexagonal lattice of Bi–Sb solid solutions is shown in Figure 2a. A hexagonal lattice system is conventionally used with $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$, and $\vec{c}$ lattice vectors. The angles between the $\vec{a}$ vectors equal 120° , and they lie in the plane normal to the $\vec{c}$ vector. A Cartesian coordinate system is also shown with axes denoted binary (OX), bisectrix (OY), and trigonal (OZ). The trigonal axis is aligned with the $\vec{c}$ direction in the lattices. The bisectrix axis is defined as being orthogonal to the trigonal and binary axes.

Figure 2. The main axes of the Bi–Sb crystal lattice (a) and the bending test scheme (b). (a) a_1 , a_2 , and a_3 are binary axes in a hexagonal lattice, where a_1 coincides with the OX axis, OY is the bisectrix axis, and OZ coincides with the trigonal and extrusion axes. (b) 1—loading prism, 2—sample, 3—supports, B–C—line of maximum tensile forces T_s ; h and b are the height and width of the specimen, respectively, l —distance between the supports. Bending force F_b is parallel to the extrusion axis ($F_b \parallel OZ \parallel \langle 10\bar{1} \rangle$ or $\langle \bar{1}21 \rangle$).

For n -type branches from Bi–Sb crystals, the most dangerous deformation is bending perpendicular to the direction of maximum TE efficiency, which coincides with the trigonal axis for single crystals or with the extrusion axis for crystals after plastic deformation. Therefore, from the point of view of their use as a TE material, the most important strength parameter for crystals of Bi–Sb solid solutions is the ultimate bending strength σ_b , when a bending force F_b is applied perpendicular to the trigonal or extrusion axis. Bending tests of samples by the three-point test method (Figure 2b) were carried out on an Instron 37-10-16 at temperatures of 77–300 K in a special chamber cooled with a mixture of gaseous and liquid nitrogen [9].

The surfaces of the samples undergoing bending were carefully mechanically ground and then chemically polished in a solution composed of 250 mL of H_2O + 70 mL of HCl + 83 g of CrO_3 . The thickness of the removed layer was 5–10 μm . The average grain size in polycrystals of extruded samples was determined on the basis of the number N of grains observed in a given area $S = 0.5 \times 0.5 \text{ mm}^2$, containing at least 100 grains. Then, the diameter d of a circle with an area equal to the area of one grain was determined. The value d was taken as the average grain size:

$$d = (4/\pi)^{0.5} (S/N)^{0.5} \quad (4)$$

In bending tests, Bi–Sb crystals of rectangular cross-section were used with dimensions $h = (1 \pm 0.1)$ mm, $b = (4 \pm 0.1)$ mm, $l = 10 \pm 0.1$ mm, for which $l/h \approx 10$, which justifies the application of the Equations (5) and (6) for calculation of the maximum tensile deformation ε_b and strength σ_b during bending [19]:

$$\varepsilon_b = 6 \cdot \Delta_b \cdot h / l^2, \quad (5)$$

$$\sigma_b = 1.5 \cdot F_b \cdot l / (b \cdot h^2), \quad (6)$$

where Δ_b is the maximum deflection of the specimen and F_b is the bending force.

3. Results

3.1. Crystal Structure of $\text{Bi}_{0.91}\text{Sb}_{0.09}$ Single and Polycrystalline Crystals

The dislocations within and at the boundaries of the blocks are responsible for the total rotation field of the crystal lattice. In Figure 3a, an X-ray diffraction pattern of Bi–Sb crystals is presented. The shape and width of the diffraction lines indicate the high perfection of the grown crystals. Figure 3b shows the images of diffraction spots from the crystal grown using the Schultz method. The images show images of substructural components with boundaries parallel and perpendicular to the growth axis. The size of the reflexes from individual substructural components and the width of the gaps between them were used to determine the sizes of substructural components and the angles of misorientation between them.

Figure 3. An X-ray diffraction pattern (a) and diffraction spots (b) of $\text{Bi}_{0.91}\text{Sb}_{0.09}$ grown crystals.

It was shown by the Schultz topographic method that, first, the blocks are predominantly elongated in the direction of crystal elongation; second, the transverse dimensions of the blocks are from 0.1 to 2.0 mm; third, the angles of rotation of the blocks relative to each other are in the range from several minutes to 1° . Note that a substructure in the form of weakly misoriented single-crystal blocks was also observed earlier in Bi–Sb crystals grown by the Czochralski method [5,9,12–14]. The formation of blocks is associated with the fact that the growth of Bi–Sb crystals is accompanied by the appearance of local concentration overcooling regions at the crystallization front. The results obtained using these methods indicate the presence of weakly misoriented blocks, relatively free of dislocations, with boundaries consisting of dislocation networks. The formation of blocks is due to local concentration of overcooling regions at the crystallization front. Blocks are regions that are relatively free of dislocations, and their boundaries consist of dislocation networks. The length and width of single-crystal blocks along the direction of crystal growth and perpendicular to it were 0.7–1.4 mm and 0.1–0.2 mm, respectively, at an angle of rotation of the blocks relative to each other of 3–5 arc min.

