(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 982 758 A2

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
01.03.2000 Bulletin 2000/09

(51) Int. Cl.^{7}: **H01J 61/067**

(21) Application number: **99116573.9**

(22) Date of filing: **24.08.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **24.08.1998 JP 25327798**

(71) Applicant: **TDK Corporation**
Chuo-ku, Tokyo (JP)

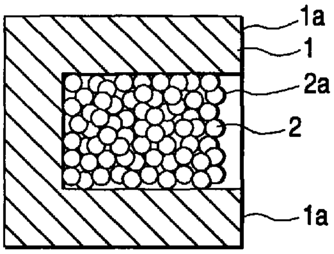
(72) Inventors:
- **Hamada, Munemitsu**
  Chou-ku, Tokyo (JP)
- **Takeishi, Akira**
  Chou-ku, Tokyo (JP)
- **Takahashi, Makoto**
  Chou-ku, Tokyo (JP)
- **Yodogawa, Masatada**
  Chou-ku, Tokyo (JP)
- **Harada, Hiraku**
  Chou-ku, Tokyo (JP)

(74) Representative:
Grünecker, Kinkeldey,
Stockmair & Schwanhäusser
Anwaltssozietät
Maximilianstrasse 58
80538 München (DE)

(54) Discharge lamp and electrode therefor

(57) The electrode for discharge lamp of the invention is that a cylindrical container 1 opening at one side is provided, and electron emission materials 2 are supported therein, the container 1 and the electron emission materials 2 are main elements of compound oxides containing, as metallic elemental components, a first component comprising at least one kind of Ba, Sr and Ca, a second component comprising at least one kind of Zr and Ti, and a third component comprising at least one kind of Ta and Nb and/or compound oxides containing nitrogen. The present electrode for discharge lamp is that the content percentage of the first component in exposed faces of the electron emission materials 2 seen from the opening side of the container 1 is higher than content percentage of the first component in an end face of the opening side of the container 1. Further, the electron emission materials are porous ones having percentage of void being 45 to 80%.

FIG. 1



Printed by Xerox (UK) Business Services
2.16.7/3.6

Description

BACKGROUND OF THE INVENTION

[0001] The invention relates to an electrode for discharge lamp and a discharge lamp having the electrode to be used to a back light of a liquid crystal display apparatus, a fluorescent lamp of electric bulb or a small sized fluorescent discharge lamp to be employed as a reading light source of facsimile or scanner.

[0002] Recently, social demands for saving energy, natural resources and others have been raised, and in response thereto, curtailment of energy of display or general illuminating light source has positively been progressed. For example, it has rapidly been advanced to substitute liquid crystal display of less energy consumption for CRT or substitute fluorescent lamps of electric bulb of higher energy efficiency and longer life for incandescent lamp. Going therewith, capillary fluorescent lamps have rapidly been utilized for light source of back light of liquid crystal display or for fluorescent lamps of electric bulb.

[0003] In general, the fluorescent lamps are classified into a hot cathode fluorescent lamp utilizing arc discharge by thermo electron emission and a cold cathode fluorescent lamp utilizing glow discharge by secondary electron emission. Since the hot cathode fluorescent lamp is smaller in cathode drop voltage than the cold cathode fluorescent lamp, luminous efficiency is high to voltage. In addition, since the hot cathode fluorescent lamp makes use of the thermoelectron emission and it may take largely current density, it is easier to make high bright intensity in comparison with the cold cathode fluorescent lamp. The hot cathode fluorescent lamp is therefore suited to the light sources requiring much light flux such as the back light of the liquid crystal display of large area, the fluorescent lamp of electric bulb, the light sources for reading of facsimiles or scanners.

[0004] As the conventional electrode for the hot cathode fluorescent lamp, known is, for example, a fluorescent lamp coated with alkaline earth metal containing parts of transition metal and barium (Ba) in a tungsten coil (JP-A-59-75553). However, since the electrode described in the same starts the thermoelectron emission, it needs a preheating, and it is difficult to make the electrode capillary as the cold cathode fluorescent lamp. So, it is not easy to utilize the electrode to the liquid crystal display for note personal computers being demanded to be thin type and light weight, and unsuitable to miniaturize the fluorescent lamp of electric bulb.

[0005] On the other hand, an electrode having a structure not needing a preheating for making capillary is disclosed in JP-A-4-73853 where a double coil of tungsten is adhered with an emitter substance composed of oxides of barium, calcium and strontium. However, in a discharge lamp using the electrode of this structure, Hg ion or rare gas ion generated during discharging collide with the electrode and spatter electron emission substances, and so-called ion spattering is remarkably caused. When the ion spattering is remarkable, the electron emission substances are exhausted, and a stable arc discharge cannot be kept for a long period of time. Besides, there occurs a phenomenon that an inner wall of lamp glass tube is blackened (blackening of tube wall) by the spattered electron emission substance, and maintenance of light flux is lowered early.

[0006] U.S. Patent No.2,686,274 describes rod shaped electrodes made semiconductive by a reducing treatment of ceramics as Ba_2TiO_4. But the electrodes of the ceramic semiconductor of this structure are involved with problems that they are weak against thermal shocks, easily deteriorated by spattering by Hg ion or rare gas ion, or the current density is small.

[0007] In view of such prior hot cathode fluorescent lamps, inventors of this patent application proposed electrodes of structure supporting ceramic semiconductors in a cylindrical container opening one end and closing another end, and with respect to the electrodes and the discharge lamps using the same, they have made various improvements (JP-A-6-103627; JP-A-1-65764; JP-A-2-186550; JP-A-2-186527; JP-A-4-43546; JP-A-6-267404; JP-A-9-129117; JP-A-10-12189; JP-A-6-302298; JP-A-7-142031; JP-A-7-262963; and JP-A-10-3879). The electrode of this structure has characteristics that the pre-heating is not necessary, making capillary is possible, and a life is long because of suppressing deterioration by ion spattering or evaporation. But, for not necessitating exchange of the back light of the liquid crystal display, the life of the electrode must be longer than that of a machinery mounted with the display, and for aiming at this object, the life of the electrode should be further increased. If the fluorescent discharge lamp is considerably deteriorated by frequently repeating ON and OFF, and the life is accordingly very shortened, and for substituting an incandescent lamp, the shortening of life by repeating ON and OFF must be avoided.

SUMMARY OF THE INVENTION

[0008] Accordingly, it is an object of the invention to extend the life of the hot cathode fluorescent lamp.

[0009] The object as mentioned above can be accomplished by any of the following (1) to (8).

(1) An electrode for discharge lamp, wherein a cylindrical container opening at one side is provided, and electron emission materials are supported therein, the container and the electron emission materials are main elements of

compound oxides containing, as metallic elemental component, a first component comprising at least one kind of Ba, Sr and Ca, a second component comprising at least one kind of Zr and Ti, and a third component comprising at least one kind of Ta and Nb and/or compound oxides containing nitrogen, and content percentage of the first component in exposed faces of the electron emission discharge materials seen from the opening side of the container is higher than content percentage of the first component in an end face of the opening side of the container.

(2) An electrode for discharge lamp, wherein a container opening at one side is provided, and electron emission materials are supported therein, the container and the electron emission materials are main elements of compound oxides containing, as metallic elemental component, first component comprising at least one kind of Ba, Sr and Ca, second component comprising at least one kind of Zr and Ti, and third component comprising at least one kind of Ta and Nb and/or compound oxides containing nitrogen,
and the electron emission materials are porous ones having percentage of void being 45 to 80%.

(3) The electrode for discharge lamp as set forth in the above (1) or (2), wherein the density of the container is 60% or more in a theoretical density.

(4) The electrode for discharge lamp as set forth in any one of the above (1) to (3), wherein an average radius of curvature in the discharge face is 10 to 150μm.

(5) The electrode for discharge lamp as set forth in any one of the above (1) to (4), wherein carbides and/or nitrides containing at least one kind of Ta, Nb and Ti exist in the exposed faces of the electron emission discharge materials seen from the opening side of the container and in the end face of the opening side of the container, as well as in the outside and/or the bottom of the container.

