Hue University Journal of Science: Natural Science
Vol. 129, No. 1B, 91–98, 2020

pISSN 1859-1388
eISSN 2615-9678

FABRICATION AND ELECTRICAL CHARACTERIZATION OF LEAD-FREE $BiFe_{0.91}(Mn_{0.47}Ti_{0.53})_{0.09}O_3$–$BaTiO_3$ CERAMICS

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(Received: 28 March 2020; Accepted: 27 April 2020)

Abstract. The $(1–x)BiFe_{0.91}(Mn_{0.47}Ti_{0.53})_{0.09}O_{3–x}BaTiO_3$ (BFMT–BT) lead-free ceramics have been fabricated by using the conventional solid-state reaction method. The phase structure of BFMT–BT investigated with X-ray diffraction shows a single perovskite phase. Although 20% mol of Bi_2O_3 was added into the raw materials in excess, the evaporation of Bi^{3+} ions during calcining and sintering processes is from 20 to 30% wt. relative to other elements. The effect of $BaTiO_3$ content on the electrical properties of BFMT–BT ceramic was investigated. At a $BaTiO_3$ concentration of 0.3 M and a sintering temperature of 950 °C, the electrical properties of ceramics are best with the density (ρ) of 7.6 g/cm^3, the electromechanical coupling factor (k_p) of 0.28, and the dielectric constant (ε_r) of 1028, and the difference in polarization at the zero field is about 10.5 μC/cm^2.

Keywords: lead-free ceramics, remanent polarization, electromechanical coupling factor, dielectric constant

1 Introduction

Scientists are interested in research and application of the $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT)-based ceramics due to their excellent piezoelectric properties and many applications in piezoelectric actuators and transformers in recent years [1-3]. However, the use of lead-based ceramics has caused serious environmental problems because of the high toxicity of lead oxide. Therefore, it is necessary to develop lead-free ceramics with good ferroelectric and piezoelectric properties for the replacement of the lead-related ceramics [4-10].

$BiFeO_3$ (BFO) thin films have been reported to show excellent ferroelectric properties due to the compressive stress imposed by the bottom electrode, which has a smaller lattice constant than that of BFO [11-18]. However, the piezoelectric properties of BFO bulk ceramics are not consistent in many reports and are very sensitive to process conditions and impurities because the volatilization of some reactants leads to second phase formation and nonstoichiometry [14]. Moreover, the leakage current makes BFO undesirable for ferroelectric memories. Thus, it is not easy to measure the piezoelectric properties of BFO-based ceramics accurately because of the high leakage current [15].

To overcome this problem, various approaches have been proposed, particularly the substitution techniques by using Mn and Ti ions at the B site. In the case of Mn-substituted BFO, the well-saturated *P–E* hysteresis curves have not been found due to the large leakage current [16]. In the case of Ti-doped BFO ceramics, the *P–E* ferroelectric loops are observed at room temperature [17, 18]. Nevertheless, both of the ceramics have not yet shown the piezoelectric

properties. From these results, the fabrication of Mn and Ti- co-doped BFO (BFMT) has been expected to enhance the dielectric properties, so that its ferroelectric and piezoelectric properties could be improved.

Furthermore, $BaTiO_3$ (BT) ferroelectric ceramics show good dielectricity and piezoelectricity [19]. Therefore, $BiFe_{0.91}(Mn_{0.47}Ti_{0.53})_{0.09}O_3$–$BaTiO_3$ (BFMT–BT) ferroelectric solid solutions are attempted to fabricate by using usual solid-phase synthesis in this study.

2 Experimental

The general formula of the studied material is $(1–x)BiFe_{0.91}(Mn_{0.47}Ti_{0.53})_{0.09}O_{3–x}BaTiO_3$ (BFMT–BT) lead-free ceramics, where x is 0.0, 0.20, 0.25, 0.30, 0.35, and 0.40. Reagent grade oxide powders of Bi_2O_3, Fe_2O_3, $BaCO_3$, MnO_2, and TiO_2 (purity ≥ 99 %) were used as starting raw materials.

