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Some $A_6B_5O_{18}$ cation-deficient perovskites in the $BaO–La_2O_3–TiO_2–Nb_2O_5$ system

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Abstract

Some dielectric oxides have been synthesized and characterized in the $BaO–La_2O_3–TiO_2–Nb_2O_5$ system. Through Rietveld refinement of X-ray powder diffraction data, $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_4La_2Ti_3Nb_2O_{18}$ are identified as the $A_nB_{n-1}O_{3n}$ ($n = 6$) type cation-deficient perovskites with space group $R\bar{3}m$ and lattice constants $a = b = 5.7106(1)$ Å, and $c = 42.0666(5)$ Å for $Ba_5LaTi_2Nb_3O_{18}$; $a = b = 5.6602(1)$ Å, and $c = 41.8296(5)$ Å for $Ba_4La_2Ti_3Nb_2O_{18}$, respectively. Their ceramics exhibit high dielectric constant up to 57 and high quality factors (Qf) up to 21,273 GHz. The temperature coefficient of resonant frequency (τ_f) of these ceramics is decreased with the increase of B-site bond valence.

Keywords: Cation-deficient perovskite; Dielectric materials; X-ray powder diffraction

1. Introduction

Recently, the microwave dielectric properties of some $A_5B_4O_{15}$ type cation-deficient hexagonal perovskites such as $Ba_5Nb_4O_{15}$, $Ba_{5-x}Sr_xNb_4O_{15}$, $Ba_5Ta_4O_{15}$, $ALa_4Ti_4O_{15}$ ($A = $ Ca, Sr and Ba) have attracted much attention because of their important application as microwave dielectric resonators and filters [1–6], while only two $A_6B_5O_{18}$ type perovskites ($A_2La_4Ti_5O_{18}$, with $A = $ Ca, Ba) so far have been reported [7–9]. Both ceramics are characterized by high dielectric constant (ε_r) up to 50.6, high quality factors (Qf) up to 31,839 GHz, and low temperature coefficient of resonant frequency τ_f in the range -36.4 to $+6\,\mathrm{ppm\,^\circ C^{-1}}$. It is worthwhile to investigate whether other $A_6B_5O_{18}$ perovskites might have equivalent or superior properties. The authors recently investigated some new $A_6B_5O_{18}$ oxides in the $BaO–La_2O_3–TiO_2–Nb_2O_5$ system, the present ceramics exhibit high dielectric constant up to 56.6, high quality factors and a positive temperature coefficient of resonant frequency τ_f in the range $+65$–$+142\,\mathrm{ppm\,^\circ C^{-1}}$ [10,11], in contrast with $A_6B_{10}O_{30}$-type filled tungsten-bronze compounds, such as $Ba_5LaTi_3Nb_7O_{30}$ and $Ba_4La_2Ti_4Nb_6O_{30}$, which show ferroelectric nature with high loss at microwave frequency and large temperature coefficient [12,13]. These $A_6B_5O_{18}$-type ceramics have great potential in microwave application if the temperature coefficient can be suppressed to an acceptable level ($-20\,\mathrm{ppm\,^\circ C^{-1}} < \tau_f < +20\,\mathrm{ppm\,^\circ C^{-1}}$), and the understanding of their crystal structures is a key point for such property modification. In the present paper, we report the structure characterization of $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_4La_2Ti_3Nb_2O_{18}$ together with the microwave dielectric properties.

2. Experimental

$Ba_5LaTi_2Nb_3O_{18}$ and $Ba_4La_2Ti_3Nb_2O_{18}$ were synthesized through solid state reaction from the high-purity

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powders of $BaCO_3$ (>99.95%), La_2O_3 (>99.99%), TiO_2 (>99.99%), and Nb_2O_5 (>99.99%). The stoichiometric mixtures of starting powders were weighed and ball milled in distilled water medium for 12 h in a plastic bottle using zirconia balls. The wet mixtures were dried at 120 °C then calcined at 1350 °C in air for 24 h. These heated powders were pressed into discs of different thickness in the range 5–6 and 11 mm in diameter under a pressure of 180 MPa after grinding and then were sintered at 1420 °C for $Ba_5LaTi_2Nb_3O_{18}$ and 1450 °C for $Ba_4La_2Ti_3Nb_2O_{18}$ in air for 8 h to yield dense polycrystalline ceramics. The basic reaction for the synthesis could be represented by Eqs. (1) and (2).

