# United States Patent [19]

**Tomita et al.**

[11] **3,820,487**

[45] **June 28, 1974**


[54] **LIGHT SOURCE LAMP CATHODE FOR ATOMIC LIGHT ABSORPTION ANALYSIS FORMED BY COMPRESSING POWDER OF $Cd_3$ Cu WITH ONE OFTHE POWDERS OF $Pb_3Ba$, $Pb_3CA$ OR $Pb_3Sr$**


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[73] Assignee: **Hitachi, Ltd.**, Tokyo, Japan



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[21] Appl. No.: **358,546**

[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** ..... **313/209**, 313/218, 313/311, 252/518, 252/521

[51] **Int. Cl.** ..... **H01j 61/08**

[58] **Field of Search** ..... 313/209, 311, 218, 346; 252/521



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*Attorney, Agent, or Firm*—Craig and Antonelli



[57] **ABSTRACT**

A hollow cathode lamp for atomic light absorption analysis which includes a hollow cathode fabricated by mixing and compressing the powder of $Cd_3Cu$ with at least one of the powders of $Pb_3Ba$, $Pb_3Ca$ and $Pb_3Sr$ in a predetermined volume ratio into a hollow cathode shape.


**3 Claims, 7 Drawing Figures**

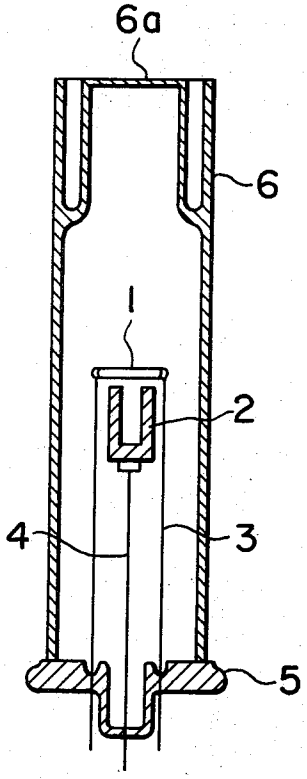


FIG. 1

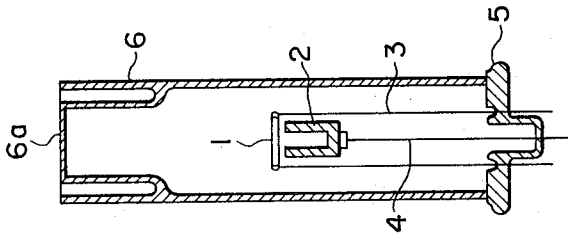

6
2
3
5
6a
1
4

FIG. 2

