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(71) Applicant: **Akademia Gorniczo-Hutnicza im. Stanislawa Staszica w Krakowie**
30-059 Krakow (PL)

(72) Inventors:
- **WOJCIECHOWSKI, Krzysztof**
  32-082 Wieckowice, ul. Spacerowa 37 (PL)
- **PARASHCHUK, Taras**
  31-221 Krakow, ul.Bialopradnicka 28D/50 (PL)
- **CHERNIUSHOK, Oleksander**
  30-065 Krakow,ul. Tokarskiego 4/216A (PL)

(74) Representative: **Kowal, Elzbieta et al**
Polservice
Kancelaria Rzecznikow
Patentowych sp. z o.o.
Bluszczanska 73
00-712 Warszawa (PL)

(54) GAMMA-ARGYRODITE STRUCTURE MATERIAL FOR THERMOELECTRIC CONVERSION AND THE METHOD OF OBTAINING THE SAME

(57) The material with the γ-argyrodite structure for thermoelectric conversion is characterized by the chemical formula of $Cu_{8-\delta}SiS_xSe_{6-x}$ for $x = 0 \div 6$ and $\delta = 0 \div 0.5$.

The method of obtaining a material with the γ-argyrodite structure for thermoelectric conversion is characterized by the fact that vacuum encapsulation is carried out, during which the elements Cu, Si, S, and Se of high purity above 99.99% are weighed in atomic ratios Si : Cu : S : Se - 1 : 7.5÷8 : 0÷6 : 0÷6, with the total amount of S and Se being 6 times the amount of Si, after which the elements are mixed and sealed in a reactor. Next, a melting process is carried out, during which the batch is heated to a temperature in the range of 1200-1600 K and kept at this temperature for at least 5 hours, to allow liquid synthesis to take place, after which the batch is cooled in free mode to room temperature. Subsequently, an annealing heat treatment process is carried out, during which the previously formed batch is ground into powder, which is cold pressed and annealed for 20-1000 hours at 700-1000 K under vacuum, after which it is subjected to free cooling to room temperature to obtain a homogeneous material. Finally, a pressure-assisted sintering process is carried out, during which the annealed material is ground into a fine powder, which is placed in a graphite mold and heated to a temperature of 900-1100 K, and densified at a pressure of 20-200 MPa, for 10-600 minutes, after which the material is slowly cooled at a cooling rate of 1-30 K/min. Heating of the annealed material ground into a fine powder, during the pressure-assisted sintering process, is carried out by the spark plasma sintering (SPS) method.

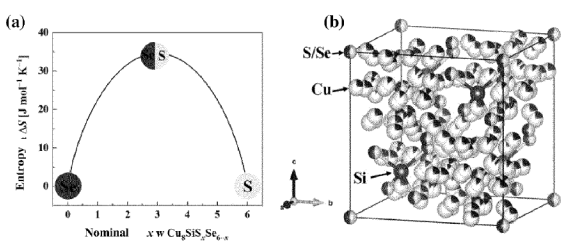

Fig. 1

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Description

[0001] The subject of the invention is a material with the γ-argyrodite structure for thermoelectric conversion and a method of obtaining the same.

[0002] Compounds with an argyrodite structure with the general formula $A^{m+}_{(12-n)/m}B^{n+}Q^{2-}_6$ (A^{m+} = Li^+, Cu^+, Ag^+; B^{n+} = Ga^{3+}, Si^{4+}, Ge^{4+}, Sn^{4+}, P^{5+}, As^{5+}; Q^{2-} = S, Se, Te) show a wide range of possibilities of use in thermoelectric applications. They are produced from widely available and environmentally friendly elements. Like other ionic conductors, argyrodites also have many polymorphic modifications. The γ-modification with high symmetry is more favorable for thermoelectric applications compared to the α-modification due to its higher thermoelectric conversion efficiency.

