

# Dielectric properties of low-firing $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3\text{-Bi}_2\text{O}_3/\text{Li}_2\text{O}$ ceramics

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Dielectric properties of low-firing  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3\text{-Bi}_2\text{O}_3/\text{Li}_2\text{O}$  ceramics are studied in this work. With the addition of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  eutectic composition, the sintering temperature of  $\text{PMN}_{1-x}\text{PT}_x$  could be lowered to  $900^\circ\text{C}$ . Relaxor behaviour of  $\text{PMN}_{1-x}\text{PT}_x$  is enhanced by the incorporation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  due to the substitution of  $\text{Bi}^{+3}/\text{Li}^+$  into the  $\text{PMN}_{1-x}\text{PT}_x$  framework.  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  eutectic composition is used as a fluxing agent, Curie shifter and depressor. Evaporation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  and  $\text{PbO}$  during firing is checked and examined via energy dispersive spectrometry (EDS) and X-ray diffraction (XRD) is used to clarify the Curie shifting and depressing effect of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ .

## 1. Introduction

It is well known that lead magnesium niobate-based ceramics [1] are promising dielectric materials for capacitors due to their high dielectric constant, small grain size, broad dielectric maximum and high insulation resistivity. Besides, PMN-based relaxors have also been proven to be promising materials for electrostrictive transducers with excellent positional reproducibility and low ageing rate but a lower electrostrictive coefficient than that of PZT [2-4]. To obtain a large electrostrictive strain, a modified plate-through type multilayered actuator has been developed.

The problems encountered in the preparation of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$  (abbreviated to  $\text{PMN}_{1-x}\text{PT}_x$ ) are the appearance of a pyrochlore phase and the poor reproducibility in consequence [5]. Control of the  $\text{PbO}$  atmosphere is also critical to prevent the formation of pyrochlore phase [6] and preserve the stoichiometry of the desired solid solution, since the sintering temperatures of  $\text{PMN}_{1-x}\text{PT}_x$  are as high as 1200 to  $1300^\circ\text{C}$  [7]. In order to eliminate the appearance of pyrochlore phase and lower the sintering temperature of  $\text{PMN}_{1-x}\text{PT}_x$  to prevent  $\text{PbO}$  evaporation and to make it possible to use a high silver-content conductor as the internal electrode of multilayered actuator or multilayer ceramic capacitor, a new processing technique instead of conventional oxide-mixing method was developed.

In the work of Swartz and Shrout [5] the "novel" fabrication technique accompanied with the addition of excess  $\text{MgO}$  was first proposed in preparing pure perovskite  $\text{PMN}_{1-x}\text{PT}_x$ . Lejune and Boilot [6] used a conventional oxide-mixing process with the addition of lead oxide to prepare pyrochlore-free  $\text{PMN}_{1-x}\text{PT}_x$ , using lead oxide as a liquid fluxing agent.  $\text{PMN}_{1-x}\text{PT}_x$  prepared by this method could be sintered at 900 to  $1000^\circ\text{C}$ .

The purpose of this work is to lower the sintering temperature of  $\text{PMN}_{1-x}\text{PT}_x$  ( $0 \leq x \leq 0.2$ ) with the

addition of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ , where  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  with a melting point of about  $700^\circ\text{C}$  is the eutectic composition of  $\text{Bi}_2\text{O}_3$  and  $\text{Li}_2\text{O}$ . A similar method to the so-called "novel" fabrication technique accompanied with the addition of 0.2 wt %  $\text{MgO}$  was used to prepare pyrochlore free  $\text{PMN}_{1-x}\text{PT}_x$  [7].

## 2. Experimental procedure

### 2.1. Preparation of $\text{PMN}_{1-x}\text{PT}_x\text{-Bi}_2\text{O}_3/\text{Li}_2\text{O}$

The raw materials used in this work were all reagent-grade oxides such as  $\text{PbO}$ ,  $\text{MgO}$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{TiO}_2$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Li}_2\text{O}$ .  $\text{MgNb}_2\text{O}_6$  columbite was first prepared by calcining the mixture of  $\text{MgO}$  and  $\text{Nb}_2\text{O}_5$  at  $1000^\circ\text{C}$  for 4 h.  $\text{PbO}$ ,  $\text{MgNb}_2\text{O}_6$ ,  $\text{TiO}_2$  and excess 0.2 wt %  $\text{MgO}$  were weighed in appropriate proportionality and then ball-milled together in acetone for 8 h. Subsequent calcination of  $\text{PMN}_{1-x}\text{PT}_x$  with  $0 \leq x \leq 0.2$  were all carried out at  $800^\circ\text{C}$  for 4 h.

The fluxing agent,  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ , was obtained by first mixing  $\text{Bi}_2\text{O}_3$  and  $\text{Li}_2\text{O}$  in a molar ratio of 89:11 and then the dried slurry was calcined at  $620^\circ\text{C}$  for 2 h. After pulverizing the calcined  $\text{PMN}_{1-x}\text{PT}_x$  and  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ , respectively, 2 to 10 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  and  $\text{PMN}_{1-x}\text{PT}_x$  were ball-milled together in acetone for 8 h. The dried powders were then mixed with 5 wt % distilled water and pressed in a steel die 1.27 cm in diameter. Six stacked disks were fired in a covered alumina crucible. The soaking time of all the firing processes in this work was fixed at 2 h.