In Figure 4, the typical diffraction pattern of the sample after deformation is compared with the isotropic polycrystalline structure of the reference sample. This indicates the

predominant orientation of the axes of trigonal crystallites in the direction of the extrusion axis, namely, the predominance of the $\langle 111 \rangle$ texture. As noted above, to quantify the degree of this texture, a magnetometric method was used in which the $W_{\langle 111 \rangle}$ content in the direction of the extrusion axis was calculated using Equation (3). With an increase in the extrusion ratio from 1.2 to 10, the value of $W_{\langle 111 \rangle}$ reduces from 88 to 50% (Table 1). The $W_{\langle 111 \rangle}$ values were determined by averaging five identically prepared samples over the results of magnetometric measurements. Table 1 also shows the root-mean-square errors of the reduced values of $W_{\langle 111 \rangle}$. The values of pole density P_{hkl} for extruded samples before and after additional annealing are presented in Table 2. Annealing was carried out at a temperature of 180 °C for 8 h in an inert gas atmosphere at a pressure of 150 kPa. In calculating P_{hkl} , only the most intense diffraction lines were taken into account. According to the data presented in Table 2, the values of the pole density P_{003} with Miller indices in multiples of (001) significantly exceed P_{hkl} of other observed diffraction lines. This indicates the predominant orientation of the trigonal axes of the crystallites along the extrusion axis or, in other words, the dominance of the $\langle 111 \rangle$ texture.

Figure 4. Diffraction patterns for a crystal $\text{Bi}_{0.91}\text{Sb}_{0.09}$ after plastic deformation. (a) Textureless reference sample, (b) sample after extrusion at $K_e = 5$ and annealing at 453 K for 8 h. Miller indices are given in the hexagonal setting for the $[111]$ planes; 2θ is the doubled Bragg angle.

Table 1. Influence of the extrusion ratio and annealing temperature for 8 h on the content of the crystallographic texture ($W_{\langle 111 \rangle} \times 100\%$) in the direction of the extrusion axis.

K_e	No Annealing	Annealing		
		150 °C	180 °C	210 °C
1.2	88 ± 4	83 ± 5	80 ± 5	72 ± 5
3	72 ± 5	62 ± 5	55 ± 5	38 ± 4
5	60 ± 5	48 ± 4	41 ± 4	23 ± 3
10	50 ± 4	33 ± 4	26 ± 4	14 ± 2

Table 2. Pole density P_{hkl} of the normals to reflecting planes (hkl) in the direction of the extrusion axis for $\text{Bi}_{0.91}\text{Sb}_{0.09}$ crystals, before and after annealing at 180 °C for 8 h.

K_e	As Extruded				After Annealing			
	1.2	3	5	10	1.2	3	5	10
P_{003}	29	21	15.2	10.1	25	16	9	5
P_{102}	0.1	0.3	0.4	0.5	0.2	0.4	0.2	0.4
P_{104}	0.1	0.2	0.4	0.6	0.2	0.2	0.4	0.3
P_{105}	0.3	0.6	0.7	0.8	0.5	0.4	0.9	1.3
P_{022}	1.4	1.6	1.3	1.2	1.7	1.9	1.1	1.6
P_{107}	0.3	0.6	0.5	0.7	0.4	0.7	1.0	1.1
P_{116}	0.2	0.3	0.3	0.5	0.2	0.3	0.6	0.4
P_{212}	0.1	0.5	0.6	0.8	0.3	0.4	0.9	1.4
P_{108}	0.8	1.0	0.9	0.8	1.2	1.3	1.2	1.0
P_{214}	0.1	0.4	0.4	0.3	0.2	0.6	0.5	0.5

Annealing of Bi–Sb extruded crystals causes a further decrease in the $W_{\langle 111 \rangle}$ values. As shown in Figure 5 and listed in Table 1, annealing of extruded samples causes intense recrystallization, leading to reorientation and coarsening of polycrystalline grains. In this case, the scattering of the $\langle 111 \rangle$ texture occurs more intensely for the samples obtained at higher values of the K_e (Figure 5).

Figure 5. Influence of the extrusion ratio on the content of the crystallographic texture $W_{\langle 111 \rangle}$ in as extruded $\text{Bi}_{0.91}\text{Sb}_{0.09}$ crystals (1) and after annealing at 453 K for 8 h (2).

