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New Thermionic Cathodes Coated with Ba-Ta-Zr-O-N System Produced by Carbothermal Reduction and Nitridation Process

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$Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ compounds for x=0～1 were produced by carbothermal reduction and nitridation process. In this process, $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ and TaC as a second phase were observed by X-ray powder diffraction patterns. Work functions and barium vaporization temperatures of the obtained powders were estimated. Work functions of the $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ compounds increased with increasing zirconium content, and the value of 1.7eV for x=0.1 was less than that of 2eV with alkaline earth oxide. Barium in the $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ compound was volatile at higher temperature than that of authentic hot cathodes coated with alkaline earth oxide. In the 4.1mm of outside diameter, 3.3mm of inside diameter, and 100mm length of glasses with 9.3kPa of argon gas and mercury, some fluorescent lamps with hot cathodes coated with $Ba(Ta_{0.8}Zr_{0.2})O_{2.2}N_{0.6}$ compound worked excellently and those has been lit for 61.2Ms, so far.

Key Words : Oxynitride, Carbothermal reduction and nitridation, Hot cathode, Fluorescent lamp

1. Introduction

It is reasonable to light in the world with fluorescent lamps in terms of less energy consumption. Tungsten coil coated with two or more of alkaline earth carbonates and zirconia is employed to develop thermionic cathodes for fluorescent lamps in these days[1]. It is said that the life of fluorescent lamps is typically about 36Ms because the barium of the cathodes is gradually disappeared at working environments. Describing the reasons for disappearing the barium, it is known that additional heating due to ion bombardment and I^2R losses introduce to vaporize barium of oxide coated cathodes. The barium vapor forms amalgam in the lamp tubes[2], so the lamps contain excess mercury to replenish activated mercury. It is worth to produce stable materials for coated cathodes at working conditions in terms of less mercury consumption.

In the 8th International Symposium on the Science & Technology of Lighe Sources (LS-8), Hamada presented new structural cathodes with new materials of Ba-Ta-Zr-O system[3]. It should be mentioned that less vaporization of barium was found and long life was expected for this system. Besides, de-carbonating process is not required while producing fluorescent lamps. These remarkable features are possibly applied to fluorescent lamps with authentic cathodes, although Hamadas' cathodes are inconvenient to be built in a structural point of view. However, compounds to emit thermionic electrons have not been recognized, because the cathodes consisted of mixture of several unidentified compounds.

Recently, we have finally identified a thermionic compound related with $BaTaO_2N$ of a perovskite structure. In 1986, it is reported that Marchand et al synthesized $BaTaO_2N$ compound by flowing heated ammonia gas[4]. Regarding mass-producebility, it is disadvantageous that heat treatment with ammonia gas is required. This paper shows how we developed the $BaTaO_2N$ compounds by carbothermal reduction and nitridation that is the process to compose Sialon[5-6].

As we think about applying the $BaTaO_2N$ compounds to oxide coated cathodes in fluorescent lamps, it is useful to evaluate their work functions and barium vapor temperatures. In this paper, we will provide these informative values as well as producing light bulbs.

2. Experimental Procedures

A. Sample preparations

Figure 1 shows preparation of powders by carbothermal reduction and nitridation process. $BaCO_3$, Ta_2O_5, and ZrO_2 in powder forms were carefully weighed. The raw materials and deionized water were dumped into a plastic bottle with ZrO_2 grinding media, and were mixed for 72ks. After separating ZrO_2 media from the mixture of raw materials and water, the slurry was dried up in oven at 373K for 57.6ks. Carbon black to remove oxygen during the process was added into the dried raw materials, and mixed in alumina mortar. The mixture was pressed in disk shapes of 15mm diameter and 10mm thickness. To induce the carbothermal reduction and nitridation process, firing was carried out between 1473K and 1673K for 18ks flowing nitrogen gas while the pressed disks were sat into a carbon crucible. Flow rate of the nitrogen gas was 4.7mm/s. After firing, the disks were powdered in porcelain mortar by hand.