### 2.2. Examination of evaporated low melting-point phases

To check if the added  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  or other low melting point phases might evaporate during sintering, an alumina (96%  $\text{Al}_2\text{O}_3$ ) substrate was covered above the pressed ceramic powder and used as a collector for the evaporated phases during firing, as shown in Fig. 1. The composition of the ceramic sample was  $\text{PMN}_{0.85}\text{PT}_{0.15}$  added with 4 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . Low

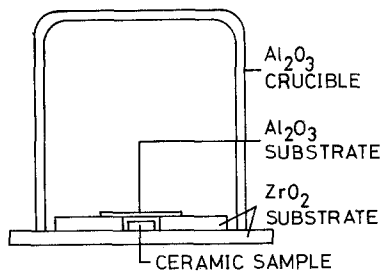


Figure 1 Arrangement for the collection of the evaporated phase from  $\text{PMN}_{0.85}\text{PT}_{0.15}$  with 4 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  added.

melting phases were then evaporated under the stress of  $850^\circ\text{C}$  for 2 h. The evaporated film on the  $\text{Al}_2\text{O}_3$  substrate was analysed qualitatively with the help of the energy dispersive spectrometer (EDS) and X-ray diffraction (XRD) method.

### 2.3. Measurement of dielectric properties

Dielectric properties were measured from the 1 mm-thick disk-type specimens with silver electrodes fired on both sides. The dielectric constant and loss tangent were obtained from an HP4192A LF impedance analyser at 1 KHz with 1 V r.m.s. Insulation resistance was measured with a TOA SM-5E super megohm meter 2 min after applying 1000 V d.c.

## 3. Results and discussion

### 3.1. Dielectric properties of $\text{PMN}_{1-x}\text{PT}_x$ with $0.1 \leq x \leq 0.2$

Figure 2 shows the temperature dependence of dielectric constant and loss tangent of  $1270^\circ\text{C}$ -fired  $\text{PMN}_{1-x}\text{PT}_x$  with  $0.1 \leq x \leq 0.2$ . The apparent Curie temperature of  $\text{PMN}_{1-x}\text{PT}_x$  for  $x = 0.1, 0.15$  and  $0.2$  are  $40, 69$  and  $98^\circ\text{C}$ , respectively. From the decrease of the loss tangent maximum with the molar ratio  $x$ , it is believed that the degree of order of cation ions increased with the content of  $\text{PbTiO}_3$ . Composition of  $\text{PMN}_{1-x}\text{PT}_x$  with  $x$  less than  $0.1$  is suitable for capacitor use, because of its lower Curie temperature, broader dielectric maximum region and lower electro-

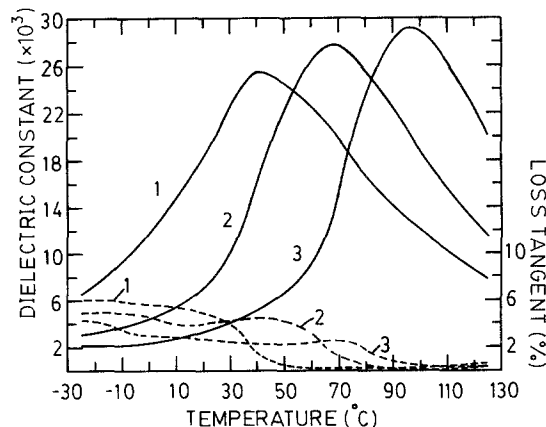


Figure 2 Temperature dependence of dielectric constant (—) and loss tangent (---) of  $1270^\circ\text{C}$ -fired  $\text{PMN}_{1-x}\text{PT}_x$ . (1)  $x = 0.1$ ; (2)  $x = 0.15$ ; (3)  $x = 0.2$ .

strictive coefficient. Composition of  $\text{PMN}_{0.9}\text{PT}_{0.1}$  with Curie region centred around room temperature exhibited superior electrostrictive properties to that of  $\text{PMN}_{1-x}\text{PT}_x$  with  $x$  larger than  $0.1$  in positional reproducibility, since the phase of  $\text{PMN}_{1-x}\text{PT}_x$  with  $x$  larger than  $0.1$  at room temperature was dominated by ferroelectric phase [2–4]. This would induce inverse hysteresis, which is inadequate for electrostrictive use. But from the power consumption point of view [8],  $\text{PMN}_{1-x}\text{PT}_x$  with a small  $x$  value, was not suitable for the actuator material application because of its high dielectric constant. For the purpose of electrostrictive use, some compromise between the above arguments have to be made and the composition with lower dielectric constant and broad dielectric maximum centred around room temperature is desired if positional reproducibility and power consumption are both taken into consideration.