Figure 6 shows examples of the structure of cleavages of Bi–Sb extruded samples at $K_e = 1.2, 3$, and 5. After annealing, on the cleavages perpendicular to the extrusion axis, there are triangular etching pits typical for the etched surface of cleavages along the (111) plane of single-crystal samples (Figure 6a). This indicates that during the extrusion process, the initial crystallographic orientation of the crystals is largely retained. Elongated grains coincide with the direction of extrusion (Figure 6b). At high magnification, the features of the cleavage of the sample extruded at $K_e 5$ show that the structure was practically isotropic in the plane perpendicular to the extrusion axis (Figure 6c). In Figure 6d, the scanning electron image of the fracture surface for the representative extruded $\text{Bi}_{0.91}\text{Sb}_{0.09}$ sample shows the excellent densification and uniform distribution of grains. No pores or cracks were identified on the surface of the sample, which is in agreement with the high density of the extruded samples, ~99% of the theoretical density. The estimated average

grain size ranges from 20 to 50 μm , and the size of the largest grains does not exceed $\sim 80 \mu\text{m}$.

Figure 6. SEM microphotographs of cleavage features (a–c) and fracture surface of a typical sample (d) in $\text{Bi}_{0.91}\text{Sb}_{0.09}$ extruded samples. (a) General view of the cleaved surface perpendicular to the extrusion axis with triangular etching pits; (b–d) annealing at 453 K for 8 h with K_e 1.2 (a), 3 (b), and 5 (c) at 1000 MPa and 300 K.

As a result of structural studies, it is shown that a strongly textured polycrystalline Bi–Sb at $K_e \leq 3$ is formed with a predominant orientation of the crystallographic axes of grains with an average size varying from 20 to 50 μm , coinciding with the orientation of the corresponding crystallographic axes of the single crystal before extrusion. At the extrusion ratio $K_e \geq 5$, the structure was practically isotropic in the plane perpendicular to the extrusion axis. For $K_e = 10$, as a result of extrusion, the axial texture $\langle 111 \rangle$ dominates in the direction of the extrusion axis, and the structure of the extruded polycrystal is practically independent of the orientation of a single crystal before extrusion.

3.2. Mechanical Properties of $\text{Bi}_{0.91}\text{Sb}_{0.09}$ Single Crystals and Polycrystalline Material

After homogenizing annealing at 453 K for 8 h, bending tests were performed on $\text{Bi}_{0.91}\text{Sb}_{0.09}$ single crystals at 77–300 K. The tested crystals were made so that the direction OZ (Figure 2b), coinciding with the trigonal axis of the crystal, was perpendicular to the direction of the bending force F_b . In a plane perpendicular to the trigonal axis, the bending force F_b was oriented along the bisectrix or binary axes (OY or OX), that is, $F_b \parallel \langle 121 \rangle$ or $F_b \parallel \langle 101 \rangle$, respectively. Ultimate bending strength σ_b of Bi–Sb extruded samples was much higher than that of single crystals and increased significantly with an increase in the extrusion ratio (Figure 7) and insignificantly with a decrease in the test temperature (Table 3). After extrusion at $K_e \geq 3$, the bending strength of the extruded crystals was practically independent of F_b orientation in the plane perpendicular to the direction of the extrusion axis.

Figure 7. Influence of the extrusion ratio on the ultimate bending strength of $\text{Bi}_{0.91}\text{Sb}_{0.09}$ crystals. The value of $K_e = 1$ corresponds to single-crystal samples. Test temperature was 80 K.

Table 3. Bending strength of extruded Bi–Sb polycrystals depending on the test temperature.

K_e	σ_b , MPa			
	300 K	200 K	150 K	80 K
1.2	27 ± 3	27 ± 3	29 ± 3	31 ± 3
3	35 ± 3	36 ± 3	38 ± 3	42 ± 3
5	48 ± 4	52 ± 4	55 ± 4	57 ± 4
10	65 ± 4	68 ± 4	70 ± 4	72 ± 4

Experimental stress–strain σ_b – ε_b dependencies (Figure 8) illustrate the main stress state during bending of samples. Fracture of the single crystals upon bending in the direction of the bisectrix axis (Figure 2, $F_b \parallel \langle 1\bar{2}1 \rangle$) occurs almost simultaneously with the appearance of the first stress breakdown at practically zero plastic deformation. In the meantime, at F_b , directed along the binary axis ($F_b \parallel \langle 10\bar{1} \rangle$), single crystals can undergo plastic deformation about 0.08%. In the directions of the binary axes of single crystals (Figure 2a, $F_b \parallel \langle 10\bar{1} \rangle$), just after the yield point at 22.7 MPa, the stress–strain curves show progressive plastic deformation with sharp drops and rises in stress (Figure 8a).