(6) The electrode for discharge lamp as set forth in any one of the above (1) to (5), wherein when the first component is expressed with M^{I}, the second component is expressed with M^{II}, and the third component is expressed with M^{III}, the container and the electron emission materials contain at least one kind of crystals selected from

$M^{I}M^{II}O_3$ type crystal,
$M^{I}_5M^{III}_4O_{15}$ type crystal,
$M^{I}_7M^{III}_6O_{22}$ type crystal,
$M^{I}M^{III}O_2N$ type crystal, and
$M^{I}_6M^{II}M^{III}_4O_{18}$ type crystal.

(7) The electrode for discharge lamp as set forth in any one of the above (6), wherein one part of M^{III} is substituted with MII and one part of M^{II} is substituted with M^{III}.

(8) A discharge lamp, having the electrode for the discharge lamp in any of the above (1) to (7).

[0010] The inventors ascertained that the ion spattering of the electrode in the hot cathode fluorescent lamp was remarkably generated at a time of the glow discharging, and found that a rapid shifting from the glow discharge to the arc discharge was possible by applying the invention they accomplished.

[0011] Specifically, by determining the containing rate of the first component in the exposed faces of the electron emission materials to be higher than the containing rate of the first component at the end face of the opening side of the container, in other words, by determining the containing rate of the first component at the end face of the opening side of the container to be low, the electric conductivity in the end face of the opening side of the container is heightened and the discharge is easily caused in the exposed face of the electron emission materials. Thus, the container sufficiently serves as an electric conductive path, and the generation of unstable discharge at the end face of the opening of the container is controlled, and a stable arc spot may be instantly formed at the exposed face of the electron emission materials. Therefore, it is possible to instantly shift from the glow discharge to the arc discharge.

[0012] Further, if the electron emission materials are made porous ones having percentage of void being 45% or more, since the heat conductivity is critically lowered, temperature is partially increased, and the rapid shift from the glow discharge to the arc discharge is enabled. If the percentage of void is too high, the electron emission material is dropped during discharging to shorten the life of the hot cathode fluorescent lamp, but if it is controlled to be 80% or less, the electron emission material is prevented from dropping, so that the long life is not impeded by shortening the glow discharge.

[0013] The invention enables to considerably check the weakening of the electrode caused at turning on, and is especially effective when the number of the glow discharging is made much by frequently repeating ON and OFF.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

Fig.1 is a cross sectional view showing a composing example of the inventive electrode for discharge lamp;

Fig.2 is a flow chart for explaining a producing process of the inventive electrode for discharge lamp;

Fig.3 is a cross sectional view showing a composing example of the discharge lamp having the inventive electrode for discharge lamp;

Fig.4 is a photograph substituting a drawing of a structure of a ceramic material, and an EPMA image showing a Ba distribution of an electrode surface for the discharge lamp;

Fig.5 is a photograph substituting a drawing of a structure of a ceramic material, and an EPMA image showing a Ta distribution of an electrode surface for the discharge lamp;

Fig.6 is a photograph substituting a drawing of a structure of a ceramic material, and an EPMA image showing a Ba distribution of an electrode surface for the discharge lamp;

Fig.7 is a photograph substituting a drawing of a structure of a ceramic material, and an EPMA image showing a Ta distribution of an electrode surface for the discharge lamp;

Fig.8 is a photograph substituting a drawing of a structure of a ceramic material, and an EPMA image showing a Ba distribution of an electrode surface for the discharge lamp;

Fig.9 is a photograph substituting a drawing of a structure of a ceramic material, and an EPMA image showing a Ta distribution of an electrode surface for the discharge lamp;

Fig.10 is a photograph substituting a drawing showing grain structure of an electrode in cross section for the discharge lamp by a scanning electron microscope;

Fig.11 is a chart of a powder X-ray diffraction of the electron emission materials;

Fig.12 is a chart of a powder X-ray diffraction of the container;

Fig.13 is a chart of a powder X-ray diffraction of the electron emission materials;

Fig.14 is a chart of a powder X-ray diffraction of the electron emission materials;

Fig.15 is a chart of a powder X-ray diffraction of the electron emission materials; and

Fig.16 is a chart of an X-ray diffraction of a disc like sintered product made under the same conditions as for the container.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The electrode for the discharge lamp

[0015] Fig.1 illustrates an example of composing the electrode for the discharge lamp of the invention. The instant electrode for discharge lamp comprises a cylindrical container 1 opening one end and electron emission materials 2 held therein. Within the tube of the electric discharge lamp, ions as Hg ion or other generated in company with discharging fly from a direction of an opposite electrode and collide with the electrode, but at this time the ions are intercepted by the container 1 and the number of the ions colliding with the electron emission materials 2 is lessened. The container 1 prevents spattering of the electron emission materials 2 by the ions and serves as an electric conductive path for supplying current to the electron emission materials 2.

[0016] The inventive container 1 and the electron emission materials 2 are each main elements of compound oxides or compound oxides containing nitrogen, and contain, as metallic elemental components, a first component comprising at least one kind of Ba, Sr and Ca, a second component comprising at least one kind of Zr and Ti, and a third component comprising at least one kind of Ta and Nb. The compound containing the first component is an electron emission component of low work function. The second component is a component necessary for making the electron emission materials have high melting points. Ti and of the second component and the third component are supply sources of compounds composing later mentioned spattering prevention layers. If the container 1 is composed of materials of the same family as the electron emission materials 2, both can be firmly combined electrically and mechanically.

[0017] The first, second and third components compose the compound oxides or the compound oxides containing nitrogen. When the first component is expressed with M^{I}, the second component is expressed with M^{II}, and the third component is expressed with M^{III}, it is desirable that the container and the electron emission materials contain at least one kind of crystals selected from

$M^{I}M^{II}O_3$ type crystal,
$M^{I}_5M^{III}_4O_{15}$ type crystal,
$M^{I}_7M^{III}_6O_{22}$ type crystal,

$M^IM^{III}O_2N$ type crystal, and
$M^I_6M^{II}M^{III}_4O_{18}$ type crystal.

There are chances that one part of M^{III} is substituted with M^{II} and one part of MII is substituted with M^{III}. The existences of these crystals can be confirmed by an X-ray diffraction. That one parts of the elements are substituted with other elements can be confirmed by the shift of the peak in the X-ray diffraction.

[0018] In the container and the electron emission materials, if the atomic ratio of the first component is X, the atomic ratio of the second component is Y, and the atomic ratio of the third component is Z for the total of the first and second and third components, preferably,

$$0.8 \le X/(Y+Z) \le 2.0$$

$$0.05 \le Y \le 0.6$$

$$0.4 \le Z \le 0.95,$$

and more preferably,

$$0.8 \le X/(Y+Z) \le 1.6$$

$$0.1 \le Y \le 0.4$$

$$0.6 \le Z \le 0.9.$$

If X/(Y+Z) is too small, the first component is early exhausted by discharging. On the other hand, if X/(Y+Z) is too large, the electron emission materials are easily evaporated and spattered during discharging, so that the tube wall of the lamp is intensively blackened to invite lowering of the lamp brightening. If Y is too small, the melting point of the electron emission materials is lowered and the closeness easily goes ahead, so that when producing the electron emission materials by baking in a reducing atmosphere, it is difficult to maintain the void percentage of the electron emission materials at appropriate values. As a result, it is difficult to make the electron emission materials porous and accordingly to maintain the discharging stable. However, if Y is too large, the resistance of the electron emission materials becomes too high, so that the maintenance of the stable discharging is difficult. If Z is too small, when producing the electron emission materials by baking in the reducing atmosphere, it is difficult to form carbides and/or nitrides on the surfaces of the container and the electron emission materials. Consequently, durability against the ion spattering is insufficient. On the other hand, if Z is too large, when producing the electron emission materials by baking in the reducing atmosphere, the container and the electron emission materials are extremely evaporated and spattered.

