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(54) **Current/voltage nonlinear resistor**

Strom/Spannung nichtlinearer Widerstand

Résistance courant/tension non-linéaire

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EP 1 798 741 B1

Description**BACKGROUND OF THE INVENTION****1. Field of the Invention**

[0001] The present invention relates to a current/voltage nonlinear resistor whose main component is zinc oxide (ZnO), and more particularly relates to a current/voltage nonlinear resistor in which improvements have been made to the composition of sub-components contained in the main component.

2. Description of the Related Art

[0002] Overvoltage protection devices such as lightning arrestors and surge absorbers are commonly incorporated into power systems or electronic device circuitry. The purpose of these devices is to protect the power system or electronic device circuitry by removing any overvoltage that has been superimposed over the normal voltage. Current/voltage nonlinear resistors are frequently used for these overvoltage protection devices. A current/voltage nonlinear resistor is a resistor with the property of exhibiting substantially insulating characteristics at ordinary voltage, but exhibiting low resistance when overvoltage is applied.

[0003] A current/voltage nonlinear resistor is a ceramic element whose main component is zinc oxide (ZnO), and the following characteristics are required of such resistors. Naturally, the resistor must have nonlinear resistance characteristics, meaning that the resistance value varies greatly with changes in voltage, but also needs to have a long enough service life that no deterioration occurs when voltage is continuously applied over an extended period, energy capability characteristics that allow it to absorb lightning surges and switching surges without damage, and so forth. Also, current/voltage nonlinear resistors are seen to have a property whereby the resistance value drops when the temperature is higher. Consequently, thermal stability with respect to high temperature is also required.

[0004] The procedure for producing a current/voltage nonlinear resistor will now be described (see Japanese Patent Publication H4-25681). The raw materials of the current/voltage nonlinear resistor are such that zinc oxide (ZnO) is the main component, and Bi_2O_3 , Co_2O_3 , MnO , Sb_2O_3 , and NiO are added as sub-components. These raw materials are thoroughly mixed along with water and a binder, then granulated with a spray dryer or the like, and these granules are molded and sintered to obtain a sinter. After this, the side faces of the sinter are coated with an insulating substance for preventing surface flashover, and this coating is heat treated to form a side face insulating layer. A current/voltage nonlinear resistor is produced by polishing the two end faces of the sinter and forming electrodes.

[0005] As demand for power and the need for stabilization have grown in recent years, reducing the size of power transmission and conversion devices has become a pressing concern. current/voltage nonlinear resistors whose main component is zinc oxide (ZnO) have been used in lightning arrestors (overvoltage protection devices) because of their excellent nonlinear resistance characteristics, but as the resistance value rises, fewer current/voltage nonlinear resistors are stacked in a lightning arrestor. In other words, increasing the resistance of a current/voltage nonlinear resistor is an essential technological key to achieving a lightning arrestor that is more compact. Also, increasing the nonlinear resistance characteristics of a current/voltage nonlinear resistor means lower the insulation layer of a power transmission and conversion system, and is therefore linked to making power transmission and conversion devices more compact.

[0006] A number of current/voltage nonlinear resistors with improved nonlinear resistance characteristics have been proposed in light of this situation. For instance, with the current/voltage nonlinear resistor disclosed in Japanese Laid-Open Patent Application 2001-307909, the amounts in which Bi_2O_3 , Co_2O_3 , MnO , Sb_2O_3 , NiO , and other such sub-components are contained are limited, and the crystal phase of the Bi_2O_3 contained in a sinter whose main component is zinc oxide (ZnO) is also limited, which allows the resistance value to be raised and superior nonlinear resistance characteristics to be obtained.

[0007] With the technology disclosed in Japanese Patents 2,933,881, 2,940,486, and 3,165,410, a rare earth oxide is added to a current/voltage nonlinear resistor whose main component is zinc oxide (ZnO) and whose sub-components are Bi_2O_3 , Co_2O_3 , MnO , Sb_2O_3 and so forth, the result of which is that the resistance value is raised and characteristics are enhanced.

[0008] EP 1 150 306 A2 relates to a current/voltage non-linear resistor comprising a sintered body having ZnO as a main component, an electrode applied to a surface of the sintered body and an insulation material applied to another surface of the sintered body, said main component containing, as auxiliary components, Bi, Co, Mn, Sb, Ni and Al in the form of their oxides, wherein a Bi_2O_3 crystalline phase in said sintered body includes an $\alpha\text{-Bi}_2\text{O}_3$ phase representing at least 80 % of the total Bi_2O_3 phase.

[0009] EP 0 029 749 A1 discloses a voltage-dependent resistor of the bulk-type, comprising a sintered body consisting essentially of, as a main constituent, zinc oxide and, as additives, Bi_2O_3 , Co_2O_3 , MnO_2 , Sb_2O_3 , Cr_2O_3 , B_2O_3 , at least one of Al_2O_3 , Ga_2O_3 , NiO and SiO_2 , wherein electrodes are applied to opposite surfaces of said sintered body.

SUMMARY OF THE INVENTION

[0010] Today, however, with the larger capacity of substations and the greater demand for underground substations, there is an increasingly great need for making power transmission and conversion devices smaller. Accordingly, the characteristics required of a current/voltage nonlinear resistor are at an even higher level, and with the prior art mentioned above, it is difficult to satisfy these requirements. More specifically, when the charging ratio (the voltage that is ordinarily applied to the current/voltage nonlinear resistor) was set high, a conventional current/voltage nonlinear resistor sometimes suffered severe deterioration, so that the service life was not long enough.

[0011] Also, a reduction in the size of power transmission and conversion devices extends to reducing the size of a lightning arrestor, of course, and the following problems have been indicated when the resistance of a current/voltage nonlinear resistor was raised due to making a lightning arrestor more compact. Because the amount of surge energy absorbed increases proportionally as the resistance of a current/ voltage nonlinear resistor is raised, the heating temperature is also raised by joule heat of the current/voltage nonlinear resistor when surge energy is absorbed.

[0012] As discussed above, because a current/voltage nonlinear resistor has a property whereby its resistance decreases as the temperature rises, if the temperature is too high, a drop in resistance occurs and there is greater current leakage. That is, since the decrease in the resistance of a current/voltage nonlinear resistor with increased resistance is greater when the temperature is raised, it has been indicated that there is a problem with thermal stability.

