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Temperature stable (1-x)$NaCa_4V_5O_{17}$-xBaV_2O_6 microwave dielectric ceramics for ULTCC applications

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ABSTRACT

Novel temperature stable (1-x)$NaCa_4V_5O_{17}$-xBaV_2O_6 ($0.8 \le x \le 0.9$, (1-x)NCV-xBV) ceramics were successfully synthesized through a high-temperature solid phase reaction route. XRD and SEM-EDS analysis demonstrated that only $NaCa_4V_5O_{17}$ and BaV_2O_6 phases were formed without any extra phase. The introduction of BaV_2O_6 not only effectively improved the τ_f of $NaCa_4V_5O_{17}$ matrix but also considerably lowered its sintering temperature to 550 °C. Typically, an approximate-zero τ_f value around −1.0 ppm/°C was achieved for 550 °C sintered 0.12NCV-0.88BV ceramics with low ε_r of 10.9 and Qxf of 15,500 GHz (at 10.3 GHz). Its good compatibility with Al electrode furthermore made 0.12NCV-0.88BV composites suitable for ULTCC applications.

1. Introduction

Nowadays, there is a growing care about the microwave dielectric ceramics, which are used in 5G wireless communications as advanced substrates, dielectric radome, dielectric filter et al. [1–3]. As the 5G era is arrival, it puts forward higher requirement for advanced dielectric materials. The dielectric materials owing low dielectric loss or high quality factor (Qxf for frequency selectivity), small dielectric permittivity ($\varepsilon_r < 15$ for fast signal transmission) and approximate-zero temperature coefficient of resonant frequency (τ_f for thermal stability) get the research hotspots [4,5]. Meanwhile, dielectric ceramics owing low heating temperature are demanded by LTCC, even ULTCC technology, which is conducive to compact electronic devices [6–8]. Hence, it is urgently required to develop dielectric materials with superior performances along with low or even ultra-low sintering temperature.

Recently, vanadium-containing compounds aroused researcher's interest once again since their low sintering temperature and good dielectric performances at microwave region [9–13]. Several vanadium host ceramics systems have been investigated for the application in LTCC domains, such as $Ba_3A(V_2O_7)_2$, (CaBi)$(MoV)O_4$, CaV_2O_6 et al. Quite recently, Xie et al. [14] reported the fabrication and spectrum properties characterization for $NaCa_4V_5O_{17}$ with triclinic structure. Later, Yin et al. first reported the dielectric performances at microwave region (ε_r = 9.7, Qxf = 51,000 GHz, τ_f = −84 ppm/°C) of 840 °C-sintered $NaCa_4V_5O_{17}$ ceramics, while they also reported the good chemical compatibility of $NaCa_4V_5O_{17}$ with Ag [15]. Yet, in our research it was found that the poor chemical compatibility between $NaCa_4V_5O_{17}$ and Ag, when prepared $NaCa_4V_5O_{17}$ using V_2O_5 as raw material, which posed challenges for LTCC applications and should be resolved [16]. However, thus far, the possible ULTCC application of $NaCa_4V_5O_{17}$ has not been investigated. Therefore, in order to make $NaCa_4V_5O_{17}$ as a possible ULTCC material, the sintering temperature of $NaCa_4V_5O_{17}$ ceramics should be below the melting point of Al (700 °C). Considering the merits of BaV_2O_6 with seldom large positive τ_f and ultralow sintering temperature of 550 °C [17], **it** was chose to modulate the τ_f and reduce the firing temperature for $NaCa_4V_5O_{17}$ matrix. In present study, the (1-x)$NaCa_4V_5O_{17}$-xBaV_2O_6 composite ceramics were fabricated, and their sintering behavior, microwave dielectric characterizations were discussed. To assess its possibility in ULTCC technology, we also studied the chemical compatibility between 0.12 $NaCa_4V_5O_{17}$ -0.88 BaV_2O_6 and Al electrode.