$$10\,BaCO_3 + La_2O_3 + 4TiO_2 + 3Nb_2O_5 \rightarrow 2Ba_5LaTi_2Nb_3O_{18} + 10CO_2\,(g), \tag{1}$$

$$4BaCO_3 + La_2O_3 + 3TiO_2 + Nb_2O_5 \rightarrow Ba_4La_2Ti_3Nb_2O_{18} + 4CO_2\,(g). \tag{2}$$

Finally, the sintered polycrystalline samples were ground to prepare the powder for X-ray diffraction analysis.

Table 1
Crystallographic parameters for $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_4La_2Ti_3Nb_2O_{18}$

Compounds	$Ba_5LaTi_2Nb_3O_{18}$	$Ba_4La_2Ti_3Nb_2O_{18}$
Space group	$R\bar{3}m$	$R\bar{3}m$
$A = b$ (Å)	5.7106(1)	5.6602(1)
c (Å)	42.0666(5)	41.8296(5)
Z	3	3
Cell volume (Å^3)	1188.04(2)	1160.57(2)
Formula weight (g/mol)	1488.14	1444.7
2θ-range, step	5–100°, 0.005°	5–100°, 0.005°
X-ray radiation	$CuK\alpha_1$ ($\lambda = 1.540598$ Å)	$CuK\alpha_1$ ($\lambda = 1.540598$ Å)
R_p, R_{wp}, χ^2 (%)	3.81, 5.16, 6.05	3.53, 4.83, 5.60

Table 2
Positional and thermal parameters for $Ba_5LaTi_2Nb_3O_{18}$

Atom	Position	$x = -y$	Z	Occu.	B_{iso}/Å^2
O1	18h	0.5058(8)	0.3032(2)	1	1.76(7)
O2	18h	0.4862(9)	0.4240(2)	1	1.76(7)
O3	18h	0.5112(11)	0.1390(2)	1	1.76(7)
Ba1	6c	0	0.3122(1)	1	0.45(1)
Ba2/La2	6c	0	0.4141(1)	0.75,0.25	0.45(1)
Ba3/La3	6c	0	0.1384(1)	0.75,0.25	0.45(1)
Nb1	6c	0	0.0523(1)	1	1.05(3)
Nb2/Ti2	6c	0	0.2225(1)	1/3,2/3	1.05(3)
Nb3/Ti3	3b	0	0.5	1/3,2/3	1.05(3)

X-ray diffraction measurements were conducted with a HUBER G670 Image Foil Guinier Camera using $CuK\alpha_1$ radiation ($\lambda = 0.1540598$ nm). To collect data suitable for Rietveld refinement, a slow step-scan was employed with a total collection time of 12 h over the 2θ range 5–100°. An initial set of lattice parameters was obtained by the least-squares refinement using WinXPOW program. Rietveld refinements were then carried out in an isotropic approximation of the thermal parameters, using the program Fullprof-Suite [14]. The

Table 3
Selected interatomic distances for $Ba_5LaTi_2Nb_3O_{18}$ (Å)

Ba1–O1:	2.881(5) × 6
Ba1–O1:	2.752(7) × 3
Ba1–O2:	3.292(7) × 3
Ba2/La2–O1:	2.728(7) × 3
Ba2/La2–O2:	2.888(6) × 6
Ba2/La2–O3:	3.015(9) × 3
Ba3/La3–O2:	2.687(7) × 3
Ba3/La3–O3:	2.858(7) × 6
Ba3/La3–O3:	2.812(9) × 3
Nb1–O1:	1.843(6) × 3
Nb1–O2:	2.406(7) × 3
Nb2/Ti2–O2:	1.733(7) × 3
Nb2/Ti2–O3:	1.943(9) × 3
Nb3/Ti3–O3:	2.109(8) × 6