[0019] Preferably, the electron emission material is porous. Being porous, the heat conductivity may be reduced, and part of temperature easily goes up, so that it is easy to shift from the glow discharge to the arc discharge and to maintain the arc discharge stable. When the electron emission material is porous, the percentage of voids is preferably 45 to 80%, and more preferably 55 to 75%. If the percentage is too low, a heat reserving effect enough for emitting thermoelectron cannot be provided, and it is difficult or probably impossible to shift from the glow discharge to the arc discharge. On the other hand, however, if the percentage of voids is too high, the electron emission material is easy to drop during discharging, resulting in short life of the electrode.

[0020] The porous electron emission material is produced, for example as later mentioned, by not compression-forming but calcining the temporarily baked granular substances. The electron emission materials produced by this process show properties that grains combining other grains with at least one part assemble, and shapes of grains are generally irregular, spherical or acicular. In such porous electron emission materials, one grain surface of plural grains is a discharging face, which plural grains exist in the surface (exposed face) at the opening side of the container. An average radius of curvature in the discharging face, that is, an average radius of curvature of grain existing at the exposed face is preferably 10 to 150μm, and more preferably 20 to 100μm. The radius of curvature when grains are irregular is a radius of circumscribing circle of said grain. The radius of curvature of the discharging face can be sought by photographs of the electrode in cross section of a scanning type electron microscope. By determining the radius of curvature of the discharging face in the above scope, the maintenance of the stable arc discharge is made easy. If the arc discharging is not stable, voltage variation and temperature variation are caused in the electrode, so that the life of the electrode is shortened. If determining the radius of curvature in the above scope, it is especially effective when lamp current is 5 to 500mA. Since the smaller the lamp current, the smaller the preferable average radius of curvature of the discharging face, a concrete and average radius of curvature may be selected appropriately from the above scope in response to the lamp current. If the lamp current is 5mA or more, it is generally sufficient for emitting thermoelectron, and when applying to a capillary lamp of 10mm or less in tube diameter, the lamp current is generally made 500mA or less.

[0021] The container may be of any shape if it is cylindrical, opening at one end and having a bottom, and is not limited to special sizes in response to the diameter of the lamp. The electrode of the invention is particularly suited to capillary lamps, and so the container has preferably a maximum diameter of 1 to 5mm, length of 0.5 to 5mm, thickness of a side wall of 0.2 to 1mm, and thickness of a bottom of 0.2 to 2mm.

[0022] At the exposed faces of the electron emission materials seen from the opening side of the container and at the end face of the opening side of the same, it is preferable that carbides containing at least one kind of Ta, Nb and Ti and/or nitrides exist. The carbides and/or nitrides compose spattering prevention layers for protecting the electron emission materials from ions flying to the electrode. Since the first component should be exposed to the exposed face of the electron emission materials, the spattering prevention layer must be porous or networked films in the at least face of the electron emission materials. Thickness of the spattering prevention layer is preferably around 3 to 10µm. Being too thin, the preventing effect is insufficient. But being too thick, it is difficult to expose the electron emission materials. The carbides and/or nitrides may exist at other than the exposed face of the electron emission materials, and further may exist other than the end face of the opening side of the container.

[0023] The carbides and nitrides for composing the spattering prevention layers are better in the electric conductivity than the container composing material. For example, by forming the layers on the container surface, as specific resistance in the surface can be 10 to 500µΩcm, the container can be sufficiently functioned as the electric conductive path. Electric supply to the electrode for discharge lamp of the invention is generally carried out through the outside and/or the bottom of the container other than the end face at the opening side thereof, and it is preferable that carbides and/or nitrides also exist at the outside and/or the bottom of the container.

[0024] As the carbides and/or nitrides containing at least one kind of Ta, Nb and Ti contained in the spattering prevention layer, other than nitride or carbide of each element, may be allowed nitrides or carbides containing components of a plurality of metallic elements or solid solutions containing together carbon and nitrogen.

[0025] In the invention, the content percentage of the first component at the exposed faces 2a of the electron emission materials seen from the opening side of the container is higher than the content percentage of the first component at the end face 1a of the opening side of the container. Preferably, the content percentage of the first component at the exposed faces 2a of the electron emission materials is larger than 1.2 times of the content percentages of the first component at the end face 1a of the opening side of the container. By giving such distribution to the content percentage of the first component, the shift from the glow discharge to the arc discharge is enabled as mentioned above.

[0026] No special definition is made to an instrument for giving the distribution to the content percentage of the first component. For example, as a first instrument, there may be enumerated a method for differing a composition of raw materials for the container and a composition of raw materials for electron emission materials. As a second instrument, a method may be recommended which makes different compositions of the spattering prevention layer in the surface of the container and the surface of the electron emission material. As a third instrument, a further method may be proposed which makes different opening rates of the spattering prevention layer of porous or networked films in the surface of the container and in the surface of the electron emission material. Depending upon the second and third instruments, the container and the electron emission materials may be of the same composition. Two or more of the first to third instruments may be used jointly.

[0027] The content percentage of the first component in the exposed faces of the electron emission materials seen from the opening side of the container and the content percentage of the first component in the end face of the opening side of the container can be measured by an electron-ray probe micro analysis (EPMA). For measuring with EPMA, an optional counting number is made a threshold value for each element, and assuming that the element exists in a range showing a count exceeding the threshold value, the content percentage of the first component is compared.

A method of producing electrodes for discharging lamp

[0028] A further reference will be made to a method of producing the electrodes.

[0029] Fig.2 shows a producing process, and a basic flow of the process is similar to a process of manufacturing ordinary ceramics.

[0030] In the present process, starting materials are weighed and mixed (Step S1) in response to compositions of the container and the electron emission materials. Compounds to be used for the starting materials may be oxides or compounds to be oxides by baking, for example, carbonate or oxalate, and ordinarily for compounds containing the first component, $BaCO_3$, $SrCO_3$ and $CaCO_3$ are preferably used, and for compounds containing the second component, ZrO_2 and TiO_2 are preferably used, and for compounds containing the third component, Ta_2O_5 and Nb_2O_5 are preferably used. The mixture may depend upon any of a ball mill method, a friction mill method, a coprecipitation method or other.

[0031] The mixed starting material is preliminary baked (Step S2). The preliminary baking conditions are not especially limited, and ordinarily 800 to 1300°C for 30 min. to 5 h. The preliminary baking may be undertaken on powders or on formed body of powders.

[0032] The obtained pre-baked materials are ground by the ball mill method or an air grinding method (Steps S3), and powders of pre-baked materials are produced and granulated (Step S4) with an aqueous solution containing organic binders as polyvinyl alcohol, polyethylene glycol or polyethylene oxide. The granulating means are not especially limited, and may depend upon, for example, a spray drying method, an extrusion granulating method, a roll granulating method or methods using mortar or pestle. By the amount of the binder to be added for granulation, the percentage of voids of the electron emission materials can be controlled. Further, this percentage can be also controlled by adding organic high polymer compounds after granulating.

[0033] Granules for the container are compressed and formed into a container shaped configuration (Step S5). Pressure therefor is preferably 20 to 500Mpa. In the formed body, granules for the electron emission materials are charged (Step S6). When charging, no pressure is preferably effected. In case of effecting pressure, destined voids cannot be formed in the electron emission materials, irrespective of amounts of binders and other high polymer compounds added when granulating, so that the heat reserving effect enough for emitting the thermoelectron cannot be available. Preheating is therefore necessary when starting the discharge. In order to avoid the electron emission materials from dropping when discharging, it is desirable that the granules within the container contact almost all of other granules in the container periphery, and for realizing such a condition, if required, pressure may be effected to an extent that granules are not deformed.

[0034] The container and the granules charged therein are reduced and baked concurrently (Step S7) to turn out sintered products (electrode) (Step S8). It is preferable that the baking atmosphere is a reducing gas as hydrogen or carbon monoxide, an inert gas as argon or nitrogen, or an inert or a neutral gases respectively containing neutral gas or reducing gas. The density of the container after baking is preferably 60% or more of a theoretical density, especially 85% or more. Here, the density of the container is obtained from the dimension of the container, while the theoretical density is obtained from the crystalline structure. The effects of the invention can be more improved by setting voids in the above said range in the electron emission materials as well as making the container close, and as later mentioned, generating amounts of carbides and nitrides in the surfaces of the container and the electron emission materials can be differed.