Figure 8. Stress–strain curves for $\text{Bi}_{0.91}\text{Sb}_{0.09}$ single crystals (a) and extruded polycrystalline material (b) at different temperatures and extrusion ratios. (a) Bending force direction is perpendicular to the trigonal axis OZ and along the binary axis OX and the bisectrix OY axis ($F_b \parallel \langle 10\bar{1} \rangle$ and $F_b \parallel \langle 1\bar{2}1 \rangle$, respectively); 200 K. (b) K_e of 3 and 10 (solid and dashed lines, respectively); 80 K (1, 2) and 300 K (3, 4).

For the samples after extrusion at K_e 3, by analogy with the case of bending of single crystals, the dependences σ_b – ε_b were investigated for two variants of orientation of the bending force F_b , namely (a) $F_b \parallel \langle 10\bar{1} \rangle$, that is, parallel to the predominant direction

of the binary axes of crystallites (Figure 2a), which coincides with the direction of these axes of the initial single crystal and (b) $F_b \parallel \langle 1\bar{2}1 \rangle$, that is, parallel to the predominant direction of the bisectrix axis OY. Both orientations of the bending force F_b were found to have little effect on bending strength of extruded samples at 80 K. For example, for $F_b \parallel \langle 10\bar{1} \rangle$ or $\langle 1\bar{2}1 \rangle$ directions, the bending strength was 31 ± 3 and 28 ± 3 MPa at $K_e 1.2$ as well as 42 ± 3 and 41 ± 3 MPa at $K_e 3$, respectively.

For samples extruded at $K_e \geq 3$, the dependences σ_b – ε_b were investigated at an arbitrary orientation of the bending force F_b in the plane perpendicular to the extrusion axis. For specimens extruded at $K_e = 1.2$, the bending force was oriented along the predominant direction of the binary axes. As a result of the extrusion of Bi–Sb crystals at $K_e \geq 5$, a TE material with an axially symmetric structure is formed. The extruded samples were investigated in the temperature range 80–300 K before and after annealing at 453 K for 8 h. For samples extruded at $K_e = 10$, the stress–strain dependences at room temperature had a relatively pronounced nonlinear region without significant disruptions of the σ_b values with increasing ε_b up to the destruction of the sample. With decreasing temperature, a decrease in the nonlinear section on the σ_b – ε_b curves was observed. At the lowest temperature of 80 K, the nonlinear section on these curves corresponding to plastic deformation was practically absent (Figure 8b). As a result of extrusion at $K_e \geq 5$, a polycrystalline structure with a high ultimate bending strength was formed, reaching values over 70 MPa in the temperature range 80–300 K.

Thus, the data obtained on the effect of extrusion on ultimate strength to bending show that plastic deformation of Bi–Sb single crystals under conditions of high hydrostatic pressure, even at low extrusion ratios, makes it possible to obtain a thermoelectric material with a significantly higher ultimate strength to bending compared to the original single crystals in the entire temperature range 80–300 K. In addition, in the same temperature range at different extrusion ratios, elongation-to-fracture (plastic deformation) of the extruded crystals increases two to three times compared to single-crystal samples, remaining rather low (Figure 9).

Figure 9. Elongation-to-fracture of single crystals ($F_b \parallel \langle 10\bar{1} \rangle$ or $\langle 1\bar{2}1 \rangle$) and extruded samples depending on temperature and extrusion ratio K_e .

4. Discussion

As follows from Figures 7–9, plasticity (elongation-to-fracture) and the strength of extruded samples at high hydrostatic pressure can reach values several times higher than those for single crystals. This is consistent with the data of compression tests of Fe_3Si single crystals [20] and AISI 4330 steel [21,22]. As reported by Lorrek and Pawelski [20], brittle materials are usually successfully deformed by additionally applying high hydrostatic pressure, which leads to an increase in the plasticity of single crystals of iron silicide by several times, especially at a certain crystallographic orientation of the sample relative to the loading axis (Figure 10a). In the Tadano and Hagihara model [21], the calculated flow

stresses under uniaxial compression are very close to the experimental results obtained by Spitzig et al. [22] at hydrostatic pressures $p = 0.552$, and 1104 MPa for AISI 4330 steel (Figure 10b). In this analysis, the hydrostatic pressure is applied as the initial stress, which means that $\sigma_{11} = \sigma_{22} = \sigma_{33} = -p$ at the initial state. In general, the ultimate plastic deformability of a material is a function of stress configuration, strain rate, and temperature. The effect of the stress configuration is the most significant and characterized by the mean normal stress $\sigma_m = 1/3 (\sigma_1 + \sigma_2 + \sigma_3)$, which may not be low enough to avoid cracking or fracture during the deformation process of a brittle material. In this case, σ_m can be reduced by applying hydrostatic pressure.

Figure 10. The effect of applied hydrostatic pressure p on true plastic strain and stress in compression tests of Fe₃Si single crystals [20] (a) and AISI 4330 steel [21] (b).

