# グラスライニング製放電電極用ガラスに関する検討

## Examination of Glass for Glass-Lined Discharge Electrodes


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各種元素をソーダガラス（$15Na_2O \cdot 15CaO \cdot 70SiO_2$）に1-3mol%添加し，それらの元素が比誘電率に及ぼす影響について調べた。グラスライニング製放電電極のコーティング層の構造に関して誘電体層の絶縁破壊電圧と比誘電率の観点から検討した。ほとんどの希土類元素（Pr，Lu，Eu，Gd，Sm）が他の元素より誘電率の増加効果が大きいことが分かった。グラスライニング層の絶縁破壊電圧の観点から，最適な改善効果を得るためには低い誘電率の下引きガラスを使用せず高い比誘電率の上引きガラスを直接母材金属上へライニングすることが望ましいことが分かった。

実験の結果 $3CoO \cdot 3NiO \cdot 3MnO_2 \cdot 3Pr_6O_{11} \cdot 30Bi_2O_3 \cdot 20BaO \cdot 50B_2O_3$（mol%；CNMPBBB）ガラスは比誘電率が16と高く，母材との優れた密着性を持っていた。CNMPBBBガラスはグラスライニング製放電電極として有望であることが分かった。

In this work, we studied the effect of various elements on the relative dielectric constant, $\varepsilon_r$, by adding 1-3mol% of an element to soda glass, $15Na_2O \cdot 15CaO \cdot 70SiO_2$, the mother glass. The structure of the dielectric coating layer for the glass-lined discharge electrode was investigated in terms of the breakdown voltage and $\varepsilon_r$. It was found that most rare-earth elements (Pr, Lu, Eu, Gd, Sm) are more effective in increasing $\varepsilon_r$ than other elements. From the viewpoint of the breakdown voltage of the glass-lined layer, it is desirable that a cover coating with a high $\varepsilon_r$ is directly coated onto the base metal without using a ground coating with the low $\varepsilon_r$, to obtain the optimum improvement effects.

As the results of experiments, the $3CoO \cdot 3NiO \cdot 3MnO_2 \cdot 3Pr_6O_{11} \cdot 30Bi_2O_3 \cdot 20BaO \cdot 50B_2O_3$ (mol%;CNMPBBB) glass was found to have a high $\varepsilon_r$ of 16 and good adhesion with steel. CNMPBBB glass is highly promising for use in the glass-lined discharge electrodes.



**Key Words:**

| | |
|---|---|
| 比誘電率 | Relative dielectric constant |
| 放電電極 | Discharge electrode |
| グラスライニング | Glass lining |
| 密着 | Adhesion |
| $Bi_2O_3 \cdot BaO \cdot B_2O_3$系ガラス | $Bi_2O_3 \cdot BaO \cdot B_2O_3$ glasses |


## Introduction

There are some devices, such as an ozonizer,[1] laser,[2] and corona discharge surface treatment device,[3] which utilize discharge between opposite dielectric coating discharge electrodes at high frequency and high voltage. Ceramic electrodes with a metal layer deposited on one side are utilized in small equipment. On the other hand, glass-lined electrodes and glass tube electrodes with a metal layer deposited inside the tube are utilized in large equipment. It is expected that the performance of such equipment will be improved by increasing the discharge power. The discharge power of the ozonizer is given by the following equation,[4)]

$$W = f \cdot C_g \cdot 2V^* \{2V_{op} - (1 + C_o/C_g) \cdot 2V^*\}$$

where $W$ is the discharge power, $f$ is the frequency of the power source, $C_g$ is the electrostatic capacity of the dielectric coating layer, $C_o$ is the electrostatic capacity of discharge space, $V_{op}$ is the crest value of applied voltage and $V^*$ is the discharge sustenance voltage.