Table 4
Positional and thermal parameters for $Ba_4La_2Ti_3Nb_2O_{18}$

Atom	Position	$x = -y$	Z	Occu.	B_{iso}/Å^2
O1	18h	0.5017(7)	0.3003(2)	1	1.80(6)
O2	18h	0.4870(9)	0.4220(2)	1	1.80(6)
O3	18h	0.4958(12)	0.1400(2)	1	1.80(6)
Ba1	6c	0.0	0.3122(1)	1	1.04(1)
Ba2/La2	6c	0.0	0.4140(1)	0.5, 0.5	1.04(1)
Ba3/La3	6c	0.0	0.1389(1)	0.5, 0.5	1.04(1)
Nb1	6c	0.0	0.0524(1)	1	0.02(3)
Ti2	6c	0.0	0.2224(1)	1	0.02(3)
Ti3	3b	0.0	0.5000	1	0.02(3)

Table 5
Selected interatomic distances for $Ba_4La_2Ti_3Nb_2O_{18}$ (Å)

Ba1–O1:	2.874(5) × 6
Ba1–O1:	2.803(6) × 3
Ba1–O2:	3.202(7) × 3
Ba2/La2–O1:	2.586(6) × 3
Ba2/La2–O2:	2.853(6) × 6
Ba2/La2–O3:	2.949(9) × 3
Ba3/La3–O2:	2.742(7) × 3
Ba3/La3–O3:	2.831(8) × 9
Nb1–O1:	1.808(5) × 3
Nb1–O2:	2.326(7) × 3
Ti2–O2:	1.770(7) × 3
Ti2–O3:	2.071(9) × 3
Ti3–O3:	1.944(8) × 6

microwave dielectric properties such as dielectric constant and unloaded Q factor were measured using an Agilent 8722ET network analyzer; the dielectric constants was calculated using TE_{011} mode under the end-shorted condition using the method suggested by Hakki and Coleman and modified by Courtney [15,16]. The τ_f was measured by noting the temperature variation of the TE_{011} resonance in the temperature range 15–85 °C.

3. Results and discussion

Through the initial least-squares refinement, the XRD patterns of $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_4La_2Ti_3Nb_2O_{18}$ were fully indexed on a trigonal lattice with unit cell parameters: $a = b = 5.7106(1)$ Å, and $c = 42.0666(5)$ Å for $Ba_5LaTi_2Nb_3O_{18}$; $a = b = 5.6602(1)$ Å, $c = 41.8296(5)$ Å for $Ba_4La_2Ti_3Nb_2O_{18}$, similar to those of $Ba_6TiNb_4O_{18}$ [17,18] and $Ba_2La_4Ti_5O_{18}$ [19,20]. All

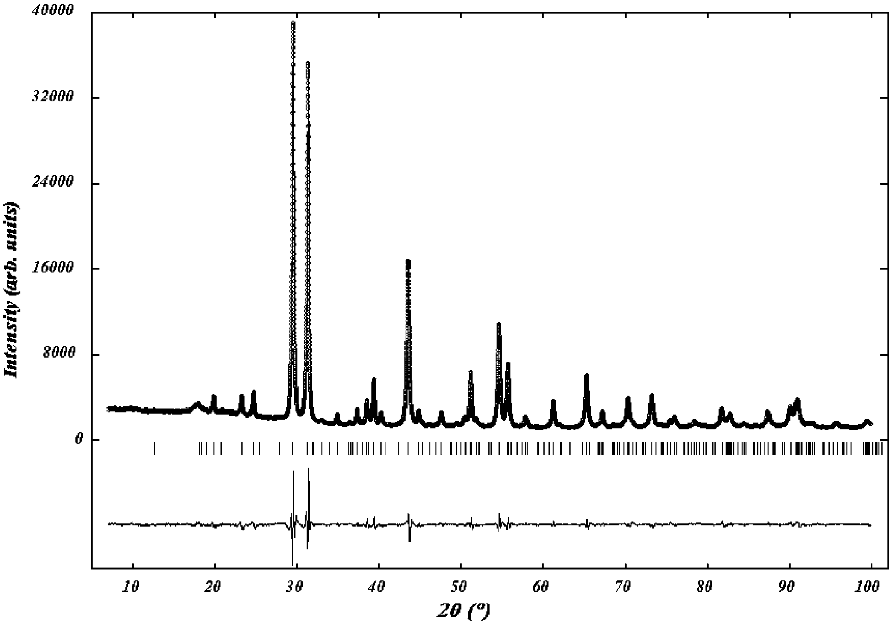

Fig. 1. Observed, calculated and difference X-ray pattern for $Ba_5LaTi_2Nb_3O_{18}$.