[0035] For forming carbides in the electrode surfaces, it is sufficient to bake them in an atmosphere of inert or neutral gases respectively containing a gas of compound containing carbon. By insufficiently removing the binder when baking, carbide may be formed by supplying carbon from the binder or the organic high polymer compound. A further carbide may be also formed by using a baking furnace partially composed of carbon, introducing carbon powders or organic high polymer compounds into the furnace, or burying formed products in carbon powders or organic high polymer compounds. Two kinds or more of the above means may be jointly used. Among them, such a means is preferable, which feeds carbon from the atmosphere, the furnace materials or the carbon powders in the furnace. On the other hand, for forming nitrides in the electrode surfaces, it is sufficient to bake them in a nitrogen atmosphere or an atmosphere including compound containing nitrogen. By jointly using the carbide forming means, carbide and nitride can be formed.

[0036] Also when the container and the electron emission materials are of the same composition, the amount of carbides per unit area of the container surface is more than the amount of carbides per unit area in the surface of the electron emission materials. The same is applicable to nitrides, because a formed product to be a container is pressed, while granules to be electron emission materials are not pressed. Carbides and nitrides grow up from crystal grain boundaries of the container and the electron emission materials to cover crystal grains, and turn out films, and at this time, since the growing more rapidly progresses in the container formed under pressure, the area covered with carbides or nitrides is wider than that of the electron emission materials. Therefore, if both are of the same composition, the content percentage of the first component is higher in the container, and in the invention, both are of the same composition for saving the producing process.

[0037] Other than the respective means, the invention employs a vacuum deposition method or a spattering method so as to form the spattering prevention layer composed of carbides and/or nitrides in the electrode surface. When using these methods, a formation of film is stopped before carbides and/or nitrides perfectly cover the electrode surface.

[0038] The baking temperature is desirably 1400 to 2000°C. Being too low, a generating reaction of compound oxide or compound oxide including nitride does not sufficiently progress, so that the electron emission materials are easily evaporated when turning on a light, and the formation of carbides or nitrides by the above means is difficult. In contrast, being too high, granules are molten, so that it is difficult to give desirable properties to the electron emission materials.

Discharge lamp

[0039] Fig.3 illustrates an example of composing the discharge lamp employing the electrode according to the present invention, and only shows vicinity near an end part of the tube. The discharge lamp has a structure enabling to make the tube capillary.

[0040] The discharge lamp is coated with a fluorescent matter on the interior and has an airtight bulb 9. The bulb 9 is sealed therein with a rare gas (at least one kind of He, Ne, Ar, Kr and Xe). Pressure of the rare gas is preferably 1330 to 22600 Pa. By determining the pressure in this range, high bright and long life are available.

[0041] A lead wire 5 is inserted into an end of the bulb 9, and is formed with an enlarged part 6 thereof within the bulb 9. The enlarged part 6 is connected with an electric conductive pipe 7. If this connection can be made with other means, the enlarged part 6 of the lead wire is not required. The electric conductive pipe 7 is desirably composed of a material of high electric conductivity. If a material of less releasing gas, e.g., Ni is used, it is preferable as a generation of gas containing impurities is checked when making the discharge lamp. The electric conductive pipe 7 may be composed of ceramic. Within the electric conductive pipe 7, the container 1 is disposed in contact therewith, and within the container 1, the electron emission materials 2 are filled up. Between the container 1 in the conductive pipe 7 and the enlarged part 6 of the lead wire, a metal pipe 4 filled with a mercury dispenser material 3 is provided. The metal pipe 4 is a cylindrical body opening both ends, and may be composed with a metal as Ni. The electric conductive pipe 7 is formed with slit like openings (not shown) at the part thereof encircling the metal pipe 4. The mercury in the mercury dispenser material 3 is evaporated by frequency heating to the metal pipe 4 and is released from the slit like openings to a discharge space 10 through between the metal pipe 4 and the enlarged part 6 of the lead wire and between the metal pipe 4 and container 1. The opening is not limited to the slit but to any shape so far as it enables to release the evaporated mercury and does not hinder the holding of the container 1. The mercury dispenser material 3 is not indispensable but may be composed to supply mercury into the bulb in a sealing process.

[0042] The inventive electrode is not limited to the discharge lamp composed as shown in Fig.3 but applicable to others, for example, various kinds of discharge lamps as already proposed in the above mentioned publications.

Example 1

[0043] As the first component, Ba was selected. As the second component, Zr was selected and as the third component, Ta was selected. As starting materials of them, $BaCO_3$, ZrO_2 and Ta_2O_5 were prepared. The starting materials for making the electron emission materials were weighed such that ratio of Ba, Zr and Ta would be

$$Ba : Zr : Ta = 1.3 : 0.2 : 0.8,$$

and wet-mixed in the ball mill for 20 hours. For making the container, the starting materials were weighed and mixed similarly such that ration would be

$$Ba : Zr : Ta = 1.0 : 0.5 : 0.5.$$

[0044] Subsequently, the mixture was dried and formed under pressure of 10Mpa. The formed substance was temporarily baked at temperature of 1100°C for 2 hours in an air. The obtained product was wet ground for 20 hours in the ball mill, dried, added with an aqueous solution containing polyvinylalcohol, pelletized with a mortar and a pestle, and granulated.

[0045] The granules for the container were formed under pressure of 200MPa to be a cylinder opening one end and closing another end (density: 3.6g/cm3). In the formed container, granules for the electron emission materials were tilled up, baked at temperature of 1600°C for 2 hours in a carbon furnace of a nitrogen gas flow atmosphere, and turned out an electrode sample No.104 shown in Table 1. The sample was sized to be 2.3mm of outer diameter, 1.7mm of inner diameter (diameter of the granule supporting part), and 1.7mm of length. The density of the container was 6.8g/cm^3 being 90% or more of the theoretical density. In this sample, the ratio of metallic elements of the electron emission materials was

$$Ba : Zr : Ta = 1.0 : 0.2 : 0.7,$$

and the ratio of metallic elements of the container was

$$Ba : Zr : Ta = 1.0 : 0.5 : 0.5.$$

These ratios were measured by the X-ray fluorescent analysis.

[0046] In Table 1, "A" designates the content percentage of the first component in exposed faces of the electron emission discharge materials seen from the opening side of the container, and "B" is the content percentage of the first component in an end face of the opening side of the container. Accordingly, the samples of $A/B > 1$ are the inventive ones. The content percentage herein is meant by abundance ratio (area ratio) of the first component measured with EPMA. For measuring with EPMA, the counting number was divided into seven levels with respect to elements to be measured, and it was judged that the elements existed in the area where the counting number was above a level 3. The level number dividing the counting number and a position determining a threshold level did not give influences a judgement as to whether A/B > 1 was satisfied or not.

[0047] The samples Nos.101 to 103 in Table 1 were produced in the same manner as No.104 except the different composition of the electron emission materials, and the lower the ratio of Ba to all metal elements, the smaller A/B is.

[0048] EPMA images used for measuring A/B are shown in Figs.4 to 9. In these images, the electrodes are seen from the opening side of the container. Figs.4 and 5 are respectively the Ba distribution and the Ta distribution of the sample No.104, Figs.6 and 7 are respectively the Ba distribution and the Ta distribution of the sample No.102, and Figs.8 and 9 are respectively the Ba distribution and the Ta distribution of the sample No.101. In each of them, areas of high bright are areas high in the element density.

[0049] Fig.4 is the inventive sample where Ba in the container surface is less while Ba in the surface of the electron emission materials is more. Fig.6 is a comparative sample where more Ba exists in not only the surface of the electron emission materials but also the container surface. Fig.8 is also a comparative sample where Ba is less in the container surface and in the surface of the electron emission materials. On the other hand, in regard to the Ta distribution, each of Figs.5, 7 and 9 shows that Ta exists in both.