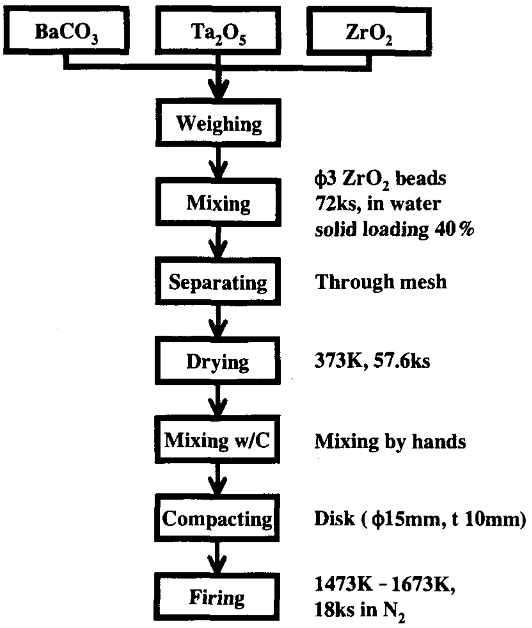


Figure 1 Steps in the carbothermal reduction and nitridation process for Ba-Ta-Zr-O-N system

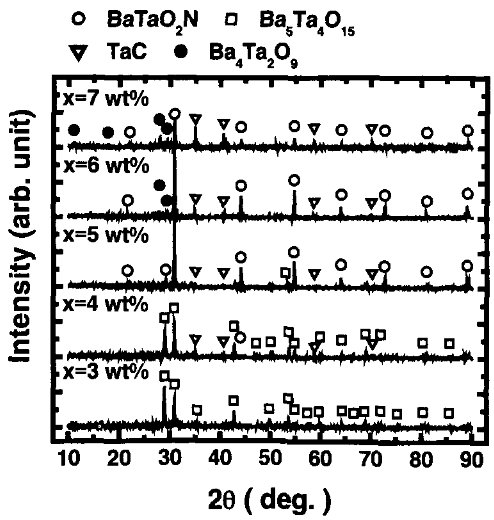


Figure 2 X-ray diffraction patterns of the samples fired at 1673K for 18ks depending on the amount of carbon black between 3wt% and 7wt%

B. Measurements

To identify the compounds we obtained, X-ray powder diffraction measurements were carried out by Cu-Kα radiation with Mac Science MXP3 system. Nitrogen and oxygen content of the compounds were determined by burning the powders in hydrogen atmosphere using Horiba EMGA-650A. Horiba EMIA-520 was used to determine carbon content. Chemical compositions were determined by X-ray fluorescence measurement using Rigaku 3550.

A sample for determining work functions was prepared by coating paste, which is a mixture of the powder with 1wt% of polyethylene glycol 200 and suitable amount of deionized water, to a tungsten coil. We adjusted the amount of added water in the paste because surface area of the powders was different. The powder coated tungsten coil, which was connected to a power supply to give a heat, was placed into a vacuum chamber. The sample as a cathode and a metal plate of stainless steel were faced in a distance of 1mm, and thermionic currents between the plate and the sample were simply measured by adding enough voltage, while the sample temperature was measured by a radiation thermometer. After the currents measurements depending upon temperatures, work functions were calculated by Richardson plots[7].

The same cathode of the tungsten coil as a sample of estimating work functions was used for evaluating barium vaporization temperatures. A lamp without a fluorescent substance was constructed, and the tungsten coil with sample powder in the lamp was placed straight in between a barium hollow cathode lamp and a spectrometer following a photomultiplier tube and multimeter. During flowing current to the tungsten coil to control temperature, the voltages at the multimeter were monitored Once the barium of the sample started volatizing, the voltage went down. We described a temperature at 90% of the initial voltage as a barium vaporization temperature.

We also developed some fluorescent lamps with the cathodes coated with the obtained powders and tested life of the fluorescent lamps in the 4.1mm of outside diameter, 3.3mm of inside diameter, and 100mm length of glasses with 9.3kPa of argon gas and mercury. The lamps were lit by 30mA of 30kHz ac current.

3. Results and Discussion

First of all, it is practical to know desirable amount of carbon black to generate $BaTaO_2N$ compound by the carbothermal reduction and nitridation process. We roughly estimated the necessary amount of carbon black by assuming chemical reaction. Equilibrium between carbon monoxide gas and carbon dioxide gas plays an important role in terms of the carbothermal reduction and nitridation at the firing temperature. Because of strong reduction capability of carbon monoxide, oxygen in the raw materials is removed during the synthesis of $BaTaO_2N$ compound.

$$BaO+\frac{1}{2}Ta_2O_5+\frac{1}{2}N_2+\frac{3}{2}CO \Leftrightarrow BaTaO_2N+\frac{3}{2}CO_2 \quad (1)$$

Assuming this chemical reaction, 4.13wt% of carbon black is required by simple math. Figure 2 shows X-ray diffraction patterns of the samples fired at 1673K for 18ks depending on the amount of carbon black between 3wt% and 7wt%. The patterns of 3wt% mostly gives $Ba_5Ta_4O_{15}$ compound, but the amount of $Ba_5Ta_4O_{15}$ compound was decreased with increasing carbon black content. While decreasing of $Ba_5Ta_4O_{15}$ compound, the behavior of generating $BaTaO_2N$ compound was contrary. The amount of TaC compound was minimized at 5wt% of carbon black content. The excess carbon black over 6wt% composed $Ba_4Ta_2O_9$ compound.