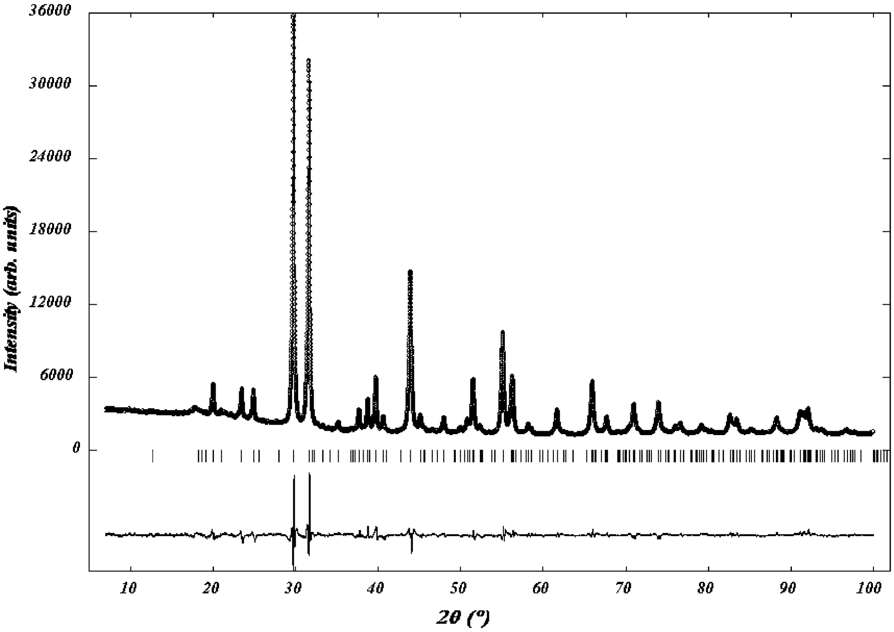

Fig. 2. Observed, calculated and difference X-ray pattern for $Ba_4La_2Ti_3Nb_2O_{18}$.

peaks were indexed and there was no evidence of any second phase(s) present such that the samples were single-phase pure.

Based on the initial crystal structure model for $Ba_6TiNb_4O_{18}$ [17] and previous studies using neutron diffraction on $Ba_2La_4Ti_5O_{18}$ [19], the Rietveld refinement was carried out in the space group $R\bar{3}m$ on the assumption that A1 sites, between two adjacent perovskite-like slabs, are exclusively occupied by larger Ba atoms, A2 and A3 sites are occupied by Ba and La. B1 sites, near the vacancy, are preferentially occupied by larger Nb atoms; B2 sites and B3 sites are randomly occupied by Nb and Ti. The thermal parameters for all atoms are refined in isotropic approximation. The refinement converged with $R\text{p} = 3.81\%$, $R\text{wp} = 5.16\%$ for $Ba_5LaTi_2Nb_3O_{18}$; and $R\text{p} = 3.53\%$, $R\text{wp} = 4.83\%$ for $Ba_4La_2Ti_3Nb_2O_{18}$. The R-factors are not corrected for background. The background are linear interpolated with 78 and 24 background points for $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_4La_2Ti_3Nb_2O_{18}$, respectively. The parameters of the Rietveld refinement and residual factors for both are given in Table 1. Positional and thermal parameters and selected interatomic distances are listed in Tables 2 and 3 for $Ba_5LaTi_2Nb_3O_{18}$ and in Tables 4 and 5 for $Ba_4La_2Ti_3Nb_2O_{18}$, respectively. Calculated and different X-ray patterns are shown in Figs. 1 and 2 for $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_4La_2Ti_3Nb_2O_{18}$, respectively. The structure of $Ba_5LaTi_2Nb_3O_{18}$ is shown in Fig. 3. Both oxides are isostructural with $Ba_6TiNb_4O_{18}$ [17] and belong to $A_6B_5O_{18}$ perovskite-related structure which can be described as consisting of identical perovskite-like blocks, five corner-sharing BO_6 octahedra thick, separated by layers of vacant octahedral [17].