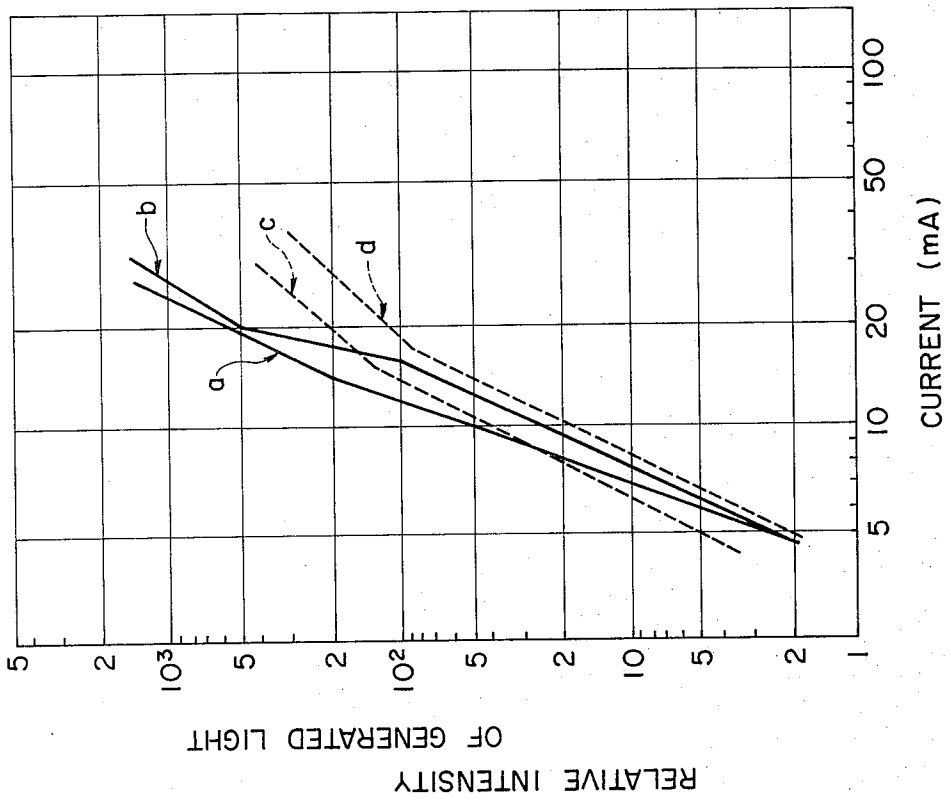

b
c
d
a
100
50
20
10
5
CURRENT (mA)
5
2
10³
5
2
10²
5
2
10
5
2
1
RELATIVE INTENSITY
OF GENERATED LIGHT

FIG. 3

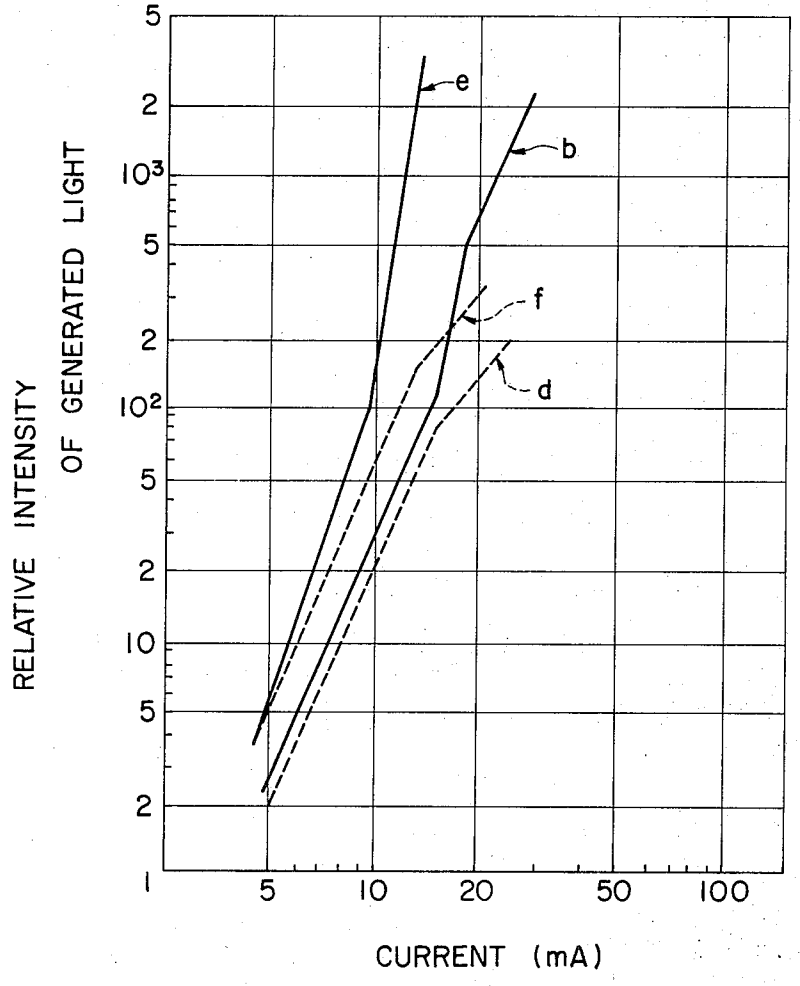

RELATIVE INTENSITY OF GENERATED LIGHT
5
2
10³
5
2
10²
5
2
10
5
2
1
5
10
20
50
100
CURRENT (mA)
e
b
f
d

FIG. 4

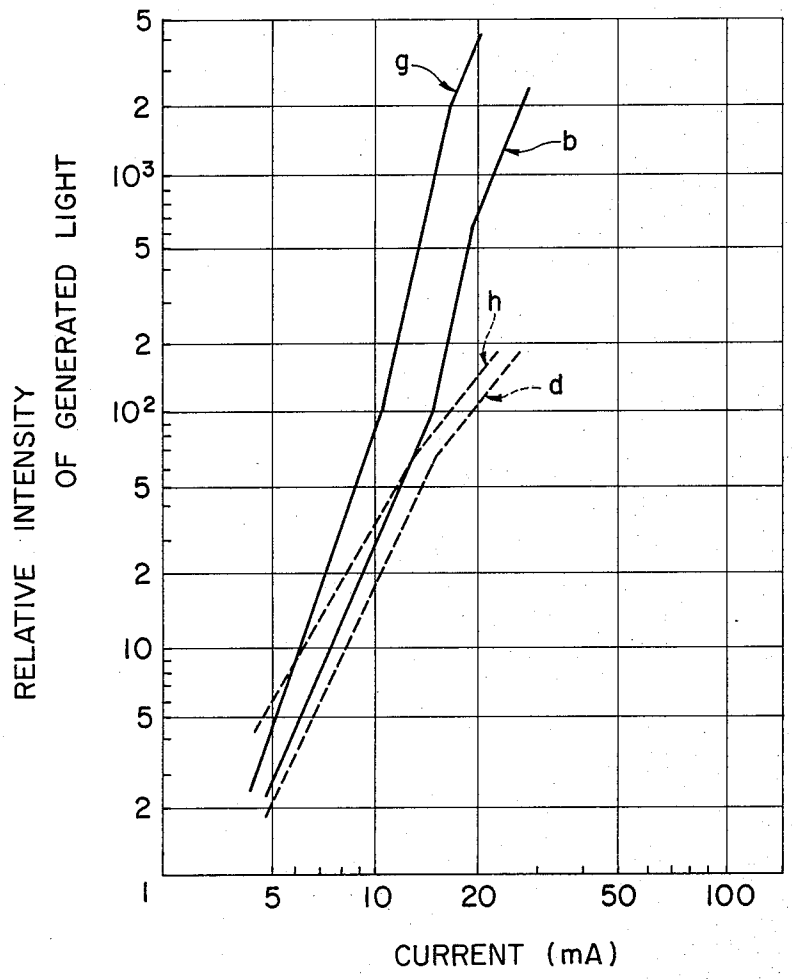

RELATIVE INTENSITY OF GENERATED LIGHT
5
2
10³
5
2
10²
5
2
10
5
2
1
5
10
20
50
100
CURRENT (mA)
g
b
h
d

FIG. 5

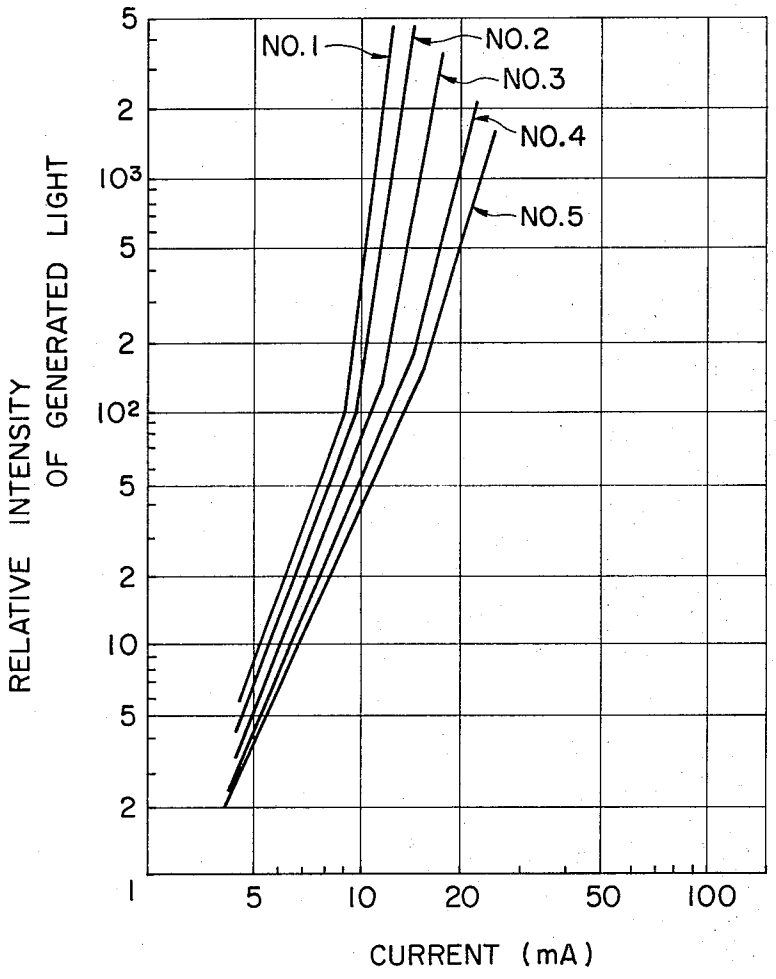

NO. 1
NO. 2
NO. 3
NO. 4
NO. 5
RELATIVE INTENSITY OF GENERATED LIGHT
5
2
10³
5
2
10²
5
2
10
5
2
1
5
10
20
50
100
CURRENT (mA)