In our previous work,  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  was used as a fluxing agent, depressor and Curie shifter [9]. To make the resultant  $\text{PMN}_{1-x}\text{PT}_x$  a promising dielectric and electrostrictive material with the incorporation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  flux agent,  $\text{PMN}_{1-x}\text{PT}_x$  with  $x$  less than

TABLE I Effect of firing temperatures and  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  content on the properties of  $\text{PMN}_{0.85}\text{PT}_{0.15}$

|  | $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ (wt %) |                         |                         |                         |                         |                         |                         |                         |                         |
|--|--|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
|  | 4  |                         |                         | 6                       |                         |                         | 8                       |                         |                         |
|  | Firing temperature ( $^\circ\text{C}$ )            |                         |                         |                         |                         |                         |                         |                         |                         |
|  | 900  | 925                     | 975                     | 900                     | 925                     | 975                     | 900                     | 925                     | 975                     |
| Density ( $\text{g cm}^{-3}$ )                                       | 7.48   | 7.49                    | 7.28                    | 7.63                    | 7.32                    | 7.18                    | 7.62                    | 7.37                    | 7.2                     |
| Dielectric constant  | 7643   | 8333                    | 10721                   | 5113                    | 7546                    | 8063                    | 4764                    | 6122                    | 7064                    |
| Loss tangent (%)   | 2.2  | 2.2                     | 2.68                    | 1.69                    | 1.0                     | 0.99                    | 1.17                    | 0.81                    | 0.68                    |
| Curie temperature ( $^\circ\text{C}$ )                               | 33   | 31                      | 24                      | 26                      | 11                      | 13                      | 20                      | 8                       | 7                       |
| Variation of capacitance (%) (at $-30, 85$ and $125^\circ\text{C}$ ) | -46.4<br>-18.6<br>-42.6                            | -45.3<br>-23.8<br>-44.7 | -48.9<br>-29.9<br>-52.5 | -38.1<br>-15.7<br>-32.9 | -36.3<br>-25.0<br>-44.9 | -41.2<br>-29.9<br>-49.1 | -33.3<br>-16.7<br>-34.4 | -28.5<br>-22.1<br>-40.1 | -34.6<br>-27.5<br>-44.4 |
| Insulation resistivity ( $\times 10^{12} \Omega \text{cm}$ )         | 0.20   | 2.33                    | 1.41                    | 0.026                   | 2.60                    | 2.05                    | 0.032                   | 2.85                    | 1.16                    |

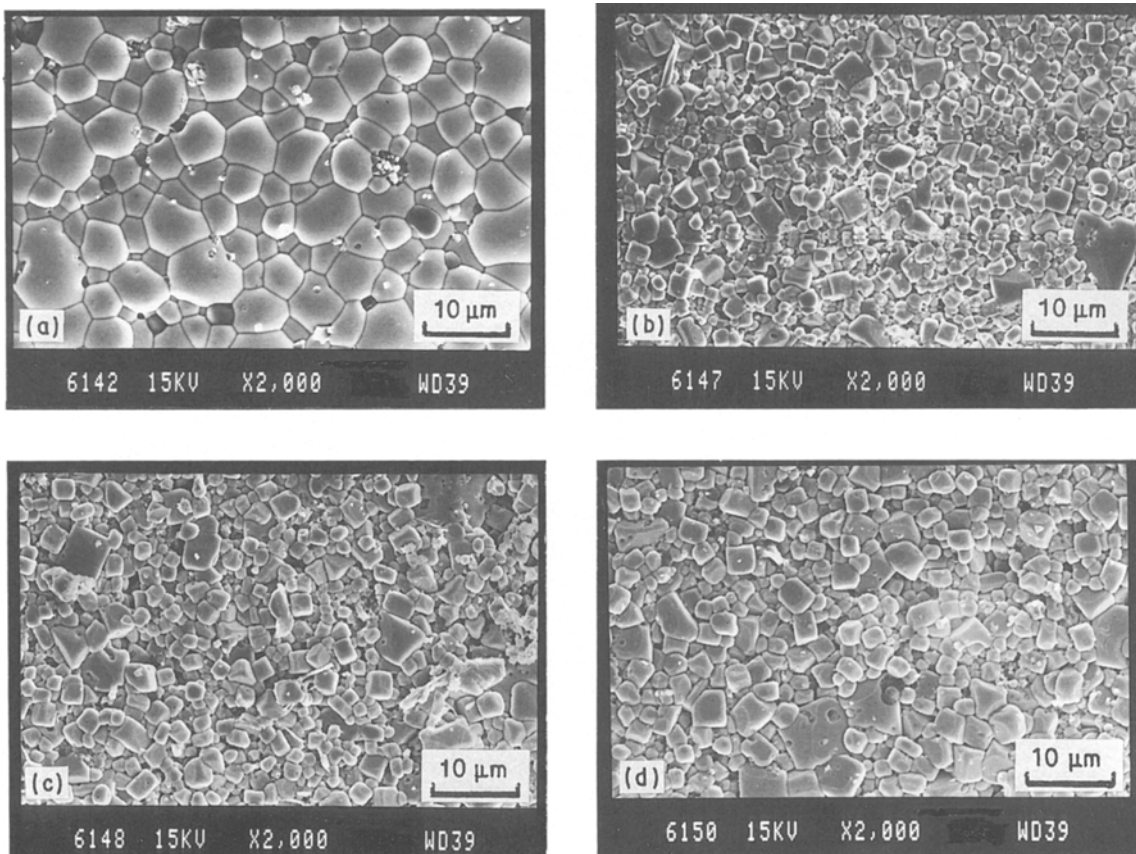


Figure 3 Free surface observation of (a)  $\text{PMN}_{0.85}\text{PT}_{0.15}$ , (b)  $\text{PMN}_{0.85}\text{PT}_{0.15}$  with the addition of 2 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ , (c) 4 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  and (d) 8 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ .

0.2 was selected as the candidate compositions based on the above mentioned compromise, since the Curie temperature of  $\text{PMN}_{1-x}\text{PT}_x$  with  $x$  less than 0.2 could be restricted in the range of  $-30$  to  $50^\circ\text{C}$  (to be seen in the following).

### 3.2. Typical dielectric properties of $\text{PMN}_{0.85}\text{PT}_{0.15}-\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$

Table I lists the typical properties of  $\text{PMN}_{0.85}\text{PT}_{0.15}$  incorporated with different amounts of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . Correlations between sintering temperature and the measured properties are also summarized in Table I. As can be seen in Table I,  $0.85\text{PMN}-0.15\text{PT}$  can be

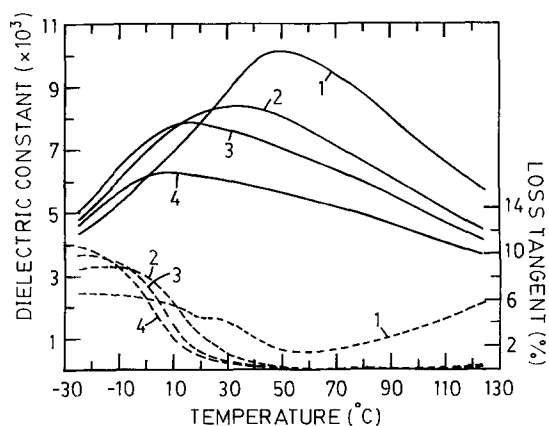


Figure 4 Temperature dependence of (—) dielectric constant and (---) loss tangent of  $925^\circ\text{C}$ -fired  $\text{PMN}_{0.85}\text{PT}_{0.15}$  with different amounts of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  added. (1) 2 wt %; (2) 4 wt %; (3) 6 wt %; (4) 8 wt %.

fired at  $900^\circ\text{C}$  with the addition of 4 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . The density obtained in this case was  $7.48\text{ g cm}^{-3}$ , while the theoretical density of  $0.85\text{PMN}-0.15\text{PT}$  is  $8.08\text{ g cm}^{-3}$ .

The composition of  $\text{PMN}_{0.85}\text{PT}_{0.15}-\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  covers the desired Curie ranges for both dielectric and electrostrictive uses. The composition of  $\text{PMN}_{0.8}\text{PT}_{0.2}$  incorporated with  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  is only suitable for electrostrictive use because its Curie temperature is about  $40^\circ\text{C}$ .

### 3.3. Fluxing agent of $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$

The scanning electron micrograph (SEM) of  $\text{PMN}_{0.85}\text{PT}_{0.15}$  with different amounts of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  added are shown in Fig. 3, where the sintering temperature of pure  $\text{PMN}_{0.85}\text{PT}_{0.15}$  and  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  added  $\text{PMN}_{0.85}\text{PT}_{0.15}$  are  $1270^\circ\text{C}$  and  $925^\circ\text{C}$ , respectively. With higher  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  content, a denser microstructure with a larger grain size are observed. From the density measurements of Table I and SEM examination of Fig. 3, the fluxing effect of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  is obvious.

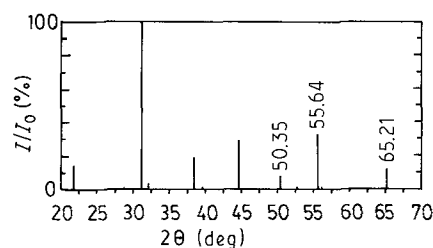


Figure 5 X-ray diffraction pattern of  $1270^\circ\text{C}$  fired  $\text{PMN}_{0.85}\text{PT}_{0.15}$ .

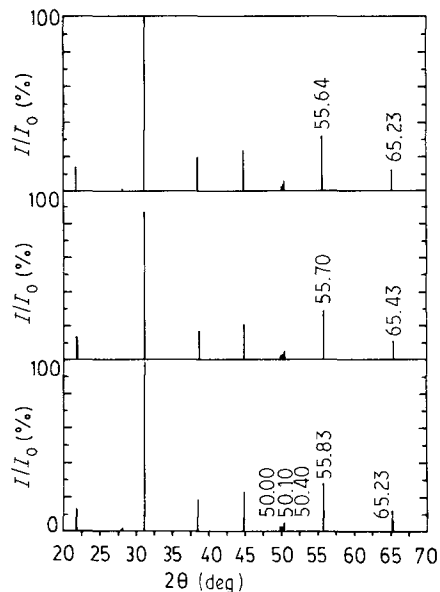


Figure 6 X-ray diffraction pattern of 925°C fired  $\text{PMN}_{0.85}\text{PT}_{0.15}$  with different amounts of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  added.