Therefore, increasing the electrostatic capacity of the dielectric coating layer is one method of effectively increasing the discharge power. It is possible to increase the electrostatic capacity of a dielectric coating layer by thinning the dielectric coating layer or by increasing the relative dielectric constant, $\varepsilon_r$. It is more advantageous to increase $\varepsilon_r$ rather than to thin the dielectric coating layer, in terms of the breakdown voltage. Some ceramics are known as high $\varepsilon_r$ materials. Coste et al.[5)] reported that the efficiency of ozonization should be improved by using high $\varepsilon_r$ ceramics as the dielectric coating layer of the discharge electrode. However, this is thought to be unsuitable for a large discharge electrode because of the restriction of the formability and workability of ceramics. It has been reported that the efficiency of ozonization can be improved by increasing $\varepsilon_r$ of a dielectric coating layer composed of a mixture of glass and barium titanate.[6)] However, $\varepsilon_r$ was not so high, about 5.8-6.6, contrary to the expectation. The reason is considered to be that a part of the high-dielectric-constant ceramics, $BaTiO_3$, changes from crystalline to amorphous due to reaction with the glass at high temperature during enameling.

In this work, we studied the effect of various elements on $\varepsilon_r$ by adding 1-3 mol% of an element to soda glass, $15Na_2O \cdot 15CaO \cdot 70SiO_2$, the mother glass. The structure of the dielectric coating layer for the glass-lined discharge electrode was investigated in terms of the breakdown voltage and $\varepsilon_r$. On the basis of the results, glasses which are suitable for use in glass-lined discharge electrodes are examined.

## 1. Experimental

Reagent grade chemicals were used as starting materials. A batch of well mixed reagents was melted in atmosphere. The frit for the glass lining was prepared by water quenching, which means that the melt was directly poured into water. On the other hand, the slip for the glass lining was prepared by milling the frit with mill additions. $15Na_2O \cdot 15CaO \cdot 70SiO_2$ (NCS; mol%) glass was selected as the mother glass. Sample glasses were prepared by adding 3 mol% of each element ($Pr_6O_{11}$, $Lu_2O_3$, $Rh_2O_3$ and $Hf_2O_3$ were 2 mol%, $Ru_2O_3$ and $Eu_2O_3$ were 1 mol%) to the mother glass.

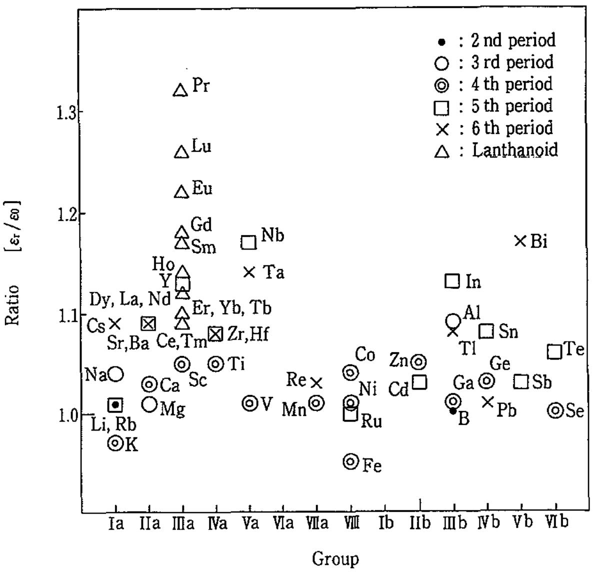
Samples for the measurements of $\varepsilon_r$ were polished to the dimensions of $15 \times 15 \times 1\ mm^3$ and silver paste was applied to both sides of the sample as electrodes. Samples for the measurements of the breakdown voltage and the adhesion were prepared by lining glass on $100 \times 100 \times 3.2\ mm^3$ shaped steel.

The relative dielectric constant was calculated from the obtained electrostatic capacity which was measured using an impedance analyzer (Yokogawa Hewlett-Packard, HP4192A). The glass transition temperature, $T_g$, and softening point were determined by differential thermal analysis (DTA; Rigaku, TG8110). The thermal expansion coefficient, $\alpha$, was determined using a thermomechanical analyzer (TMA; Rigaku, TMA8140). The breakdown voltages were measured in insulating oil using dielectric strength test equipment (Musashi Electric, IPK-50). For the evaluation of adhesion, samples were pressed by a 12.7-mm diameter hemispherical die with the load of $1.33 \times 10^4$ N and loading time of 30 s. Adhesion was evaluated from the area of the left glass layer on the impression.