FIG. 6

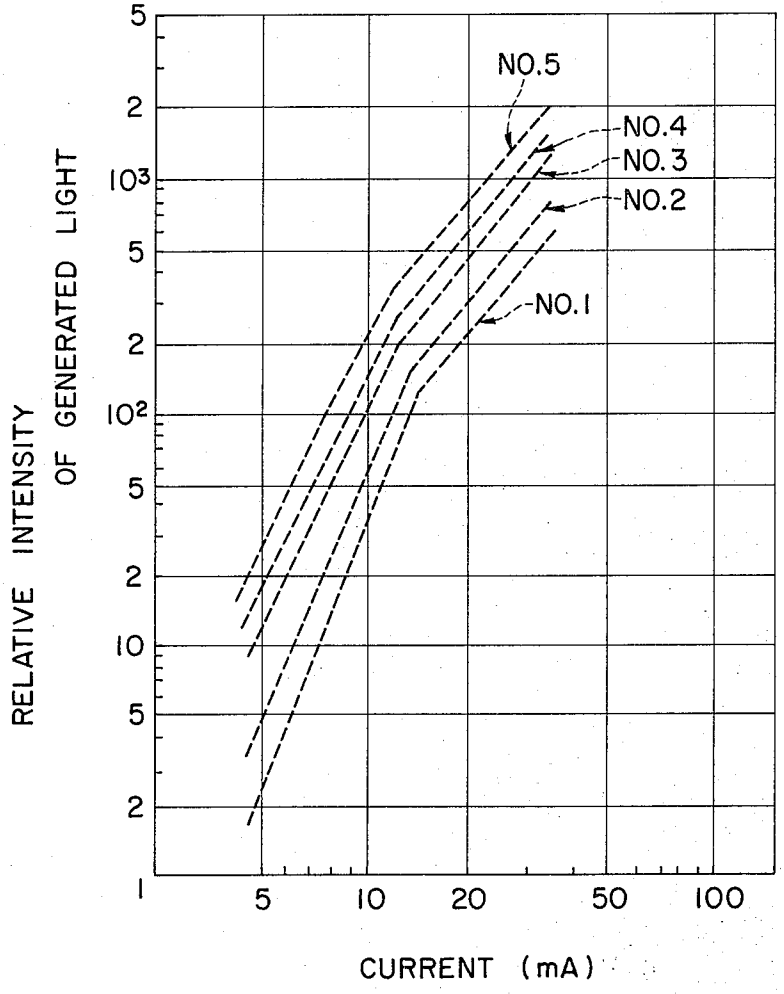
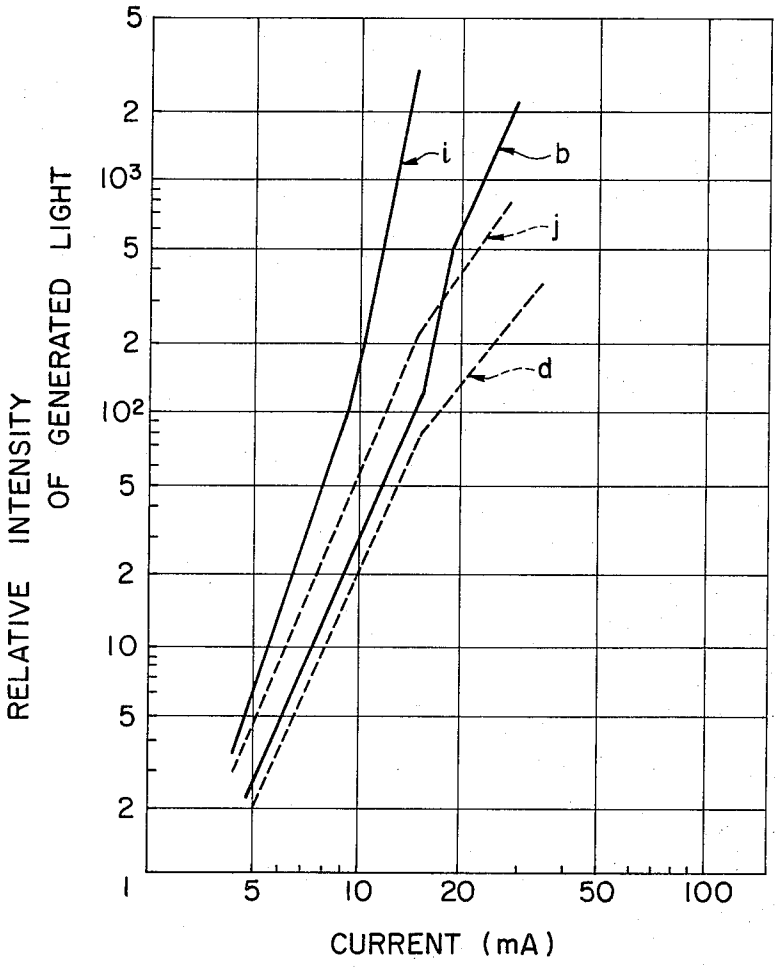

RELATIVE INTENSITY OF GENERATED LIGHT
5
2
10³
5
2
10²
5
2
10
5
2
1
NO.5
NO.4
NO.3
NO.2
NO.1
5
10
20
50
100
CURRENT (mA)

FIG. 7


RELATIVE INTENSITY OF GENERATED LIGHT
5
2
10³
5
2
10²
5
2
10
5
2
1
i
b
j
d
5
10
20
50
100
CURRENT (mA)

# LIGHT SOURCE LAMP CATHODE FOR ATOMIC LIGHT ABSORPTION ANALYSIS FORMED BY COMPRESSING POWDER OF CD CU WITH ONE OF THE POWDERS OF PB BA, PB CA OR PB SR

## FIELD OF THE INVENTION

The present invention relates to a light source for atomic light absorption analysis and more particularly to a light source provided with a new hollow cathode used in an atomic light absorption analyzer. The atomic light absorption analysis is one of the methods of quantitatively analyzing the metal salt included in a specimen solution. According to the analysis, a metal salt is decomposed by the thermal energy of flame to produce the vapors of component atoms, a light having resonance spectra is passed through the vapors to cause the component atoms to absorb the light components having wave-lengths characteristic of the atoms, and the analysis of the component atoms is optically effected by measuring the quantity of light absorbed. This method of analysis is widely used in the field of the medical, food or industrial chemistry.

For a better understanding of the present invention and for comparison between the prior art and the present invention, the specification should be read through parallel reference to the attached drawings.

