# United States Patent [19]

**Takagi et al.**

[11] **3,816,108**

[45] **June 11, 1974**


[54] **SEMICONDUCTOR GRANULES FOR USE IN ACOUSTIC-ELECTRO CONVERTING DEVICES**


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[52] **U.S. Cl.** ..... **75/134 H,** 75/149, 75/166 R

[51] **Int. Cl.** ..... **C22c 31/00**

[58] **Field of Search** ..... 75/134 H, 149, 166



[56] **References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,745,327 | 5/1956 | Mengali | 95/1.3 |
| 2,803,541 | 8/1957 | Paris | 96/1 |
| 3,228,805 | 1/1966 | Waseleski et al. | 148/2 |
| 3,629,155 | 12/1971 | Kristensen | 252/512 |



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[57] **ABSTRACT**

Semiconductor granules for use in acoustic-electro converting devices are made of alloys consisting of from 10 to 95 atomic weight percent of selenium and from 5 to 90 atomic weight percent of tellurium. The alloy may contain from 1 to 80 atomic weight percent of antimony or lead. The granules are packed in a chamber defined between a moving electrode supported by a diaphragm and a fixed electrode of an acoustic-electro converting device.


**7 Claims, 7 Drawing Figures**

FIG. 1

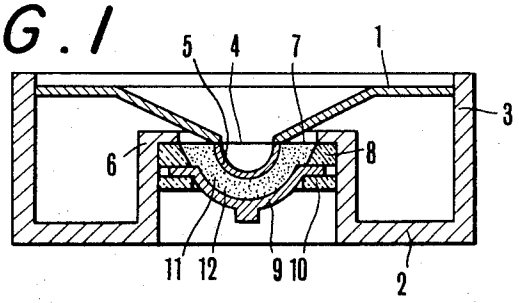

5
4
7
1
3
6
8
11
12
9
10
2

FIG. 2

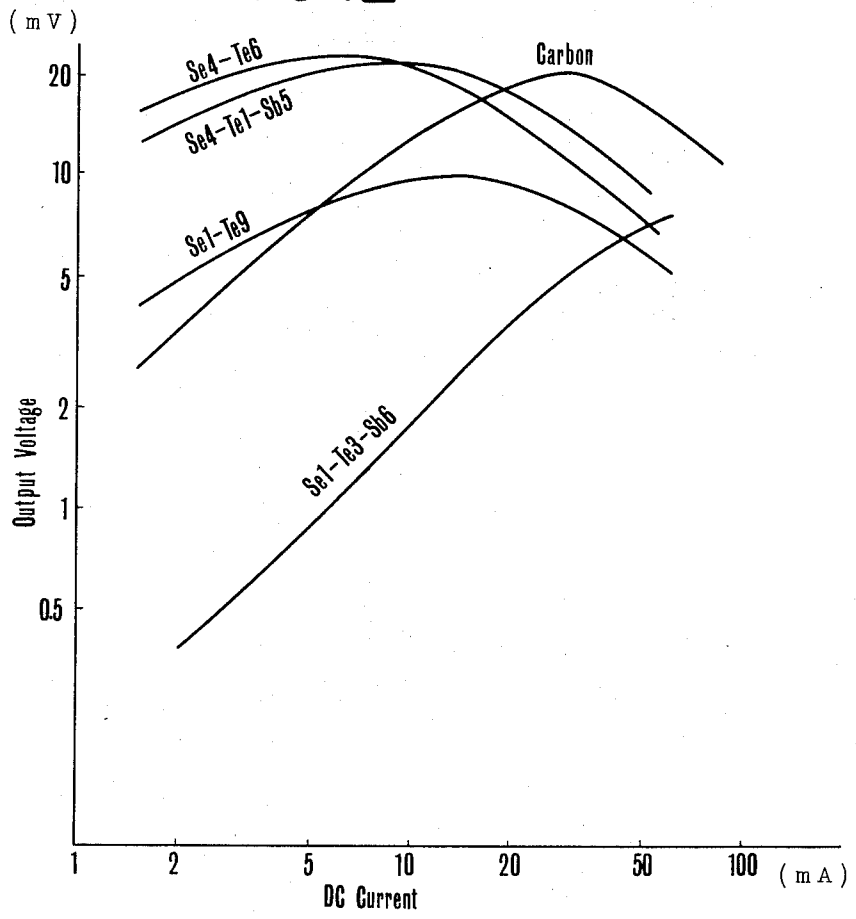

( mV )
20
10
5
2
1
0.5
Output Voltage
Se4-Te6
Se4-Te1-Sb5
Se1-Te9
Se1-Te3-Sb6
Carbon
1
2
5
10
20
50
100
( mA )
DC Current