### 3.4. Depressing and broadening effect of $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$

Figure 4 shows the temperature dependence of the dielectric constant and loss tangent of  $\text{PMN}_{0.85}\text{PT}_{0.15}$  with different amounts of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ , where the sintering temperature is 925°C. As can be seen in Fig. 4, 2 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  is not sufficient to lower the sintering temperature to 925°C, justified from its poor loss tangent against temperature characteristics. The maximum dielectric constant of  $\text{PMN}_{0.85}\text{PT}_{0.15}$  is depressed from 27600 to 10137, 8442, 7620 and 6280 with the addition of 2, 4, 6 and 8 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ , respectively. The depressing effect of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  may be ascribed to the modification of bulk composition or the segregation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  along the grain boundary (to be discussed in the following).

The X-ray diffraction pattern of 1270°C fired  $\text{PMN}_{0.85}\text{PT}_{0.15}$  and that of  $\text{PMN}_{0.85}\text{PT}_{0.15}$  added with different amounts of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  are shown in Figs 5 and 6, respectively. By comparing the results of Figs 5 and 6, changes of both the bulk composition and the phase of  $\text{PMN}_{0.85}\text{PT}_{0.15}$  by the substitution of  $\text{Bi}^{3+}/\text{Li}^+$  can be understood from the split of the diffraction peak of  $\text{PMN}_{0.85}\text{PT}_{0.15}$  at 50.35° into 50, 50.1 and 50.4° after incorporation of 8 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  into  $\text{PMN}_{0.85}\text{PT}_{0.15}$ . The shift of the diffraction peak can be visualized as the shift of d-space and thus the change of the lattice constant of  $\text{PMN}_{0.85}\text{PT}_{0.15}$  due to the modification of  $\text{PMN}_{0.85}\text{PT}_{0.15}$  by  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ .

Figure 7 shows the X-ray diffraction pattern of

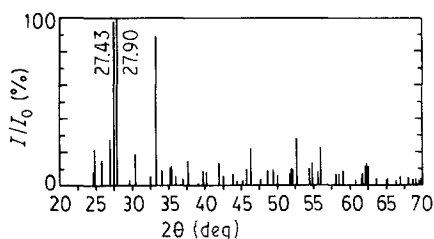


Figure 7 X-ray diffraction pattern of eutectic  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ .

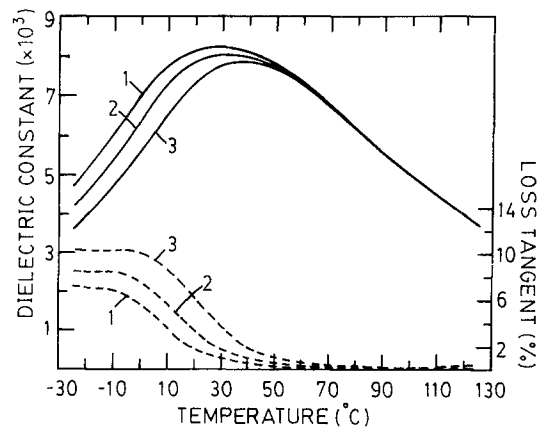


Figure 8 Relaxor behaviour of 900°C-fired  $\text{PMN}_{0.9}\text{PT}_{0.1}$  with 2 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  added. (1) 1 kHz; (2) 10 kHz; (3) 100 kHz. (—) Dielectric constants; (---) loss tangents.

680°C calcined  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . The X-ray diffraction pattern of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  is similar to that of  $\text{Bi}_2\text{O}_3$  except the relative intensity of diffraction peaks, i.e. the eutectic composition of  $\text{Bi}_2\text{O}_3$  and  $\text{Li}_2\text{O}$  is formed by the substitution of  $\text{Li}_2\text{O}$  into the matrix of  $\text{Bi}_2\text{O}_3$ . The first two maximum diffraction peaks of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  were 27.4 and 27.9°, respectively. By checking the result of Fig. 6, there are no such diffraction peaks if the content of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  in  $\text{PMN}_{0.85}\text{PT}_{0.15}$  is less than 8 wt %. But for 8 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  added  $\text{PMN}_{0.85}\text{PT}_{0.15}$ , there are two diffraction peaks at 27.8 and 28°, similar to that of the  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  phase. This result suggests that excess  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  may segregate along the grain boundary.

One interesting thing observed in Fig. 4 is that  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  shows a significant effect on the degree of order of the cations arrangement. As shown in Fig. 4, the peak value of loss tangent and the Curie region are increased and broadened, respectively, with increasing  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  content, i.e. the relaxing characteristics of  $\text{PMN}_{1-x}\text{PT}_x$ , and the diffuse phase transition is enhanced with the incorporation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . The enhancement of the diffuse phase transition could be explained as the substitution of  $\text{Bi}^{3+}/\text{Li}^+$  into  $\text{PMN}_{1-x}\text{PT}_x$ . The relaxor behaviour of 2 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ -added  $\text{PMN}_{0.9}\text{PT}_{0.1}$  is illustrated in Fig. 8.

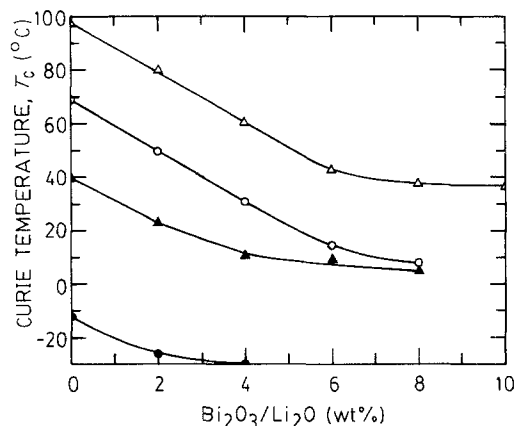


Figure 9 Effect of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  contents on the shifting of Curie temperature of  $\text{PMN}_{1-x}\text{PT}_x$ . (●)  $x = 0$ ; (▲)  $x = 0.1$ ; (○)  $x = 0.15$ ; (Δ)  $x = 0.2$ .