[0003] It is known from the publication by Chen, R.; Qiu, P.; Jiang, B.; Hu, P.; Zhang, Y.; Yang, J.; Ren, D.; Shi, X.; Chen, L. Significantly Optimized Thermoelectric Properties in High-Symmetry Cubic Cu7PSe6 Compounds: Via Entropy Engineering. J. Mater. Chem. A 2018, 6 (15), 6493-6502. https://doi.org/10.1039/c8ta00631h and from the publication by Cherniushok, O.; Parashchuk, T.; Tobola, J.; Luu, S.; Pogodin, A.; Kokhan, O.; Studenyak, I.; I, B.; Piasecki, M.; Wojciechowski, K. T. Entropy-Induced Multivalley Band Structures Improve Thermoelectric Performance in p-Cu7P(SxSe1-x)6 Argyrodites. ACS Appl. Mater. Interfaces 2021, 13 (33), 39606-39620. https://doi.org/10.1021/acsami.1c11193, a way to promote the expected polymorphic modification by increasing the configurational entropy of the system by introducing a larger number of different elements into the crystal structure of the compound. When the configurational entropy is high enough, the phase transformation from α to γ can take place significantly below room temperature, which is advantageous because this material can be used over a wide range of operating temperatures maintaining high electrical transport properties.

[0004] It is known from Chinese patent application CN107235477A by Chen Hongyi; Chen Lidong; Jiang Binbin; Qiu Pengfei; Ren Dudi; Shi Xun; Zhang Qihao a method of producing argyrodite-type thermoelectric materials involving synthesis by melting stoichiometric amounts of elements in vacuum quartz containers at 1073-1473 K followed by further annealing at 723-973 K for several days. The resulting products are crushed into fine powders and sintered into polycrystalline sinters by high-temperature high-pressure sintering at 723-1000 K for 0.1-10 hours under pressure in the range of 20-200 MPa.

[0005] It is known from Korean patent application KR20190082424A by Chung In and Zhou Chongjian; argyrodite-type material for thermoelectric applications based on the chemical formula $A^{m+}_{12-n/m}\ B^{n+}X^{2-}_{6-z}Y^{1-}_{z}$ where A is one of Cu, Ag, Na, Li, K, Cd, Hg, and B contains one or more of Ga, Ge, Si, Sn, P and As, X contains one or more of S, Se, and Te, Y is F, Cl, Br and I, where m represents the ionic value of A, n represents the ionic value of B, and z represents a real number from 0 to 1.

[0006] It is known Chinese patent application CN106098923A by Li Wen; Lin Siqi; Pei Yanzhong; argyrodite-type material for thermoelectric applications based on the chemical formula $Ag_8Sn_{1-x}Nb_xSe_6$, characterized by the fact that x=0-0.05.

[0007] It is known from Chinese patent application CN108598252A by Chen Jing; Luo Jun; Wang Chenyang; Zhang Jiye argyrodite-type material for thermoelectric applications based on the chemical formula $Ag_{9-x}Cu_yGaSe_6$, characterized by $y = 0$, $0 \le x \le 0.1$; when $y \ne 0$, $0 < x = y \le 0.9$.

[0008] It is known from Chinese patent application CN107235477A by Chen Hongyi; Chen Lidong; Jiang Binbin; Qiu Pengfei; Ren Dudi; Shi Xun; Zhang Qihao; an argyrodite-type material for thermoelectric applications based on the chemical formula $Ag_9GaSe_{6-x-y}Te_y$, characterized by $0 \le x \le 0.03$, $0 < y < 0.75$, while x and y are not 0 at the same time.

[0009] It is known from Chinese patent application CN107359231A by Li Wen; Lin Siqi; Pei Yanzhong; an argyrodite-type material for thermoelectric applications based on the chemical formula $Ag_9Ga_{1-x}M_x(Se_{1-y}S_y)_6$, characterized by the fact, that M is the chemical element selected from Cr, Cd, Zn or Ge and $0 \le x \le 0.06$, $0 \le y \le 0.10$.

[0010] The purpose of the present invention is a material that is a new polymorphic modification of γ- argyrodite with a new chemical composition, and a method for obtaining it.