## 2. Results and discussion

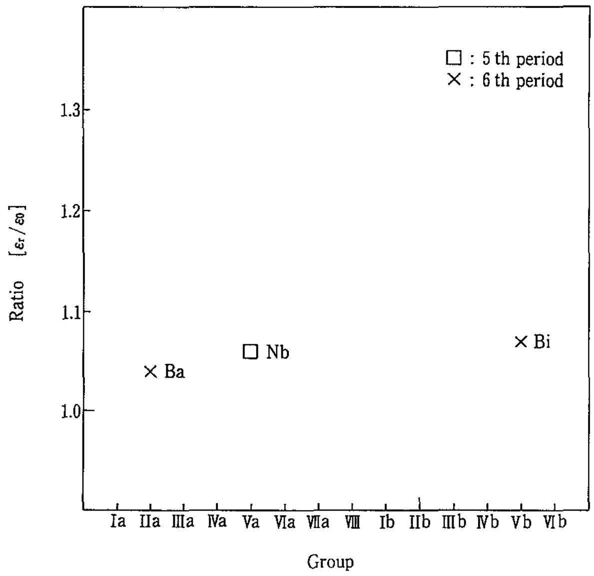
### 2. 1 Effects of each element on $\varepsilon_r$

**Figure 1** shows the effect of each added element on $\varepsilon_r$. The longitudinal axis shows the




$\varepsilon_o$ : Relative dielectric constant of $15Na_2O \cdot 15CaO \cdot 70SiO_2$ mother glasses,
$\varepsilon_r$ : Relative dielactric constant of 15 $Na_2O \cdot 15CaO \cdot 70SiO_2$ glasses containing various metal cations.

第１図　添加した元素の比誘電率への影響
**Fig. 1** Effect of adding various metal cations on relative dielectric constant.




$\varepsilon_o$ : Relative dielectric constant of $15BaO \cdot 15Na_2O \cdot 70B_2O_3$ mother glass,
$\varepsilon_r$ : Relative dielactric constant of $15BaO \cdot 15Na_2O \cdot 70B_2O_3$ glasses containing various metal cations.

第２図　添加した元素の比誘電率への影響
**Fig. 2** Effect of adding various metal cations on relative dielectric constant.

ratio of measured $\varepsilon_r$ for each sample to $\varepsilon_r$ of the mother glass, while the horizontal axis shows groups of the periodic table. It is found that most rare-earth elements (Pr, Lu, Eu, Gd, Sm) are more effective in increasing $\varepsilon_r$ than other elements. Furthermore, some non-rare-earth elements, e. g., Bi, Ti, Nb, Ta and In, also show good improvement effects on $\varepsilon_r$. It is known that the addition of Bi, Ti or Ba, increases $\varepsilon_r$ of glass.[7] In particular, Bi shows an excellent improvement of $\varepsilon_r$ in this study. However Pb, V and Te showed only a slight improvement, contrary to the expectation. This is because their vapor pressures during melting are higher than those of other elements. For the borate glass system, Ba, Bi and Nb were added to the mother glass of $15BaO \cdot 15Na_2O \cdot 70B_2O_3$ (BNB; mol%) and the effects of each element on $\varepsilon_r$ were investigated. The behavior of $\varepsilon_r$ improved in the borate glass system, showing a tendency similar to the silicate glass system, as shown in **Fig. 2.**