The significant stability of the structure of the samples obtained by extrusion of single crystals in a high pressure liquid medium at $K_e \leq 3$ is explained by the fact that the all-round hydrostatic compression used in the process of extrusion increases the uniformity of crystal plastic deformation, which leads to the formation of a more stable polycrystalline structure of extruded samples, consisting of blocks with an orientation main crystallographic directions close to the original single crystal.

As follows from Figure 5, annealing of the extruded samples causes a decrease in the specific content of the crystallographic texture $W_{\langle 111 \rangle}$, which reflects intense recrystallization leading to reorientation and coarsening of polycrystalline grains. However, such heat treatment improves the TE properties of the alloy [1,2]. Of course, the value of $W_{\langle 111 \rangle}$ reaches the maximum if the trigonal axis of the single crystals is directed along the extrusion axis.

At low values of extrusion ratio ($K_e \leq 3$), Bi–Sb polycrystalline alloy is strongly textured and has a preferred orientation of the crystallographic axes of grains coinciding with the orientation of the corresponding crystallographic axes of the single crystal before extrusion. However, a higher plastic deformation of single crystals ($K_e \geq 5$) leads to practically isotropic grains in the plane perpendicular to the extrusion axis (Figure 6c). At the highest plastic deformation of the single crystal at $K_e = 10$, the axial texture $\langle 111 \rangle$ dominates in the direction of the extrusion axis, and the structure of the polycrystalline extruded material is practically independent of the orientation of a single crystal before extrusion.

At room temperature, elastic elongation of Bi_{0.91}Sb_{0.09} alloy depends on applied stress, which can be calculated from Young's modulus and is about 0.08% (Figure 8). Gopinathan and Padmini [23] observed anomalous variations in elastic properties in the Sb concentration range from 2.2 to 14.89 at.%, in which, for example, Young's modulus (E) varied nonmonotonically from 25 to 37.5 GPa. In this defined region of critical concentrations, this is interpreted in terms of changes in lattice parameter and carrier concentration. In accordance to Woodcox et al. [24], the E values for the Bi_{0.91}Sb_{0.09} alloy are in the range from 26 to 32 GPa. Taking the modulus value equal to 30 GPa, and stress at the transition point of the linear dependence σ_b – ϵ_b into the nonlinear one (yield point) equal to 23 MPa, we find elastic deformation is $23 \times 100\% / 30,000 = 0.077\%$. Thus, the plastic deformation

(elongation-to-fracture) of extruded samples at 300 K, obtained at extrusion ratios of 3 and 10, is 0.08 and 0.28%, respectively (Figures 8b and 9). At 80 K, the plastic deformation of the extruded samples is zero and 0.09% for the K_e values of 3 and 10, respectively.

As shown above in Figure 8a, at bending force directed along the binary axis OZ ($F_b \parallel \langle 10\bar{1} \rangle$), the stress–strain curves of single crystals show sharp drops and rises after the yielding point at 22.7 MPa. The occurrence of sharp sawtooth stress drops or serrations during compression and tension deformations of bismuth and antimony single crystals due to twinning was indicated earlier [25–28]. Klassen-Neklyudova [25] summarized that elastic and residual twinning is formed under loading of bismuth and antimony crystals. Slonaker and Smutz [26] found that the transition from slip to twinning as the predominant deformation mechanism of 99.99% Bi was observed at tensile deformation when the angle Θ between the normal to the true cleavage plane (111), and the major axis of the single crystal equals 70° . The value of the critical resolved shear stress for slip on the (111) plane in bismuth at room temperature, obtained by Steegmuller and Daniel [27], is in agreement with the results of Slonaker and Smutz [26]. Deformation modes observed after compression tests at the strain rate of 1.7×10^{-4} on bismuth crystals of various orientations, mainly at the temperature -80°C (193 K) and more, are slip on (111) plane and twinning along the (011), (101), and (110) planes [27]. In the tensile test, twinning easily occurs at a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ [28] and is suppressed at a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$ or lower [29,30].

The destruction of single crystals upon bending when $F_b \parallel \langle 1\bar{2}1 \rangle$ occurs almost simultaneously with the appearance of the first breakdown of stress at a deformation of about 0.05%, while with F_b directed along the binary axis ($F_b \parallel \langle 10\bar{1} \rangle$) single crystals can undergo plastic deformation three times greater. Thus, when the bending force F_b is directed along the binary or bisectrix axis of the single crystal, differences in σ_b values are apparently determined by the conditions for the formation of microcracks μ (Figure 11) in the vicinity of the B–C line (Figure 2b), where maximum tensile forces T and stresses act upon the bending of single crystals [19,31].

Figure 11. Scheme of the formation of a microcrack μ during bending of Bi–Sb single crystals: (a) The formation of a microcrack μ along the binary axis $\langle 10\bar{1} \rangle$ in the region of intersection of twins S and S'. (b,c) The location of the microcrack μ in the ABCD plane near the line of maximum tensile stresses at $F_b \parallel \langle 1\bar{2}1 \rangle$ and $F_b \parallel \langle 10\bar{1} \rangle$, respectively.