In figure 2, three different compounds such as $BaTaO_2N$, $Ba_5Ta_4O_{15}$, and TaC were identified as large volumes on each carbon content. To determine optimum carbon content, figure 3 summarizes intensities of representative X-ray diffraction peaks of $BaTaO_2N$, $Ba_5Ta_4O_{15}$, and TaC, depending on the amount of carbon black with the firing temperatures, respectively. The representative Miller indices were chosen such as (200) of $BaTaO_2N$ ($2\theta=44°$), (103) of $Ba_5Ta_4O_{15}$ ($2\theta=29°$), and (111) of TaC ($2\theta=35°$), respectively. The intensities of X-ray diffraction peaks are proportional to volume fractions of compounds, assuming that the powders in a sample holder are isotropic. The amount of $BaTaO_2N$ compound was maximized at the carbon black content from 5wt% to 6wt% at 1673K. On the contrary, the amount of $Ba_5Ta_4O_{15}$ compound at the range of carbon black content was reduced rapidly. At firing temperature of 1573K, the range of carbon black content that generated $BaTaO_2N$ compound was narrower. The amount of TaC compound was quickly increased with increasing the carbon black content over 6wt%. It is observed that firing the sample with the carbon black content of 6wt% at 1573K is suitable to maximize the amount of $BaTaO_2N$ compound. It should be mentioned that the amount of 6wt% required to maximize the amount of $BaTaO_2N$ compound was larger than that of carbon black content estimated by simple math. The excess carbon black was consumed not only by producing TaC compound, but by the less efficiency in the carbothermal reduction and nitridation.

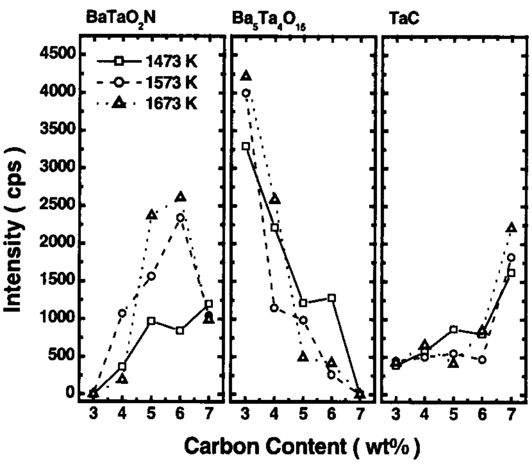


Figure 3 Intensities of representative X-ray diffraction peaks of $BaTaO_2N$, $Ba_5Ta_4O_{15}$, and TaC, depending on the amount of carbon black with firing temperatures

Zirconium plays a key role for authentic cathodes coated with barium oxide in terms of expanding life of fluorescent lamps. On the same idea, it is interesting to develop $Ba(Ta_{1-x}Zr_x)O_2N$ compounds by carbothermal reduction and nitridation process. The ratio of ZrO_2 to Ta_2O_5 in the Ba-Ta-Zr-O-N system was x. : (1-x)/2 Figure 4 shows X-ray diffraction patterns of the samples between x=0.2 and 1.0 fired at 1673K for 18ks and that for x=0 fired at 1573K. Desirable carbon content between 3.6wt% and 6wt% were added for the each samples. Perovskite-type $Ba(Ta_{1-x}Zr_x)O_2N$ compounds were obtained in the range between x=0 and 1, although small amounts of TaC compound were recognized. The results from X-ray fluorescence measurements displayed good agreement with the initial chemical compositions. At x=1, the pattern was reasonably fitted with that of $BaZrO_3$ compound. When the pattern of x=0.6 was carefully analyzed, each peak consisted of two peaks. Figure 5 shows calculated lattice constants of the samples depending on zirconium content for x=0~1. The