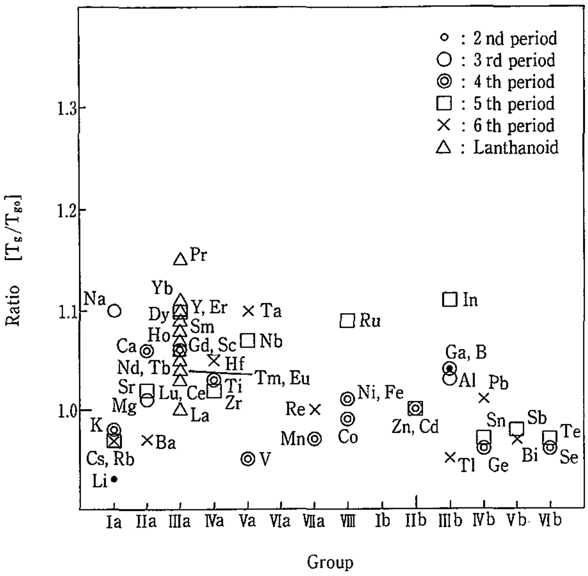
## 2. 2 Effects of each element on $T_g$ and $\alpha$

The effect of various elements added to NCS on $T_g$ is shown in **Fig. 3.** The effect of various elements added to NCS on $\alpha$ is shown in **Fig. 4.** As expected, elements which cause a rise of $T_g$ decrease $\alpha$. Rare-earth elements which greatly increase $\varepsilon_r$ also tend to raise $T_g$ but decrease $\alpha$, while Bi greatly increases $\varepsilon_r$, decreases $T_g$ and increases $\alpha$. Based on the above results, Bi is suitable as an additive to the glass lining to increase $\varepsilon_r$ and to adjust $\alpha$ of the glass to that of the base metal.

## 2. 3 Composition of glass for glass lining

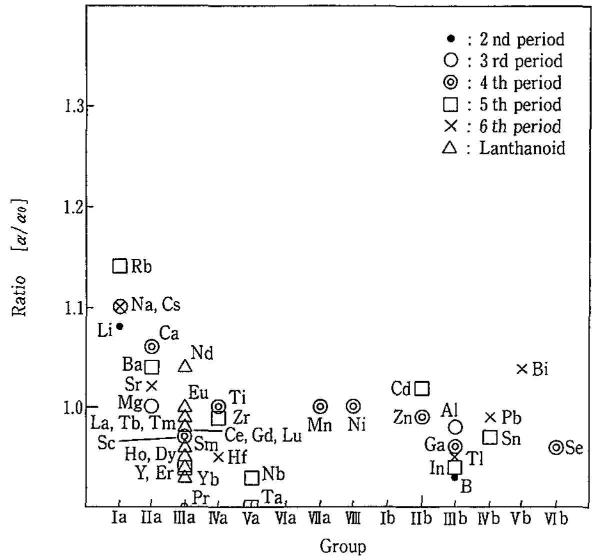
### 2. 3. 1 Silicate glasses

The borosilicate glasses have large thermal expansion coefficients between $T_g$ and the softening point. Therefore they tend to generate the crack defect called the strain-line during enameling. Generally the corrosion resistance of the borate glasses are inferior to those of silicate glasses and borosilicate glasses. Therefore silicate glasses were investigated first. The




$T_{go}$ : Glass transition temperature of $15Na_2O \cdot 15CaO \cdot 70SiO_2$ mother glass,
$T_g$ : Glass transition temperature of $15Na_2O \cdot 15CaO \cdot 70SiO_2$ glasses containing various metal cations.

第3図　添加した元素のガラス転移点への影響
**Fig. 3** Effect of adding various metal cations on glass transition temperature.




$\alpha_o$ : Thermal expansion coefficient of $15Na_2O \cdot 15CaO \cdot 70SiO_2$ mother glass,
$\alpha$ : Thermal expansion coefficient of $15Na_2O \cdot 15CaO \cdot 70SiO_2$ glasses containing various metal cations.