FIG. 3

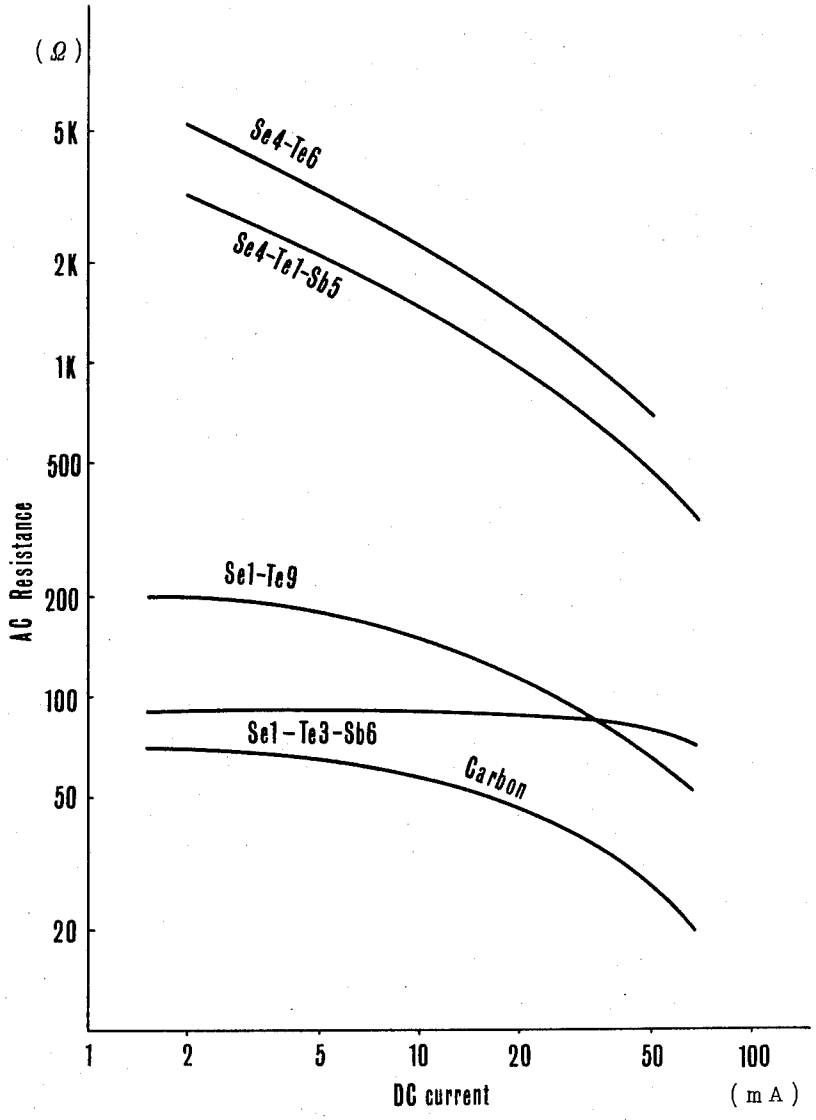
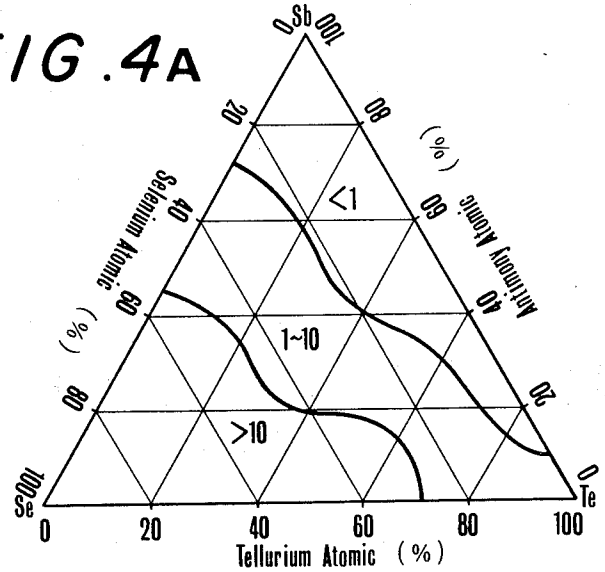
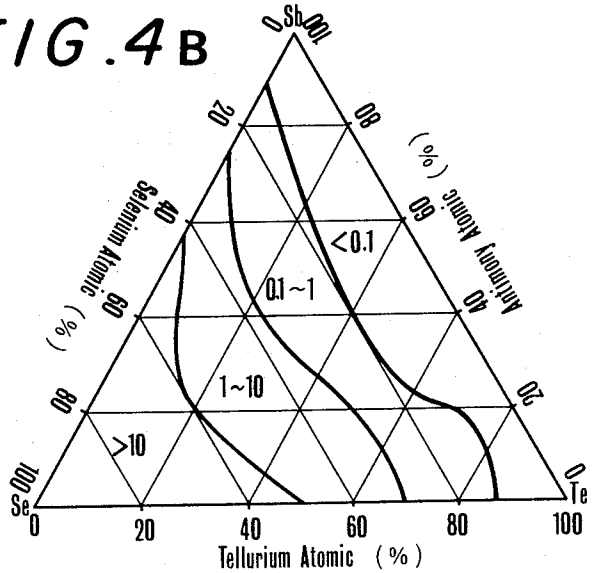