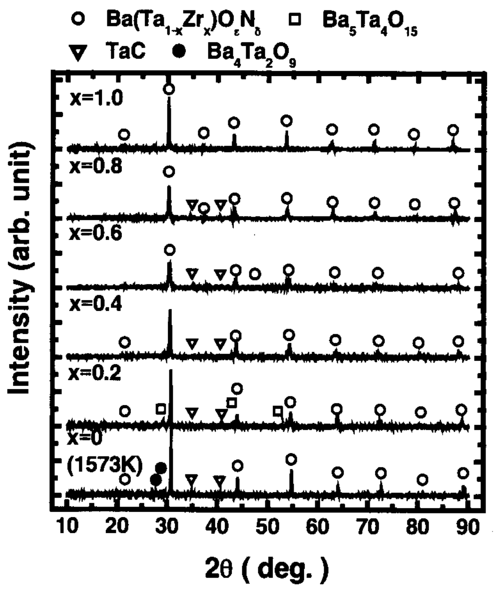


Figure 4 X-ray diffraction patterns of the $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ samples between x=0.2 and 1.0 fired at 1673K for 18ks and for x=0 fired at 1573K

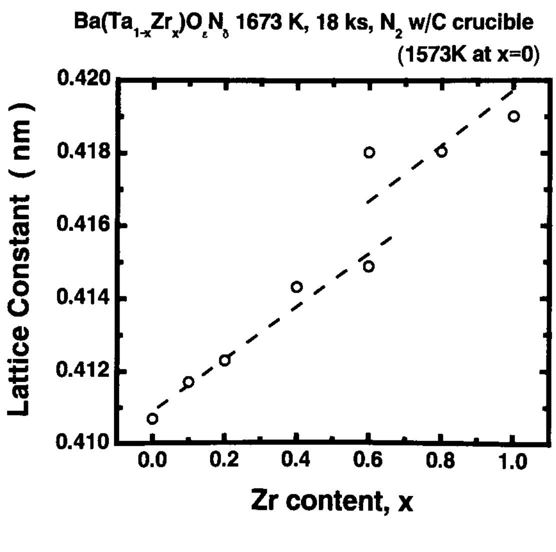


Figure 5 Calculated lattice constants of the samples depending on zirconium content for x=0~1

lattice constants proportionally increased with increasing zirconium content, though there was a gap at x=0.6. It was reported that the same behavior for the samples prepared by firing in ammonia gas was observed by Grins, except for the behavior at x=0.6[8].

Oxygen, nitrogen, and carbon content of $Ba(Ta_{1-x}Zr_x)O_2N$ compounds were investigated. Figure 6 shows nitrogen and oxygen content of the samples with zirconium content for x=0~1. Nitrogen content decreased with increasing zirconium content, although oxygen content increased with increasing zirconium content contrary. At x=1, almost no nitrogen content was detected. The suffixes, ε and δ, for the oxygen and nitrogen of $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ were estimated by these results. The measurement displayed a maximum carbon content of 0.46wt% at

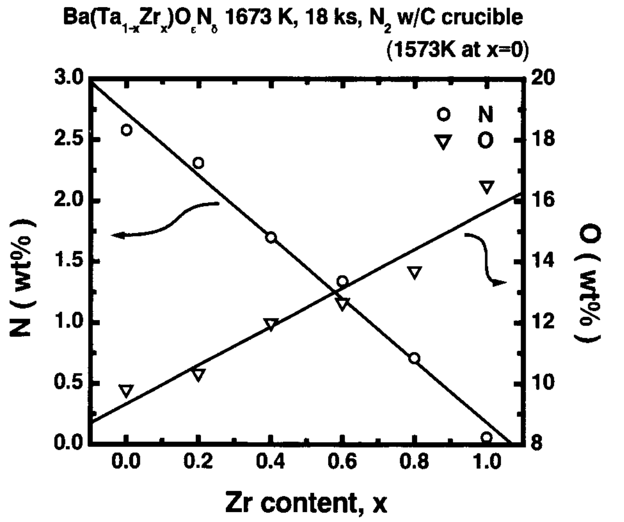


Figure 6 Nitrogen and oxygen content of the $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ samples with zirconium content for x=0~1