[0011] The essence of the material with γ- argyrodite structure for thermoelectric conversion is that it has the chemical formula $Cu_{8-\delta}SiS_xSe_{6-x}$, where $x = 0 \div 6$ and $\delta = 0 \div 0.5$.

[0012] The essence of the method of obtaining γ-argyrodite-structure material for thermoelectric conversion is that a vacuum encapsulation is carried out, during which the elements Cu, Si, S, and Se of high purity above 99.99% are weighed in atomic ratios Si : Cu : S : Se - 1 : 7.5÷8: 0÷6 : 0÷6, with the total amount of S and Se being 6 times of the amount of Si, after which the elements are mixed and sealed in a reactor. Then a melting process is carried out, during which the batch is heated to a temperature in the range of 1200 to 1600 K and kept at this temperature for at least 5 hours, to allow the synthesis to occur in a liquid state. After this is done, the batch is cooled in free mode to room temperature. Subsequently, an annealing process is carried out, during which the previously formed batch is ground into powder, which is cold pressed and annealed for 20-1000 hours at 700-1000 K under vacuum, after which it is subjected to free cooling to room temperature to obtain a homogeneous material. Finally, a pressure-assisted sintering process is carried out, during which the annealed material is ground into a fine powder, which is placed in a graphite mold and heated to a temperature of 900 - 1100 K, and densified at a pressure of 20-200 MPa, for a time of 10-600 minutes, after which the material is subjected

to slow cooling at a cooling rate of 1-30 K/min.

[0013] Advantageously, the heating of the annealed material ground into a fine powder during the pressure-assisted sintering process is carried out by the spark plasma sintering (SPS) method.

[0014] The developed thermoelectric materials are produced from environmentally harmless and relatively inexpensive chemical elements, enabling the manufacture of thermoelectric converters for common applications (e.g., waste heat recovery, solar and geothermal energy conversion).

[0015] By optimizing the composition and synthesis conditions, a modification of γ-argyrodite $Cu_8SiS_xSe_{6-x}$, with good thermoelectric properties is obtained. The concentration of charge carriers is optimized by introducing an appropriate deficiency of Cu, which makes it possible to achieve a high energy conversion efficiency of 13%. In comparison, the efficiency of commercially available thermoelectric modules based on Bi_2Te_3 alloys is only 5-6%. In addition, the high-performance $Cu_{8-\delta}SiS_xSe_{6-x}$ material contains only low-cost and environmentally friendly elements, significantly reducing thermoelectric device prices.

[0016] Adding sulfur in place of selenium in $Cu_8SiS_xSe_{6-x}$ (x = 0.1-3) stabilizes the favorable high-temperature γ-polymorphic modification and improves the thermoelectric power factor of this material over the entire temperature range. Optimization of the carrier concentration by Cu deficiency defects further improves the thermoelectric efficiency of η. The $Cu_{8-\delta}SiS_xSe_{6-x}$ has a high efficiency η = 13% at 773 K with a temperature difference from 298 K to 773 K.

Embodiment

[0017] The object of the invention is presented in the drawing in which Fig. 1 (a) shows the entropy change in the system due to the substitution of selenium by sulfur and (b) the y - argyrodite crystal structure of $Cu_8SiS_3Se_3$; Fig. 2 shows an electron microscope image of the selected sample after sintering; the graph in Fig. 3 shows the dependence of the material efficiency on the temperature difference ΔT.

[0018] The argyrodite thermoelectric copper-silicon-sulfur-selenium material with the chemical formula $Cu_{7.95}SiS_3Se_3$ is obtained by the following procedure:

(1) Powders of copper of 5.3312 g, silicon of 0.3242 g, sulfur of 1.1104 g, and selenium of 2.7342 g with a purity of 99.99% are mixed and then sealed under a vacuum of 10^{-5} mbar in a quartz ampoule coated inside with graphite;

(2) The quartz ampoule containing the raw material is placed in a high-temperature muffle furnace, which is slowly heated to 1400 K for 10 hours, and maintained at this temperature for 5 hours, which allows the components to react in a liquid state, followed by free cooling to room temperature to obtain the first ingot;

(3) The resulting ingot is ground to powder, cold-pressed, and annealed for 170 hours at 873 K in quartz ampoules under vacuum to obtain a homogeneous material. The material is then cooled freely to room temperature;

(4) The annealed material is ground into a fine powder, placed in a graphite mold, and heated at a rate of 70 K/min to 1023 K. It is then densified by spark plasma sintering (SPS) method at 60 MPa, for 60 minutes. The resulting sinter is subjected to slow cooling at a rate of 15 K/min.