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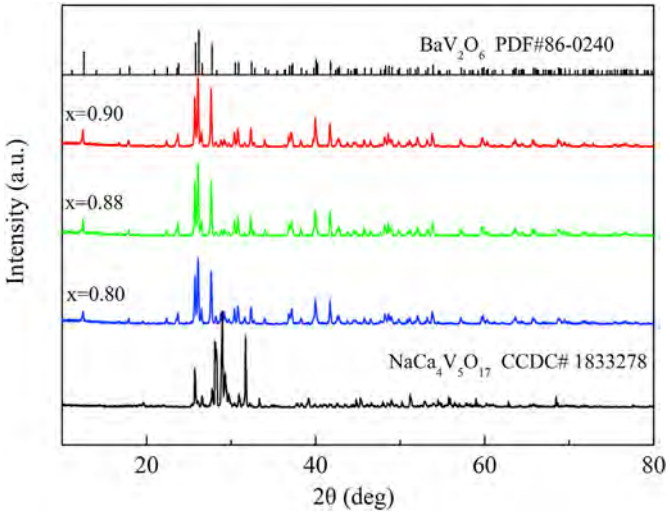

Fig. 1. PXRD patterns of 800 °C sintered $NaCa_4V_5O_{17}$ ceramics and 550 °C sintered (1-x)$NaCa_4V_5O_{17}$-xBaV_2O_6 ($0.8 \le x \le 0.9$) ceramics.

Table 1
The measured and calculated ε_r and τ_f values of (1-x)$NaCa_4V_5O_{17}$-xBaV_2O_6 ceramics sintered at 550 °C for 4 h.

Composition x	ε_r	ε_{cal}	τ_f (ppm/°C)	$\tau_{f\ cal}$ (ppm/°C)
0.80	10.86	10.74	−12.7	−14.1
0.85	10.96	11.02	1.0	3.0
0.90	10.97	11.10	3.0	8.0

2. Experimental procedure

The (1-x)$NaCa_4V_5O_{17}$-xBaV_2O_6 (x = 0.8, 0.88, 0.9) composite ceramics were fabricated through a high-temperature solid phase reaction method. High-purity oxides or carbonates: $BaCO_3$ (99%), Na_2CO_3 (99.8%), V_2O_5 (99%) and $CaCO_3$ (99%) were doped as raw materials. Predried starting materials in stoichiometric $NaCa_4V_5O_{17}$ (NCV) and BaV_2O_6 (BV) compositions were mixed with ethanol in a nylon jar and stirred for 8 h using ZrO_2 balls. The NCV and BV powders were presintered under 600 °C holding for 4 h and 460 °C for 3 h, individually. Then, pre-sintered NCV and BV powders were blended in different molar fraction, and re-milled for 8 h. After drying, the mixture powders were mixed with 5 wt% polyvinylalcohol solution as binder, granulated and pressed into cylindrical disks (Φ10 mm × 6 mm) at 200 MPa. Finally, the (1-x)NCV-xBV disks were sintered from 525 to 600 °C with an interval of 25 °C in air.

The phase constitutions, surface morphologies and main chemical composition of fired samples along with their compatibility with Al powders were identified by powder X-ray diffraction (PXRD, Smartlab, Japan), scanning electron microscope, (SEM, Gemini300, Germany) and energy dispersive spectrometer (EDS). Archimedes-method was used to gauge the bulk density of obtained ceramics. The ε_r, Qxf and τ_f values of (1-x)NCV-xBV composite were tested through a vector network analyzer (Keysight Tech., E5071C ENA) at 9.0–11.3 GHz equipped with the TE_{018} shielded cavity. The τ_f was computed according to the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \times 10^6 \quad (1)$$

3. Results and discussion

Fig. 1 gives the PXRD profiles of 800 °C sintered $NaCa_4V_5O_{17}$ ceramics and 550 °C sintered (1-x)$NaCa_4V_5O_{17}$-xBaV_2O_6 ($0.8 \le x \le 0.9$) composite ceramics. As seen in Fig. 1, there were no extra diffraction peaks except for the diffraction peaks of $NaCa_4V_5O_{17}$ (CCDC# 1,833,278) and BaV_2O_6 (JCPDS# 86–0240), indicating that a stable $NaCa_4V_5O_{17}$–BaV_2O_6 diphasic ceramics was achieved, as was also demonstrated by later SEM results. The good chemical compatibility between $NaCa_4V_5O_{17}$ and BaV_2O_6 could attribute to their diverse crystal structure, that is, $NaCa_4V_5O_{17}$ exhibits a triclinic structure, whereas BaV_2O_6 crystallizes in a orthorhombic structure [14,17]. The good chemical compatibility between $NaCa_4V_5O_{17}$ and BaV_2O_6 is conducive to modulation of the dielectric properties of $NaCa_4V_5O_{17}$ matrix, particularly for its τ_f [18], which is well presented in our cases.