第4図　添加した元素の熱膨張係数への影響
**Fig. 4** Effect of adding various metal cations on thermal expansion coefficient.

addition of Ba induces a large improvement of $\varepsilon_r$ and barium carbonate is available as the starting material. The melting temperature is expected to decrease, and the agitation effect is also induced by evaporation of carbon dioxide during melting when using a carbonate as a starting material. As a result of the experiments, Bi was found to induce the largest improvement effect on $\varepsilon_r$, other than rare-earth elements. The addition of Bi is easier for adjusting $\alpha$ to that of the base metal than the addition of other effecive elements. Therefore the $Bi_2O_3$-$BaO$-$SiO_2$ glass system was investigated. The glass formation region for the $Bi_2O_3$-$BaO$-$SiO_2$ glass system is relatively wide.[8] For the glass lining, slow heating and cooling are generally required in order to prevent the introduction of defects since the base metal possesses the large heat capacity. In particular, more time than in the usual application is necessary for heating and cooling with the glass-lined electrode application, to prevent distortion. Therefore the crystallization of the glass is difficult to avoid in this glass system.

### 2. 3. 2 Borate glasses

The borate glass system was also similarly investigated as in the case of the silicate glass system. The low corrosion resistance is a problem in borate glasses. However, the electrode is mostly used under the dry atmosphere condition, like the electrode of an ozonizer, so it is decided that the borate glasses can be used in electrode application. The $Bi_2O_3$-$BaO$-$B_2O_3$ glass system was selected for the same reason as in the case of the silicate glass system. It was found that $30Bi_2O_3 \cdot 20BaO \cdot 50B_2O_3$ (BBB; mol%) glass is suitable for adjusting the thermal expansion coefficient to approximately $1 \times 10^{-5}$ /℃ in order to line the steel and for preventing crystallization during the glass lining process. To induce a large improvement effect on $\varepsilon_r$, Pr was also added to the BBB glass. Therefore $3Pr_6O_{11} \cdot 30Bi_2O_3 \cdot 20BaO \cdot 50B_2O_3$ (PBBB; mol%) glass was selected from the compositions of Pr added to BBB. **Table 1** shows the physical properties of PBBB glass. The relative dielectric constant of conventional glasses used as the glass lining for steel is estimated to be approximately 6 to 8. On the other hand, $\varepsilon_r$ of PBBB glass is 17. The firing temperature of PBBB glass is 570℃ which is 200℃ lower than that of conventional glasses. The lower firing temperature is advantageous for electrode applications due to reduced distortion.

### 2. 4 Voltage assignment and breakdown condition of multilayer

The glass lining layer consists of two layers called the ground coat layer G/C and the cover coat layer C/C. The function of the G/C is to maintain a good adhesion with the base metal, while C/C has properties which are suitable for the intended application. When the step voltage $V$ is applied at time=0, the change on standing of electric field, $E$, is expressed as follows,[9] where the values of thicknesses of G/C and C/C are $d_1$ and $d_2$, the respective electric fields are $E_1$ and $E_2$, the respective conductivities are $\sigma_1$ and $\sigma_2$, the respective relative dielectric constants are $\varepsilon_1$ and $\varepsilon_2$ and the external applied AC voltage is $V$.

| | |
|---|---|
| C/C | $d_1$, $E_1$, $\sigma_1$, $\varepsilon_1$ |
| G/C | $d_2$, $E_2$, $\sigma_2$, $\varepsilon_2$ |

$$E_1=\frac{\sigma_2}{\sigma_1 d_2+\sigma_2 d_1}V+\left(\frac{\varepsilon_2}{\varepsilon_1 d_2+\varepsilon_2 d_1}-\frac{\sigma_2}{\sigma_1 d_2+\sigma_2 d_1}\right)\times V\cdot exp\left(-\frac{t}{\tau}\right)$$

where, $\tau=(\varepsilon_1 d_2+\varepsilon_2 d_1)/(\sigma_1 d_2+\sigma_2 d_1)$.