Firstly, the mixture of BT was prepared by reacting $BaCO_3$ with TiO_2 at 1200 °C for 2 h after milling the mixture for 8 h. Secondly, Bi_2O_3, Fe_2O_3, MnO_2, and TiO_2 were weighed and milled (the PM 400/2 milling machine) for 8 h with zirconia balls and ethanol as the medium. The addition of Bi_2O_3 to compensate evaporation during heating is 20% mol. Then, the powders were calcined at 750 °C for 2 h. Thirdly, the calcined product of the BFMT was mixed with BT calcined ceramics at the ratio of BT/BFMT equal to $(1–x)/x$ mole. As it is well known, Bi_2O_3 is easy to evaporate at a low temperature of about 600 °C. On the other hand, BFO needs to be calcined at relatively high temperatures to attain the transition of ferroelectric phases. Therefore, it is necessary to seek the minimum temperature enabling the phase transition and limiting the Bi^{3+} evaporation.

To identify the temperature for calcining BFMT–BT, we investigated the data of thermal gravimetric (TG) and thermal analysis (DTA) of BFMT–BT powders (Fig. 1). As the above results, the TG curve exhibits a linear decrease in the total mass of the studied powder. However, the DTA curve shows an endothermic peak at 824.95 °C, corresponding to the ion evaporation. To ensure the phase creation in the sample, the mixture powder was calcined at temperatures a little higher than 850 °C after being milled for 8 h and pressed into pellets.

The calcined BFMT–BT powder was milled for 16 h with zirconia balls and ethanol as the medium. The ground materials were pressed into circular pellets with a diameter of 12 mm and a thickness of 1.5 mm under 100 MPa; then, they were sintered in a sealed alumina crucible at 900, 950, 1000, and 1050 °C for 2 h.

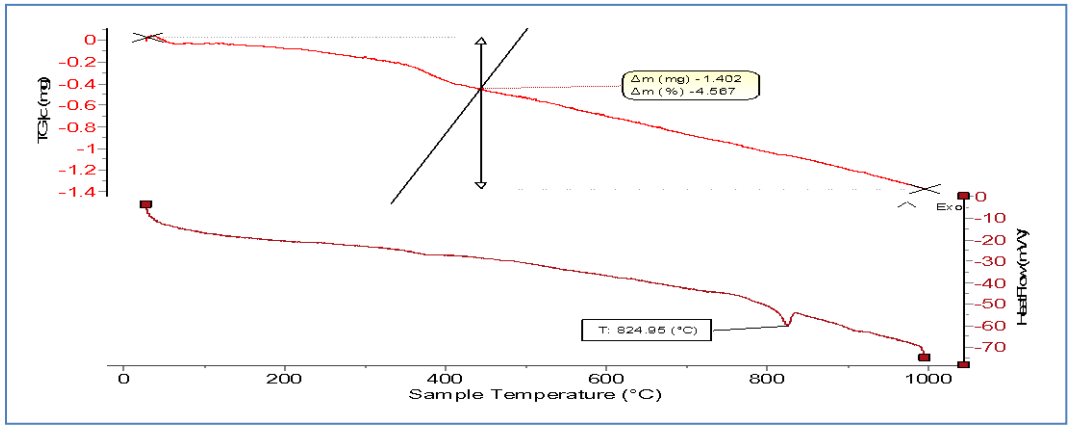

Fig. 1. TG and DTA curve of BFMT–BT power at 10 °C/min heating rate

pISSN 1859-1388
eISSN 2615-9678

The density of the samples was measured by using the Archimedes method. The synthesized pellets were polarized in a silicone oil bath at 120 °C by applying a DC electric field of 30 kV·cm^{-1} for 20 min, then cooling down to room temperature. They were aged for 24 h prior to testing. The crystalline property was determined by using X-ray diffraction (XRD) analysis (Rigaku RINT2000) at room temperature. The morphology was studied with a field emission scanning electron microscope (FESEM; JSM-6340F). The relative ratio of elements in BEMT–BT was identified by using X-ray energy-dispersive spectra (EDS) analysis (Hitachi S-3400N). The piezoelectric properties were determined via resonance and antiresonance frequencies with an impedance analyzer (Agilent 4196B and RLC HIOKI 3532). The ferroelectric properties were measured by using the Sawyer–Tower method.