Table 1 summarizes the measured and calculated ε_r and τ_f values of 550 °C for 4 h sintered (1-x)$NaCa_4V_5O_{17}$-xBaV_2O_6 composite ceramics. The τ_f could be continuously tuned with the change of the blend mixture proportion of $NaCa_4V_5O_{17}$ and BaV_2O_6. Typically, a near zero τ_f

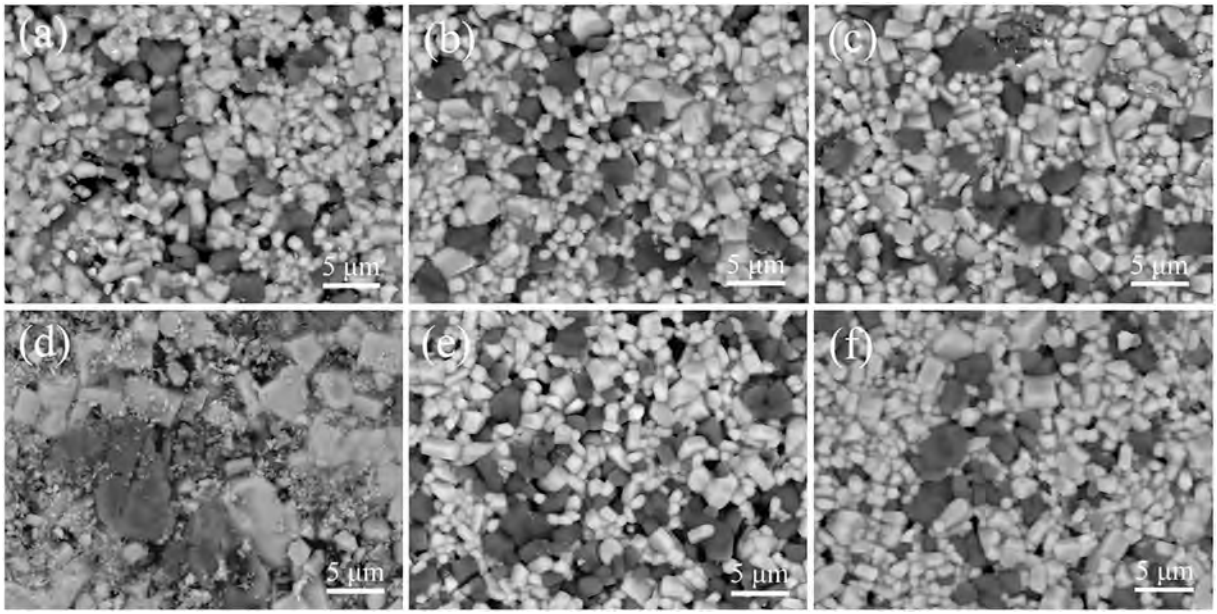

Fig. 2. Typical backscattered electron micrographs of (1-x)$NaCa_4V_5O_{17}$-xBaV_2O_6 composite ceramics sintered at diverse temperatures: (a) x = 0.88, 525 °C; (b) x = 0.88, 550 °C; (c) x = 0.88, 575 °C; (d) x = 0.88, 600 °C; (e) x = 0.8, 550 °C; (f) x = 0.9, 550 °C.