Under the action of sufficient compression or tension stresses directed along one of the equivalent $\langle 100 \rangle$ axes, twins can be formed in Bi–Sb single crystals with a rhombohedral lattice symmetry in the form of thin interlayers with twinning planes {110} and twinning directions $\langle 100 \rangle$ [25]. With this bending scheme, one of the {110} twinning planes makes an angle of 71° with the (111) plane, and one of the twinning directions $\langle 100 \rangle$ is perpendicular

to the binary or bisector axis coinciding with the B–C line, depending on the orientation F_b . When a single crystal is bent, tensile forces T act in the vicinity of the B–C line. As a result, conditions are realized for the formation of twinning layers along the $\{110\}$ plane. The symmetry of the tensile forces upon bending of single crystals with respect to the middle cross-section ABCD (Figure 11), which coincides with the (111) plane, leads to the formation of a twin structure symmetric with respect to the ABCD plane. As a result, twin intersection regions appear in the vicinity of the BC line.

In the region of intersection of twins, there is a high density of dislocations and the appearance of cavities—Rose channels [32]—that have been actually reported as early as 1868 by Rose, who described these channels, or voids, formed by intersecting twins in calcite [24,31]. These were later described as microcracks in body-centered cubic (BCC) metals by Priestner [33], and by Sleeswyk [34] to explain ductile–brittle fracture transition in BCC iron through a complex emissary dislocation proposed mechanism. These cavities can penetrate the crystal in the direction of the binary axis at macroscopic distances and are the nuclei of microcracks. Therefore, when a single crystal is bent, a microcrack μ will most likely appear along the direction of the binary axis $\langle 10\bar{1} \rangle$. As a result, firstly, microcracks μ most likely arise along the B–C line, which coincides with the direction of one of the binary axes, when $F_b \parallel \langle 12\bar{1} \rangle$, and secondly, when $F_b \parallel \langle 10\bar{1} \rangle$, then the line B–C coincides with one of the bisectrix axes $\langle 1\bar{2}1 \rangle$ (Figure 11c) in this case, while microcracks μ most likely occur along a binary axis oriented at an angle of 30° to the B–C line.

Obviously, in the case of $F_b \parallel \langle 12\bar{1} \rangle$, the action of tensile stresses during bending of a single crystal, which form and open a microcrack μ , is more effective than in the case of $F_b \parallel \langle 10\bar{1} \rangle$. This explains the higher values of the ultimate bending strength observed during bending of single crystals, when $F_b \parallel \langle 10\bar{1} \rangle$, compared with bending of single crystals, when $F_b \parallel \langle 12\bar{1} \rangle$.

Plastic deformation at compression by an all-round load can develop both due to sliding and due to twinning depending on the orientation of single crystals, temperature, and other factors. For example, for Bi single crystals deformed at a rate of $\sim 10^{-4} \text{ s}^{-1}$, Steegmuller and Daniel [27] found a slip mode at room temperature for the crystal orientation $\{\bar{1}11\}$, (111) , and $\{100\}$ and twinning mode for orientations (011) , (101) , and (110) .

In the process of bending of extruded samples, the increased density of dislocations and other structural defects and the development of grain boundaries (GBs) determine a significant resistance to twinning. The twins that appear in individual grains are small in size, and in the areas of their intersection, extended microcracks—which can become nuclei of the destruction of the entire polycrystal—cannot form. This apparently explains the absence of sharp drops in σ_b during bending of extruded specimens, regardless of the orientation of F_b . In addition, GBs, dislocation pile-ups and other defects that prevent the development of microcracks increase the ultimate strength σ_b .

Thus, as previously reported [9], the TE properties of the $\text{Bi}_{0.91}\text{Sb}_{0.09}$ alloy obtained by extrusion at high hydrostatic pressure are close to those of single crystals, while having several times higher strength (Figures 7 and 8). For example, the dimensionless thermoelectric figure of merit ZT at 80 K decreases from 0.42 to 0.36 with an increase in the extrusion ratio K_e from 1.2 to 10, compared to 0.44 for single crystals measured without a transverse magnetic field. Recently, a unique thermoelectric solid-state multistage cooler for operating temperatures up to ~ 140 K was developed. In this case, the two-stage TE module for 140–200 K temperature range was developed on the n -type $\text{Bi}_{0.91}\text{Sb}_{0.09}$ crystal after plastic deformation and p -type $\text{Bi}_{1.6}\text{Sb}_{0.4}\text{Te}_3$ extruded crystal [35].

5. Conclusions

- (1) A new method was developed to significantly improve the mechanical properties of such effective thermoelectric (TE) materials as $\text{Bi}_{(1-x)}\text{Sb}_x$ single crystals due to their plastic deformation by extrusion under all-round hydrostatic compression at room temperature in a liquid medium.