3 Results and discussion

Fig. 2 shows the X-ray diffraction patterns of the 0.7BFMT–0.3BT ceramics sintered at 950 °C for 2 h. These ceramics have pure perovskite phases and no trace of the second phase with a rhombohedral structure characterized by a peak $(200)_R$ at $2\theta \approx 44.5°$.

It is clear that the obtained BFMT–BT ceramics are composed of Bi, Fe, Ti, and Ba (Fig. 3). Moreover, the improved ferroelectric properties of the BFMT–BT ceramics will be shown in this study. These results confirm that the qualitative and quantitative chemical composition of the synthesized ceramics is quite good. Calculating the molar ratios between Bi and other elements from the data of the spectrum analysis and comparing them with the corresponding ratios in the chemical formula of $0.7BiFe_{0.91}(Mn_{0.47}Ti_{0.53})_{0.09}O_3–0.3BaTiO_3$, we can identify the relative loss of Bi compared with other elements in the ceramics due to evaporation (Table 1).

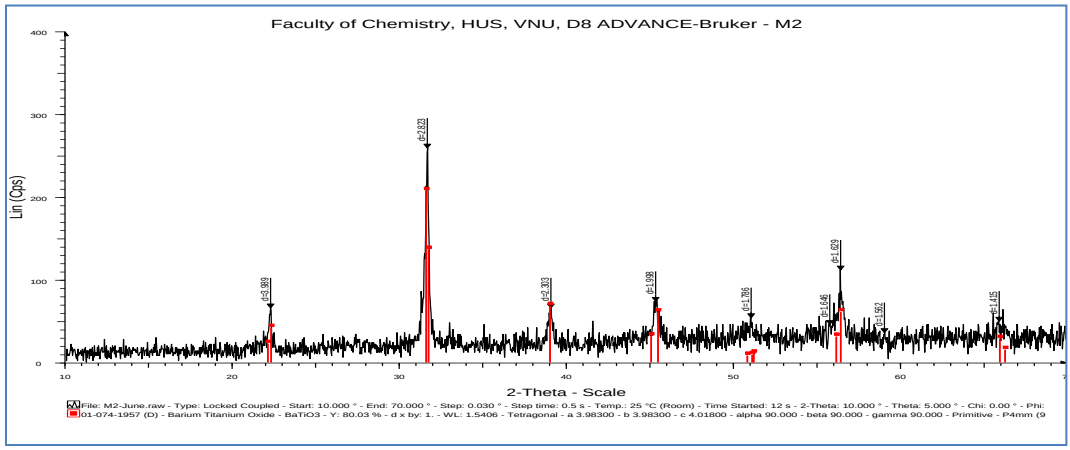

Fig. 2. X-ray diffraction patterns of 0.7BFMT–0.3BT ceramics sintered at 950 °C for 2 h

Table 1. Comparison of the ratios between Bi and other elements in 0.7BFMT–0.3BT sintered at 950 °C for 2 h

0.7BFMT–0.3BT	**Molar ratios**		
	Bi/Ba	**Bi/Ti**	**Bi/Fe**
Chemical formula	2.333	2.210	1.099
Practical composition	1.658	0.576	0.711
Relative loss in mol, %	28.2	19.1	26.3

Fig. 3 and Table 1 show that the relative loss of Bi compared with other elements by evaporation during the synthesis of the BFMT–BT ceramic is from 19.1 to 28.2% mol. The loss increases from Ba, Fe, Ti, and Bi. It is also disadvantageous for the synthesis of ferroelectric ceramics related to Bi at high temperatures.

It can be seen that the densities of the BFMT–BT ceramics change with the sintering temperature and the amount of $BaTiO_3$ (Fig. 4). The density of BFMT–BT samples increases with increasing the amount of $BaTiO_3$ and the sintering temperature. It attains a maximum value (ϱ = 7.2 g/cm^3) at a $BaTiO_3$ composition of 0.3 mol when sintered at 950 °C and then decreases. The density of BFMT–BT samples sintered at a higher temperature than 950 °C decreases, and this might be caused by the evaporation of Bi_2O_3 during sintering at higher temperatures. According to these results, the optimal sintering temperature of $(1–x)BFMT_{1–x}BT$ would be 950 °C.