## BRIEF DESCRIPTION OF THE DRAWING

FIG. **1** shows in cross section a hollow cathode lamp used in an ordinary atomic light absorption analyzer.

FIG. **2** graphically shows the relative intensities of lights generated by the use of a hollow cathode lamp of a $Pb_3Ba$-$Cd_3Cu$ cathode according to the present invention and of a conventional Cd-Pb composite cathode.

FIG. **3** graphically shows the relative intensities of lights generated by the use of a hollow cathode lamp of a $Pb_3Ca$-$Cd_3Cu$ cathode according to the present invention and of a conventional Cd-Pb composite cathode.

FIG. **4** graphically shows the relative intensities of lights generated by the use of a hollow cathode of a $Pb_3Sr$-$Cd_3Cu$ cathode according to the present invention and of a conventional Cd-Pb composite cathode.

FIGS. **5** and **6** respectively show the relative intensities of light generated from cadmium Cd and lead Pb by the use of a hollow cathode lamp of a $Pb_3Ca$-$Cd_3Cu$ cathode when the ratio by volume of Pb to Cd is varied.

FIG. **7** comparatively shows the resonance spectra from lead Pb and cadmium Cd by the use of a hollow cathode lamp according to the present invention and of a conventional composite cathode, respectively.

## DESCRIPTION OF THE PRIOR ART

The general structure of a light source used in an atomic light absorption analyzer is as shown in FIG. **1.** Reference numerals **1** and **2** designate an anode and a cathode, respectively. The anode **1** is a hollow disc and the cathode **2** is a hollow cylinder with one end closed. The anode **1** and the cathode **2** are hermetically sealed in a discharge tube consisting of a quartz envelope **6** and a socket **5,** and an anode terminal **3** and a cathode terminal **4** are connected with the anode **1** and the cathode **2** and led out through the socket **5.** The inner space of the discharge tube is filled with a small quantity of an inert gas such as argon gas.



When discharge is caused between the anode **1** and the cathode **2** by the application of a voltage therebetween, the inert gas in the tube is ionized to create positive ions, which hit the inner surface of the hollow cathode to cause the cathode metal to be vaporized. The atoms of the vaporized metal are excited by a strong electric field near the cathode and generate spectral lines or resonance spectral lines from the hollow of the cathode **2.** The spectral lines are passed through a window **6***a* of the quartz envelope **6** to be used for atomic light absorption analysis. It is necessary for the light source of an atomic light absorption analyzer, and especially the composite cathode used therein to produce a plurality of resonance spectral lines, to produce as strong spectral lines as possible. Since, however, there exists a plurality of elements in the cathode, the intensities of lights corresponding to the respective elements are usually lowered.

In order to obtain more than two kinds of lights with a single lamp having a composite cathode as mentioned above, it is necessary that the intensities of the respective lights should be almost equal for lamp currents of the same order.

The present invention has been made to obtain a light source having a single cathode which can produce several resonance spectral lines corresponding to different elements having such low melting points that each of them may not solely form the cathode body, and especially to obtain a cathode to produce resonance spectral lines corresponding to Pb and Cd.

The melting point of Pb is 327°C and that of Cd is 321°C. Therefore, if only one of them is used as a solid cathode, it will be melted and deformed at operating temperatures of about 500°C. In order to solve this problem encountered in the simultaneous analysis of Pb and Cd, there is used a cathode comprising a porous body of metal having a high melting temperature such as Cu or Ni and Pb-Cd alloy fused into and solidified in the pores of the body. With this structure of the cathode, however, the quantity of the metal having a high melting point is too small so that the intensity of light having a corresponding resonance spectral line is unsatisfactory.

## SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a light source provided with a nei hollow cathode, which can solely produce resonance spectral lines corresponding to Pb and Cd with sufficiently high intensities.

Another object of the present invention is to provide a hollow cathode lamp whose cathode is formed of a mixture of $Cd_3Cu$ powder and at least one of $Pb_3Ba$, $Pb_3Ca$ and $Pb_3Sr$ powder.

A further object is to provide a hollow cathode whose composite cathode formed of the powders of $Cd_3Cu$ and at least one of $Pb_3Ba$, $Pb_3Ca$ and $Pb_3Sr$, the ratio by volume of the powder of $Cd_3Cu$ to one of $Pb_3Ba$, $Pb_3Ca$ and $Pb_3Sr$ being in the range of 1:3 to 1:10 in order to obtain lights having stable strong intensity.

A still further object is to provide a hollow cathode lamp provided with a composite cathode which is made of a molded article of a powder mixture of $Cd_3Cu$ and at least one of $Pb_3Ba$, $Pb_3Ca$ or $Pb_3Sr$, the grain diame-

ter being smaller than 500 $\mu$ and especially smaller than 200 $\mu$.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Prior to explaining concrete embodiments according to the present invention, it should be generally noted about the materials and the other items to be adopted in the present invention as follows.