The conductance of the glass used for the glass lining is very small, approximately $10^{-13}$ $Sm^{-1}$, therefore the strength of electric fields is decided by the capacity of each layer during a short period. When the high-frequency AC voltage is applied to the glass-lined layer, the electric field in each layer is shown as follows;

$$E_1=\frac{\varepsilon_2}{\varepsilon_1 d_2+\varepsilon_2 d_1}V,$$

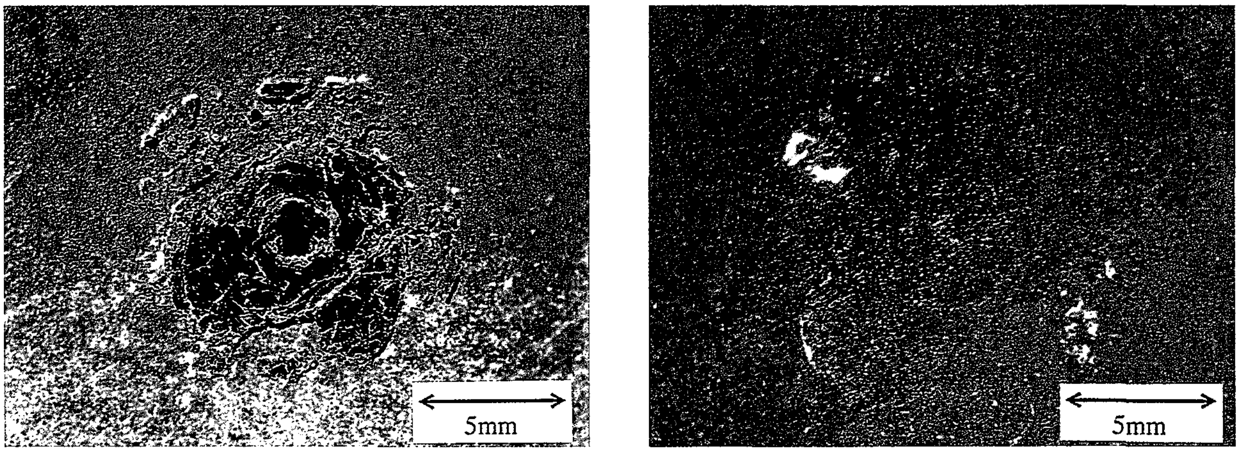
第 1 表 $3Pr_6O_{11}$・$30Bi_2O_3$・$20BaO$・$50B_2O_3$ガラスの物性

**Table 1** Physical Properties of $3Pr_6O_{11}\cdot30Bi_2O_3\cdot20BaO\cdot50B_2O_3$ glass

| Properties | Measured values |
|---|---|
| Relative dielectric constant (at 150kHz) | 17 |
| tan $\delta$ (at 150kHz) | $4\times10^{-3}$ |
| Breakdown voltage | 14 MV/m |
| Firing temperature | 570 ℃ |
| Thermal expansion (50～400℃) | $1.07\times10^{-5}$/℃ |
| Corrosion resistance | no deliquescence in atmosphere |

$$E_2=\frac{\varepsilon_1}{\varepsilon_1 d_2+\varepsilon_2 d_1}V.$$

Consequently, the ratio of G/C to C/C is $E_2:E_1=\varepsilon_1:\varepsilon_2$. When the breakdown voltages of G/C and C/C are approximately equal, it is possible that the layer which has the smaller $\varepsilon_r$ will be broken down. A multilayer which consists of the two layers corresponds to a series connection of condensers as the equivalent circuit. Therefore the electrostatic capacity of the multilayer is strongly affected by the layer which has the smaller $\varepsilon_r$. If $\varepsilon_r$ of only one layer is raised, the electrostatic capacity of the multilayer does not become high. When C/C with high $\varepsilon_r$ overlies G/C with low $\varepsilon_r$, $\varepsilon_r$ of the multilayer is not high. Furthermore, if G/C is broken down due to unequal voltage assignment, the high voltage will be applied only to C/C, breaking it down. Normally the thickness of G/C is 0.2 mm, while the thickness of C/C is 0.8 mm. If $\varepsilon_r$s of G/C and C/C are, respectively, 7 and 17, $\varepsilon_r$ of the multilayer is estimated to be approximately 13. If a high voltage $V_h$ is applied, the electric field of G/C is estimated to be 1.89 $V_h$ MV/m and the electric field of C/C to be 0.78 $V_h$ MV/m. If the values of breakdown voltage of G/C and C/C are almost equal at approximately 14 MV/m, it is necessary that the maximum applied voltage is below 7.4 kV (= 14/1.89) to prevent the breakdown of G/C. In the case of using G/C with low $\varepsilon_r$, it is necessary




A B

A : $3CoO \cdot 3NiO \cdot 3MnO_2 \cdot 3Pr_6O_{11} \cdot 30Bi_2O_3 \cdot 20BaO \cdot 50B_2O_3$ (mol% ; CNMPBBB) glass,
B : $3Pr_6O_{11} \cdot 30Bi_2O_3 \cdot 20BaO \cdot 50B_2O_3$ (mol% ; PBBB) glass.