[0019] Fig. 1a shows the changes in the configurational entropy of the $Cu_8SiS_xSe_{6-x}$ system depending on the amount of sulfur and selenium. Calculations show that the compound with composition $Cu_8SiS_3Se_3$ has the highest configurational entropy and (the largest disorder in the Se/S sublattice) which is shown schematically in the crystal structure drawing (Fig. 1b). Such a chemical composition causes the obtained compound to have the structure of the polymorphic modification of γ-argyrodite already at room temperature, which was confirmed by X-ray diffraction XRD and differential scanning calorimetry DSC methods. Fig. 2. shows an example of a scanning electron microscope SEM image obtained after sintering of the material. The values of energy conversion efficiencies for $Cu_8SiS_xSe_{6-x}$ samples determined from measurements of electrical and thermal properties are shown in Fig. 3. The obtained materials with the composition of $Cu_8SiS_xSe_{6-x}$ have significantly higher thermoelectric power factor and ultra-low thermal conductivity compared to undoped Cu_8SiS_6 and Cu_8SiSe_6. A maximum efficiency of 10.2% is achieved for a composition with x = 3 at 773 K. Nevertheless, the material has a too-small number of p-type carriers.

[0020] Further optimization of the concentration of p-type charge carriers allows for an additional increase in efficiency. The optimal concentration of carriers (holes) was achieved by intentionally created deficiency of copper in the $Cu_{8-\delta}SiS_3Se_3$. As a result, the efficiency (Fig. 3) for the $Cu_{8-\delta}SiS_3Se_3$ samples reached a value of ~13% at 773 K for a sample with δ = 0.05. This value of efficiency is the highest value reported to date for materials with a p-type argyrodite structure. In summary, the estimated efficiency (Fig. 3) for the components made of the obtained materials at a temperature difference of 475 K shows that α-Cu_8SiS_6 has an efficiency of 2.3%, α-Cu_8SiSe_6 - 8.3%, while the γ-$Cu_8SiS_3Se_3$ modification shows an efficiency of 10.2%. On the other hand, with the optimal composition of $Cu_{7.95}SiS_3Se_3$, the efficiency increases to 13.0 %.

Claims

1. A material with the γ-argyrodite structure for thermoelectric conversion is **characterized by** the chemical formula of $Cu_{8-\delta}SiS_xSe_{6-x}$ for x = 0 ÷ 6 and δ = 0 ÷ 0.5.

2. A method of obtaining a material with γ-argyrodite structure for thermoelectric conversion, **characterized in that** vacuum encapsulation is carried out, during which the elements Cu, Si, S and Se are weighed in atomic ratios Si : Cu : S : Se - 1 : 7.5÷8 : 0÷6 : 0÷6, with the total amount of S and Se being 6 times the amount of Si, after which these elements are mixed and sealed in a reactor, then a melting process is carried out, during which the batch is heated to a temperature in the range of 1200 to 1600 K and kept at this temperature to allow liquid synthesis to take place, after which the batch is cooled in free mode to room temperature, then a processing is carried out, during which the previously formed batch is ground into powder, which is pressed and annealed for 20-1000 hours at a temperature of 700-1000 K under vacuum, and finally a pressure-assisted sintering process is carried out, during which the annealed material is ground into fine powder, which is placed in a mold and heated to a temperature of 900 - 1100 K, and densified at a pressure of 20-200 MPa, for a period of 10-600 minutes, after which the material is subjected to slow cooling at a cooling rate of 1-30 K/min.

