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# The reaction sequence and dielectric properties of $BaSm_2Ti_4O_{12}$ ceramics

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**Abstract**

To establish the correct reaction sequence of BaO–$Sm_2O_3$–4$TiO_2$, phases present in different calcining temperatures are identified by X-ray diffraction patterns. When different calcining temperatures are used, the source phase BaO ($BaCO_3$) consumes below 850°C, the source phases $TiO_2$ and $Sm_2O_3$ consume at 1000 and 1150°C; the intermediate phases $BaTiO_3$, $BaTi_4O_9$, and $Sm_2Ti_2O_7$ consume at 1050, 1200, and 1250°C, respectively. The $BaSm_2Ti_4O_{12}$ phase starts to reveal at the 1100°C-calcined powder. The integrating intensity of $BaSm_2Ti_4O_{12}$ phase increases with the raising of calcining temperatures, accompanying with the decrease of integrating intensities of the source and intermediate phases. As the sintering temperature increases, the densities, quality values, and dielectric constants of $BaSm_2Ti_4O_{12}$ ceramics increase and saturate at 1325ºC. The $BaSm_2Ti_4O_{12}$ ceramics sintered at 1325°C have the properties of $Q^*f = 5180$, $\varepsilon_r = 81.8$, and $\tau_f = -19.2$ ppm/°C. © 2000 Elsevier Science Limited and Techna S.r.l. All rights reserved.

*Keywords:* C: Dielectric properties; $BaSm_2Ti_4O_{12}$ ceramics; Reactions

## 1. Introduction

Microwave dielectric ceramics with a high dielectric constant are needed to satisfy very high technical demands. They should possess extremely low loss to achieve high quality factor ($Q$), a small temperature coefficient of resonant frequency ($\tau_f$), and a dielectric constant higher than 80. The dielectric constant of rutile $TiO_2$ was high, about 104, but it has a $\tau_f$ value of $\sim +427$ ppm/°C. Because of the high $\tau_f$ values the $TiO_2$ was not suitable for real application. Many ceramic dielectrics developed so far for microwave application were composed of mixed phases consisting of $TiO_2$-based compounds in multicompoent systems. $(Zr,Sn)TiO_4$ [1], $Ba(Zn,Mg)_{1/3}Ta_{2/3}O_3$ components [2], and a series of complex perovskite families of $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ [3], satisfied the above requirements. High permittivity microwave ceramics were also obtained in the solid solution series $Ba_{6-x}Re_{8+2/3x}$ $Ti_{18}O_{54}$ [4,5], where the $x$ value depended on the lanthanide (Re). In the BaO–$Re_2O_3$–$n$$TiO_2$ system the ceramics composition was the most important parameter in tailoring of its microwave properties. The BaO–$Re_2O_3$–4$TiO_2$ ceramics (Re = Sm, Nd, and Gd) were developed based on $Ba_{6-x}Re_{8+2/3x}$ $Ti_{18}O_{54}$ ternary compound known as microwave resonator material corresponds exactly to $x = 0.5$ [6].

In the ternary BaO–$Sm_2O_3$–$n$$TiO_2$, the occurrence of six ternary compounds had been reported. The BaO–$Sm_2O_3$–4$TiO_2$ was a promising dielectric in microwave regions, there remains some uncertainty concerning the occurrence of a ternary compound with higher $TiO_2$ content in this system, i.e., 1:1:4 or 1:1:5 [6,7], and the later could be supposed from the experimental results obtained in the identical BaO–$Sm_2O_3$–$n$$TiO_2$ system. The coprecipitation method is one of the most popular and convenient procedures to prepare homogeneous powders. In order to minimize the compositional deviation from stoichiometry, the coprecipitation method that we had established in the studies of the BaO–$Sm_2O_3$–4$TiO_2$ system. Unfortunately, very few studies had been conducted on the powder preparation and controlled fabrication of the mixed phase dielectrics in such complicated BaO–$Sm_2O_3$–4$TiO_2$ systems. In the BaO–$Re_2O_3$–4$TiO_2$ system only Takahashi et al. developed the reaction sequence [8]. In this study, the reaction sequence of BaO–$Sm_2O_3$–4$TiO_2$ composition was developed. The sintering characteristics and the microwave

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dielectric properties of BaO–$Sm_2O_3$–4$TiO_2$ systems were also developed in this study.