第5図 密着テスト後のテストピース表面写真
**Fig. 5** Surface photographs after adhesion test.

that the applied voltage is set at a low level even if C/C with high $\varepsilon_r$ is used. From the viewpoint of the breakdown voltage of the glass-lined layer, it is desirable that C/C with high $\varepsilon_r$ is directly lined on the base metal without using a G/C with low $\varepsilon_r$, to achieve optimum improvement effects.

### 2. 5 Improvement of the adhesion between the glass and the base metal

Normally Co, Ni and Mn are added to the conventional G/C in order to increase the adhesion between the glass and the base metal,[10] because the adhesion is generally preferred to be very high. Therefore Co, Ni and Mn were added to PBBB glass to improve the adhesion, in the form of a compound with the composition of $3CoO \cdot 3NiO \cdot 3MnO_2 \cdot 3Pr_6O_{11} \cdot 30Bi_2O_3 \cdot 20BaO \cdot 50B_2O_3$ (mol%;CNMPBBB). The result of the adhesion test is shown in **Fig. 5.** It can be seen from the figure that a part of the CNMPBBB glass layer remained after pressing, while the PBBB glass layer was completely removed after pressing. Moreover, the properties of the CNMPBBB glass system given in **Table 2** show that $\varepsilon_r$ of CNMPBBB glass is 16 which is lower than $\varepsilon_r$ of PBBB glass due to the addition of Co, Ni and Mn. In conclusion, from the viewpoint of $\varepsilon_r$ and adhesion, CNMPBBB glass is highly promising for use in glass-lined discharge electrodes.

**第2表** $3C_0o \cdot 3NiO \cdot 3MnO_2 \cdot 3Pr_6O_{11} \cdot 30Bi_2O_3 \cdot 20BaO \cdot 50B_2O_3$ガラスの物性
**Table 2** Physical Properties of $3C_0o \cdot 3NiO \cdot 3MnO_2 \cdot 3Pr_6O_{11} \cdot 30Bi_2O_3 \cdot 20BaO \cdot 50B_2O_3$ glass

| Properties | Measured values |
|---|---|
| Relative dielectric constant (at 150kHz) | 16 |
| tan $\delta$ (at 150kHz) | $4 \times 10^{-3}$ |
| Breakdown voltage | 14 MV/m |
| Firing temperature | 570 ℃ |
| Thermal expansion (50～400℃) | $1.05 \times 10^{-5}$/℃ |
| Corrosion resistance | no deliquescence in atmosphere |

### Conclusion

The results of this study are summarized as follows.

(1) The effect of various elements on the relative dielectric constant ($\varepsilon_r$) was investigated by adding 1-3 mol% of an element to soda glass. It was found that most rare-earth

elements (Pr, Lu, Eu, Gd, Sm) are more effective in increasing $\varepsilon_r$ than other elements.

(2) From the viewpoint of the breakdown voltage of the glass-lined layer, it is desirable that a cover coat with high $\varepsilon_r$ is directly lined on the base metal without using a ground coat with low $\varepsilon_r$, in order to obtain the optimum improvement effects.

(3) $3CoO \cdot 3NiO \cdot 3MnO_2 \cdot 3Pr_6O_{11} \cdot 30Bi_2O_3 \cdot 20BaO \cdot 50B_2O_3$ (mol%; CNMPBBB) glass has a high $\varepsilon_r$ of 16 and good adhesion with steel. CNMPBBB glass is highly promising for use in glass-lined discharge electrodes.

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