The unit cell parameters and unit-cell volume of $Ba_5LaTi_2Nb_3O_{18}$, $Ba_4La_2Ti_3Nb_2O_{18}$ and $Ba_2La_4Ti_5O_{18}$ slightly decrease as the content of La^{3+} and Ti^{4+} ions increase since the Shannon's effective ionic radius [21] of La^{3+} (1.36 Å) is smaller than that of Ba^{2+} (1.61 Å) at A site and the radius of Ti^{4+} (0.605 Å) is smaller than that of Nb^{5+} (0.64 Å) at B site. In $Ba_5LaTi_2Nb_3O_{18}$, the Ba/La–O bonds range from 2.687(7) to 3.292(7) Å and the (Ti, Nb)–O bonds range from 1.733(7) to 2.406(7) Å. Similarly, in $Ba_4La_2Ti_3Nb_2O_{18}$, the Ba/La–O bonds range from 2.586(6) to 3.202(7) Å, and the Ti/Nb–O bonds range from 1.770(7) to 2.326(7) Å.

The microwave dielectric properties of $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_4La_2Ti_3Nb_2O_{18}$ ceramics are shown in Table 6. Both ceramics exhibit high dielectric constant in the range 55.1–57.3, high quality factors with Qf in the range 18,456–21,273 GHz. Compared with our previous work [10–11], the dielectric constant and quality factors Qf for both ceramics have been slightly increased by increasing the times of calcination and sintering, respectively, and this might be concerned with the increased crystallinity and relative densities.

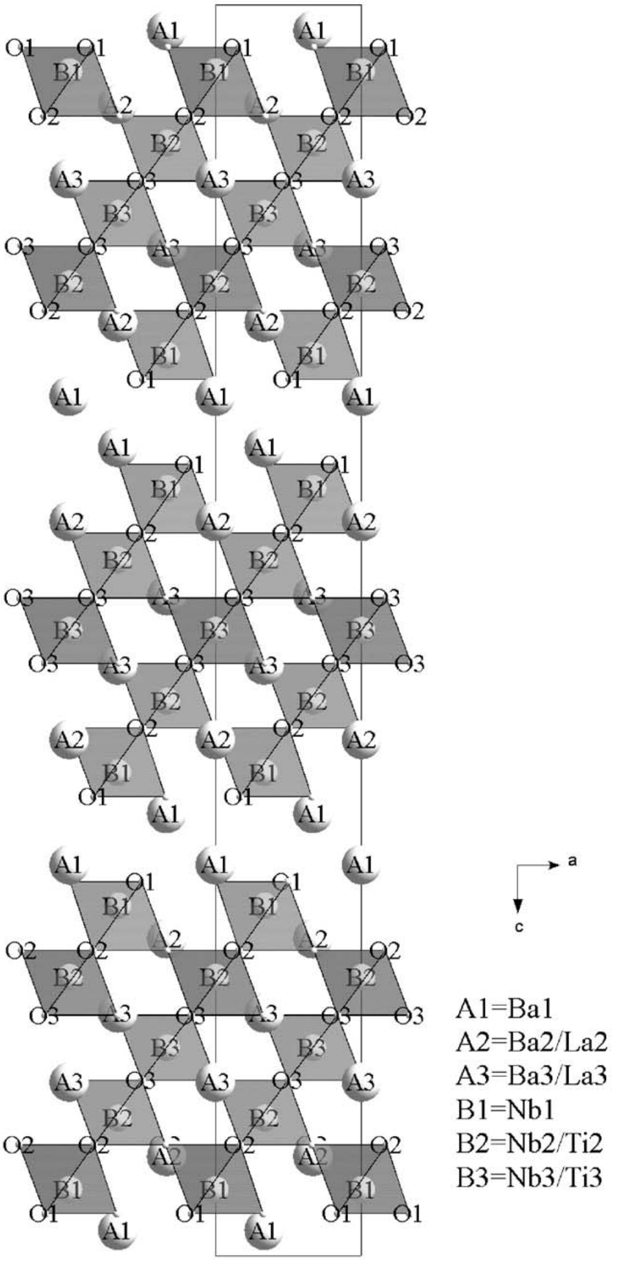

Fig. 3. Crystal structure of $Ba_5LaTi_2Nb_3O_{18}$.