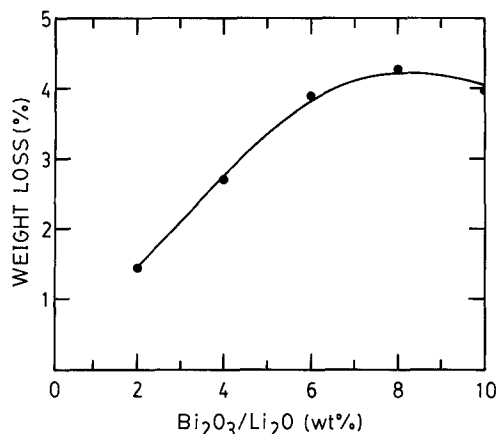


Figure 10 Weight losses of 925°C-fired  $\text{PMN}_{0.8}\text{PT}_{0.2}$  with different amounts of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  added.

### 3.5. Curie shifting effect of $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$

As can be seen in Fig. 4, the Curie temperature of  $\text{PMN}_{1-x}\text{PT}_x$  is shifted from 69°C to 48, 33, 11 and 8°C with the addition of 2, 4, 6 and 8 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ , respectively. It is evidenced that  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  could be used as Curie shifter of  $\text{PMN}_{1-x}\text{PT}_x$ . The effect of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  on the shifting of the Curie temperature of  $\text{PMN}_{1-x}\text{PT}_x$  is shown in Fig. 9, where the sintering temperature was 925°C. Curie temperature of  $\text{PMN}_{1-x}\text{PT}_x$  is first decreased almost linearly with the content of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  and then approaches to a stable value with further increments of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . For  $\text{PMN}_{0.8}\text{PT}_{0.2}$  added with 8 and 10 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ , the Curie temperatures are 38°C and 37°C, respectively, i.e. the dissolving of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  into the  $\text{PMN}_{1-x}\text{PT}_x$  grains would not be increased with further increments of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . Excess  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  may segregate along the grain boundary or evaporate due to its low melting point of about 700°C.

Figure 10 shows the weight loss of 925°C-fired  $\text{PMN}_{0.8}\text{PT}_{0.2}$  incorporated with different  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  contents. The trend of weight loss with  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  content is similar to that of Curie temperature. Weight losses are first increased almost linearly and then

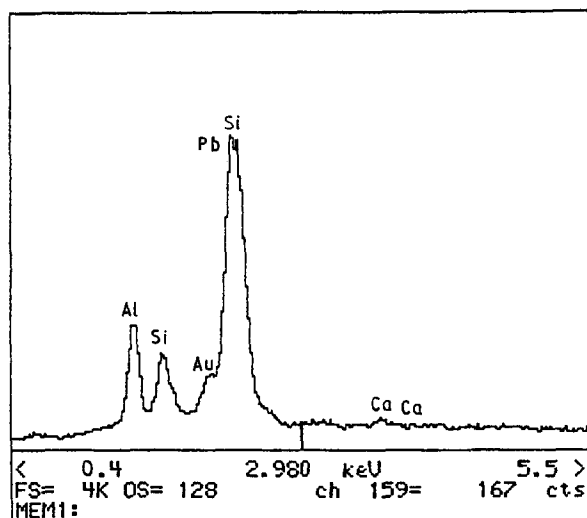


Figure 11 Energy dispersive spectrum of collected phases from the evaporation of 850°C-fired  $\text{PMN}_{0.85}\text{PT}_{0.15}$  with 4 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  added.

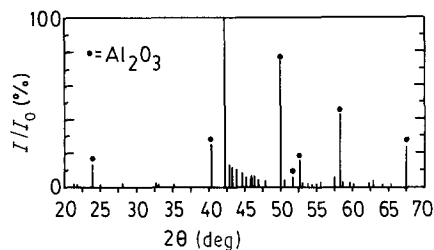


Figure 12 X-ray diffraction pattern of the evaporated film on  $\text{Al}_2\text{O}_3$  substrate.

increased slowly with further increments of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . The insignificant variations of both weight loss and Curie temperature imply that excess  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  is segregated along the grain boundary. In Fig. 10, the weight loss of 8 wt % added  $\text{PMN}_{0.8}\text{PT}_{0.2}$  is about 4.3 wt % i.e. there is at most 3.7 wt % in  $\text{PMN}_{0.8}\text{PT}_{0.2}$ . From this, the solubility of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  in  $\text{PMN}_{0.8}\text{PT}_{0.2}$  could be estimated to be not more than 3.7 wt % at the sintering temperature of 925°C.