Fig. 5 shows the SEM images of the fractured surface of the BFMT–BT ceramics at various $BaTiO_3$ concentrations and sintering temperatures. It is observed from the micrographs that the average grain size of the samples increases with the sintering temperature, and the samples become denser. However, the figure also shows that further increasing the sintering temperature to 1000 °C leads to a large number of pores, and the density of ceramic reduces. The grain sizes and thus the density of ceramics have a strong effect on the dielectric, piezoelectric, and ferroelectric properties of the ceramic.

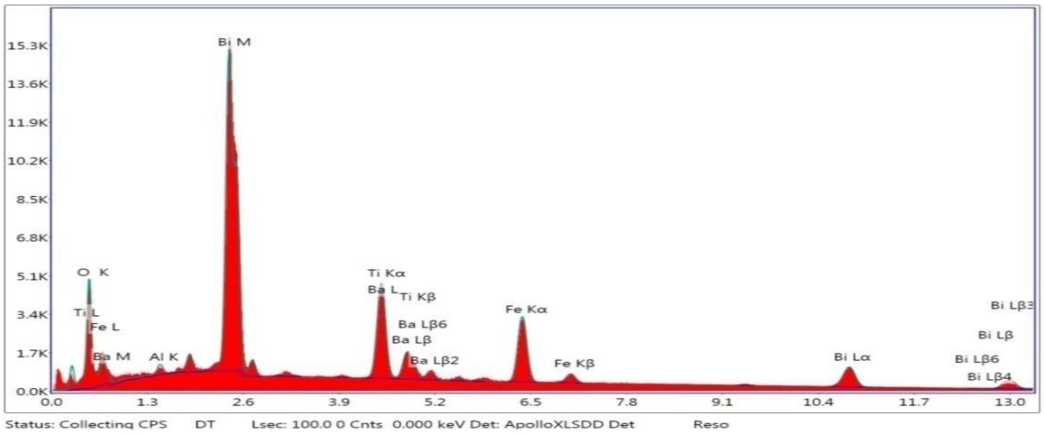

Fig. 3. EDS spectrum of 0.7BFMT–0.3BT ceramics sintered at 950 °C for 2 h

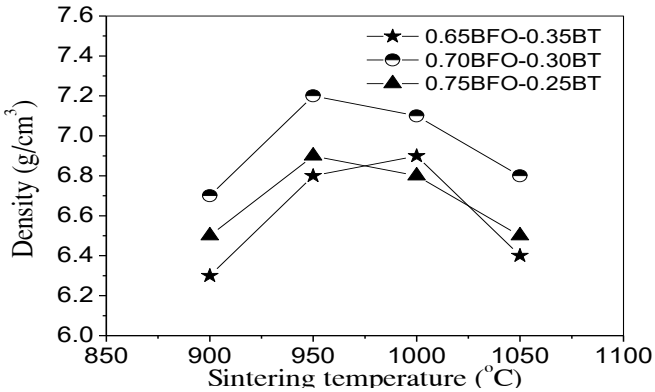

Fig. 4. Density of the BFMT–BT ceramics as a function of sintering temperature

pISSN 1859-1388
eISSN 2615-9678

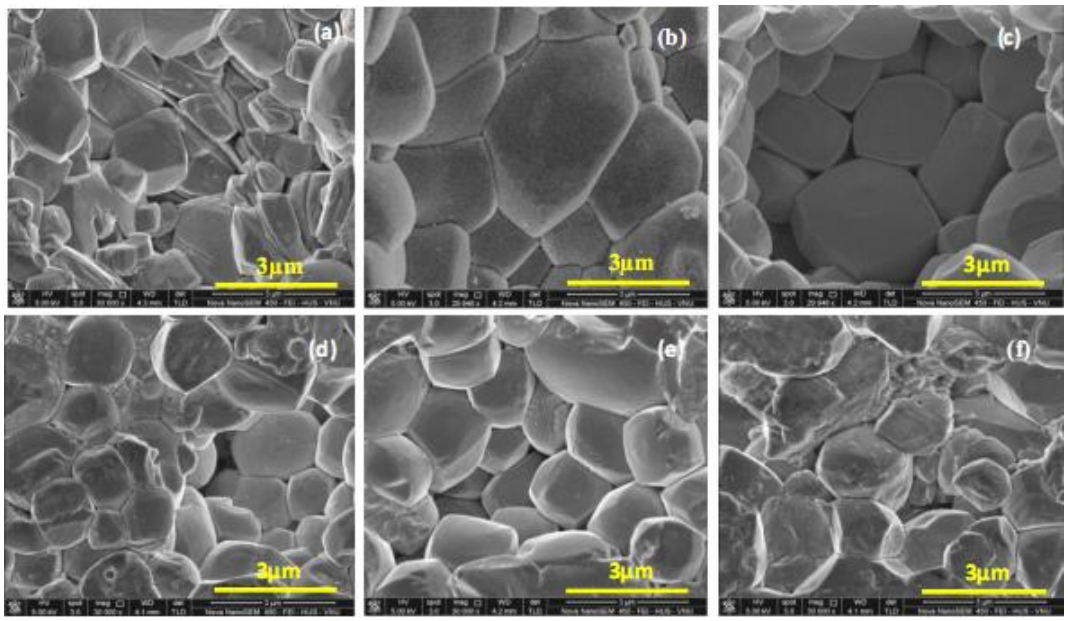

Fig. 5. Surface morphologies observed from SEM images of BFMT–BT ceramics at various ratios of $BaTiO_3$ and sintering temperatures: (a) 0.7BFMT–0.3BT (900 °C), (b) 0.7BFMT–0.3BT (950 °C), (c) 0.7BFMT–0.3BT (1000 °C); (d) 0.7BFMT–0.3BT (1050 °C); (e) 0.65 BFMT–0.35BT (950 °C), and (f) 0.75 BFMT–0.25BT (950 °C)