[0013] As a result, current of commercial frequency after the absorption of surge energy causes thermal runaway, and this increases unevenness of heating in the current/voltage nonlinear resistor. This invites an increase in thermal stress, which can lead to the breakdown of the current/voltage nonlinear resistor. Therefore, unless excellent thermal stability has been ensured, the resistance of the current/ voltage nonlinear resistor cannot be raised high enough, and it is difficult to reduce the size of a lightning arrestor.

[0014] The present invention was proposed in light of these problems, and it is an object thereof to provide a current/voltage nonlinear resistor with which the resistance value, nonlinear resistance characteristics, and thermal stability can be improved by specifying the compositional range of sub-components, and the size of a lightning arrestor can be reduced.

[0015] The present invention was conceived in an effort to achieve the stated object. According to the present invention, a current voltage nonlinear resistor includes a sinter, wherein said sinter consists essentially of zinc oxide (ZnO) as the main component and bismuth (Bi), cobalt (Co), manganese (Mn), antimony (Sb), nickel (Ni), gallium (Ga), and a rare earth element (R) as sub-components in proportions, calculated as Bi_2O_3 , Co_2O_3 , MnO , Sb_2O_3 , NiO , Ga^{3+} , and R_2O_3 , of 0.3 to 1.5 mol% Bi_2O_3 , 0.3 to 2.0 mol% Co_2O_3 , 0.4 to 3.0 mol% MnO , 0.5 to 4.0 mol% Sb_2O_3 , 0.5 to 4.0 mol% NiO , 0.0005 to 0.02 mol% Ga^{3+} , and 0.05 to 1.0 mol% R_2O_3 , wherein the current voltage nonlinear resistor is in the form of a disk, wherein the relationship between the added amount of Ga^{3+} and the diameter of the disk is such as claimed in claim 1.

[0016] With the present invention, the reason for specifying the sub-components to the above compositional ranges is that the inventors conducted various research into the compositions of current/voltage nonlinear resistors in an effort to achieved the above object, and as a result learned that keeping the proportions within the above ranges yields good resistance, nonlinear resistance characteristics, and thermal stability, and conversely that the above characteristics suffer when the proportions are outside the above ranges. Specifically, if the compositional proportions of the sub-components are kept within the above ranges, high resistance can be ensured and the nonlinear resistance characteristics and thermal stability are improved, and this makes it possible to attain the high level of characteristics required at the current time.

[0017] The present invention provides a current/voltage nonlinear resistor with which the sub-components, namely, bismuth (Bi), cobalt (Co), manganese (Mn), antimony (Sb), nickel (Ni), gallium (Ga), and a rare earth element (R), are contained in the compositional proportion ranges given above, and this affords excellent resistance, nonlinear resistance characteristics, and thermal stability, which in turn allows a current/voltage nonlinear resistor to be provided that can contribute to making lightning arrestors smaller.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

FIG. 1 is a cross section of the current/voltage nonlinear resistor pertaining to the present invention; and
FIG. 2 is a graph of nonlinearity and the Ga^{3+} added amount coefficient A.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] Embodiments of the present invention will now be described in specific terms through reference to FIGS. 1 and 2 and Tables 1 to 5. Tables 1 to 5 show evaluation indicators and contained amounts of current/voltage nonlinear

resistors produced with varying amounts of sub-components contained. Of the sample numbers given in the tables, those marked with an asterisk have sub-components that are outside the compositional ranges pertaining to the present invention, and are comparative samples produced for the sake of comparison. Those not marked with an asterisk, meanwhile, have sub-components within the compositional ranges corresponding to the present invention.

(1) First Embodiment

[0020] A first embodiment related to the present invention will be described through reference to FIG. 1 and Tables 1 and 2. FIG. 1 is a cross section of the current/voltage nonlinear resistor pertaining to this embodiment.

Constitution

[0021] In this embodiment, zinc oxide (ZnO) was used as the main component. Bismuth (Bi), cobalt (Co), manganese (Mn), antimony (Sb), nickel (Ni), and gallium (Ga), were used as sub-components, and the final amounts in which these were contained, calculated as Bi_2O_3 , Co_2O_3 , MnO, Sb_2O_3 , NiO, and Ga^{3+} were within the following ranges.

[0022] The product contained 0.3 to 1.5 mol% Bi_2O_3 , 0.3 to 2.0 mol% Co_2O_3 , 0.4 to 3.0 mol% MnO, 0.5 to 4.0 mol% Sb_2O_3 , 0.5 to 4.0 mol% NiO, and 0.0005 to 0.02 mol% Ga^{3+} .

[0023] Furthermore, at least one type of rare earth oxide (R) selected from about dysprosium (Dy), europium (Eu), erbium (Er), thulium (Tm), gadolinium (Gd), yttrium (Y), holmium (Ho), and ytterbium (Yb) were contained in an amount of 0.05 to 1.0 mol%, calculated as R_2O_3 .

Production Procedure

[0024] The procedure for producing the current/voltage nonlinear resistors pertaining to this embodiment and comparative samples will now be described in specific terms. Bi_2O_3 , Co_2O_3 , MnO, Sb_2O_3 , NiO, Dy_2O_3 , and Ga^{3+} or Al^{3+} were measured out as sub-components in specific amounts with respect to the ZnO main component such that the amounts in which the components were contained in the current/voltage nonlinear resistors ultimately obtained were as indicated for sample numbers 1 to 44 in Tables 1 and 2. These raw materials were mixed in a mixer along with water and an organic binder, and each slurry was adjusted to a uniform consistency. The Ga^{3+} or Al^{3+} here was added as a nitrate aqueous solution.

[0025] Next, each of the slurries thus obtained was spray granulated in a spray dryer to produce a granulated powder with a grain size of about 100 μm . The granulated powder thus obtained was put in a metal mold and pressed into a disk with a diameter of 125 mm and a thickness of 30 mm, and this molded disk was heated to 500°C to remove the organic binder that had been added.

[0026] After this, the disk was fired for 2 hours at 1100°C to obtain the sinter 1 shown in FIG. 1. The side faces of the sinter 1 were coated with an inorganic insulating substance, and these coatings were heat treated to form side face insulating layers 2. Finally, the upper and lower end faces of the sinter 1 provided with the side face insulating layers 2 were polished to a specific thickness, after which electrodes 3 were thermal sprayed onto the polished faces of the sinter 1 to produce a current/voltage nonlinear resistor.