In accordance with the present invention, both Pb and Cd are in the form of a metal-to-metal alloy or an intermetallic compound since each of them has a melting point higher in alloy than in a single substance. The melting points of the intermetallic compounds mentioned above are sufficiently higher than the operating temperatures of the hollow cathode lamp. The reason why the metal compound of Pb is limited to $Pb_3Ba$, $Pb_3Ca$ or $Pb_3Sr$, is that if Pb is alloyed with alkaline earth metals then the voltage to maintain glow discharge can be decreased by 200 to 300 volts so that the sputtering of Pb is stabilized. Pb can be combined with metal Se or Te belonging to the group IV elements of the periodic table, but Pb-Se or Pb-Te alloy cannot show the effect of stabilizing the sputtering of Pb. In addition, the reason why the metal compound of Cd is limited to $Cd_3Cu$, is as follows. Namely, the vapor pressure of Cd is high so that sputtering does not produce the free atoms of Cd but an excessive amount of the vapor thereof. Consequently, such a large quantity of the vapor increases self-absorption, which makes the intensity of generated light unstable and deteriorates the sensitivity in detection. Therefore, Cd must be alloyed with some other metal so as to lower the vapor pressure and to stabilize the intensity of generated light. For this reason, Cd should be used in the form of $Cd_3Cu$ or CdSb. In the case of CdSb, however, the vapor pressure of Sb is high so that the intensity of generated light cannot be stabilized. Thus, $Cd_3Cu$ proves to be a preferable compound.

Incidentally, pressure of higher than 500 kg/cm$^2$ is applied to make the mixed powders into shape and the shaped cathode is lightly heated to increase the mechanical strength of the cathode.

## EMBODIMENT 1

A Pb-Cd composite cathode in the form of a hollow cylinder has been fabricated according to the following procedure, the external diameter of the hollow cylinder being 8 mm, the length 20 mm, the diameter of the cylindrical hollow 4 mm, and the depth of the hollow 15 mm. Pb with purity of 99.9 percent and Ba with purity of 99 percent are melted in an atmosphere of Ar to form $Pb_3Ba$ ingot consisting of 75 atomic percent of Pb and 25 atomic percent of Ba (hereafter atomic percent is designated by at. percent for brevity's sake). The melting point of the intermetallic compound $Pb_3Ba$ is about 610°C. The crucible used for fusing is made of ion and the mould used for shaping is of copper. The ingot is ground by means of a stamp mill placed in an Ar atmosphere, into powder having a grain diameter of less than about 100 $\mu$. On the other hand, Cd with purity of 99.9 percent and Cu with purity of 99.9 percent are melted in the atmosphere of Ar to form an intermetallic compound $Cd_3Cu$ ingot consisting of 75 at. percent of Cd and 25 at. percent of Cu. The melting point of $Cd_3Cu$ is about 530°C. The fusing crucible is of transparent quartz and the mould is of copper. The ingot is then crushed by means of a stamp mill placed in an Ar atmosphere into powder having a grain diameter of less than about 100 $\mu$. Next, the $Pb_3Ba$ powder and the $Cd_3Cu$ powder are mixed in the ratio by volume of 3 to 1 and then the mixed powder is compressed at a pressure of $2.5 \times 10^3$ kg/cm$^2$ and shaped into a hollow cathode having a predetermined configuration. The shaping is performed by pressing the powder contained in a metal mould.

For the purpose of comparison, a Pb-Cd composite cathode is formed according to the conventional procedure wherein Pb-Cd alloy consisting of Pb-Cd in the ratio by volume of 3 to 1 is impregnated into the pores of a porous body of Cu having a porosity of about 60 percent.

The two kinds of cathodes formed according to the methods described above are mounted in discharge tubes having a structure as shown in FIG. 1 and the measurement of the strength of the spectral light generated is performed with the discharge tubes. FIG. 2 shows the relative intensities of light having wavelengths of 2,833 A and 2,288 A corrresponding respectively to the resonance spectral lines of Pb and Cd, solid curves and dashed curves corresponding to the cathode formed according to the present invention and the conventional cathode. In FIG. 2, the abscissa represents the current flowing between the anode and the cathode and the ordinate gives the relative value of the strength of light in logarithmic graduation.

An increase in the strength of light with an increase in the current, as is seen in FIG. 2, means that the sputtering is intensified with the increase in temperature. The rate of increase of the strength falls for the values of current above a certain threshold. This is possibly because too much metal vapor produced by sputtering gives rise to the self-absorption of generated light. In FIG. 2, the curves *a*, *b*, *c* and *d* correspond to the Cd of the $Pb_3Ba$-$Cd_3Cu$ cathode, the Cd of the conventional Pb-Cd composite cathode, the Pb of the $Pb_3Ba$-$Cd_3Cu$ cathode and the Pb of the conventional Pb-Cd composite cathode, respectively. The reference value for relative intensity is adopted with respect to the resonance spectral line corresponding to the Pb of the $Pb_3Ba$-$Cd_3Cu$ cathode, that is, the value of 5 corresponds to the case where a current of 5 mA is drawn through the cathode to cause the Pb of the cathode to luminesce. It is thus apparent from the result plotted in FIG. 2 that the strengths of lights corresponding to Pb and Cd obtained by the use of the cathode according to this embodiment are about 2 to 5 times as great as those obtained with the impregnation cathode.