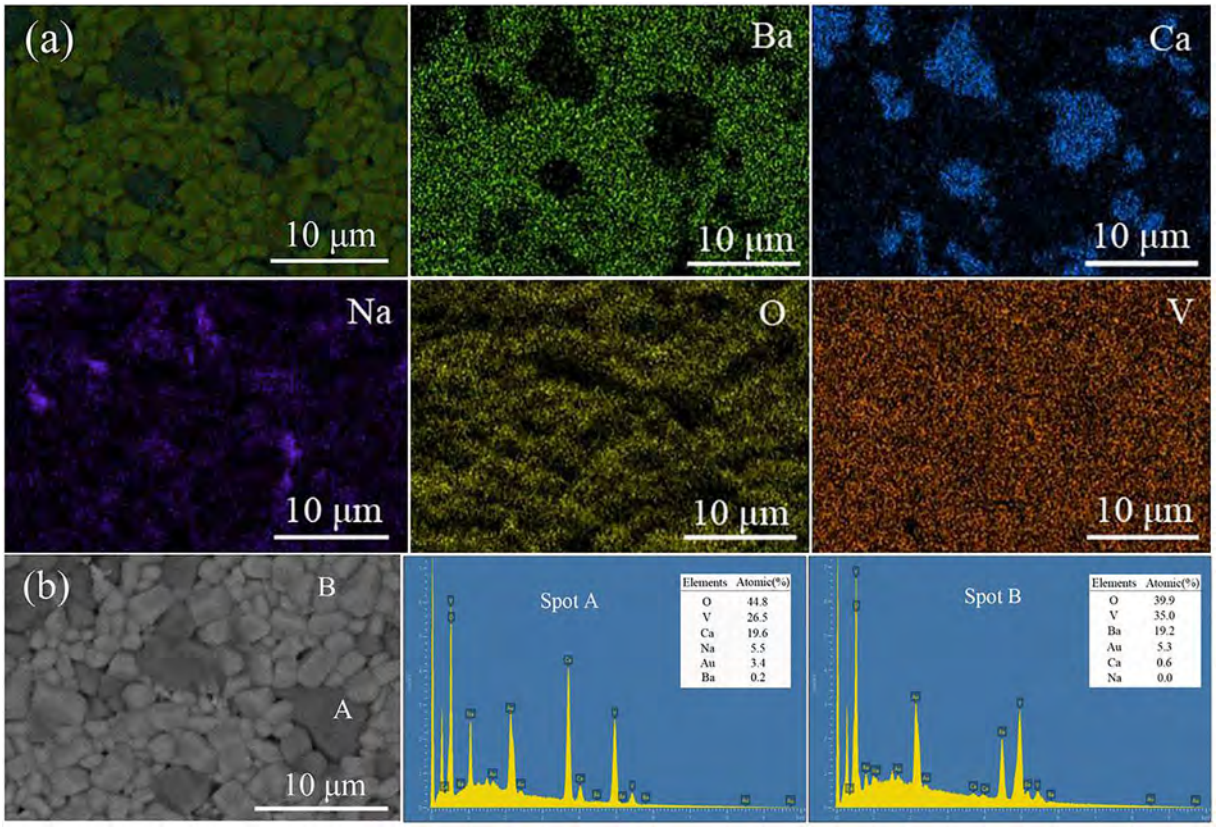

Fig. 3. (a) EDS (elements) mapping, (b) EDS spectra of $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ samples sintered at 550 °C.

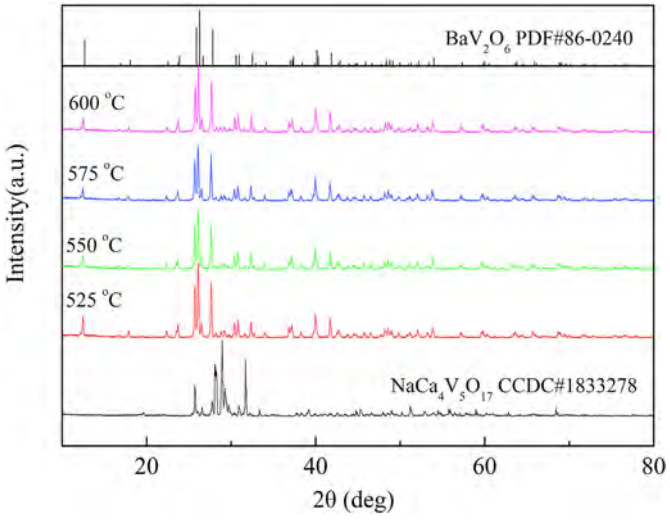

Fig. 4. PXRD patterns of $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ ceramics heated at different temperatures.

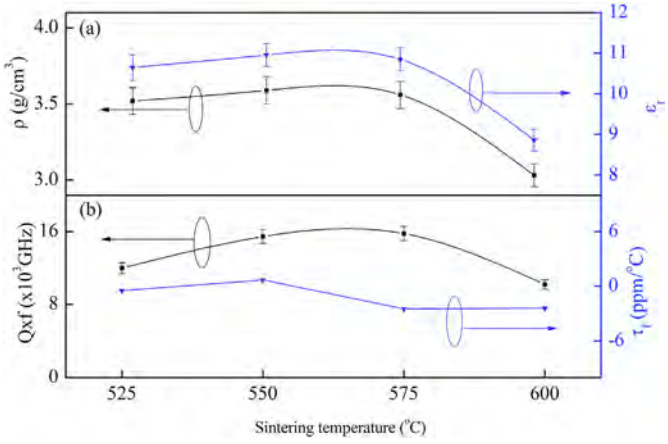

Fig. 5. Variation of the density and microwave dielectric properties of the $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ ceramics versus firing temperature.

could be obtained for $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ composite ceramics.