Evaluation of Resistance

[0027] The characteristics of the various current/voltage nonlinear resistors produced by the above procedure were evaluated as follows. First, the resistance of the current/voltage nonlinear resistor was evaluated by measuring the initial operating voltage of the current/voltage nonlinear resistor (the voltage when 1 mA of AC current was applied; $V_{1\text{mA}}$). The higher the initial operating voltage, the fewer current/voltage nonlinear resistors that need to be stacked in a lightning arrester, so this voltage is effective as an index for ascertaining how compact a lightning arrester can be made.

Evaluation of Nonlinear Resistance Characteristics

[0028] The voltage when a 10 kA impulse current of 8 x 20 μs was applied ($V_{10\text{kA}}$) was measured, and the ratio of this to the initial operating voltage $V_{1\text{mA}}$ ($V_{10\text{kA}}/V_{1\text{mA}}$) was evaluated as a nonlinearity coefficient. The smaller the value of this nonlinearity coefficient, the better the nonlinear resistance characteristics.

Evaluation of thermal stability

[0029] The thermal stability of the current/voltage nonlinear resistor was evaluated by measuring the resistance leakage current when AC voltage that was 90% of the initial operating voltage was applied in a 200°C thermostatic tank. Spe-

EP 1 798 741 B1

cifically, the less leakage current at high temperature there is at 200°C, the better the thermal stability. The compositions of ten elements with each added component composition were measured, and the average thereof was used for the compositional value. The measurement results are given in Tables 1 and 2.

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Table 1

Sample number	Amounts of sub-components contained (mol%)							Initial operating voltage (V _{1mA})	Nonlinearity V _{10kA} /V _{1mA}	Leakage current at high temperature (mA)
	Bi ₂ O ₃	Sb ₂ O ₃	MnO	NiO	Co ₂ O ₃	Ga ³⁺	Al ³⁺			
1*	0.20	2.00	1.00	2.00	1.00'	0.003	0	813	1.560	25.0
2	0.30	2.00	1.00	2.00	1.00	0.003	0	625	1.453	13.4
3	0.50	2.00	1.00	2.00	1.00	0.003	0	552	1.458	10.3
4	1.00	2.00	1.00	2.00	1.00	0.003	0	498	1.467	9.7
5	1.50	2.00	1.00	2.00	1.00	0.003	0	405	1.472	8.9
6*	1.80	2.00	1.00	2.00	1.00	0.003	0	350	1.492	8.0
7*	0.50	0.30	1.00	2.00	1.00	0.003	0	368	1.502	7.4
8	0.50	0.50	1.00	2.00	1.00	0.003	0	402	1.475	8.9
9	0.50	1.00	1.00	2.00	1.00	0.003	0	502	1.462	9.2
10	0.50	3.00	1.00	2.00	1.00	0.003	0	598	1.468	11.2
11	0.50	4.00	1.00	2.00	1.00	0.003	0	605	1.487	13.5
12*	0.50	5.00	1.00	2.00	1.00	0.003	0	698	1.521	16.5
13*	0.50	2.00	0.20	2.00	1.00	0.003	0	444	1.524	8.7
14	0.50	2.00	0.40	2.00	1.00	0.003	0	478	1.492	9.1
15	0.50	2.00	0.80	2.00	1.00	0.003	0	542	1.458	9.2
16	0.50	2.00	2.00	2.00	1.00	0.003	0	578	1.472	9.1
17	0.50	2.00	3.00	2.00	1.00	0.003	0	595	1.482	11.5
18*	0.50	2.00	4.00	2.00	1.00	0.003	0	602	1.542	14.8
19*	0.50	2.00	1.00	0.30	1.00	0.003	0	395	1.501	9.8
20	0.50	2.00	1.00	0.50	1.00	0.003	0	488	1.492	8.2
21	0.5	2.00	1.00	1.00	1.00	0.003,	0	502	1.472	9.2
22	0.50	2.00	1.00	3.00	1.00	0.003	0	580	1.443	11.2
23	0.50	2.00	1.00	4.00	1.00	0.003	0	602	1.440	13.5
24*	0.50	2.00	1.00	5.00	1.00	0.003	0	621	1.502	17.9

Table 2

Sample number	Amounts of sub-components contained (mol%)							Initial operating voltage V_{1mA} (V/mm).	Nonlinearity V_{10kA}/V_{1mA}	Leakage current at high temperature (mA)
	Bi_2O_3	Sb_2O_3	MnO	NiO	Co_2O_3	Ga^{3+}	Al^{3+}			
25*	0.50	2.00	1.00	2.00	0.20	0.003	0	458	1.542	12.3
26	0.50		1.00	2.00	0.30	0.003	0	498	1.490	9.2
27	0.50	2.00	1.00	2.00	0.50	0.003	0	524	1.462	9.2
28	0.50	2.00	1.00	2.00	1.50	0.003	0	575	1.442	11.2
29	0.50	2.00	1.00	2.00	2.00	0.003	0	592	1.432	13.5
30*	0.50	2.00	1.00	2.00	2.50	0.003	0	618	1.502	21.5
31*	0.50	2.00	1.00	2.00	1.00	0.0003	0	645	1.592	13.4
32	0.50	2.00	1.00	2.00	1.00	0.0005	0	618	1.472	19.9
33	0.50	2.00	1.00	2.00	1.00	0.001	0	584	1.468	10.9
34	0.50	2.00	1.00	2.00	1.00	0.005	0	542	1.460	9.9
35	0.50	2.00	1.00	2.00	1.00	0.01	0	51	1.490	9.7
36	0.50	2.00	1.00	2.00	1.00	0.02	0	495	1.497	11.2
37*	0.50	2.00	1.00	2.00	1.00	0.03	0	46.2	1.582	10.9
38*	0.50	2.00	1.00	2.00	1.00	0	0.003	552	1.459	18.2
39*	0.50	2.00	1.00	2.00	1.00	0.003	0	342	1.502	7.2
40	0.50	2.00	1.00	2.00	1.00	0.003	0	443	1.495	8.1
41	0.50	2.00	1.00	2.00	1.00	0.003	0	492	1.482	9.2
42	0.50	2.00	1.00	2.00	1.00	0.003	0	524	1.462	9.9
43	0.5	2.00	1.00	2.00	1.00	0.003	0	59.1	1.489	12.5
44*	0.50	2.00	1.00	2.00	1.00	0.003	0	594	1.524	20.1

[0030] As discussed above, the current/voltage nonlinear resistors with the sample numbers marked with an asterisk in Tables 1 and 2 had compositions outside the ranges of the present invention, and were samples produced for the sake of comparison. As is clear from the results in Tables 1 and 2, the characteristics of the comparative samples do not satisfy the conditions of an excellent current/voltage nonlinear resistor as specified above.