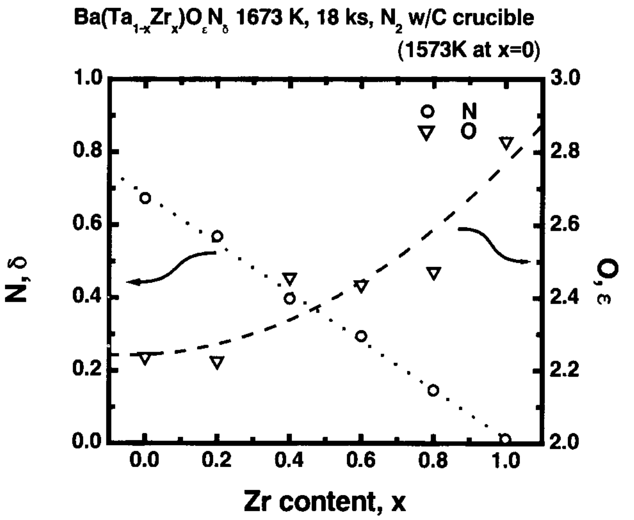


Figure 7 δ for nitrogen and ε for oxygen ratio calculated based on the results in figure 6

x=0 though the results from the measurements were less than 0.23wt% at x=0.2~1.0 in this system. Assuming that whole amount of 0.46wt% carbon at x=0 existed as TaC compound, the maximum ratio of TaC was 7.3wt%. There were three detectable phases at x=0 in figure 4, though the amount of $Ba_4Ta_2O_9$ compound was relatively small. Therefore, the phase except for TaC and $Ba_4Ta_2O_9$ compound should be $BaTaO_2N$ compound in this assumption. And excess barium and/or excess zirconium might compose oxides and/or nitrides, but it was negligible that imperceptibly small X-ray diffraction patterns for the oxides and/or nitrides were presented. It should be noted that we cannot say precise error values for the suffixes of ε and δ. Based on these assumptions above, the numbers for x=0 said that ε for oxygen ratio and δ for nitrogen were 2.2 and 0.7, respectively. The sum of total nitrogen and oxygen was less than 3, although ABO_3 is generally represented with perovskite structure. It is feasible to say that small amounts of defects exist in these systems. Figure 7 represents δ for nitrogen and ε for oxygen ratio calculated based on the results in figure 6 and carbon content.

Capability of $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ compounds as a thermionic material was investigated. Work function determines emission of cathode concerned. Figure 8 shows work functions of the samples as a function of zirconium content. The work functions increased with increasing zirconium content, despite of large error bars.

It is favorable to put larger working currents of the coated cathodes in terms of better efficiency in lumen output. As long as the latest cathodes based on barium oxide coated are applied, working temperature must be less than around 1323K to avoid vaporization of the barium. Figure 9 shows barium vaporization temperatures of the samples depending on zirconium content. Compared to the behavior of BaO as an authentic hot cathode material, $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ compounds give higher barium vaporization temperatures over 270K than that of BaO.

The newly developed cathodes coated with $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ compounds don't require activation process such as heating tungsten filaments with the compounds to generate excess barium and to reduce the work function. According to the report for

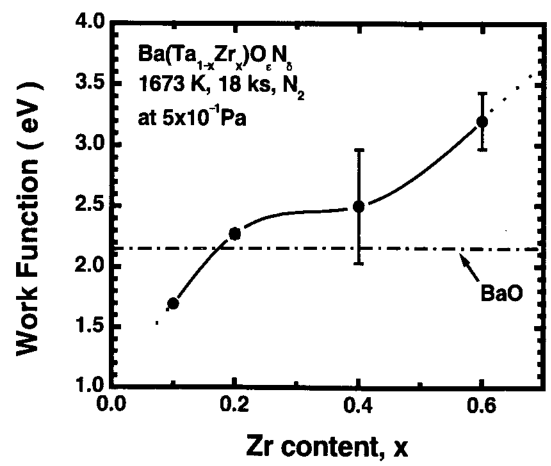


Figure 8 Work functions of the $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ samples as a function of zirconium content

authentic cathodes[7], excess barium plays an important role to accelerate the thermionic emission of electrons.

At last, we developed some fluorescent lamps with the cathodes coated with $Ba(Ta_{0.8}Zr_{0.2})O_{2.2}N_{0.6}$ compound to test life. Photo 1 describes an image of the cathode dipped in the water-based slurry with $Ba(Ta_{0.8}Zr_{0.2})O_{2.2}N_{0.6}$ compound. Arc spots about $100\mu m$ diameter were generated under the condition of 30mA of ac current in the 4.1mm of outside diameter, 3.3mm of inside diameter, and 100mm length of lamps with 9.3kPa of argon gas and mercury, as shown in photo 2. The life of these lamps is over 61.2Ms, so far.