## 2. Experimental procedures

Samples were prepared from reagent-grade $BaCO_3$, $Sm_2O_3$ (cubic), and $TiO_2$ (anatase). The powders were weighted according to the ratio BaO:$Sm_2O_3$:$TiO_2$ = 1:1:4 (mol ratio), which was equivalent to a composition of Ba–$Sm_2O_3$–4$TiO_2$. The powders were milled in a plastic jar with deionized water for 8 h, then the powders were dried and ground to force through a 250-mesh sieve. These powders were then heated for 4 h from 850 to 1300°C at a step of 50°C. After crushing and grinding, the crystalline phases of calcining powders were determined by X-ray diffraction patterns (XRD). XRD patterns were taken at $2\theta = 4°$ per min using Cu$K_\alpha$ radiation. For sintering, the mixed powders were calcined at 1100°C were used as the base composition. After grinding and sieving, the powders were pressed to form pellets and then the pellets were sintered at 1275~1375°C for 6 h. Crystalline phases of the sintered $BaSm_2Ti_4O_{12}$ ceramics were also investigated using XRD patterns. The densification behaviors of the $BaSm_2Ti_4O_{12}$ ceramics as a function of sintering temperature were evaluated by determining the bulk density using the Archimedes method. The microstructures of sintered samples were directly observed from the scanning electronic micrograph (SEM). Dielectric properties at microwave frequencies (7.25~9.31 GHz) were evaluated by the modified Hakki–Coleman dielectric resonator method [9]. For convenience, the $Q^*f$-factor was used for evaluating the loss quality, where $f$ was the resonant frequency. The temperature change of the resonant frequency $\Delta f_o/f_o$ and temperature coefficient of resonant frequency $\tau_f$ were defined as follows.

$$\Delta f_o/f_o = (f_T - f_o)/f_o \tag{1}$$

where $f_T$ and $f_o$ are the resonant frequency at 85 and 0°C, respectively.

$$\tau_f = \Delta f_o/(f_o^* \Delta T) \tag{2}$$

## 3. Results and discussion

The conventional solid-state-reaction process for synthesizing $BaSm_2Ti_4O_{12}$ compounds were commonly based on the following reaction:

$$BaCO_3 + Sm_2O_3 + 4TiO_2 \rightarrow BaSm_2Ti_4O_{12} \tag{3}$$

However, the real solid reaction processes are usually more complex, and some intermediate reaction phases might happen. The XRD patterns of BaO–$Sm_2O_3$–4$TiO_2$ powders calcined at various temperatures are shown in Fig. 1, and the phase analyses are summarized in Table 1. As various calcining temperatures are used, various phases are observed in calcined BaO–$Sm_2O_3$–4$TiO_2$ powders. Calcining BaO–$Sm_2O_3$–4$TiO_2$ powder at 850°C the source phases of $TiO_2$ and $Sm_2O_3$ are residual, and $TiO_2$ and $Sm_2O_3$ consume ("consume" means that the higher temperature can find the composition) at 1000 and 1150°C, respectively. The $BaTiO_3$, $BaTi_4O_9$, and $Sm_2Ti_2O_7$ start to reveal at 850-, 850-, and 900°C-calcining powders. These results suggest that the intermediate phases of $BaTiO_3$, $BaTi_4O_9$, and $Sm_2Ti_2O_7$ form before the $BaSm_2Ti_4O_{12}$ phase. Proceeding calcination at 1100°C the $BaSm_2Ti_4O_{12}$ forms and coexists with the