Fig. 6 shows the room temperature dielectric constant ε_r and the dielectric loss tanδ at 1 kHz of BFMT–BT ceramics at different sintering temperatures. The ε_r increases with the sintering temperature and reaches the highest value of 1028 at 950 °C with x = 0.3 and then decreases. This is a result of the large and homogeneous grain size and the highest densification of the 0.7BFMT–0.3BT ceramics. Larger grain has a larger domain size and less domain boundary, and thus the polarization is larger [1].

The *P–E* hysteresis loops display the ferroelectric properties of the 0.7BFMT–0.3BT ceramics (Fig. 7a). A sharp increase in P_r is observed for the samples sintered at 900–950 °C (Fig. 7b). For the 0.7BFMT–0.3BT ceramic sintered at 950 °C, the difference in the polarization at the zero field is about 10.5 µC/cm² with the coercive electric field of 29.4 kV/cm. This agrees well with the dielectric and piezoelectric properties of the samples.

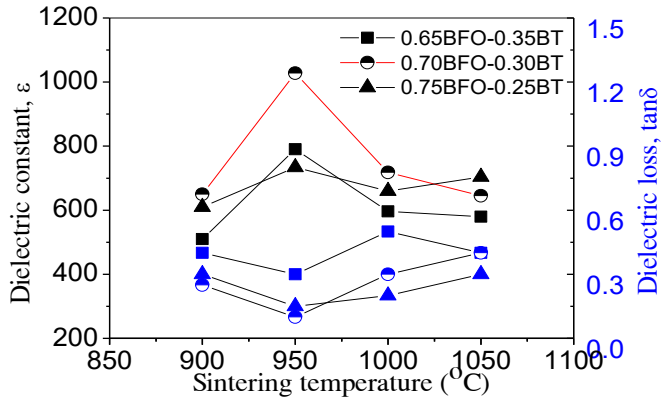

Fig. 6. Dielectric constant and loss of ceramics with different amounts of $BaTiO_3$