The temperature coefficients of resonant frequency τ_f of $Ba_4La_2Ti_3Nb_2O_{18}$, $Ba_5LaTi_2Nb_3O_{18}$ compared with $Ba_2La_4Ti_5O_{18}$ ceramic [7] and their B-site bond valence (V_{Nb}, V_{Ti}) values are listed in Table 7. The details on the valences (V_i) of B-site ions in these crystal structures were determined by the bond valence sum, calculated using Brown's method [22] (see Eqs. (3) and (4)).

$$s_{ij} = \exp(R_0 - R_{ij})/B, \tag{3}$$

$$V_i = \sum_j s_{ij}, \tag{4}$$

where R_0 and B are known as the bond valence parameters of various cations, and a constant value

Table 6
Microwave dielectric properties of $Ba_5LaTi_2Nb_3O_{18}$ and $Ba_4La_2Ti_3Nb_2O_{18}$

Composition	Sintering conditions	Density (% theor.)	ε_r	Q	f (GHz)	Qf (GHz)
$Ba_5LaTi_2Nb_3O_{18}$	1420 °C, 6h	96.7	57.3	3950	4.6725	18456
$Ba_4La_2Ti_3Nb_2O_{18}$	1450 °C, 6h	95.3	55.1	4180	5.0894	21273

Table 7
B-site bond valance of three perovskites

Composition	R_{Nb}(Å)	R_{Ti}(Å)	$R_{B\text{-}O}$(Å)	B(Å)	V_{Nb}	V_{Ti}	$V_{unit\text{-}cell}$ (Å^3)	τ_f(ppm °C^{-1})
$Ba_5LaTi_2Nb_3O_{18}$	1.911	1.815	2.024	0.37	4.42	3.41	1188.04(2)	+138
$Ba_4La_2Ti_3Nb_2O_{18}$	1.911	1.815	1.977	0.37	5.02	3.87	1160.57(2)	+61
$Ba_2La_4Ti_5O_{18}$ [7,19]		1.815	1.955	0.37		4.11	1107.42	−36.4

(0.37 Å), respectively, and then R_{ij} means the interatomic distance between cation i and j. In this paper R_{ij} is the mean bond length of B–O.

It has been reported that the τ_f could be effectively evaluated by the *B*-site bond valence in the perovskite structure [23]. It is clear that the τ_f of these ceramics gradually decrease with an increase in *B*-site bond valances due to a decrease in unit-cell volumes with increasing content of La and Ti ions. Therefore, the τ_f might be controlled with the increase of *B*-site bond valence in $A_6B_5O_{18}$ cation-deficient perovskite compounds in the $BaO–La_2O_3–TiO_2–Nb_2O_5$ system, which is similar to the results in some ABO_3 perovskite compounds [23,24]. Further, a near-zero τ_f might be achieved in the ceramics of intermediate compositions between $Ba_4La_2Ti_3Nb_2O_{18}$ and $Ba_2La_4Ti_5O_{18}$, and this work is in progress.

4. Conclusions

$Ba_5LaTi_2Nb_3O_{18}$ and $Ba_4La_2Ti_3Nb_2O_{18}$ have been synthesized and identified as $A_6B_5O_{18}$ type cation-deficient perovskites with space group $R\bar{3}m$ and their lattice constants are $a = b = 5.7106(1)$ Å, $c = 42.0666(5)$ Å; and $a = b = 5.6602(1)$ Å, $c = 41.8296(5)$ Å, respectively. The polycrystalline samples of these compounds exhibit high dielectric constant and low dielectric loss. The τ_f of these ceramics gradually decrease with an increase in *B*-site bond valance due to the decrease in unit-cell volumes with increasing content of La and Ti ions, and this suggests the potential for microwave application of the present materials.

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