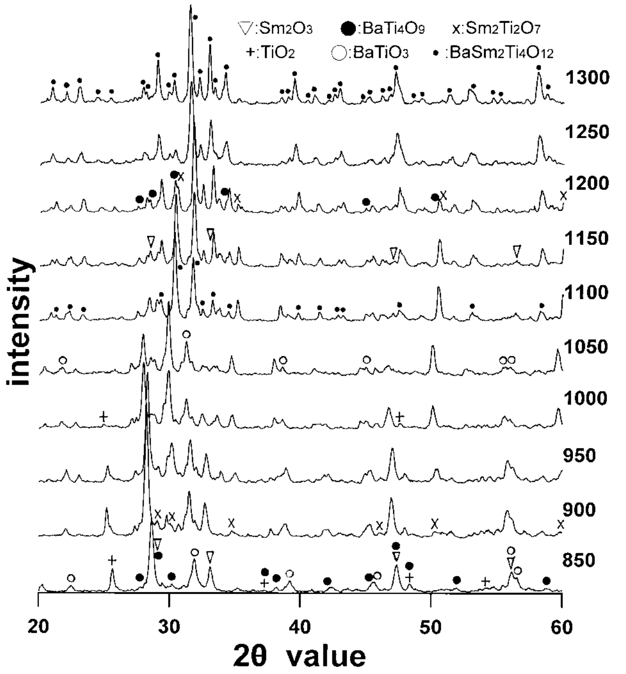

Fig. 1. The crystalline phases of the calcined BaO–$Sm_2O_3$–4$TiO_2$ powder.

Table 1
The phases of calcined $BaSm_2Ti_4O_{12}$ powders[a]

| Temperature (°C) | $Sm_2O_3$ | $BaTiO_3$ | $TiO_2$ | $BaTi_4O_9$ | $Sm_2Ti_2O_7$ | $BaSm_2Ti_4O_{12}$ |
|---|---|---|---|---|---|---|
| 850 | **O** | **O** | **O** | **O** | **X** | **X** |
| 900 | **O** | **O** | **O** | **O** | **O** | **X** |
| 950 | **O** | **O** | **O** | **O** | **O** | **X** |
| 1000 | **O** | **O** | **O** | **O** | **O** | **X** |
| 1050 | **O** | **O** | **X** | **O** | **O** | **X** |
| 1100 | **O** | **O** | **X** | **O** | **O** | **O** |
| 1150 | **O** | **O** | **X** | **O** | **O** | **O** |
| 1200 | **X** | **X** | **X** | **O** | **O** | **O** |
| 1250 | **X** | **X** | **X** | **X** | **X** | **O** |
| 1300 | **X** | **X** | **X** | **X** | **X** | **O** |

[a] **O**, exist; **X**, not exist.

source phases ($Sm_2O_3$) and the intermediate phases ($BaTi_4O_9$ and $Sm_2Ti_2O_7$). Further raising the calcining temperature, the intermediate phases $BaTiO_3$ consumes at 1150°C. Even though 1200°C is used as the calcining temperatures, the $BaTi_4O_9$ and $Sm_2Ti_2O_7$ phases are still residual. The XRD pattern of powder calcined at 1300°C is similar to one calcined at 1250°C, and only one crystalline phase of $BaSm_2Ti_4O_{12}$ is revealed as the calcined temperature is higher than 1250°C.

Fig. 2 shows the integrating intensity of all phases revealing at the calcining temperatures of 850~1300°C. As Fig. 2 shows, the integrating intensities of $Sm_2O_3$ and $TiO_2$ phases decrease with the raise of calcining temperatures. The integrating intensities of $BaTiO_3$, $BaTi_4O_9$, and $Sm_2Ti_2O_7$ phases first increase with the calcining temperature. The integrating intensities of $BaTiO_3$, $BaTi_4O_9$, and $Sm_2Ti_2O_7$ phases reach a maximum at 900, 950, and 1100°C, respectively, then decrease with the raise of calcining temperatures. The integrating intensity of $BaSm_2Ti_4O_{12}$ phase first reveals at 1100°C, increases with the calcining temperature, and then saturates at about 1250°C. In the range of 1100~1250°C the intensity of $BaSm_2Ti_4O_{12}$ phase increases accompanying with the decrease of intensities of $BaTi_4O_9$ and $Sm_2Ti_2O_7$ phases. These results suggest that the formation of $BaSm_2Ti_4O_{12}$ phase is at the consumption of the $BaTi_4O_9$ and $Sm_2Ti_2O_7$ phases. From Figs. 1 and 2, the reaction sequence to form $BaSm_2Ti_4O_{12}$ can be summarized as:

$$BaCO_3 \rightarrow BaO + CO_2 \quad (4)$$

$$BaO + TiO_2 \rightarrow BaTiO_3 \quad (5)$$

$$BaTiO_3 + 3TiO_2 \rightarrow BaTi_4O_9 \quad (6)$$

$$Sm_2O_3 + 2TiO_2 \rightarrow Sm_2Ti_2O_7 \quad (7)$$

$$Sm_2Ti_2O_7 + BaTi_4O_9 \rightarrow BaSm_2Ti_4O_{12} \quad (8)$$

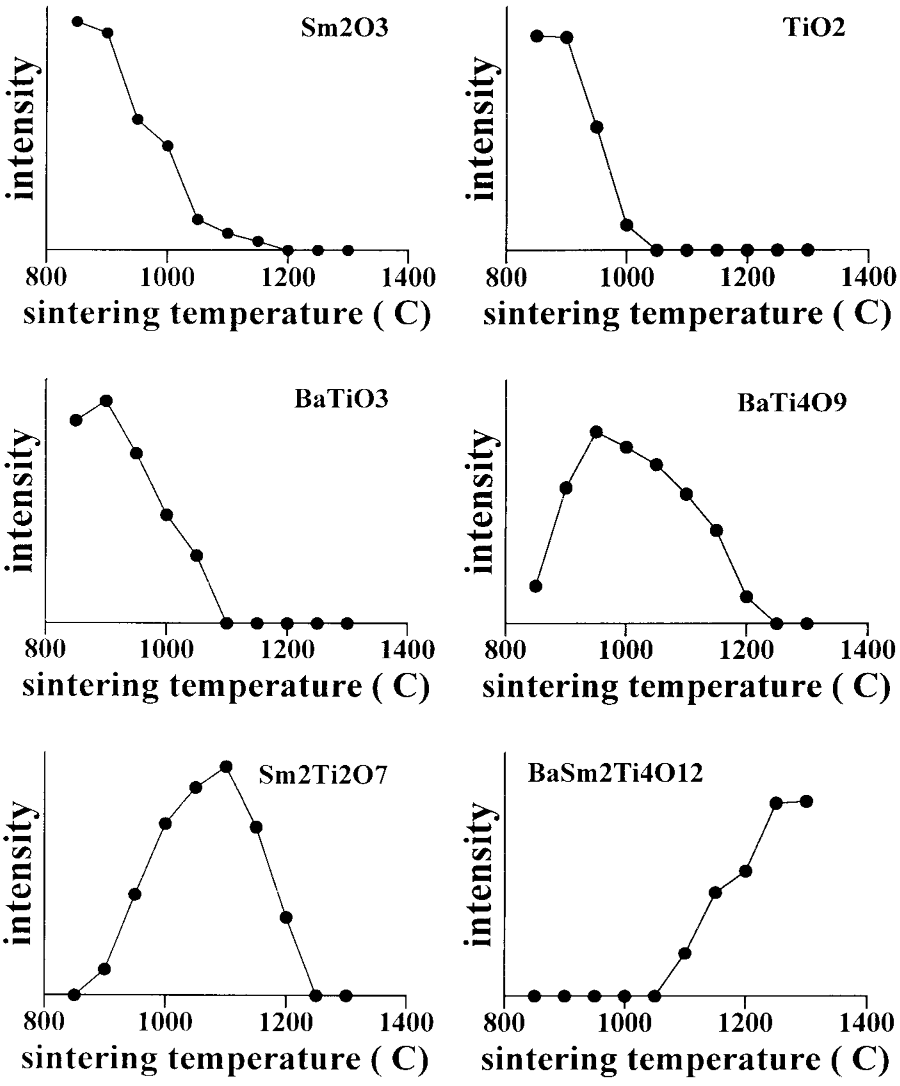

Fig. 2. The integrating intensity of all phases.

This was consistent with the previous reports. When the calcining temperatures were higher than 1250°C, some minor phases may be existed in the calcined powder, however, they could not be differentiated from the major phase of $BaSm_2Ti_4O_{12}$ because of overlapping with the mainly crystalline phase.