Initial operating voltage (V_{1mA}) > 400 V/mm
 Nonlinearity coefficient (V_{10kA}/V_{1mA}) < 1.50
 Leakage current at high temperature (200°C) < 15 mA

[0031] In contrast, the current/voltage nonlinear resistors with sample numbers not marked with an asterisk in Tables 1 and 2 were within the compositional ranges specified in the claims of the present invention, and therefore exhibited excellent results for initial operating voltage, nonlinearity coefficient, and leakage current at high temperature. Specifically, the current/voltage nonlinear resistors pertaining to this embodiment can be considered to have high resistance and excellent nonlinear resistance characteristics and thermal stability.

[0032] Let us now discuss the role of the various sub-components contained in this embodiment, and also mention that the characteristics of this embodiment are not attained with the comparative samples.

Role of Bi_2O_3 (see Table 1)

[0033] Bi_2O_3 is a component that is present at the boundary of the zinc oxide (ZnO), which is the main component of the sinter, and is responsible for nonlinear resistance characteristics. The role of this component is to promote the growth of ZnO crystal grains. If we compare sample numbers 1 to 6 here, we see that when the amount of Bi_2O_3 was less than 0.3 mol% (sample number 1), the material was in the liquid phase during sintering, and the amount of Bi_2O_3 was inadequate to improve sintering.

[0034] Accordingly, excellent characteristics were not obtained in terms of nonlinearity and leakage current at high temperature. Also, when the amount of Bi_2O_3 was over 1.5 mol% (sample number 6), the growth of ZnO particles proceeded too much during sintering, so a sufficiently high initial operating voltage could not be obtained.

Role of Sb_2O_3 (see Table 1)

[0035] Sb_2O_3 is a component that controls and makes uniform the growth of ZnO crystal grains during sintering by forming spinel ($Zn_7Sb_2O_{12}$) particles along with zinc oxide (ZnO). Its role is to improve nonlinear resistance characteristics and, at the same time, suppress the growth of ZnO crystal grains.

[0036] A comparison of sample numbers 3 and 7 to 12 reveals that if the Sb_2O_3 content is less than 0.5 mol% (sample number 7), there will be too few spinel particles capable of suppressing grain growth during sintering, so excellent characteristics cannot be obtained in terms of initial operating voltage and nonlinearity. If the amount of Sb_2O_3 is over 4 mol% (sample number 12), however, it will act as an insulating component in the sinter, and there will be too many spinel particles, so excellent characteristics cannot be obtained in terms of nonlinearity and leakage current at high temperature.

Role of MnO (see Table 1)

[0037] MnO is a component that primarily forms a solid solution with spinel particles and improves nonlinear resistance characteristics. A comparison of sample numbers 3 and 13 to 18 reveals that if the MnO content is less than 0.4 mol% (sample number 13), the electrical characteristics are unstable at the ZnO grain boundary, so excellent nonlinearity cannot be obtained. If the amount of MnO is over 3 mol% (sample number 18), however, here again it is impossible to obtain excellent nonlinearity characteristics.

Role of NiO (see Table 1)

[0038] NiO is similar to MnO in that it primarily forms a solid solution with spinel particles and improves nonlinear resistance characteristics. A comparison of sample numbers 3 and 19 to 24 reveals that if the NiO content is less than 0.5 mol% (sample number 19), the very little NiO will form a solid solution with the spinel particles, so excellent initial operating voltage and nonlinearity cannot be obtained. If the amount of NiO is over 4 mol% (sample number 24), however, the electrical characteristics are unstable at the ZnO grain boundary, so excellent nonlinearity characteristics and leakage current at high temperature characteristics cannot be obtained.

Role of Co_2O_3 (see Table 2)

[0039] Co_2O_3 also is a component that primarily forms a solid solution with spinel particles and improves nonlinear resistance characteristics. A comparison of sample numbers 3 and 25 to 30 reveals that if the Co_2O_3 content is less than 0.3 mol% (sample number 25), the electrical characteristics are unstable at the ZnO grain boundary, so excellent nonlinearity cannot be obtained, but if the amount of Co_2O_3 is over 2 mol% (sample number 30), here again the electrical characteristics are unstable at the ZnO grain boundary, making it impossible to obtain excellent nonlinearity characteristics or leakage current at high temperature characteristics.

Role of Ga^{3+} (see Table 2)

[0040] Ga^{3+} serves to improve nonlinear resistance characteristics by forming a solid solution in the ZnO particles and lowering the electrical resistance of the ZnO particles. Aluminum (Al) has often been used in prior art as a component with a similar purpose, but improving nonlinear resistance characteristics by adding gallium gives a current/voltage nonlinear resistor with better thermal stability than by adding aluminum.

[0041] A comparison of sample numbers 3 and 31 to 38 reveals that if the Ga^{3+} content is less than 0.0005 mol% (sample number 31), not enough Ga^{3+} will form a solid solution in the ZnO particles in the sinter, so the electrical resistance of the ZnO particles will be high and excellent nonlinearity cannot be obtained.

[0042] If the amount of Ga^{3+} is over 0.02 mol% (sample number 37), however, the Ga^{3+} will precipitate at the ZnO grain boundary and adversely affect the electrical characteristics of the ZnO grain boundary, so excellent nonlinearity cannot be obtained. Furthermore, compared to when Al^{3+} is added (sample number 38), adding Ga^{3+} allows better leakage current at high temperature characteristics to be obtained.

Role of Dy_2O_3 (see Table 2)

[0043] If the above-mentioned Sb_2O_3 , Co_2O_3 , NiO, and MnO are added in too large an amount in an effort to raise the resistance of a current/voltage nonlinear resistor, the resistance value will be highly dependent on temperature, so thermal stability will decrease.