[0050] The void percentages in Table 1 are those of the electron emission materials of the samples in cross section available in photographs of the scanning electron microscope. The void percentages were adjusted by filling the organic high polymer compound (phenol resin powder) in the formed body in addition to granules and controlling the filling amount. In regard to the sample No.104, Fig.10 shows a photograph of the scanning electron microscope in cross section parallel with an axial direction. It is seen from the same that the electron emission materials are acicular and unitary with the container. The average radius of curvature of the discharging surface of the samples were 10 to 50μm.

[0051] These electrode samples were incorporated in the discharge lamp of full length of the bulb: 100mm, outer diameter: 5mm, sealed gas: Ar, sealing pressure: 9.3 kPa, sealed matter: Hg, frequency of a drive source: 30kHz, and lamp current: 30mA so as to measure the shift time TGA from the glow discharge to the arc discharge. Results are shown in Table1.

Table 1

Sample No.	A/B	Void (%)	TGA (Sec.)
101 (Comparative)	0.7	60	≥5
102 (Comparative)	1.0	60	≥2
103	1.2	60	≤0.5
104	5.0	60	≤0.1

[0052] It is seen from Table 1 that being A/B > 1, the shift time TGA is very short as 0.5 seconds or less.

[0053] In regard to the sample No.104, the powder X-ray diffraction was undertaken. The powder X-ray diffraction was carried out on the electrode samples produced in the same manner as the sample No.104 except at least partial changing of the compositions of the electron emission materials, the composition of the container and the baking conditions. As a result, in each of the electron emission materials and the container, confirmed was crystal of at least one kind of $Ba_7Ta_6O_{22}$, $BaTaO_2N$, $Ba_5Ta_4O_{15}$, $Ba_6ZrTa_4O_{18}$ and $BaZrO_3$. From the shift of the peak position in the X-ray diffraction, it was assumed that a substitution of Zr for a part of Ta and a substitution of Ta for a part of Zr occurred in each of crystals. Among charts of the X-ray diffraction provided in this measuring, those of the electron emission materials and the container of the sample No.104 are exemplified in Figs.11 and 12, and those of the electron emission materials of other samples are exemplified in Figs.13 to 15. Fig.15 is a chart by Cr-Kα, and other are Cu-Kα. Figs. 12, 14, 15 show a chart of a X-ray diffraction of composite oxide materials not containing nitride. Fig. 13 shows a chart of a X-ray diffraction of composite oxide materials containing nitride. Fig. 11 shows a chart of a X-ray diffraction of a material containing both of of composite oxide materials not containing nitride and composite oxide materials containing nitride. As existence of carbides in the container surface could not clearly confirmed by the powder X-ray diffraction, disc like sintered bodies were made with the same composition, forming pressure and baking condition, and the X-ray diffraction was performed thereon. Results are shown in Fig.16 from which it is seen that TaC film is formed on the sintered surface. Observing the TaC film by the scanning electron microscope, it was a crystal film. Measuring the specific resistance of the TaC film by a 4 terminal method, it was 60 to 180μΩcm. Thickness was 3 to 5μm.

Example 2

[0054] A sample of the electrode was made in the same manner as the sample No.104 except mixing the starting materials such that a ratio of the metallic elements was

$$\mathrm{Ba} : \mathrm{Zr} : \mathrm{Ta} = 1.2 : 0.3 : 0.7.$$

Namely, in this sample, the mixing ratio of the starting materials was the same in the electron emission materials and the container. A/B of the instant sample was 2.0 and included in the inventive range.

Example 3

[0055] Samples of the electrode were made in the same manner as the sample No.104 of the example 1 excepting that the void ratio is as shown in Table 2. In regard to them, the shift time TGA were monitored same as the example 1. Additionally, time duration of the arc discharge was monitored to check the life of arc discharge. Result is shown in Table 2.

Table 2

Sample No.	Void (%)	TGA(Sec.)	Lives of Arc discharge (Hours)
201 (Comparative)	40	≥10	≤70
202	45	≤0.1	≥4000
104	60	≤0.1	≥4000
203	70	≤0.1	≥4000
204	80	≤0.1	≥4000
205 (Comparative)	85	≤0.1	≤2900

[0056] From Table 2, it is seen that by determining the void percentage to be 45 to 80%, TGA is short as 0.1 seconds or less the arc discharging life of 4000 hours or more is available. In contrast, if the void percentage is 40%, TGA is remarkably long as exceeding 10 seconds, and the life is very shortened. Even if the void percentage is 85%, the life is shortened, because the electron emission materials drop during lighting the lamp.

[0057] A/B of the samples in Table 2 is all above 5.

Example 4

[0058] Samples of the electrode were made in the same manner as the sample No.104 in Table 2 excepting that the average radius of curvature of the discharge face is as shown in Table 3. The average radius of curvature of the discharge face was changed by classifying pelletized granules and controlling granular sizes.

[0059] In regard to them, the lamp currents had values as in Table 3, and stability of arc spots was checked. Results are shown in Table 3. Valuations shown in Table 3 are

○ : The arc spot is not moved for more than 10 hours,

△ : The arc spot is moved within 5 minutes,

X : No arc discharging (only glow discharge where the whole of electrode is discharged)

Table 3

Average radius of curvature (μm)	Lamp current (mA)						
	5	15	30	50	100	300	500
5	△	△	△	△	△	△	△
10	○	△	△	△	△	△	△
15	○	○	○	△	△	△	△
30	○	○	○	○	△	△	△
75	X	○	○	○	○	○	△
100	X	X	○	○	○	○	○
150	X	X	X	X	X	○	○
250	X	X	X	X	X	X	X

[0060] From Table 3, it is seen that when the lamp current is 5 to 500mA, if the average radius of curvature of the discharge face is selected from the range of 10 to 150μm, the discharge can be maintained for a long period of time without shift of the arc spot. If the arc spot is moved, voltage variation occurs and the ion spattering is easily caused, and thermal shock is given to the electron emission materials, resulting in shortening the life of the electrode.

Claims

1. An electrode for discharge lamp comprising:

    a cylindrical container opening at one end; and
    electron emission materials accommodated in said cylindrical container,
    wherein said container and said electron emission materials contains main elements including one of compound oxides and compound oxides containing nitrogen, which contains, as metallic elemental components, a first component comprising at least one of Ba, Sr and Ca, a second component comprising at least one of Zr and Ti, and a third component comprising at least one of Ta and Nb, and
    content percentage of the first component at exposed faces of the electron emission materials seen from the opening side of the container is higher than content percentage of the first component at an end face of the opening side of the container.

2. The electrode for discharge lamp as set forth in claim 1, wherein the density of the container is 60% or more of a theoretical density.

3. The electrode for discharge lamp as set forth in any one of claims 1, wherein an average radius of curvature in the discharge face is 10 to 150μm.

4. The electrode for discharge lamp as set forth in any one of claims 1, wherein carbides and/or nitrides containing at least one kind of Ta, Nb and Ti exist in the exposed faces of the electron emission materials seen from the opening side of the container and in the end face of the opening side of the container, as well as in the outside and/or the bottom of the container.

5. The electrode for discharge lamp as set forth in any one of claims 1, wherein when the first component is expressed with M^{I}, the second component is expressed with M^{II}, and the third component is expressed with M^{II}, the container and the electron emission materials contain at least one kind of crystals selected from

    $M^{I}M^{II}O_3$ type crystal,
    $M^{I}_5M^{III}_4O_{15}$ type crystal,
    $M^{I}_7M^{III}_6O_{22}$ type crystal,
    $M^{I}M^{III}O_2N$ type crystal, and

$M^{I}_{6}M^{II}M^{III}_{4}O_{18}$ type crystal.

6. The electrode for discharge lamp as set forth in any one of claim 5, wherein one part of M^{III} is substituted with M^{II} and one part of M^{II} is substituted with M^{III}.

7. An electrode for discharge lamp comprising:

a cylindrical container opening at one end; and
electron emission materials accommodated in said cylindrical container;
wherein said container and said electron emission materials contains main elements of compound oxides and compound oxides containing nitrogen, which contains, as metallic elemental component, first component comprising at least one of Ba, Sr and Ca, second component comprising at least one of Zr and Ti, and third component comprising at least one of Ta and Nb, and
said electron emission materials are porous ones having percentage of void being 45 to 80%.