(Ω)
5K
2K
1K
500
200
100
50
20
AC Resistance
Se4-Te6
Se4-Te1-Sb5
Se1-Te9
Se1-Te3-Sb6
Carbon
1
2
5
10
20
50
100
DC current
(mA)

FIG. 4A




Tellurium Atomic (%)
AC Output Voltage (mV)
(I=5mA)

FIG. 4B




Tellurium Atomic (%)
AC Resistance (KΩ)

FIG. 4c

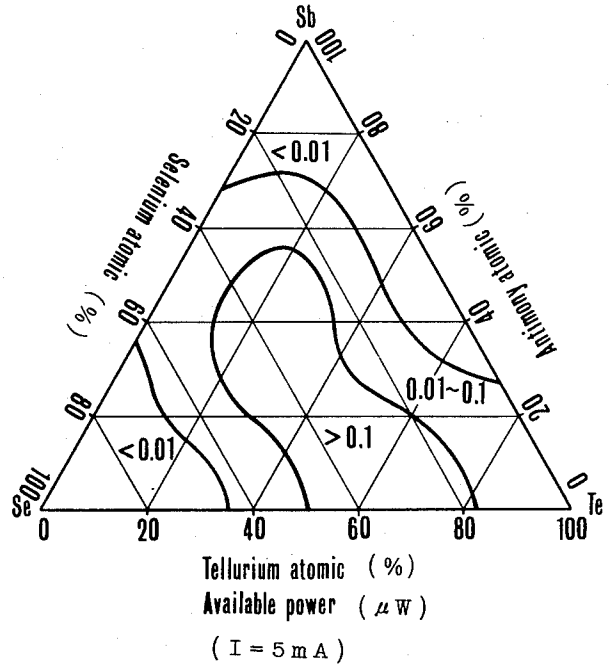
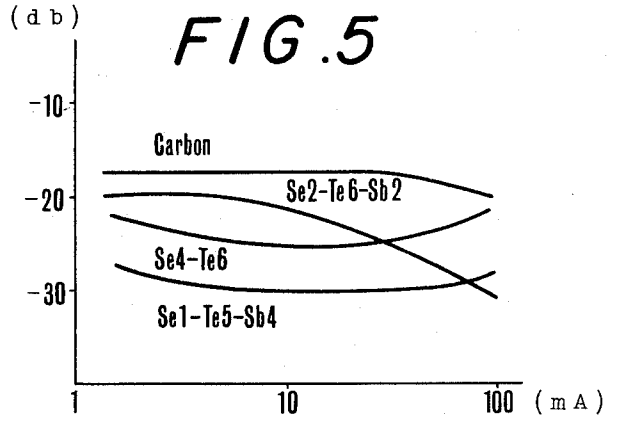

Sb
0
100
20
80
40
60
60
40
80
20
100
0
Se
Te
Selenium atomic (%)
Antimony atomic (%)
< 0.01
0.01~0.1
< 0.01
> 0.1
0
20
40
60
80
100
Tellurium atomic (%)
Available power (μW)
(I = 5 mA)

FIG. 5


(db)
-10
-20
-30
Carbon
Se2-Te6-Sb2
Se4-Te6
Se1-Te5-Sb4
1
10
100
(mA)

# SEMICONDUCTOR GRANULES FOR USE IN ACOUSTIC-ELECTRO CONVERTING DEVICES

## BACKGROUND OF THE INVENTION

This invention relates to semiconductor granules for use in acoustic-electro converting devices such as transmitters.