## EMBODIMENT 2

A Pb-Cd composite cathode in the form of a hollow cylinder, 8 mm across the external diameter of the hollow cylinder, 20 mm in length, 4 mm across the cylindrical hollow and 15 mm in the depth of the hollow, has been fabricated according to the following procedure. Pb with purity of 99.9 percent and Ca with purity of 99 percent are melted in an atmosphere of Ar to form $Pb_3Ca$ ingot constituted of 75 at. percent of Pb and 25 at. percent of Ca. The melting point of $Pb_3Ca$ is about 660°C. The crucible used for fusing is made of iron and the mould for shaping is of copper. The ingot is ground by means of a stamp mill placed in an Ar atmosphere, into powder having a grain diameter of less than about 100 $\mu$. On the other hand, Cd with purity of 99.9 per-

cent and Cu with purity of 99.9 percent are melted in an atmosphere of Ar to form $Cd_3Cu$ ingot consisting of 75 at. percent of Cd and 25 at. percent of Cu. The melting point of $Cd_3Cu$ is about 530°C. The fusing crucible is made of transparent quartz and the shaping mould is of copper. The ingot is then crushed by means of a stamp mill placed in an Ar atmosphere, into powder having a grain diameter of less than about 100 $\mu$. Next, the $Pb_3Ca$ powder and $Cd_3Cu$ powder are mixed in the ratio by volume of 3 to 1 and then the mixed powder is compressed at a pressure of $2.5 \times 10^3$ kg/cm$^2$ and shaped into a hollow cathode. The shaping is performed by pressing the powder in a metal mould. The thus finished cathode is mounted in a discharge tube having a structure as shown in FIG. **1** and the strength of the spectral light is measured with a discharge tube.

FIG. **3** shows strength of spectral lights having wavelengths of 2,833 A and 2,288 A corresponding respectively to the resonance spectral lines of Pb and Cd, solid curves and dashed curves corresponding to the cathode formed according to the present embodiment and the conventional cathode. In FIG. **3,** the abscissa represents the current flowing between the anode and the cathode and the ordinate gives the relative value of the strength of light in a logarithmic scale. The curves *e* and *f* in FIG. **3** correspond to the Cd and Pb of the $Pb_3Ca$-$Cd_3Cu$ cathode, respectively. The reference value for the strength is adopted with respect to the reference spectral line corresponding to the Pb of the $Pb_3Ca$-$Cd_3Cu$ cathode, that is, the value of 5 is taken for the case where a current of 5 mA is drawn through the cathode to cause the Pb of the cathode to luminesce. It is understood from the result shown in FIG. **3** that the strengths of lights corresponding to Pb and Cd obtained by the use of the cathode according to the present embodiment are about 2 to 7 times as great as those obtained with the conventional cathode according to impregnation method.

## EMBODIMENT 3

A Pb-Cd composite cathode in the form of a hollow cylinder, 8 mm across the external diameter of the hollow cylinder, 20 mm in length, 4 mm across the cylindrical hollow and 15 mm in the depth of the hollow, has been fabricated according to the following procedure. Pb with purity of 99.9 percent and Sr with purity of 99 percent are melted in the atmosphere of Ar to form a $Pb_3Sr$ ingot consisting of 75 at. percent of Pb and 25 at. percent of Sr. The melting point of $Pb_3Sr$ is about 670°C. The fusing crucible is made of iron and the shaping mould of copper. The ingot is crushed by means of a stamp mill placed in an atmosphere of Ar, into powder having a grain diameter of less than about 100 $\mu$. On the other hand, Cd with purity of 99.9 percent and Cu with purity of 99.9 percent are melted in an atmosphere of Ar to form $Cd_3Cu$ ingot consisting of 75 at. percent of Cd and 25 at. percent of Cu. The melting point of $Cd_3Cu$ is about 530°C. The fusing crucible is made of transparent quartz and the shaping mould of copper. The ingot is then crushed by means of a stamp mill placed in an Ar atmosphere, into powder having a grain diameter of less than about 100 $\mu$. Next, the $Pb_3Sr$ powder and the $Cd_3Cu$ powder are mixed in the ratio by volume of 3 to 1 and then the mixed powder compressed at a pressure of $2.5 \times 10^3$ kg/cm$^2$ and shaped into a hollow cathode. The shaping is performed by pressing the powder contained in a metal mould.

The thus fabricated cathode is mounted in a discharge tube having a structure as shown in FIG. **1** and the strength of the spectral light generated is measured with a discharge tube.