[0044] In view of this, in this embodiment, higher resistance is achieved by adding Dy_2O_3 , which is a rare earth oxide that has the effect of raising resistance, the added amounts of Sb_2O_3 , Co_2O_3 , NiO, and MnO are effectively reduced and the temperature dependence of resistance is thereby lessened, and the thermal stability of the current/voltage nonlinear resistor can be increased.

[0045] A comparison of sample numbers 3 and 39 to 44 reveals that if the Dy_2O_3 content is less than 0.3 mol% (sample number 39), there will not be enough Dy_2O_3 to have the effect of suppressing grain growth, so excellent initial operating voltage and nonlinearity cannot be obtained. If the amount of Dy_2O_3 is over 1.0 mol% (sample number 44), however, the electrical characteristics will be unstable at the ZnO grain boundary, making it impossible to obtain excellent characteristics in terms of nonlinearity or leakage current at high temperature.

[0046] Furthermore, an oxide of dysprosium (Dy) was used as a rare earth oxide in this embodiment, but oxides of other rare earth elements, namely, europium (Eu), erbium (Er), thulium (Tm), gadolinium (Gd), yttrium (Y), holmium (Ho), and ytterbium (Yb), may also be used, and these will have the same effect as an oxide of dysprosium (Dy). Also, as long as the amount in which the various rare earth oxides are contained ends up being within a range of 0.05 to 1.0 mol%, the combination thereof may be selected as desired.

[0047] As described above, in this embodiment zinc oxide (ZnO) is the main component and the final amounts of sub-components are within the ranges given above, which makes it possible to obtain a current/voltage nonlinear resistor that has high resistance and excellent thermal stability and nonlinear resistance characteristics. Accordingly, the number of stacked layers of current/voltage nonlinear resistor can be reduced while maintaining high reliability, and this contributes to making a lightning arrester smaller.

(2) Second EmbodimentConstitution and Production Procedure

[0048] Next, a second embodiment related to the present invention will be described through reference to Table 3. This embodiment is characterized by being composed of a sinter containing 0.005 to 0.05 wt% silver (Ag), calculated as Ag_2O .

[0049] Specifically, Bi_2O_3 (0.5 mol%), Co_2O_3 (1.0 mol%), MnO (1.0 mol%), Sb_2O_3 (2 mol%), NiO (2 mol%), Dy_2O_3 (0.5 mol%), and Ga^{3+} (0.003 mol% as a nitrate aqueous solution) were measured out as sub-components in the final proportions given in parentheses above, and these components were added to the ZnO main component. Ag_2O was

further added to this base composition so as to be contained in an amount of 0.001 to 0.1 wt%, and the current/voltage nonlinear resistors of sample numbers 45 to 50 shown in Table 3 were produced by the method described in the first embodiment above.

Evaluation of Service Life Characteristics

[0050] The service life characteristics of these current/voltage nonlinear resistors were evaluated. This was accomplished by continuously applying the voltage (V_{1mA}) when a 1 mA current was flowing, in an air atmosphere at 120°C for 3000 hours, and measuring the percentage change in the leakage current (I_r) before and after the application of V_{1mA} . The results are given in Table 3.

[0051] The percentage change here is expressed by the following formula.

$$\frac{(I_r \text{ (after 3000 hours)} - I_r \text{ (initial value)})}{I_r \text{ (initial value)}} \times 100$$

[0052] If the change in leakage current here is a negative value, this indicates that the current/voltage nonlinear resistor has excellent service life characteristics.

Table 3

Sample number	Ag ₂ O content (wt%)	Percentage change in leakage, current (%)
45*	0.0001	9.2
46	0.005	-1.2
47	0.010	-5.4
48	0.020	-9.2
49	0.050	-0.6
50*	0.100	4.9

Effect

[0053] The current/voltage nonlinear resistors of sample numbers 45 and 50, which are marked with an asterisk in Table 3, have compositions outside the scope of the claims of the present invention. As is clear from the results given in Table 3, the characteristics of the comparative samples indicate that the percentage change in leakage current is a positive value, and the service life characteristics are low. In other words, when the added amount of silver, calculated as Ag₂O, was less than 0.005 wt%, there was no effect of improving service life characteristics. When the amount was over 0.05 wt%, though, this had the opposite effect of causing the service life characteristics to deteriorate.

[0054] In contrast, with this embodiment (sample numbers 46 to 49) in which the Ag₂O content was from 0.005 to 0.05 wt%, the percentage change in leakage current was a negative value (see Table 3), and it is clear that current/voltage nonlinear resistors with excellent service life characteristics were obtained.

[0055] Specifically, with this embodiment, adding silver in an amount of 0.005 to 0.05 wt%, calculated as Ag₂O, reduces the change over time in leakage current and improves the service life characteristics. Furthermore, in this embodiment, the effect of adding silver on the service life characteristics was only discussed for the base composition given in the Constitution and Production Procedure above, but the same effect will be obtained as long as the composition is within the range of the base composition given in Claim 1.

(3) Third Embodiment

Constitution and Production Procedure

[0056] Next, a third embodiment related to the present invention will be described through reference to Table 4. This embodiment is characterized by being composed of a sinter containing 0.005 to 0.05 wt% boron (B), calculated as B₂O₃.

[0057] Specifically, Bi₂O₃ (0.5 mol%), Co₂O₃ (1.0 mol%), MnO (1.0 mol%), Sb₂O₃ (2 mol%), NiO (2 mol %), Dy₂O₃ (0.5 mol %), and Ga³⁺ (0.003 mol% as a nitrate aqueous solution) were measured out as sub-components in the final

proportions given in parentheses above, and these components were added to the ZnO main component. Up to this point this embodiment is the same as the second embodiment above.

[0058] B_2O_3 was further added to this base composition so as to be contained in an amount of 0.001 to 0.1 wt%, and the current/voltage nonlinear resistors of sample numbers 51 to 56 shown in Table 4 were produced by the method described in the first embodiment above. That is, in the third embodiment, B_2O_3 was contained, instead of the Ag_2O used in the second embodiment, in amounts between 0.001 and 0.1 wt%.

Evaluation of Service Life Characteristics

[0059] The service life characteristics of these current/voltage nonlinear resistors were evaluated by the method given in the second embodiment. Table 4 shows the percentage change in leakage current in this third embodiment.