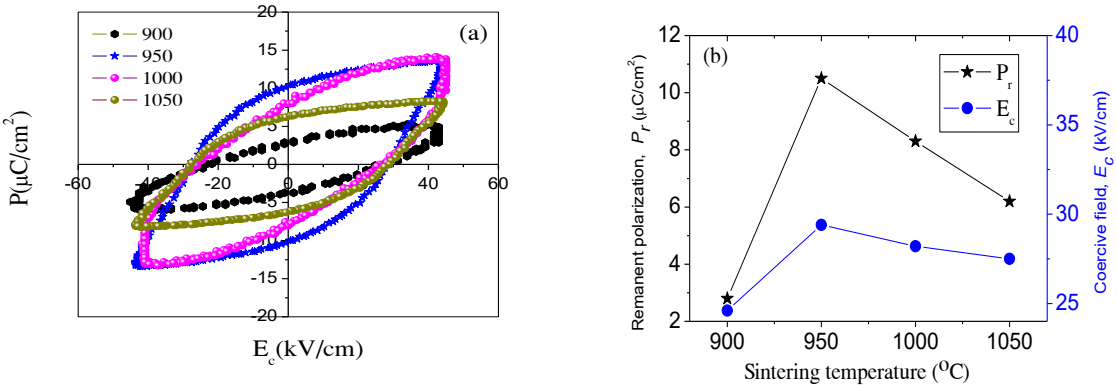

Fig. 7. P–E hysteresis loops of BFMT-BT ceramic samples sintered at various temperatures

To determine the piezoelectric properties of ceramics, resonant vibration spectra of the samples were measured at room temperature (Fig. 8a), and from these resonant spectra, the piezoelectric parameters of the samples were determined (Fig. 8b). It can be observed that the electromechanical coupling factor (k_p) and the mechanical quality factor (Q_m) depend on the amount of $BiTiO_3$ and sintering temperature. The mechanical quality and electromechanical coupling factors of the BFMT–BT ceramics are markedly improved. The largest values for k_p (0.24) and Q_m (115) are obtained at x = 0.3 and the sintering temperatures of 950 °C. This is probably related to the characteristics of the density and the increasing grain size [1]. During sintering, the presence of the liquid phase enhances the density and grain size, leading to a decrease in the energy loss and improvement of the electrical properties.

4 Conclusions

We fabricated the $(1–x)BiFe_{0.91}(Mn_{0.47}Ti_{0.53})_{0.09}O_3–_xBaTiO_3$ ceramics with x from 0 to 0.4 at various sintering temperatures. The 0.7BFMT–0.3BT ceramics sintered at 950 °C for 2 h have pure perovskite phases with a rhombohedral structure characterized by a peak $(200)_R$ at the $2\theta \approx 44.5°$. The largest grain size of 0.7BFMT–0.3BT ceramics was obtained at 1000 °C for 2 h. Generally, the ceramics possessing the largest grain size may show good dielectric, piezoelectric, and ferroelectric properties. In this study, the ceramics sintered at temperatures lower than 950 °C show the best

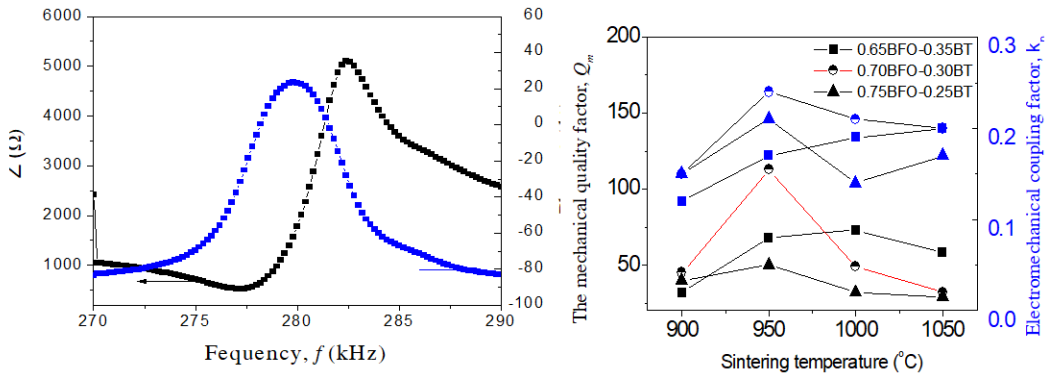

Fig. 8. The electromechanical coupling factor k_p (a) and the mechanical quality factor Q_m (b) of BFMT-BT ceramics

pISSN 1859-1388
eISSN 2615-9678

properties due to the increase of the evaporation of Bi^{3+} large quantity with sintering temperature. Hence, the hysteresis loops of the 0.7BFMT–0.3BT ceramics sintered at 950 °C for 2 h show relatively good ferroelectricity, and their difference in polarization at the zero field of is about 10.5 $\mu C/cm^2$. These piezoelectric properties of the ceramics were also analyzed by identifying the value of mechanical quality and electromechanical coupling factors, which are 0.24 and 115, respectively.

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