Fig. 2 displays the typical backscattered electron micrographs of (1-x)$NaCa_4V_5O_{17}$-xBaV_2O_6 composite ceramics sintered at diverse temperatures. A porous structure or abnormal grain growth were observed for the ceramics sintered at temperature below 550 °C or above 575 °C, respectively, which would resulted in low bulk density. However, from Fig. 2(b) and (c), a pretty compact microstructure without any obvious pores was obtained when samples sintered at 550–575 °C, facilitating the dielectric performance of ceramics [19]. Meanwhile, two different colors grains were observed for all specimens: bright and dark grains, indicating the different phase constitution.

EDS (elements) mapping and spectra of $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ samples sintered at 550 °C were conducted to indentify the phase constitution of the distinct color grains. The corresponding results are presented in Fig. 3. As indicated in Fig. 3(a), the O and V elements are uniformly distributed over in all the grains, whereas the Na and Ca elements are mainly distributed on the dark grains and Ba element on the white grains, respectively. According to the quantitative EDS spectra (Fig. 3(b)), the dark (marked A) and white grains (marked B) approximately corresponded to $NaCa_4V_5O_{17}$ and BaV_2O_6 separately, which was in accordance with PXRD results.

Fig. 4 depicts the PXRD patterns of $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ composite ceramics heated at different temperatures. As shown in Fig. 4, with sintering temperature raised, all samples displayed mixed