Table 4

Sample number	B_2O_3 content (wt%)	Percentage change in leakage current (%)
51*	0.0001	9.8
52	0.005	-21
53	0.010	-3.5
54	0.020	-8.2
55.	0.050	-6.9
56*	0.100	12.5

Effect

[0060] The current/voltage nonlinear resistors of sample numbers 51 and 56, which are marked with an asterisk in Table 4, have compositions outside the scope of the claims of the present invention. As shown in Table 4, the characteristics of the comparative samples indicate that the percentage change in leakage current is a positive value, and the service life characteristics are low.

[0061] In other words, the service life characteristics were low when the added amount of boron, calculated as B_2O_3 , was less than 0.005 wt%, and when it was more than 0.05 wt%. In contrast, with this embodiment (sample numbers 52 to 55) in which the B_2O_3 content was from 0.005 to 0.05 wt%, the percentage change in leakage current was a negative value (see Table 4), and current/voltage nonlinear resistors with excellent service life characteristics were obtained.

[0062] Specifically, with this embodiment, adding boron in an amount of 0.005 to 0.05 wt%, calculated as B_2O_3 , improves the service life characteristics, just as in the second embodiment. Furthermore, in this embodiment, the effect of adding boron on the service life characteristics was only discussed for the above-mentioned base composition, but the same effect will be obtained as long as the composition is within the range of the base composition given in Claim 1. Also, instead of adding silver or boron alone, both may be added at the same time, as long as the combined amount is between 0.005 and 0.05 wt%.

(4) Fourth Embodiment

Constitution and Production Procedure

[0063] A fourth embodiment related to the present invention will now be described. In this embodiment, Bi_2O_3 (0.5 mol%), Co_2O_3 (1.0 mol%), MnO (1.0 mol%), Sb_2O_3 (2 mol%), NiO (2 mol%), Dy_2O_3 (0.5 mol%), and Ga^{3+} (0.003 mol%) were measured out as sub-components in the final proportions given in parentheses above, these components were added to the ZnO main component, and current/voltage nonlinear resistors were produced by the method described in the first embodiment above. This embodiment is characterized in that Ga^{3+} is added as a nitrate aqueous solution.

Evaluation of Resistance Stability

[0064] The stability of the resistance value is evaluated in this fourth embodiment. Specifically, the initial operating voltage (V_{1mA}) was measured for 100 current/voltage nonlinear resistors in which Ga^{3+} had been added as a nitrate aqueous solution, and the standard deviation of this initial operating voltage was calculated. As a comparative example, the initial operating voltage (V_{1mA}) was measured for 100 current/voltage nonlinear resistors in which Ga^{3+} had been

added not as an aqueous solution, but as an oxide, and the standard deviation of this initial operating voltage was calculated.

Effect

[0065] In this embodiment and the comparative example, the standard deviation was calculated, and as a result the standard deviation of V_{1mA} when the Ga^{3+} was added as a nitrate aqueous solution was 585, while the standard deviation of V_{1mA} when the Ga^{3+} was added as an oxide was 2406. Specifically, a current/voltage nonlinear resistor with vastly less variance in its characteristics could be obtained by adding the Ga^{3+} as a nitrate aqueous solution.

[0066] Because gallium (Ga) was added in an extremely small amount, when gallium oxide (Ga_2O_3), which is an oxide of gallium (Ga), was added, it was difficult to mix uniformly with the other raw materials, and there was a great deal of variance in the characteristics. In contrast, when gallium nitrate ($Ga(NO_3)_3$), which is a water-soluble gallium raw material, was added, it mixed as gallium ions with the other raw materials, which is believed to be why the characteristics were so stable.

(5) Fifth Embodiment

Constitution and Production Procedure

[0067] A fifth embodiment related to the present invention will be described through reference to Table 5. In this embodiment, Bi_2O_3 (0.5 mol%), Co_2O_3 (1.0 mol%), MnO (1.0 mol%), Sb_2O_3 (2 mol%), NiO (2 mol%), and Dy_2O_3 (0.5 mol%) were measured out as sub-components in the final proportions given in parentheses above, and these components were added to the ZnO main component.

[0068] Ga^{3+} was added as a nitrate, with the added amount varied, and the current/voltage nonlinear resistors of sample numbers 57 to 71 in Table 5 were produced by the method described in the first embodiment above. Here, the disk diameter of the current/voltage nonlinear resistors was either 35, 60, or 100 mm, and the added amount of Ga^{3+} was varied with the disk diameter.

[0069] The nonlinearity (V_{10kA}/V_{1mA}) of these current/voltage nonlinear resistors was evaluated by the method given in the first embodiment above, and the results are given in Table 5. The coefficient A in Table 5 is a coefficient in the following relational formula with the added amount of Ga^{3+} .

[0070] This embodiment is characterized in that the above-mentioned coefficient A is between 5 and 14.

$$\text{Added amount of } Ga^{3+} \text{ (mol\%)} = (A - 0.042 \times D) / 1000$$

(A: coefficient; D: disk diameter (mm))

(A: coefficient; D: disk diameter (mm))

Table 5

Sample number	D (mm)	Ga^{3+} added amount (mol%)	Coefficient A	Nonlinearity V_{10kA}/V_{1mA}
57*	35	0.002	3.47	1.742
58	35	0.004	5.47	1.672
59	35	0.008	9.47	1.652
60	35	0.12	13.47	1.672
61*	35	0.015	16.47	1.729
62*	60	0.002	4.52	1.568
63	60	0.003	5.52	1.502
64	60	0.005	7.52	1.492
65	60	0.01	12.52	1.502
66*	60	0.013	15.52	1.584
67*	100	0.0003	4.50	1.542

(continued)

Sample number	D (mm)	Ga ³⁺ added amount (mol%)	Coefficient A	Nonlinearity V_{10kA}/V_{1mA}
68	100	0.0008	5.00	1.468
69.	100	0.003	7.20	1.458
70	100	0.008	12.20	1.468
71*	100	0.012	16.20	1.521

Effect

[0071] FIG. 2 shows the relation between the coefficient A and nonlinearity. As shown in FIG. 2, nonlinearity obviously varies with the amount in which gallium (Ga) is added. Here, when the current/voltage nonlinear resistor is disk shaped, added amount of gallium at which nonlinearity is good varies with the diameter of the disk. This is because the current density in the current/voltage nonlinear resistor varies with the disk diameter, and the optimal added amount of gallium is within the range of the relational formula given above.