Typical semiconductor granules utilized in conventional acoustic-electro converting devices are carbon granules. Although carbon granules have a high sensitivity they are manufactured by utilizing natural anthracite as the raw material so that it is difficult to obtain carbon granules of definite quality at a high yield. Further, prior art carbon granules manifest a large hysteresis for supplied current and sound pressure as well as a large non-linear distortion so that their acoustic-electro converting operation is not stable.

Among acoustic-electro converting devices utilizing semiconductors other than carbon granules may be mentioned those utilizing PN junctions and those utilizing the piezoelectric effect or the piezo-resistance effect of the semiconductor bulk. However, the sensitivity of the acoustic-electro converting devices utilizing these materials is much lower than that of the devices using carbon granules.

## OBJECTS OF THE INVENTION

Accordingly, it is an object of this invention to provide novel semiconductor granules for use in acoustic-electro converting devices having an extremely small hysteresis for the supply voltage and sound pressure as well as small non-linear distortion.

Another object of this invention is to provide improved semiconductor granules for use in acoustic-electro converting devices which can generate a larger output voltage than prior art carbon granules for a comparably small supply current and for a definite sound pressure.

Still another object of this invention is to provide improved semiconductor granules for use in acoustic-electro converting devices which have uniform quality, can be manufactured at a high yield and have smaller vapor adsorption than carbon granules and hence are more stable.

A further object of this invention is to provide novel semiconductor granules for use in acoustic-electro converting devices capable of producing a large output for a given value of supply direct current and sound pressure applied thereto.

Still further object of this invention is to provide semiconductor granules for use in acoustic-electro converting devices capable of manifesting extremely large attenuation for harmonics of the input audio frequency.

Another object of this invention is to provide a novel acoustic-electro converting device capable of providing a high sensitivity by utilizing the resistance variation of the semiconductor granules themselves as well as the variation in the contact resistance between the granules. The invention is based on the discovery that the semiconductor substances of the selenium-tellurium alloy have a large piezoresistance effect and a suitable electrical resistance.

According to this invention there are provided semiconductor granules for use in acoustic-electro converting devices, which are made of alloys consisting essentially of from 10 to 95 atomic weight percent of selenium and from 5 to 90 atomic weight percent of tellurium. Further, the alloys may contain from 1 to 80 atomic weight percent of antimony or lead. In a typical application the semiconductor granules of this invention are packed between a moving electrode supported by a diaphragm and a fixed electrode of the acoustic-electro converting device.



## BRIEF DESCRIPTION OF THE DRAWINGS

Further objects and advantages of the invention will be better understood from the following detailed description taken in conjunction with the accompanying drawings in which:

FIG. **1** is a sectional view of an acoustic-electro converting device using the novel semiconductor granules;

FIG. **2** is a graph showing the direct current-output voltage characteristics of the novel semiconductor granules;

FIG. **3** is a graph showing the direct current-resistance characteristics of the novel semiconductor granules;

FIGS. **4A**, **4B** and **4C** show the relationship between the composition of the alloy and AC output voltage, AC resistance and available power, respectively; and

FIG. **5** is a plot showing the attenuation characteristics of the second harmonic of the audio frequency of the acoustic-electro converting devices utilizing the semiconductor granules embodying the invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

An acoustic-electro converting device using the semiconductor granules of this invention comprises a cone-shaped duralumin diaphragm **1** having an outer periphery mounted on the inside of the outer wall **3** of an aluminum casing **2**. The diaphragm **1** is provided with a central openging **4** which is covered by a semispherical hollow moving electrode **5**. An annular sheet **7** of silk is provided between the inner wall **6** of the casing **2** and the moving electrode **5**. A semispherical hollow fixed electrode **9** is secured concentric with the moving electrode **5** by an annular insulation washer **8** located below sheet **7**. The stationary electrode **9** is clamped between annular insulation washers **8** and **10**. Accordingly, a chamber **11** is defined by silk sheet **7**, moving electrode **5**, insulation washer **8** and fixed electrode **9**. The chamber **11** has a volume of about 0.45 cc, for example, and is packed with the semiconductor granules to be described later.