8. The electrode for discharge lamp as set forth in claim 7, wherein the density of the container is 60% or more of a theoretical density.

9. The electrode for discharge lamp as set forth in any one of claims 7, wherein an average radius of curvature in the discharge face is 10 to 150μm.

10. The electrode for discharge lamp as set forth in any one of claims 7, wherein carbides and/or nitrides containing at least one kind of Ta, Nb and Ti exist in the exposed faces of the electron emission materials seen from the opening side of the container and in the end face of the opening side of the container, as well as in the outside and/or the bottom of the container.

11. The electrode for discharge lamp as set forth in any one of claims 7, wherein when the first component is expressed with M^{I}, the second component is expressed with M^{II}, and the third component is expressed with M^{II}, the container and the electron emission materials contain at least one kind of crystals selected from

$M^{I}M^{II}O_{3}$ type crystal,
$M^{I}_{5}M^{III}_{4}O_{15}$ type crystal,
$M^{I}_{7}M^{III}_{6}O_{22}$ type crystal,
$M^{I}M^{III}O_{2}N$ type crystal, and
$M^{I}_{6}M^{II}M^{III}_{4}O_{18}$ type crystal.

12. The electrode for discharge lamp as set forth in any one of claim 6, wherein one part of M^{III} is substituted with M^{II} and one part of M^{II} is substituted with M^{III}.