- (2) A detailed study of *n*-type Bi–Sb solid solutions in a wide temperature range shows a significant increase in the mechanical strength of Bi–Sb crystals after extrusion in comparison with high-quality Bi–Sb single crystals. The increase in the strength of the Bi–Sb single crystals after plastic deformation is associated with the development of numerous grains with a high boundary surface as well as structural defects, such as dislocations that accumulate at grain boundaries.
- (3) The significant stability of the structure of the extruded samples can be explained by the uniformity of the plastic deformation of the crystal under all-round hydrostatic compression, which leads to the formation of a more stable polycrystalline structure of the thermoelectrics, consisting of blocks with the orientation of the main crystallographic directions close to the original single crystal.
- (4) Strengthening of Bi–Sb crystals after plastic deformation under all-round compression, as reported earlier, makes it possible to develop a unique thermoelectric solid-state multistage cooler for operating temperatures up to $T \sim 140$ K for the first time.

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References

1. Goldsmid, H.J. *Introduction to Thermoelectricity*, 2nd ed.; Springer-Verlag: Berlin/Heidelberg, Germany, 2016; Volume 121. [\[CrossRef\]](#)
2. Lenoir, B.; Scherrer, H. An Overview of Recent Developments for Bi–Sb Alloys. *Semicond. Semimet.* **2001**, *69*, 101–137. [\[CrossRef\]](#)
3. Yim, W.M.; Amith, A. Bi–Sb Alloys for Magneto-Thermoelectric and Thermomagnetic Cooling. *Solid-State Electron.* **1972**, *15*, 1141–1165. [\[CrossRef\]](#)
4. Zemskov, V.S.; Belaya, A.D.; Beluy, U.S.; Kozhemyakin, G.N. Growth and Investigation of Thermoelectric Properties of Bi–Sb Alloy Single Crystals. *J. Cryst. Growth* **2000**, *212*, 161–166. [\[CrossRef\]](#)
5. Sidorenko, N.A.; Ivanova, L.D. Bi–Sb Solid Solutions: Potential Materials for High-Efficiency Thermoelectric Cooling to below 180 K. *Inorg. Mater.* **2001**, *37*, 331–335. [\[CrossRef\]](#)
6. Smith, G.E.; Wolfe, R. Thermoelectric Properties of Bismuth–Antimony Alloys. *J. Appl. Phys.* **1962**, *33*, 841–846. [\[CrossRef\]](#)
7. Belaya, A.D.; Zayakin, S.A.; Zemskov, V.S.; Kopiev, I.M. Ultimate Bending Strength of Single Crystals of Bi–Sb Solid Solutions. *Izv. Acad. Sci. USSR Met.* **1990**, *4*, 166–169.
8. Sidorenko, N.A. Thermoelectric Materials for Peltier Cryogenic Coolers. *Cryogenics* **1992**, *32*, 40–43. [\[CrossRef\]](#)
9. Sidorenko, N.; Parashchuk, T.; Maksymuk, M.; Dashevsky, Z. Development of Cryogenic Cooler Based on *n*-Type Bi–Sb Thermoelectric and HTSC. *Cryogenics* **2020**, *112*, 103197. [\[CrossRef\]](#)
10. Martin-Lopez, R.; Zayakin, Z.; Lenoir, B.; Brochin, F.; Dauscher, A.; Scherrer, H. Mechanical Properties of Extruded Bi₈₅Sb₁₅ Alloy Prepared by Mechanical Alloying. *Philos. Mag. Lett.* **1998**, *78*, 283–287. [\[CrossRef\]](#)
11. Ivanova, L.D.; Petrova, L.I.; Granatkina, Y.V.; Zemskov, V.S.; Sokolov, O.B.; Skipidarov, S.Y.; Duvankov, N.I. Extruded Materials for Thermoelectric Coolers. *Inorg. Mater.* **2008**, *44*, 687–691. [\[CrossRef\]](#)
12. Czochralski, J. Ein Neues Verfahren zur Messung der Kristallisationsgeschwindigkeit der Metalle. *Z. Physikal. Chem.* **1918**, *92*, 219–221. [\[CrossRef\]](#)
13. Mayanov, E.P.; Gasanov, A.A.; Naumov, A.V. The Czochralski Method (cz): History and Development. *Mater. Electron. Eng.* **2018**, *19*, 59–70. [\[CrossRef\]](#)
14. Zemskov, V.S.; Belaya, A.D.; Kozhemyakin, G.N.; Lyuttsaw, V.G.; Kostyukova, Y.P. Growth of Single Crystals of Bismuth–Antimony Alloys by Chochralski Method. *J. Cryst. Growth* **1985**, *71*, 243–245. [\[CrossRef\]](#)
15. Schulz, L.G. A Direct Method of Determining Preferred Orientation of a Flat Reflection Sample Using a Geiger Counter X-ray Spectrometer. *J. Appl. Phys.* **1949**, *20*, 1030–1033. [\[CrossRef\]](#)