4. Conclusions

$Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ compounds for x=0~1 were produced by carbothermal reduction and nitridation process. In this process, $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ and TaC as a second phase were observed with optimum carbon content by X-ray powder diffraction patterns. Feasibility of applying fluorescent lamps showed lower work functions and higher volatile temperatures than those of authentic material as barium oxide. Work functions of the $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ compounds increased with increasing zirconium content, and the value of 1.7eV for x=0.1 was less than that of 2eV with alkaline earth oxide. Barium in the $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ compound was volatile at higher temperature than that of authentic hot cathodes coated alkaline earth oxide. In the 4.1mm of outside diameter, 3.3mm of inside diameter, and 100mm length of glasses with 9.3kPa of argon gas and mercury, some fluorescent lamps with hot cathodes coated with $Ba(Ta_{0.8}Zr_{0.2})O_{2.2}N_{0.6}$ compound worked excellently and those has been lit for 61.2Ms, so far.

Photo 1 A Cathode coated with $Ba(Ta_{0.8}Zr_{0.2})O_{2.2}N_{0.6}$ compound

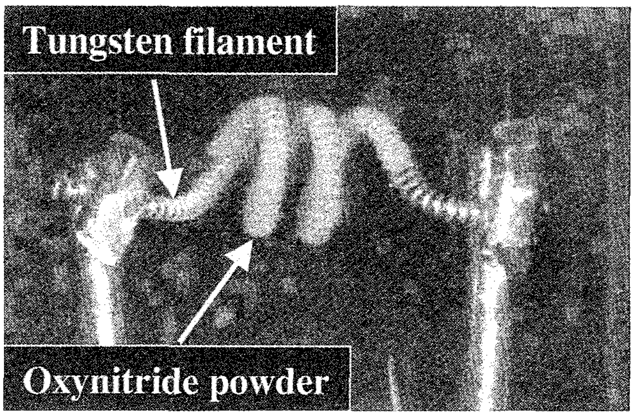
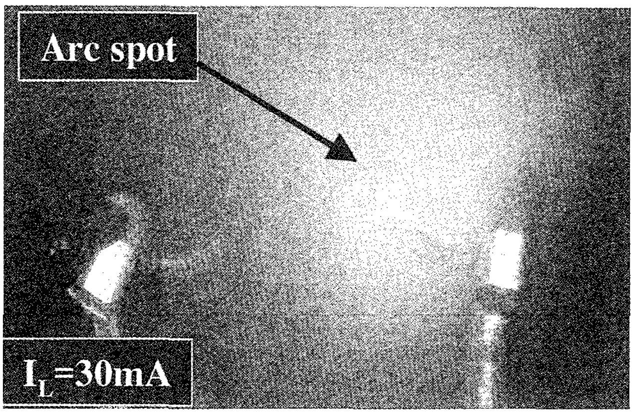


Photo 2 A working cathode coated with $Ba(Ta_{0.8}Zr_{0.2})O_{2.2}N_{0.6}$ compound under the condition of 30mA of ac current in the 4.1mm of outside diameter, 3.3mm of inside diameter, and 100mm length of lamps with 9.3kPa of argon gas and mercury



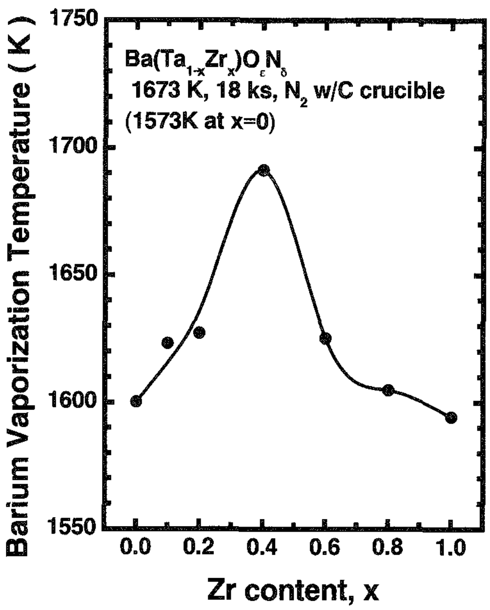


Figure 9 Barium vaporization temperatures of the $Ba(Ta_{1-x}Zr_x)O_\varepsilon N_\delta$ samples depending on zirconium content

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