3. The method of obtaining a material with the γ-argyrodite structure for thermoelectric conversion, according to claim 2 **characterized in that** the heating of the annealed material ground into a fine powder during the pressure-assisted sintering process is carried out by the spark plasma sintering (SPS) method.

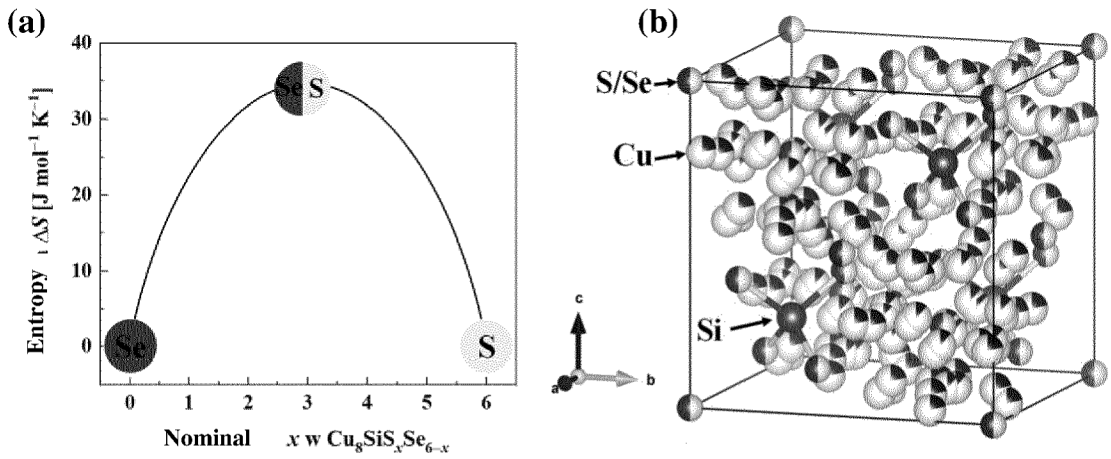
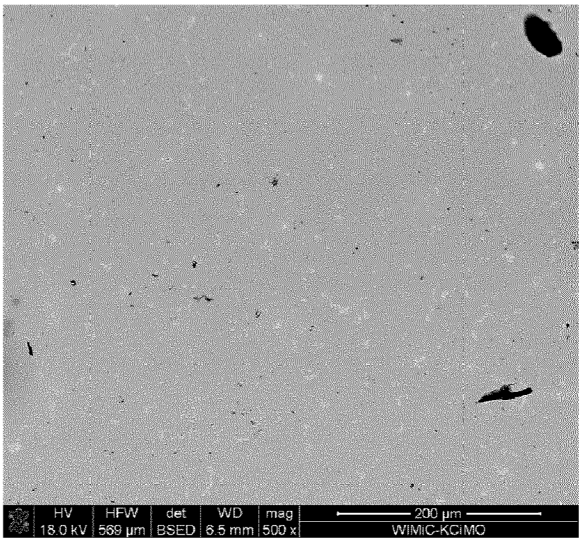

(a)
40
30
20
10
0
Entropy $_t\Delta S$ [J mol^{-1} K^{-1}]
Se
S
Se
S
0
1
2
3
4
5
6
Nominal x w $Cu_8SiS_xSe_{6-x}$
(b)
S/Se
Cu
Si
c
a
b