FIG. **4** shows the relative strengths of light having wavelengths of 2,833 A and 2,288 A corresponding respectively to the resonance spectral lines of Pb and Cd, solid and dashed curves corresponding to the cathode formed according to the present embodiment and the conventional cathode. In FIG. **4,** the abscissa represents the current flowing between the anode and the cathode and the ordinate gives the relative value of the strength of light in a logarithmic scale. The curves *g* and *h* in FIG. **4** correspond to the Cd and Pb of the $Pb_3Sr$-$Cd_3Cu$ cathode according to this embodiment, respectively. The reference value for the strength is adopted with respect to the Pb of the conventional Cd-Pb composite cathode, that is, the value of 2 is taken for the case where a current of **5** mA is drawn. It is apparent from FIG. **4** that the strength of light corresponding to Pb obtained by the use of the cathode according to this embodiment is about 2 to 5 times as great as that obtained with the conventional cathode according to an impregnation method.

## EMBODIMENT 4

Five examples of a cathode using such powders of $Pb_3Ca$ and $Cd_3Cu$ as mentioned in EMBODIMENT 2 mixed with each other according to the composition shown in the table given below, and formed through compression at a pressure of $2.5 \times 10^3$ kg/cm$^2$. The shaping of the cathode is performed by pressing the mixed powder contained in a metal mould.

TABLE

| CATHODE NO. | VOLUME RATIO | | | | | |
|---|---|---|---|---|---|---|
| 1 | $Pb_3Ca$ | 2 | vs. | $Cd_3Cu$ | 1 |
| 2 | do. | 3 | do. | do. | 1 |
| 3 | do. | 5 | do. | do. | 1 |
| 4 | do. | 10 | do. | do. | 1 |
| 5 | do. | 15 | do. | do. | 1 |

The thus completed cathode is mounted in a discharge tube having a structure as shown in FIG. **1,** and the strength of the spectral light generated is measured with a discharge tube.

FIG. **5** and FIG. **6** show respectively the strengths of light having wavelengths of 2,288 A and 2,833 A corresponding respectively to the resonance spectral lines of the Cd and Pb of the respective cathodes No. **1** to No. **5.** In FIGS. **5** and **6,** the abscissae represent the current and the ordinates give the relative value of the light strength in logarithmic scale. The reference value for the light strength is adopted with respect to the Cd resonance spectral line of the No. **4** cathode, that is, the value of 5 is taken for the case where a current of **5** mA is drawn. As is apparent from FIGS. **5** and **6,** all the No. **2** to No. **4** cathodes generate the light having a strength of the same order for the same current value, but the No. **1** cathode emits a strong spectral line for Cd and a weak spectral line for Pb while the No. **5** electrode produces a strong spectral line for Pb and a weak spectral line for Cd. Consequently, it has been proved that

the No. 2 to No. 4 cathode are of the highest quality.

## EMBODIMENT 5

A Pb-Cd composite cathode in the form of a hollow cylinder, 8 mm across the external diameter of the hollow cylinder, 20 mm in length, 4 mm across the cylindrical hollow and 15 mm in the depth of the hollow, has been fabricated according to the following procedure. The $Pb_3Sr$ powder used in the third embodiment, the $Pb_3Ca$ powder used in the second embodiment and the $Cd_3Cu$ powder used in the second embodiment, are mixed in the ratio in volume of 2:2:1 and the mixed powder is compressed at a pressure of $2.5 \times 10^3$ kg/cm$^2$ to form a solid cathode. The thus prepared cathode is mounted in a discharge tube having a structure as shown in FIG. 1 and the strength of the spectral light generated is measured with the discharge tube.

FIG. 7 shows the strengths of light having wavelengths of 2,833 A and 2,288 A corresponding respectively to the resonance spectral lines of Pb and Cd, solid and dashed curves corresponding to the cathode formed according to the present embodiment and the conventional cathode according to an impregnation method. In FIG. 7, the abscissa represents the current flowing through the anode and the cathode and the ordinate gives the relative value of the strength of light in logarithmic scale. In FIG. 7, the curves *i* and *j* represent respectively the relative strengths of light from the Cd and the Pb of the cathode according to the present embodiment while the curves *b* and *d* give the strengths of the light from the Cd and the Pb of the conventional cathode according to an impregnation method. The strengths of light corresponding to Pb and Cd obtained with the cathode according to the present embodiment are about 2 to 5 times as great as those obtained with the conventional cathode, as seen from FIG. 7.

We claim:

1. A light source lamp for atomic light absorption analysis comprising a cathode having a hollow portion formed therein, an anode provided adjacent to said cathode, a hermetically sealed envelope containing said cathode and said anode, and an inert gas atmosphere confined in said envelope, wherein said cathode is formed in a predetermined contour by a molded body of an intermetallic compound powder, said powder comprising a first powder of at least one member selected from the group consisting of $Pb_3Ba$, $Pb_3Ca$ and $Pb_3Sr$, and a second powder of $Cd_3Cu$.

2. A light source lamp according to claim 1, wherein a volume ratio of said first powder to said second powder is 3 to 10 per one.

3. A light source lamp according to claim 1, wherein said molded body comprises said first and second powders in such a relation that the light intensities of lead and cadmium which are irradiated from said cathode are substantially equal to each other.

* * * * *