In this study, the powder calcined at 1100°C is used as the initial $BaSm_2Ti_4O_{12}$ powder for sintering. The XRD patterns of $BaSm_2Ti_4O_{12}$ pellets sintered at 1275 to 1375°C are shown in Fig. 3, these results are similar to the powders calcined at temperatures higher than 1250°C. During sintering, the intermediate phases of $BaTiO_3$, $BaTi_4O_9$, and $Sm_2Ti_2O_7$ all consume and only the $BaSm_2Ti_4O_{12}$ phase is left. It also notes that the some peak-intensity of $BaSm_2Ti_4O_{12}$ phase increases with the raising of sintering temperature.

Fig. 4 reveals the as-sintered surfaces at two different sintering temperatures. As 1325°C is used as the sintering temperature, the main crystals are bar-shaped grains with the occasional appearance of block-shaped grains, as Fig. 4(a) shows. With the raise of sintering temperature from 1325 to 1350°C, as Fig. 4(b) shows, the length of the bar-shaped grains tends to increase and the small block-shaped grains decreases. The bulk density of samples sintered at 1275~1375°C are shown in Fig. 5, showing that the bulk density has maximum values at temperatures around 1350°C. Either higher or lower sintering temperatures may cause the bulk density to decrease. As sintering temperatures are lower than 1350°C, the decrease of the porosity may cause this result; As 1375°C is used as the sintering temperature, long grains grow at the expense of short ones, which result in the formation of new and larger voids where the short grains are originally located. As the long bar grains come into contact, continual growth push them away from one another, which causes expansion of the sintered compacts and results in decreases in bulk densities.

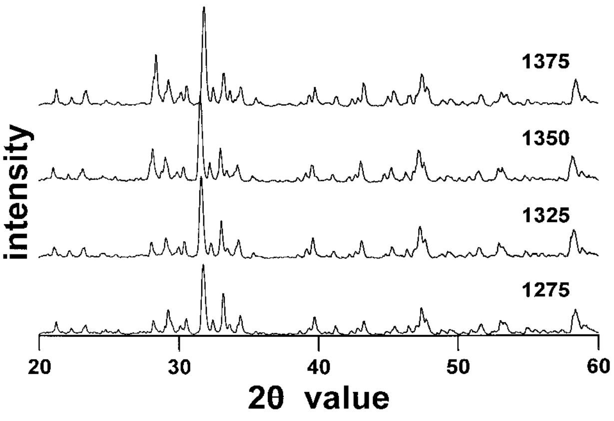

Fig. 3. The XRD patterns of sintered $BaSm_2Ti_4O_{12}$ ceramics.

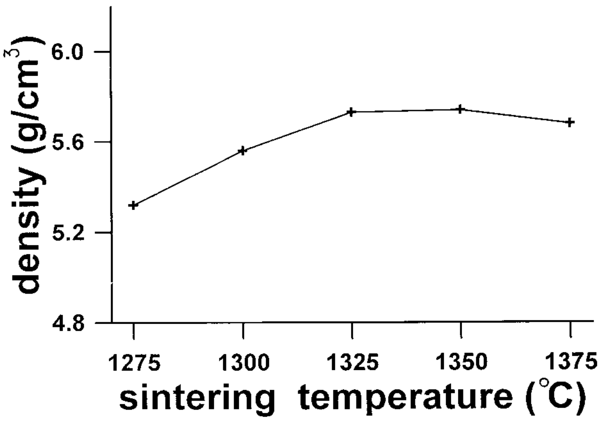

Fig. 5. The density of sintered $BaSm_2Ti_4O_{12}$ ceramics as a function of sintering temperatures.