### 3.6. Identification of evaporated low melting-point phases

The energy dispersive spectrum (EDS) of the evaporated film on the  $\text{Al}_2\text{O}_3$  substrate is shown in Fig. 11. The elements in the evaporated film on  $\text{Al}_2\text{O}_3$  substrate are identified as Al, Si, Ca, Au, Pb and Bi. Al, Si and Ca came from the 96%  $\text{Al}_2\text{O}_3$  substrate. Au is the evaporated gold film on the specimen surface for SEM observation. Pb and Bi originate from the phase of  $\text{PbO}$  and  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ , respectively. This confirms the possibility of evaporation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  during firing. Both the X-ray diffraction pattern and scanning electron micrograph of the evaporated film are shown in Figs 12 and 13, respectively. In addition to the diffraction peaks of  $\text{Al}_2\text{O}_3$ , another residual unknown single-crystal-like diffraction peak is neither that of  $\text{PbO}$  nor  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . According to the result of Fig. 11, this unknown phase is believed to be a solid solution of  $\text{PbO}$  and  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . However, whether this solid solution is formed before being evaporated on to alumina surface or after is not clarified in this work.

### 3.7. Variation of capacitance with temperature

Figure 14 shows the temperature dependencies of capacitance variations for  $\text{PMN}_{0.85}\text{PT}_{0.15}$  incorporated with different amounts of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ , where the sintering temperature is 925°C. As can be seen in Fig. 14, capacitance variations are restricted within the range of 2.6 to 40% from -25 to 125°C with the addition of 8 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . This composition could be used as dielectrics for capacitor with stable temperature characteristics. An electrostrictive material with stable temperature characteristics, low power consumption and excellent positional reproducibility could be achieved with the aid of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . For low content  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ -added  $\text{PMN}_{1-x}\text{PT}_x$ , the broadening of the capacitance temperature characteristics may be attributed to the change of bulk composition by the substitution of  $\text{Bi}^{3+}/\text{Li}^+$  into  $\text{PMN}_{1-x}\text{PT}_x$ . For higher

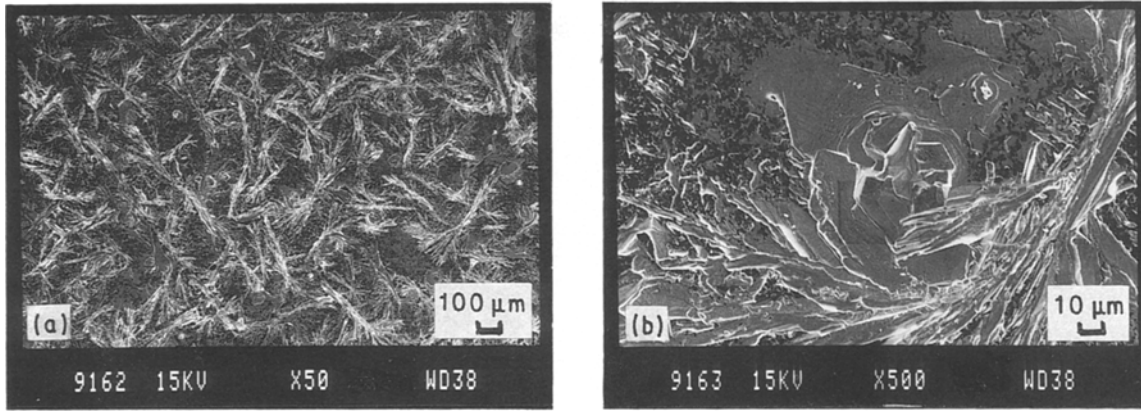


Figure 13 Scanning electron micrograph of the evaporated film on  $\text{Al}_2\text{O}_3$  substrate with magnification of (a)  $\times 50$  and (b)  $\times 500$ .

content  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ -added  $\text{PMN}_{1-x}\text{PT}_x$ , the broadening of capacitance against temperature characteristics might result from the segregation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ .

### 3.8. Effect of sintering temperature on the dielectric properties of $\text{PMN}_{1-x}\text{PT}_x$ - $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$

Figure 15 shows the temperature dependence of dielectric constant and loss tangent of 4 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ -added  $\text{PMN}_{0.85}\text{PT}_{0.15}$  fired at different temperatures. With increasing sintering temperature, more  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  may dissolve into the  $\text{PMN}_{1-x}\text{PT}_x$  grain. Curie temperature is thus decreased with firing temperature. The change of Curie temperature and weight loss of 8 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ -added  $\text{PMN}_{0.8}\text{PT}_{0.2}$  against firing temperature are delineated in Fig. 16.

Weight loss increased with firing temperature, but Curie temperature does not change significantly with firing temperature. This confirms the fact that dissolving of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  into the  $\text{PMN}_{1-x}\text{PT}_x$  grain is compensated by the evaporation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . Under higher firing temperature such as  $1000^\circ\text{C}$ , dissolving of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  into the  $\text{PMN}_{1-x}\text{PT}_x$  grain become insignificant. Consequently, Curie temperature is shifted back to higher temperature at  $1000^\circ\text{C}$ .

Figure 17 shows the temperature dependence of the capacitance variations of 4 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ -added

$\text{PMN}_{0.85}\text{PT}_{0.15}$  fired at different temperatures. The higher the firing temperature, the greater the evaporation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . As a result, possible segregation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  could not take place at a higher firing temperature. There is an abrupt capacitance change of about 10% at  $125^\circ\text{C}$  due to the lack of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  along the grain boundary when the firing temperature increased up to  $975^\circ\text{C}$ .