Although the theory of operation of the mechanism of the acoustic-electro converting device shown in FIG. **1** is not yet fully understood, the following phenomena were noted. When a sound pressure is applied to diaphragm **1** while a dc voltage is supplied between moving and fixed electrodes **5** and **9**, a pressure is applied upon the semiconductor granules packed in the chamber **11**. Then the resistance of the semiconductor granules themselves and contact resistance between granules vary to in turn vary the electrical resistance between electrodes **5** and **9** thereby producing an output signal corresponding to the applied sound pressure.

The raw materials of the semiconductor granules of this invention comprises selemium, tellurium and antimony. Preferably these raw materials have a purity, for example, of 99.999 percent. The components are

weighed at a predetermined ratio and the mixture of the components is packed in a glass ampoule with one end closed. After evacuating the ampoule to a vacuum of about $10^{-6}$ Torr, the open end of the ampoule is sealed. Then, the sealed ampoule is placed in an electric furnace to heat the mixture of the components to a temperature substantially higher than the melting point of the mixture. When the melting point of the raw material is higher than 500°C, a quartz ampoule is substituted for the glass ampoule. The ampoule is vibrated in the electric furnace to agitate and admix the molten metal. Thereafter, the ampoule is cooled to room temperature at a rate of about 1°C per minute thus producing the desired alloy crystals. The crystals are then pulverized to form granules having a particle size of from 0.1 to 0.4 mm.

One example of the characteristics of granules of selenium- tellurium alloy is as follows. In one case, 1.7 g of granules having a grain size of 60 to 100 mesh of a selenium-tellurium alloy containing these elements at an atomic weight ratio of 1 : 9 (Se 1 - Te 9) was packed in chamber **11** whereas in the other case 1.4 g of the granules having a grain size of 60 to 100 mesh of a selenium-tellurium alloy containing these elements at an atomic weight ratio of 4 : 6 (Se 4 - Te 6) was packed in chamber **11**. The acoustic-electro characteristics of these alloys were measured and the results are shown in the following Tables. The measurements were carried out by supplying a dc current across electrodes **5** and **9** and by applying a sound pressure of about one microbar to the diaphragm at a frequency of 1 $kH_z$.

TABLE 1.

| | AC output voltage (mV) FIG. 2 | | | | |
|---|---|---|---|---|---|
| Supplied Current (mA) | 2 | 5 | 10 | 20 | 50 |
| Se 1 : Te 9 | 5 | 7.8 | 9.5 | 9.1 | 5.8 |
| Se 4 : Te 6 | 17 | 21 | 20 | 14 | 7 |

TABLE 2.

| | AC resistance (ohm) FIG. 3 | | | | |
|---|---|---|---|---|---|
| Supplied Current (mA) | 2 | 5 | 10 | 20 | 50 |
| Se 1 : Te 9 | 200 | 175 | 150 | 110 | 64 |
| Se 4 : Te 6 | 5000 | 3200 | 2200 | 1300 | 700 |

The following example illustrates alloys of selenium-tellurium- antimony. In one case, 1.3 g of the granules having a particle size of 60 to 100 mesh of a selenium-tellurium-antimony containing these elements at an atomic weight ratio of 1 : 3 : 6 (Se 1-Te 3-Sb 6) was packed in chamber **11** whereas in the other case **1.4** g of the granules of the particle size of 60 to 100 mesh of a selenium-tellurium-antimony alloy containing these elements at an atomic weight ratio of 4 : 1 : 5 (Se 4-Te 1-Sb 5) was packed in chamber **11**. The measured values of the acoustic-electro characteristics of these alloys under the same measuring conditions as in the preceding example are shown in Tables 3 and 4 below.

TABLE 3.

| | AC output voltage (mV) FIG. 2 | | | | |
|---|---|---|---|---|---|
| Supplied Current (mA) | 2 | 5 | 10 | 20 | 50 |
| Se 1-Te 3-Sb 6 | 0.38 | 0.9 | 1.8 | 3.5 | 7 |
| Se 4-Te 1-Sb 5 | 14 | 20 | 21 | 17 | 8.6 |

TABLE 4.

| | AC resistance (ohm) FIG. 3 | | | | |
|---|---|---|---|---|---|
| Supplied Current (mA) | 2 | 5 | 10 | 20 | 50 |
| Se 1-Te 3-Sb 6 | 90 | 90 | 90 | 89 | 78 |
| Se 4-Te 1-Sb 5 | 3100 | 2100 | 1420 | 950 | 460 |

These Tables (1–4) show typical data obtained and these data are plotted in FIGS. **2** and **3**. FIG. **2** shows a plot of DC current-AC output voltage characteristics. As can be noted from FIG. **2**, with the exception of the alloy Se 1-Te 3-Sb 6, the novel semiconductor granules show a larger AC output voltage for a small DC current when compared with the well known carbon granules. As shown in FIG. **3** which illustrates the AC resistance characteristics of the novel semiconductor granules, these granules manifest a larger AC resistance than do carbon granules.