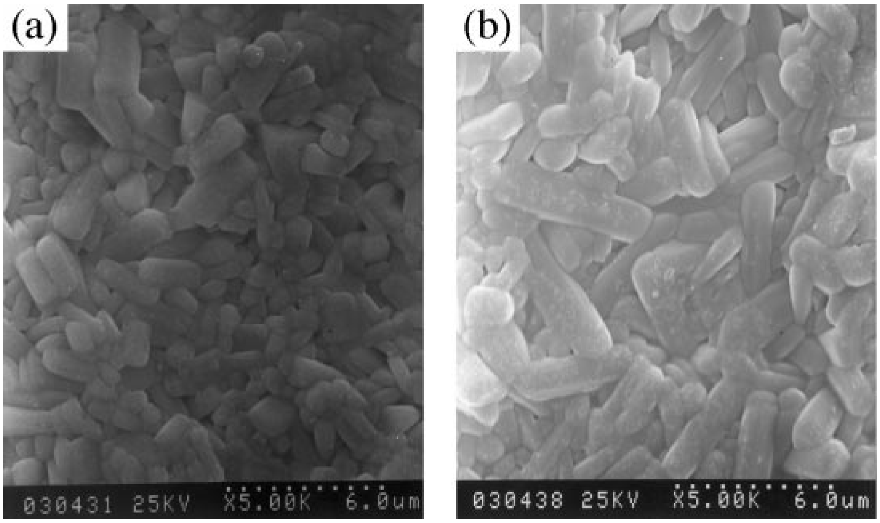

Fig. 4. The micrographs of sintered $BaSm_2Ti_4O_{12}$ ceramics: (a) sintered at 1325°C and (b) sintered at 1350°C.

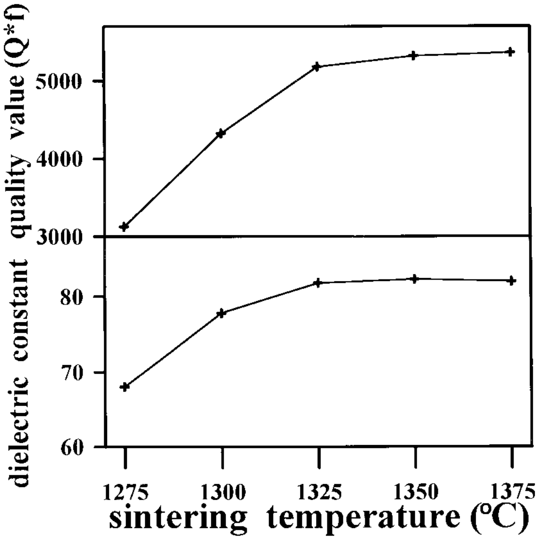

Fig. 6. The dielectric constant ($\varepsilon_r$ value) and quality ($Q^*f$) values of the $BaSm_2Ti_4O_{12}$ ceramics as a function of sintering temperature.

The dielectric constant ($\varepsilon_r$ value) and quality values ($Q^*f$) of the $BaSm_2Ti_4O_{12}$ ceramics are estimated as a function of sintering temperature and the results are shown in Fig. 6. For $BaSm_2Ti_4O_{12}$ ceramics, the $\varepsilon_r$ values increase with the raise of sintering temperature. It maybe caused by that the densities increase with the raise of sintering temperature. The $Q^*f$ values of $BaSm_2Ti_4O_{12}$ ceramics also increase with the raise of sintering temperatures and saturate at about 1325°C. The increase of $Q^*f$ values with the raise of sintering temperature maybe caused by the larger grain growth and the more uniform in grain size. Because as the grain size increases, the pores and grain boundary area decreases, that will reduce the lattice imperfections and than increase the $Q^*f$ values. However, such significant changes in dielectric properties are hardly explained only by the lattice imperfection or boundary defects. In this study, 1325°C is enough to sinter $BaSm_2Ti_4O_{12}$ ceramics, because the microwave characteristics of $BaSm_2Ti_4O_{12}$ ceramics saturate at about 1325°C. For example, the temperature coefficient of resonant frequency ($\tau_f$) of $BaSm_2Ti_4O_{12}$ ceramics sintered at 1325, 1350, and 1375°C are $-19.2$, $-18.9$, and $-18.8$ ppm/°C, respectively.

## 4. Conclusions

a. 1100°C is enough for $BaO–Sm_2O_3–4TiO_2$ powder to form $BaSm_2Ti_4O_{12}$ phase.
b. Using 1275°C as the sintering temperature of the 1100°C-calcined BST powder the source phase $Sm_2O_3$ and $TiO_2$ and the intermediate phases $BaTiO_3$, $BaTi_4O_9$, and $Sm_2Ti_2O_7$ consume. Only the single $BaSm_2Ti_4O_{12}$ phase is revealed in the sintered ceramics.
c. The densities and the microwave characteristics (dielectric constant, quality value, and $\tau_f$ values) of $BaSm_2Ti_4O_{12}$ ceramics saturate at about 1325°C, i.e. 1325°C is enough to sinter $BaSm_2Ti_4O_{12}$ ceramics.

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