### 4. Conclusion

The sintering temperature of  $\text{PMN}_{1-x}\text{PT}_x$  could be lowered to  $900^\circ\text{C}$  via liquid phase sintering by adding the eutectic  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ . In addition to the fluxing effect of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ ,  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  also could be visualized as a depressor and a Curie shifter. By comparing the relationships of weight loss against  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  content and Curie temperature against  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  content, the depressing effect under low  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  content is ascribed to the substitution of  $\text{Bi}^{3+}/\text{Li}^+$  into the bulk grain, which is the same reason as for the shifting of the Curie temperature. The depressing effect under higher  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  content may be correlated to the segregation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  along the grain boundary. The shift of the Curie temperature back to a higher temperature is relevant to the evaporation of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ .

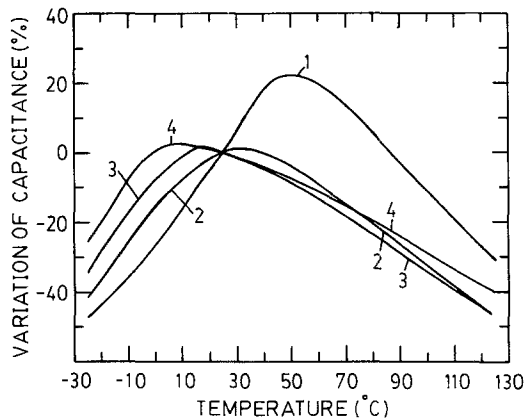


Figure 14 Temperature dependence of the capacitance variation for  $\text{PMN}_{0.85}\text{PT}_{0.15}$  with different amounts of  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  added. (1) 2 wt %; (2) 4 wt %; (3) 6 wt %; (4) 8 wt %.

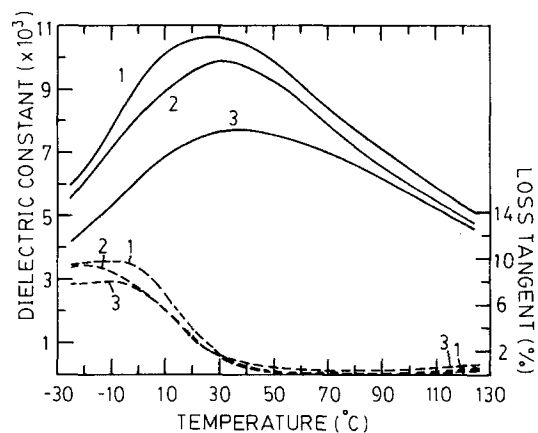


Figure 15 Temperature dependence of dielectric constant and loss tangent of 4 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ -added  $\text{PMN}_{0.85}\text{PT}_{0.15}$  fired at different temperature. (1)  $975^\circ\text{C}$ ; (2)  $950^\circ\text{C}$ ; (3)  $900^\circ\text{C}$ . (—) Dielectric constants; (---) loss tangents.

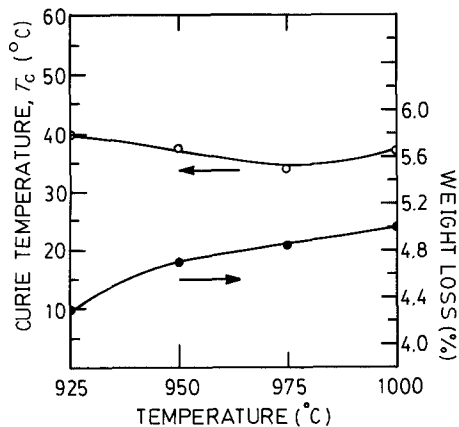


Figure 16 Firing temperature dependence of Curie temperature and weight loss of 8 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ -added  $\text{PMN}_{0.8}\text{PT}_{0.2}$ .

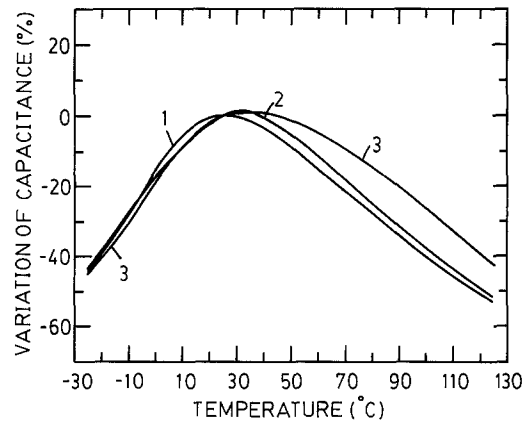


Figure 17 Temperature dependence of the capacitance variation of 4 wt %  $\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$ -added  $\text{PMN}_{0.85}\text{PT}_{0.15}$  fired at different temperature. (1) 975°C; (2) 950°C; (3) 900°C.

Resultant composition would be suitable for the dielectric uses with stable temperature characteristics and high resistivity.  $\text{PMN}_{1-x}\text{PT}_x-\text{Bi}_2\text{O}_3/\text{Li}_2\text{O}$  may also be used as electrostrictive material with stable temperature characteristics, low power consumption and excellent positional reproducibility.

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