From the results of a number of measurements made on granules of alloys of compositions differing in proportions from those described above, it has been possible to make a clear analysis of the acoustic-electro converting characteristics of the semiconductor granules of the selenium-tellurium-antimony system. The results of this analysis are shown by the diagrams in FIGS. **4A**, **4B** and **4C**. FIG. **4A** shows the composition dependency of the AC output voltage where a DC current of 5 m A was supplied between the moving **5** and the fixed electrodes **9** when a sound pressure of about 1 microbar at a frequency of 1 $kH_z$ was applied to the diaphragm. FIG. **4B** shows the composition dependency of the AC resistance by illustrating the AC resistance between the electrodes at a frequency of 1 $kH_z$ whereas FIG. **4C** shows the composition dependency of the output power at a DC current of 5 m A.

The hysteresis of the novel semiconductor granules for DC current and sound pressure is much smaller than that of conventional carbon granules. Thus, the operation of the semiconductor granules is extremely stable. Moreover, the distortion in the output voltage

with respect to the waveform of the input sound pressure of the acoustic-electro converting device utilizing the semiconductor granules of this invention is smaller than that of the carbon transmitter. Especially, the attenuation characteristic of the second harmonic of the input sound wave is excellent. FIG. **5** shows the attenuation characteristics of the second harmonic output with reference to the fundamental frequency output of the acoustic-electro converting devices using the novel semiconductor granules and carbon granules, respectively.

While the invention has been described in terms of selenium-tellurium alloys and selenium-tellurium-antimony alloys, it was found that lead could be substituted for antimony with equal satisfactory results. For example, when 2 atomic weight percent of lead was incorporated in a 49 : 49 selenium-tellurium alloy, the output voltage was increased 10 percent whereas the AC resistance was decreased 20 percent when compared with selenium-tellurium alloys.

As described above, alloys containing higher percentages of selenium have higher output voltages. Especially under a low supplied current of less than 15 m A, larger output voltages are obtained than with carbon granules. As pointed out above, the electrical resistance increases with the selenium concentration. It has been found that it is possible to adjust the electrical resistance of the novel alloy semiconductor granules by incorporating a halogen into the selenium-tellurium type alloy. For example, when 0.05 percent by weight, of chlorine is added to an alloy containing selenium and tellurium at an atomic weight ratio of 3 : 7, the output voltage scarcely varied while the AC resistance decreased about 20 percent. The quantity of incorporation of the chlorine may be very small, 0.001 to 0.1 percent being preferred for chlorine.

We claim:

**1.** An article of manufacture comprising acoustic-electric converting device semiconductor granules for use in acoustic-electric converting devices, said granules being made of an alloy consisting essentially of from 10 to 95 atomic weight percent of selenium and from 5 to 90 atomic weight percent of tellurium, and characterized in being granulated into granules having diameters of the order from 0.1 to 0.4 mm.

**2.** The semiconductor granules according to claim **1**, wherein said alloy further contains from 1 to 80 atomic weight percent of antimony.

**3.** The semiconductor granules according to claim **1**, wherein said alloy further contains from 1 to 80 atomic weight percent of lead.

**4.** The semiconductor granules according to claim **1**, wherein said alloy further contains from 0.001 to 0.1 percent by weight of halogen.

**5.** The semiconductor granules according to claim **2**, wherein said alloy further contains from 0.001 to 0.1 percent by weight of halogen.

**6.** The semiconductor granules according to claim **4**, wherein said halogen is chlorine.

**7.** An article of manufacture comprising acoustic-electric converting device semiconductor granules for use in acoustic-electric converting devices, the said granules consisting essentially of from 10 to 40 atomic weight percent of selenium, from 10 to 30 atomic wieght percent of tellurium and from 50 to 60 atomic weight percent of antimony, and characterized in having diameters of the order of from 0.1 to 0.4 mm.

* * * * *