Fig. 1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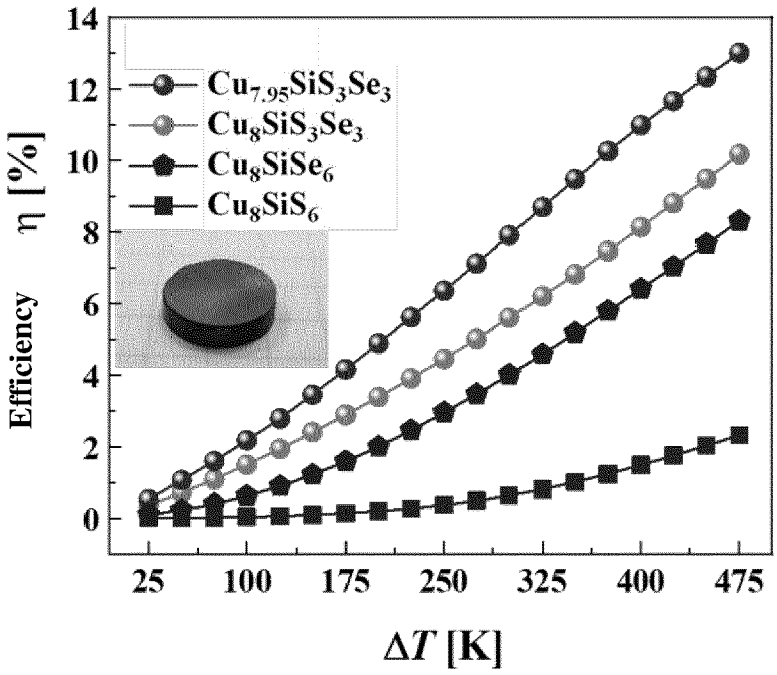
HFW
589 µm
det
BSED
WD
6.5 mm
mag
500 x
200 µm
WIMiC-KCiMQ

Fig. 2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ΔT [K]
Cu7.95SiS3Se3
Cu8SiS3Se3
Cu8SiSe6
Cu8SiS6
0
2
4
6
8
10
12
14
25
100
175
250
325
400
475

Fig. 3.

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EUROPEAN SEARCH REPORT

Application Number
EP 22 21 1900

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	ISHII M ET AL: "Structure and vibrational spectra of argyrodite family compounds Cu"8SiX"6 (X=S, Se) and Cu"8GeS"6", SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY. AMSTERDAM; NL, NL, vol. 121, no. 1-4, 2 June 1999 (1999-06-02), pages 11-18, XP004166450, ISSN: 0167-2738, DOI: 10.1016/S0167-2738(98)00305-1	1	INV. C01B33/00 H10N10/852 C01B19/00 H10N10/01
A	* abstract * * Experimental * * the whole document *	2,3	
X	ISHII M ET AL: "Vibrational spectra and phase transitions of Cu"8MX"6 (M=Si, Ge; X=S, Se) and Cu"4GeS"4", SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY. AMSTERDAM; NL, NL, vol. 136-137, 2 November 2000 (2000-11-02), pages 403-407, XP004225959, ISSN: 0167-2738, DOI: 10.1016/S0167-2738(00)00469-0	1	TECHNICAL FIELDS SEARCHED (IPC) C01B H01L H10N
A	* abstract * * Experimental * * the whole document *	2,3	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	8 August 2023	Straub, Thomas

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 22 21 1900

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	BRAMMERTZ G ET AL: "Fabrication and characterization of ternary Cu8SiS6and Cu8SiSe6thin film layers for optoelectronic applications", THIN SOLID FILMS, vol. 616, 24 September 2016 (2016-09-24), pages 649-654, XP029812157, ISSN: 0040-6090, DOI: 10.1016/J.TSF.2016.09.049	1	
A	* abstract * * Experimental * * the whole document *	2,3	
T	TARAS PARASHCHUK ET AL: "Discovery of the high thermoelectric performance in low-cost Cu8SiSxSe6-x argyrodites", ARXIV.ORG, CORNELL UNIVERSITY LIBRARY, 201 OLIN LIBRARY CORNELL UNIVERSITY ITHACA, NY 14853, 4 July 2023 (2023-07-04), XP091555088, * the whole document *		TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	8 August 2023	Straub, Thomas

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REFERENCES CITED IN THE DESCRIPTION

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- KR 20190082424 A, Chung In and Zhou Chongjian **[0005]**
- CN 106098923 A, Li Wen; Lin Siqi; Pei Yanzhong **[0006]**
- CN 108598252 A, Chen Jing; Luo Jun; Wang Chenyang; Zhang Jiye **[0007]**
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