13. A discharge lamp comprising the electrode for the discharge lamp in any of claims 1 to 12.

FIG. 1

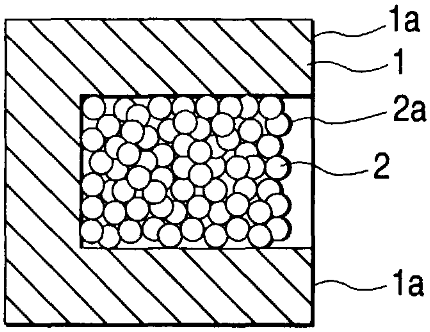


FIG. 2

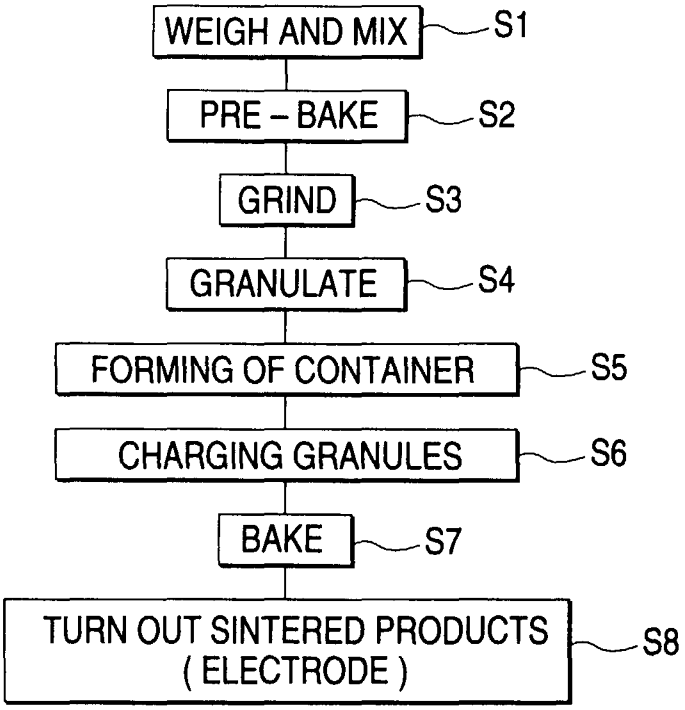


FIG. 3

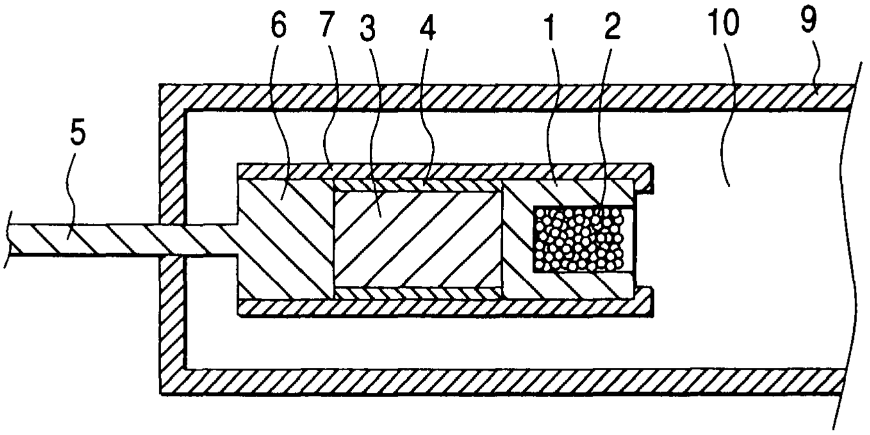


FIG. 4

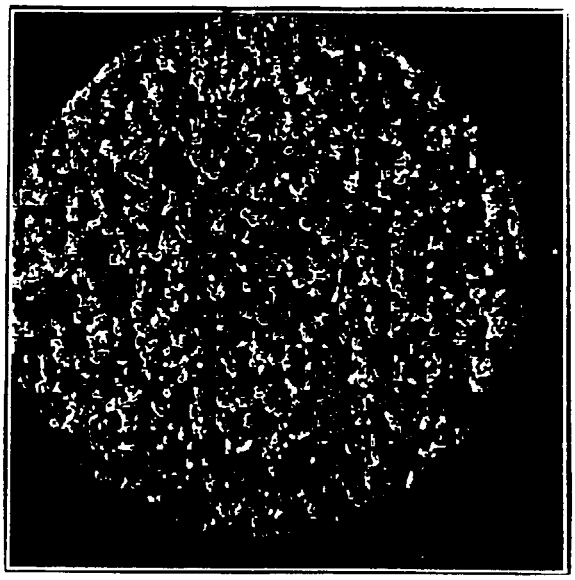


FIG. 5

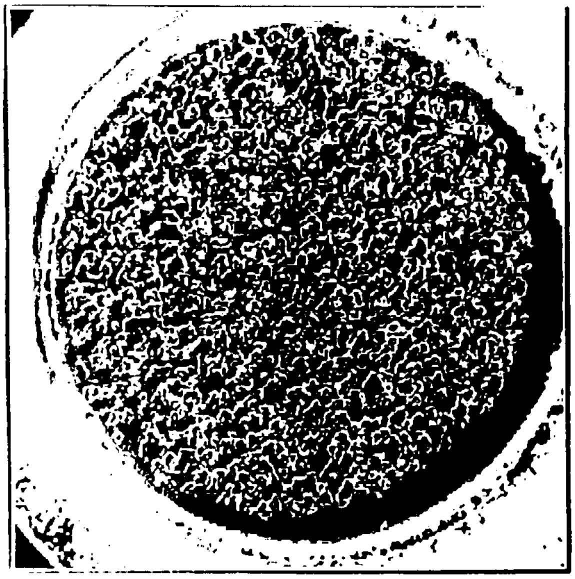


FIG. 6

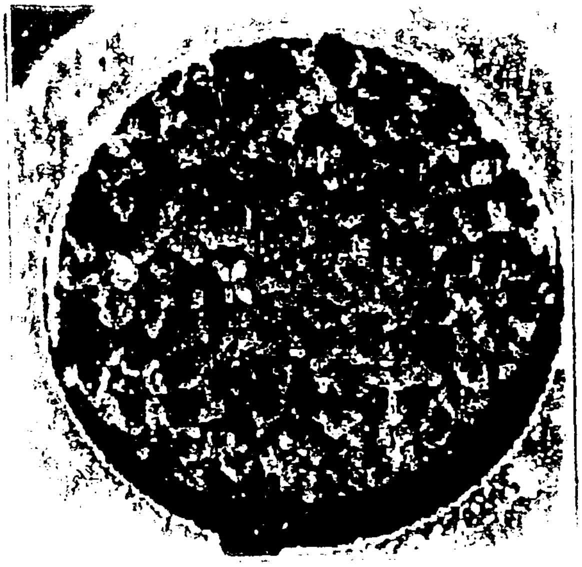


FIG. 7

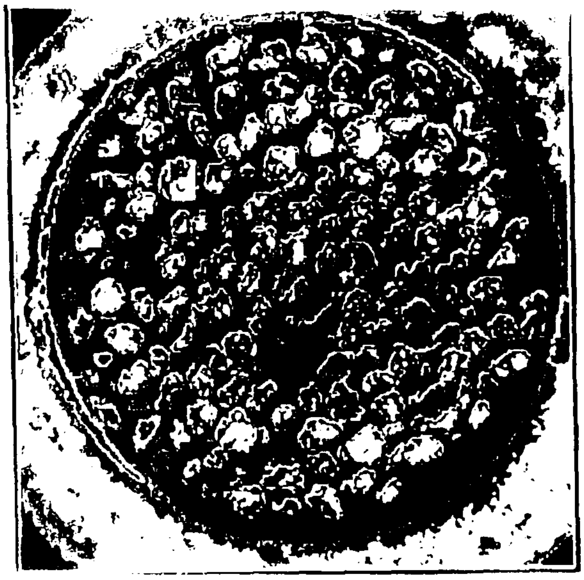


FIG. 8

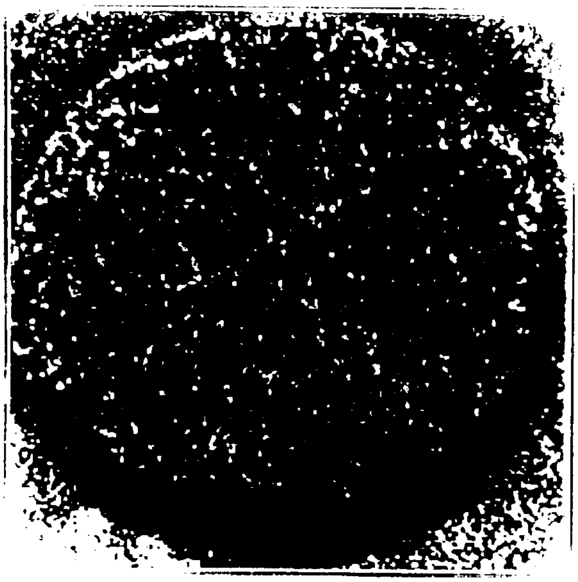


FIG. 9

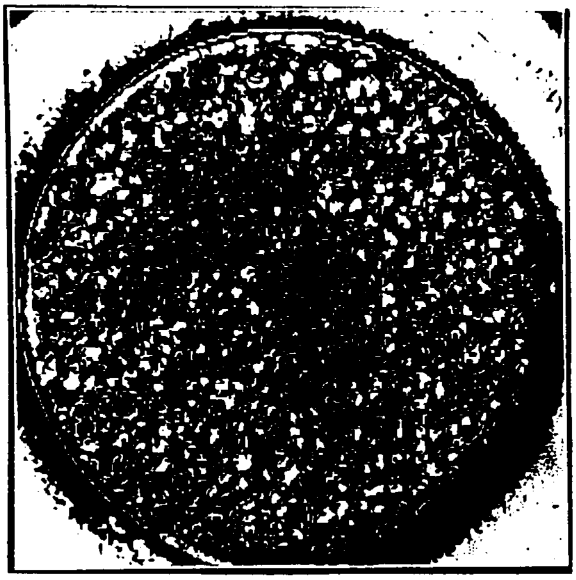


FIG. 10

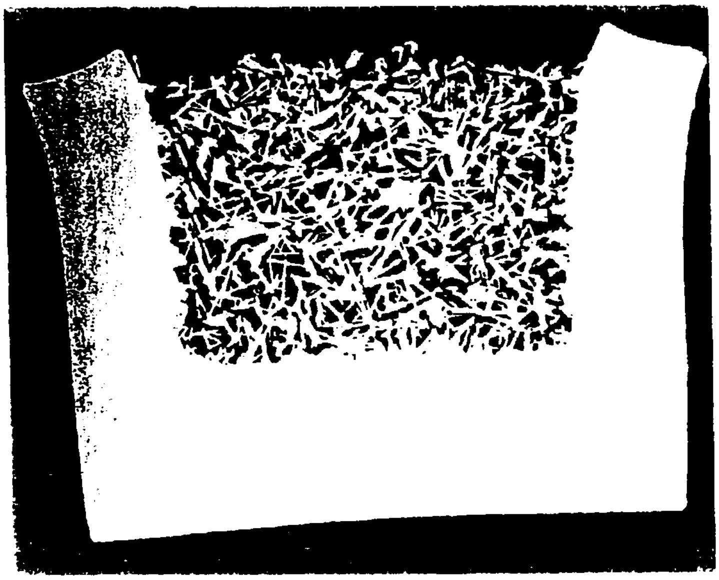


FIG. 11

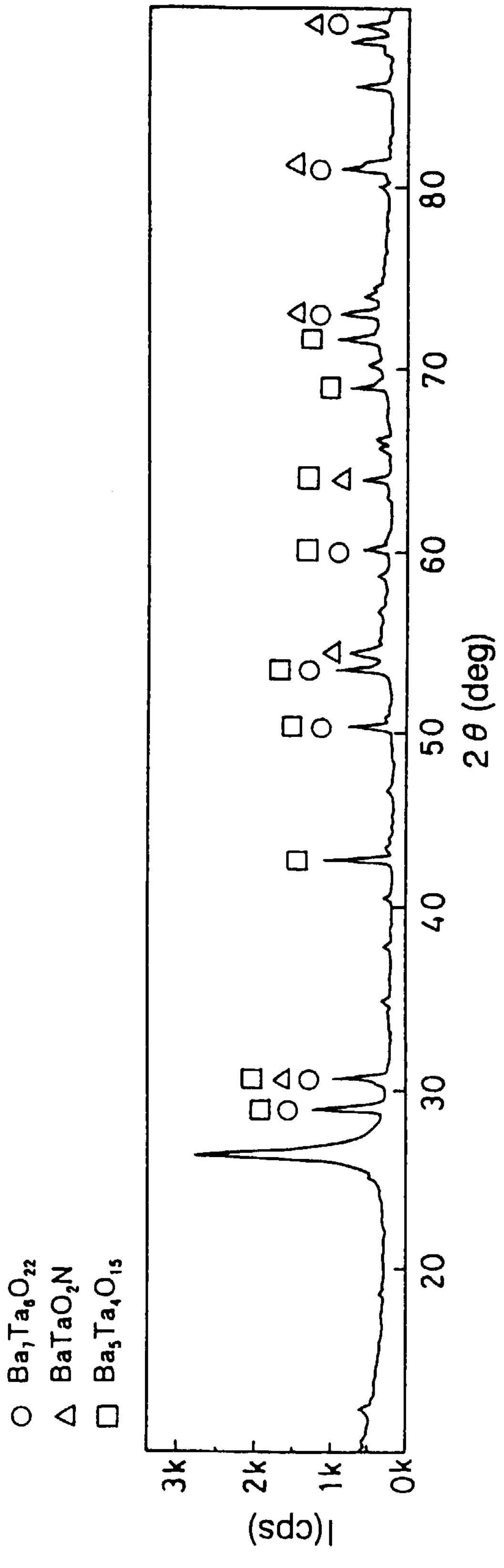

○ $Ba_7Ta_6O_{22}$
△ $BaTaO_2N$
□ $Ba_5Ta_4O_{15}$
I (cps)
3k
2k
1k
0k
20
30
40
50
60
70
80
2θ (deg)