16. Raghothamachar, B.; Dhanaraj, G.; Bai, J.; Dudley, M. Defect Analysis in Crystals Using X-ray Topography. *Microsc. Res. Tech.* **2006**, *69*, 343–358. [[CrossRef](#)]
17. Weissmann, S.; Lee, L.H. Applications of the Divergent Beam X-ray Technique. *Prog. Cryst. Growth Charact.* **1989**, *18*, 205–226. [[CrossRef](#)]
18. Sidorenko, N.A.; Tsvetkova, N.A.; Dashevskii, Z.M. A Method for Preferential Structural Orientation Measurement in Thermo-electric Materials. *Supercond. Sci. Technol.* **1993**, *6*, 62–66. [[CrossRef](#)]
19. Callister, W.D., Jr. *Materials Science and Engineering*, 6th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2003.
20. Lorrek, W.; Pawelski, O. The Influence of Hydrostatic Pressure on the Plastic Deformation of Metallic Materials. In Proceedings of the Fifteenth International Machine Tool Design and Research Conference; Palgrave: London, UK, 1975; pp. 703–712.
21. Tadano, Y.; Hagihara, S. Hydrostatic Pressure Dependent Crystal Plasticity by Homogenization-based Finite Element Method. *ISIJ Int.* **2016**, *56*, 700–707. [[CrossRef](#)]
22. Spitzig, W.A.; Sober, R.J.; Richmond, O. Pressure Dependence of Yielding and Associated Volume Expansion in Tempered Martensite. *Acta Metall.* **1975**, *23*, 885–893. [[CrossRef](#)]
23. Gopinathan, K.K.; Padmini, A.R.K.L. Ultrasonic Studies on Bismuth-Antimony Alloys. *J. Phys. D Appl. Phys.* **1974**, *7*, 32–40. [[CrossRef](#)]
24. Woodcox, M.; Young, J.; Smeu, M. Ab Initio Investigation of the Elastic Properties of Bismuth-Based Alloys. *Phys. Rev. B* **2019**, *100*, 104105. [[CrossRef](#)]
25. Klassen-Neklyudova, M.V. *Mechanical Twinning of Crystals*; Springer: Berlin/Heidelberg, Germany, 1964; p. 213.
26. Slonaker, R.E.; Smutz, M. Factors Affecting the Growth and the Mechanical and Physical Properties of Bismuth Single Crystals. *J. Less Common Met.* **1965**, *8*, 327–338. [[CrossRef](#)]
27. Steegmuller, C.; Daniel, J.S. Slip in Bismuth. *J. Less Common Met.* **1972**, *27*, 81–85. [[CrossRef](#)]
28. Yanaka, Y.; Kariya, Y.; Watanabe, H.; Hokazono, H. Plastic Deformation Behavior and Mechanism of Bismuth Single Crystals in Principal Axes. *Mater. Trans.* **2016**, *57*, 819–823. [[CrossRef](#)]
29. Motohashi, I.; Otake, S. Plastic Deformation and Dislocation Etch-Pit Distribution Due to the (001) <110> Glide System for Bismuth Single Crystals. *J. Jpn. Inst. Met.* **1973**, *37*, 978–985. [[CrossRef](#)]
30. Otake, S.; Namazue, H.; Matsuno, N. Critical Resolved Shear Stresses of Two Slip Systems in Bismuth Single Crystals. *Jpn. J. Appl. Phys.* **1980**, *19*, 433–437. [[CrossRef](#)]
31. ASTM International. *Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials*; ASTM International: West Conshohocken, PA, USA, 2003.
32. Rose, G. *Über die im Kalkspat Vorkommenden Hohlen Canäle*; Akademie Der Wissenschaften: Berlin, Germany, 1868; Volume 23, pp. 57–79.
33. Priestner, R. The Relationship between Brittle Cleavage and Deformation Twinning in BCC Metals. In *Deformation Twinning*; Reed-Hill, R.E., Hirth, J.P., Rogers, H.C., Eds.; Gordon and Breach Science: New York, NY, USA, 1964; pp. 321–355.
34. Sleeswyk, A.W. Emissary Dislocations: Theory and Experiments on the Propagation of Deformation Twins in α -Iron. *Acta Metall.* **1962**, *10*, 705–725. [[CrossRef](#)]
35. Parashchuk, T.; Sidorenko, N.; Ivantsov, L.; Sorokin, A.; Maksymuk, M.B.; Dzundza, B.; Dashevsky, Z. Development of Solid-State Multi-Stage Thermoelectric Cooler. *J. Power Sources* **2021**, *496*, 229821. [[CrossRef](#)]