[0072] In other words, as is clear from FIG. 2, if the coefficient A is between 5 and 14, this is the optimal region for obtaining excellent nonlinearity, regardless of the disk diameter of the current/voltage nonlinear resistor. This embodiment, in which Ga³⁺ is added in an amount at which the coefficient A will be from 5 to 14, allows exceedingly good nonlinear resistance characteristics to be obtained.

(6) Other Embodiments

[0073] The present invention is not limited to the embodiments given above, and various modifications are possible as long as the sub-components bismuth (Bi), cobalt (Co), manganese (Mn), antimony (Sb), nickel (Ni), gallium (Ga), and a rare earth element (R), and silver (Ag) and boron (B) are within the compositional range given in the claims.

[0074] It is explicitly stated that all features disclosed in the description and/or the claims are intended to be disclosed separately and independently from each other for the purpose of original disclosure as well as for the purpose of restricting the claimed invention independent of the composition of the features in the embodiments and/or the claims. It is explicitly stated that all value ranges or indications of groups of entities disclose every possible intermediate value or intermediate entity for the purpose of original disclosure as well as for the purpose of restricting the claimed invention, in particular as limits of value ranges.

Claims

1. A current/voltage nonlinear resistor including a sinter (1), said sinter consisting essentially of zinc oxide (ZnO) as the main component and bismuth (Bi), cobalt (Co), manganese (Mn), antimony (Sb), nickel (Ni), gallium (Ga), and a rare earth element (R) as sub-components, wherein the sub-components, calculated as Bi₂O₃, Co₂O₃, MnO, Sb₂O₃, NiO, Ga³⁺, and R₂O₃, are contained in the following proportions:

Bi₂O₃: 0.3 to 1.5 mol%,
 Co₂O₃: 0.3 to 2.0 mol%,
 MnO: 0.4 to 3.0 mol%,
 Sb₂O₃: 0.5 to 4.0 mol%,
 NiO: 0.5 to 4.0 mol%,
 Ga³⁺: 0.0005 to 0.02 mol%, and
 R₂O₃: 0.05 to 1.0 mol%,

wherein the current/voltage nonlinear resistor is in the form of a disk, whereby the relationship between the added amount of Ga³⁺ and the diameter of the disk is such that the added amount of Ga³⁺ (mol%) $\leq (A - 0.042 \times D)/1000$ (where A = 5 to 14, and D = the disk diameter (mm)).

2. The current/voltage nonlinear resistor according to Claim 1, wherein the sinter (1) further contains 0.005 to 0.05 wt% silver (Ag), calculated as Ag₂O₃.

3. The current/voltage nonlinear resistor according to Claim 1, wherein the sinter (1) further contains 0.005 to 0.05 wt% boron (B), calculated as B_2O_3 .
4. The current/voltage nonlinear resistor according to any one of Claims 1 to 3, wherein (R) is at least one member of the group consisting of dysprosium (Dy), europium (Eu), erbium (Er), thulium (Tm), gadolinium (Gd), yttrium (Y), holmium (Ho), and ytterbium (Yb).
5. The current/voltage nonlinear resistor according to any one of Claims 1 to 4, wherein a water-soluble raw material is used as a gallium (Ga) addition raw material.

Patentansprüche

1. Strom/Spannung-nichtlinearer Widerstand, der einen Sinterkörper (1) umfasst, wobei der Sinterkörper im Wesentlichen aus Zinkoxid (ZnO) als Hauptkomponente und Bismuth (Bi), Cobalt (Co), Mangan (Mn), Antimon (Sb), Nickel (Ni), Gallium (Ga) und einem Seltenerdelement (R) als Nebenkomponten besteht, wobei die Nebenkomponten, berechnet als Bi_2O_3 , Co_2O_3 , MnO, Sb_2O_3 , NiO, Ga^{3+} und R_2O_3 , in den folgenden Anteilen enthalten sind:

Bi_2O_3 : 0,3 bis 1,5 mol-%

Co_2O_3 : 0,3 bis 2,0 mol-%

MnO: 0,4 bis 3,0 mol-%

Sb_2O_3 : 0,5 bis 4,0 mol-%

NiO: 0,5 bis 4,0 mol-%

Ga^{3+} : 0,0005 bis 0,02 mol-% und

R_2O_3 : 0,05 bis 1,0 mol-%,

wobei der Strom/Spannung-nichtlineare Widerstand in der Form einer Scheibe vorliegt, wodurch die Beziehung zwischen der zugesetzten Ga^{3+} -Menge und dem Durchmesser der Scheibe derart ist, dass

die zugesetzte Ga^{3+} -Menge (mol-%) $\leq (A - 0,042 \times D)/1000$ ist

(wobei A = 5 bis 14 und D = Scheibendurchmesser (mm)).

2. Strom/Spannung-nichtlinearer Widerstand nach Anspruch 1, wobei der Sinterkörper (1) ferner 0,005 bis 0,05 Gew.-% Silber (Ag), berechnet als Ag_2O_3 , enthält.

3. Strom/Spannung-nichtlinearer Widerstand nach Anspruch 1, wobei der Sinterkörper (1) ferner 0,005 bis 0,05 Gew.-% Bor (B), berechnet als B_2O_3 , enthält.

4. Strom/Spannung-nichtlinearer Widerstand nach einem der Ansprüche 1 bis 3, wobei (R) mindestens ein Element der Gruppe, bestehend aus Dysprosium (Dy), Europium (Eu), Erbium (Er), Thulium (Tm), Gadolinium (Gd), Yttrium (Y), Holmium (Ho) und Ytterbium (Yb), ist.

5. Strom/Spannung-nichtlinearer Widerstand nach einem der Ansprüche 1 bis 4, wobei als zuzusetzendes Gallium (Ga)-Ausgangsmaterial ein wasserlösliches Ausgangsmaterial verwendet wird.