FIG. 12

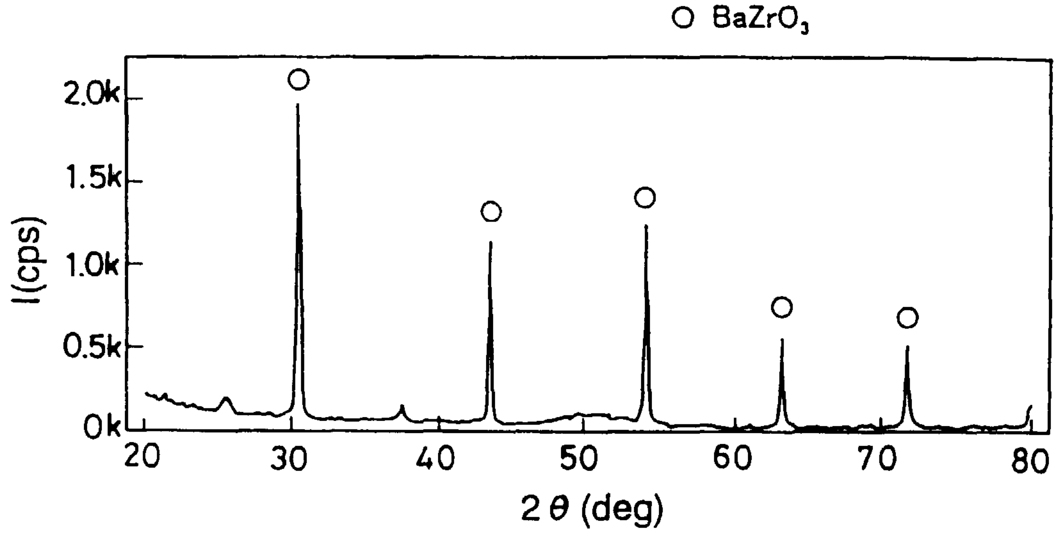


FIG. 13

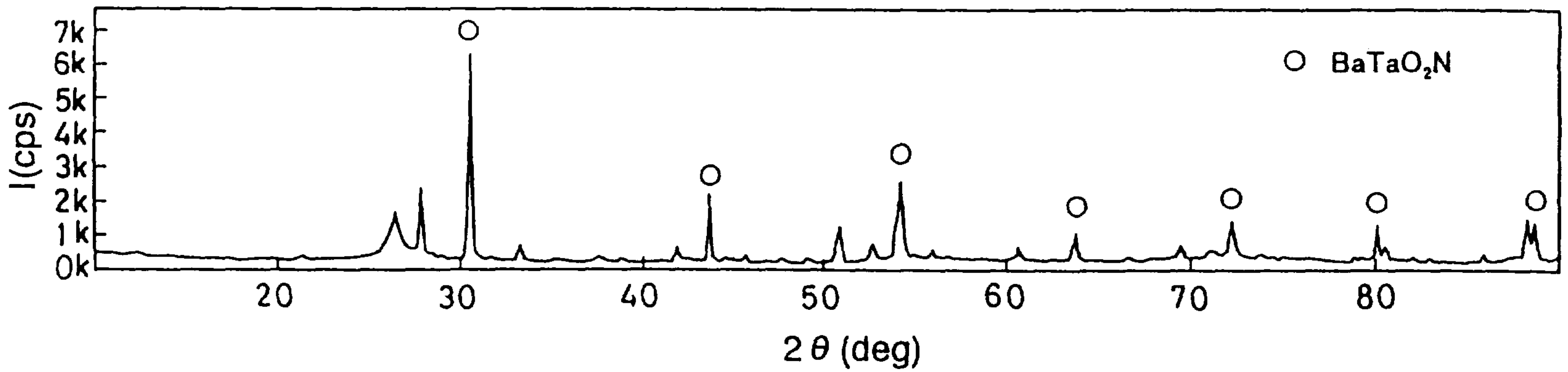


FIG. 14

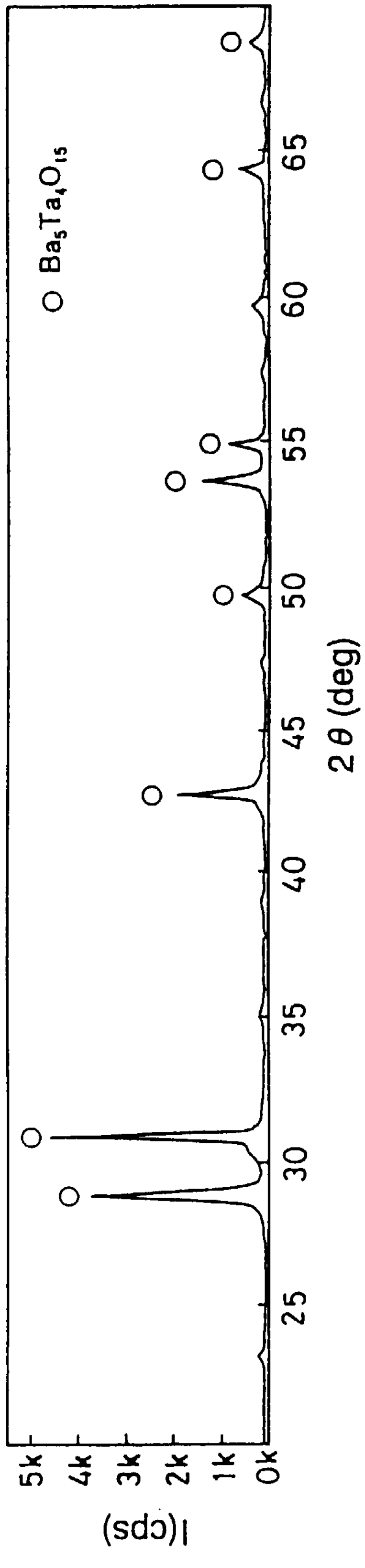


FIG. 15

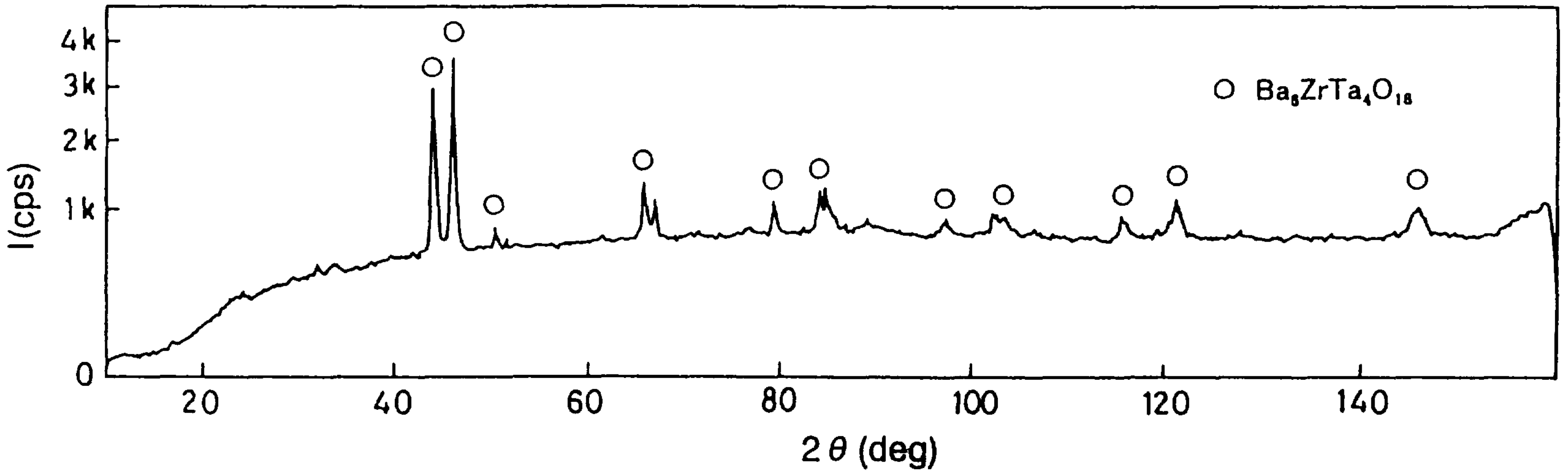


FIG. 16