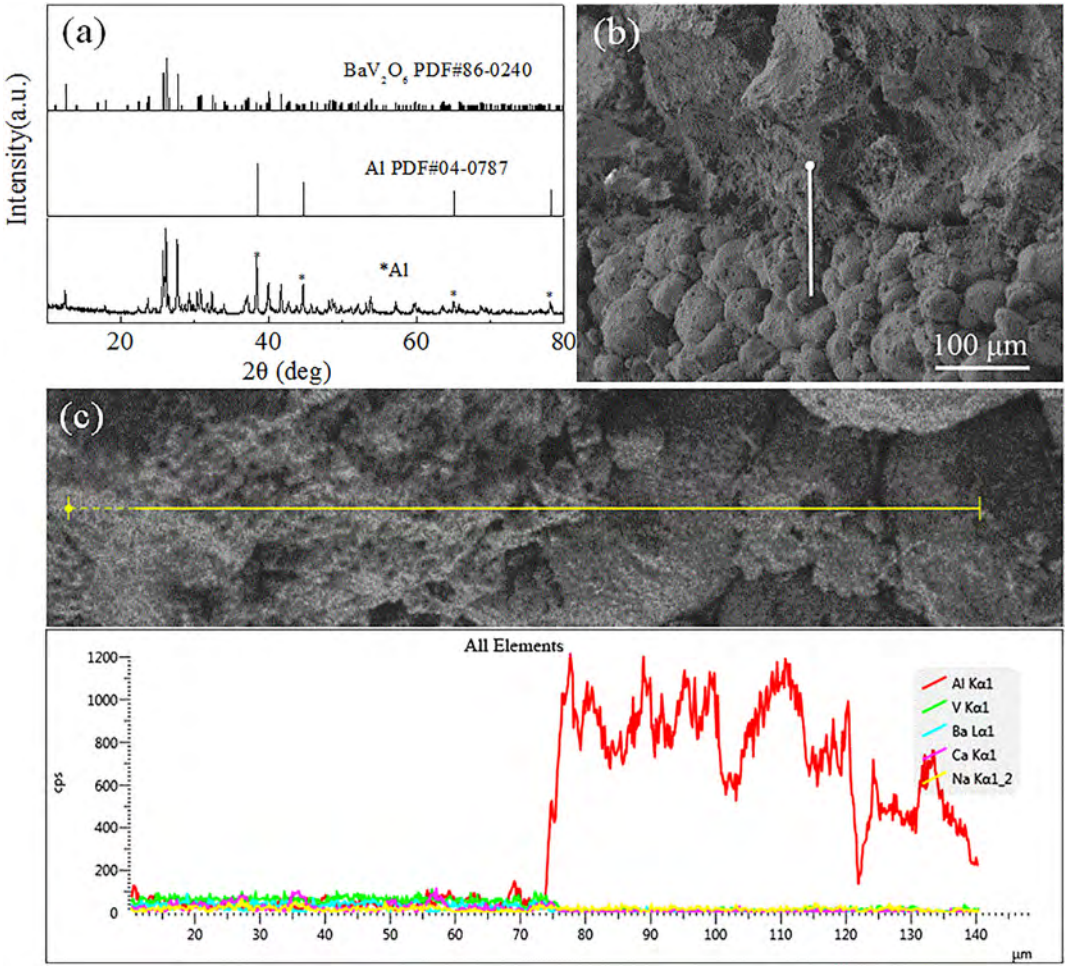

Fig. 6. (a) PXRD, (b) **fracture SEM images, (c) EDS line-scans** of $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ composites co-fired with 20 wt% Al powders at 550 °C.

phases and remained identical, including the main phase BaV_2O_6 with orthorhombic structure and small amount of triclinic $NaCa_4V_5O_{17}$ phase.

The plots of dielectric properties of $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ composite ceramics versus firing temperature are represented in Fig. 5. As shown in Fig. 5 (a), the bulk density initially ascended, reached saturated values at 550–575 °C, and thereafter descended with an elevated temperature. The change in bulk density was consistent with the morphology analysis aforementioned. The changes of ε_r and Qxf with an elevated temperature presented a resemble tendency as that of bulk density. The supreme values of ε_r and Qxf corresponded to the maximum density, implying the close rely of ε_r and Qxf on density. Thus, the elevated density may be responsible for the increment of ε_r and Qxf values, whereas the rapid growth of partial grains corresponded to the decline of ε_r and Qxf values [20]. In addition, as seen in Fig. 5 (b), the τ_f value of the $0.12NaCa_4V_5O_{17}$-0.88 BaV_2O_6 composite ceramics waved ~ −1.0 ppm/°C indifferently to sintering temperature variation, which was due to the invariable phase composition [21]. Compared to Refs. [15], the introduction of an amount of BaV_2O_6 in $NaCa_4V_5O_{17}$ not only improved the τ_f value but also remarkably lowered the sintering temperature of $NaCa_4V_5O_{17}$-basic ceramics. This may make the $NaCa_4V_5O_{17}$-basic ceramics as a potential ULTCC material.

The chemical compatibility with Al electrode is the essential require of ULTCC material [22]. Therefore, we carried out the research on the chemical compatibility of $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ composites with Al powders. Fig. 6 shows the PXRD and **fracture SEM images coupled with EDS line-scans** of 550 °C sintered $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ composites doped with 20 wt% Al powders. There were no additional phases except for those of the Al (JCPDS #04–0787) and composite ceramics, as shown in Fig. 6 (a). **The interface was well maintained and no diffusion occurred between $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ and Al during the firing process, as confirmed in** Fig. 6 (b) and (c). The absence deficiency of any extra phases including Al and no diffusion indicated the good chemical compatibility between $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ composites and Al electrode, suggesting it could serve in ULTCC applications.

4. Conclusions

Temperature stable (1-x)$NaCa_4V_5O_{17}$-xBaV_2O_6 ($0.8 \le x \le 0.9$) have been fabricated through a conventional solid phase reaction route. The impacts of sintering temperature and composition on crystalline phases, microstructure, microwave dielectric characteristics of (1-x) $NaCa_4V_5O_{17}$-xBaV_2O_6 were investigated. Coexistence of $NaCa_4V_5O_{17}$ and BaV_2O_6 phases as well as its chemical compatibility with Al powders were verified by the XRD and SEM-EDS analyses. The BaV_2O_6 addition could improve the τ_f and lower the sintering temperature of $NaCa_4V_5O_{17}$-basic ceramics simultaneously. Favorable dielectric properties were achieved in the 0.12 $NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ composite ceramics fired at 550 °C: ε_r~10.9, Qxf~ 15,500 GHz (at 10.3 GHz), τ_f ~ −1.0 ppm/°C. Its well compatible with Al electrode further rendered the $0.12NaCa_4V_5O_{17}$-$0.88BaV_2O_6$ composites suitable for ULTCC applications.

Declaration of competing interest

The authors declare that they have no known competing financial interestsor personal relationships that could have appeared to influence the work reported in this paper.

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