Revendications

1. Résistance courant/tension non-linéaire comprenant une fritte (1), ladite fritte étant constituée essentiellement d'oxyde de zinc (ZnO) comme composant principal et de bismuth (Bi), de cobalt (Co), de manganèse (Mn), d'antimoine (Sb), de nickel (Ni), de gallium (Ga) et d'un élément de terre rare (R) comme sous-composants, dans laquelle les sous-composants, calculés pour Bi_2O_3 , Co_2O_3 , MnO, Sb_2O_3 , NiO, Ga^{3+} , et R_2O_3 , sont contenus dans les proportions suivantes :

Bi_2O_3 : 0,3 à 1,5% en mole,

Co_2O_3 : 0,3 to 2,0% en mole,

MnO : 0,4 à 3,0 % en mole,

Sb_2O_3 : 0,5 à 4,0 % en mole,

NiO : 0,5 à 4,0 % en mole,

Ga^{3+} : 0,0005 à 0,02 % en mole,

EP 1 798 741 B1

et R_2O_3 : 0,05 à 1,0% en mole,
dans laquelle la résistance courant/tension non-linéaire a la forme d'un disque,
la relation entre la quantité ajoutée de Ga^{3+} et le diamètre du disque étant telle que
la quantité ajoutée de Ga^{3+} (% en mole) $\leq (A - 0,042 \times D) / 1000$ (où $A = 5$ à 14 et $D =$ diamètre du disque (mm)).

2. Résistance courant/tension non linéaire selon la revendication 1, dans laquelle la fritte (1) contient en outre 0,005 à 0,05 % en poids d'argent (Ag), calculé pour Ag_2O_3 .
3. Résistance courant/tension non linéaire selon la revendication 1, dans laquelle la fritte (1) contient en outre 0,005 à 0,05 % en poids de bore (B), calculé pour B_2O_3 .
4. Résistance courant/tension non linéaire selon l'une quelconque des revendications 1 à 3, dans laquelle (R) est au moins un élément du groupe constitué du dysprosium (Dy), de l'euporium (Eu), de l'erbium (Er), du thulium (Tm), du gadolinium (Gd), de l'yttrium (Y), de l'holmium (Ho) et de l'ytterbium (Yb).
5. Résistance courant/tension non linéaire selon l'une quelconque des revendications 1 à 4, dans laquelle un matériau brut soluble dans l'eau est utilisé sous la forme d'un matériau brut additionnel de gallium (Ga).

FIG. 1

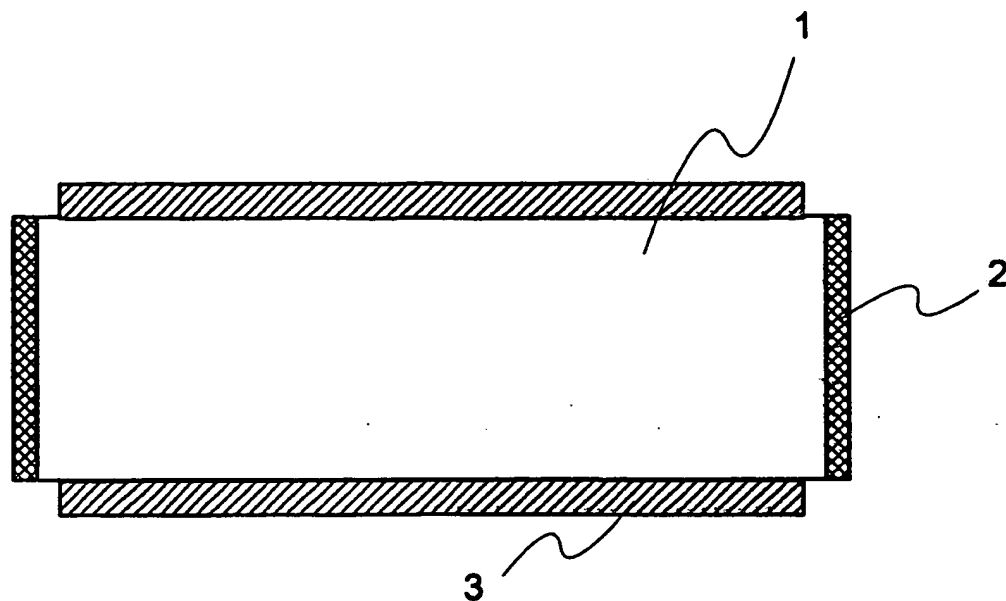
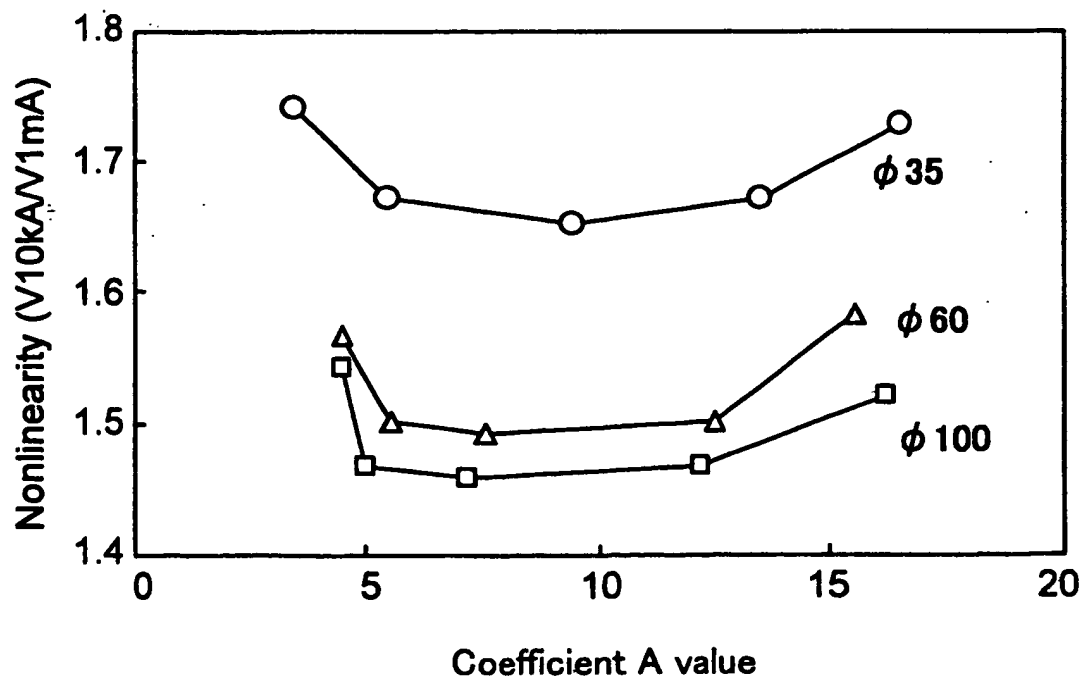


FIG. 2



REFERENCES CITED IN THE DESCRIPTION

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