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A novel ultra-low temperature sintered Li_2CO_3 doped $Ba_3V_2O_8$ microwave ceramics

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Abstract

Novel $Ba_3V_2O_8$ + x wt.% Li_2CO_3 ($0 \leq x \leq 12$) ceramics were synthesized at ultra-low sintering temperatures. The doping effect of Li_2CO_3 on microwave properties and the principle of ultra-low temperature sintering was investigated. The XRD refinement demonstrated that Q × f value showed a strong relationship with packing fraction, bond energy of V-O, and lattice energy as a function of Li_2CO_3 content. An appropriate amount of Li_2CO_3 dramatically reduced the sintering temperature of $Ba_3V_2O_8$ ceramic from 1200 to 660 °C. Li_2CO_3 addition could modify the τ_f value of $Ba_3V_2O_8$ to reach the near-zero value. The 8 wt.% Li_2CO_3 doped $Ba_3V_2O_8$ ceramic sintered at 660 °C displayed good microwave properties: ε_r = 13.07, Q × f = 33,000 GHz, and τ_f = 13.0 ppm/°C.

Keywords: ceramics, sintering, crystal structure, microwave property

1. Introduction

Previously, $Ba_3V_2O_8$ ceramic needed the high sintering temperature of 1600°C to acquire the dielectric constant (ε_r) of 11, Q × f of 62,347 GHz, and temperature coefficient of resonant frequency

(τ_f) of 28.8 ppm/°C [1]. Further, the 0.5 wt.% B_2O_3 added $Ba_3V_2O_8$ was sintered well at 950°C and achieved good microwave properties of ε_r= 12.5, Q × f = 41,065 GHz, and τ_f = 38.8 ppm/°C [1]. It can be seen that the addition of low-melting-point compound can reduce the sintering temperature of $Ba_3V_2O_8$ ceramic. Accordingly, Li_2CO_3 with low-melting-point of 723 °C [2] was chose as sintering aid in our work and applied to reduce the sintering temperature of $Ba_3V_2O_8$ ceramic to 670 °C for the first time. Novel $Ba_3V_2O_8$ + x wt.% Li_2CO_3 ($0 \leq x \leq 12$) ceramics have been developed for ultra-low temperature co-fired ceramics (ULTCC) [3-4]. The influence of Li_2CO_3 addition on microstructures and microwave properties for $Ba_3V_2O_8$ ceramic was studied specifically.

2. Experimental procedure

$BaCO_3$, V_2O_5, and Li_2CO_3 with 99.9 % purity were starting materials and the solid-state reaction method was employed. According to the chemical formula, the weighed powders of $BaCO_3$ and V_2O_5 were ball-milled for 7 hours in nylon jars using zirconium media. The $Ba_3V_2O_8$ powders were produced by calcining the dried blend at 800 °C for 2 hours. After that, the $Ba_3V_2O_8$ powders were mixed with x wt.% Li_2CO_3 (x = 0, 6, 8, 10, 12) powders and re-milled for 7 hours. Thereafter, the dried powders were grounded with 15 wt.% of PVA and formed into pellets at 15MPa, and then fired at different temperature (640 ~ 1200 °C) for 4 hours. Crystalline phases were investigated by the X-ray diffraction (XRD, PANalytical PW3040/60, Netherland). Raman spectra were recorded by the Raman Microscope (inVia, Renishaw, UK). Differential scanning calorimetry (DSC, Netzsch STA 449C, Germany) was applied to study the chemical reaction under 1000 °C. Microwave properties were obtained from the network analyzer (Agilent E5071C, US) using the Hakki-Coleman dielectric resonator method. The surface microstructure of specimens was investigated via scanning electron microscopy (SEM, FEI

Inspect F, UK). The morphology and crystal structure was further researched using the high-resolution transmission electron microscope (HRTEM, FEI Tecnai G2 F20 S-Twin, USA).

3. Results and discussion

Figure 1a presents the XRD patterns of $Ba_3V_2O_8$ + x wt.% Li_2CO_3 ($0 \le x \le 12$) ceramics fired at the optimal temperatures. Clearly, a small amount of Li_2CO_3 cannot change the constitution of the crystalline phase and the crystallized $Ba_3V_2O_8$ phase (PDF # 82-2057) keeps the hexagonal system. Furthermore, the Rietveld refinement was implemented by GSAS-EXPGUI. The calculated data including lattice parameters, bond length, and cell volume are listed in Table 1. The refined pattern of $Ba_3V_2O_8$ + 8 wt.% Li_2CO_3 ceramic is depicted as a representative in Figure 1b. Besides, Raman spectra for $Ba_3V_2O_8$ + x wt.% Li_2CO_3 ($0 \le x \le 12$) ceramics are drawn in Figure 1c. It is noticed that the vibration corresponding to $(VO_4)^{3-}$ group originated from the structure of $Ba_3V_2O_8$ are detected at 837 cm^{-1} and 328 cm^{-1}. The packing fraction, the bond energy of V-O, and the lattice energy can be calculated by following formulas.

The packing fraction is obtained from the formula below:

$$Packing\ \ fraction\ (\%) = 4\pi \times \frac{3\times r_{Ba}^3 + 2\times r_V^3 + 8\times r_O^3}{3\times unit\ cell\ volume} \times Z \quad (1)$$

where Z is the number of units per unit cell. The $E\mu\ b$ is determined by the $E\mu\ c$(the nonpolar covalence energy) and the $E\mu\ i$(the complete ionic energy) [5-7]:

$$E_b^{\mu} = \mathrm{t}_c E_c^{\mu} + t_i E_i^{\mu} \quad (2)$$

$$1 = \mathrm{t}_c + t_i \quad (3)$$

$$t_i = \left| \frac{(S_A + S_B)/\Delta S_B}{2} \right| \quad (4)$$

where t_c and t_i are the covalent and ionic blending coefficients, S_A and S_B are the electronegativities of A and B ions, ΔS_B is the change for complete loss of an electron, respectively. Among them, the $E\mu$ c part is calculated from the formula as follows:

$$E_c^{\mu} = \frac{(r_{cA} + r_{cB})}{d^{\mu}} (E_{A-A} E_{B-B})^{1/2} \tag{5}$$

where r_{cA} and r_{cB} are the covalent radii [8]. The homonuclear bond energies $E_{A\text{-}A}$ and $E_{B\text{-}B}$ are chosen as $E_{V\text{-}V}$ = 269.3 kJ/mol, $E_{O\text{-}O}$ = -497.375 kJ/mol, according to the handbook [9]. The $E\mu$ i part is calculated by:

$$E_{\mathrm{i}}^{\mu} = \frac{33200}{d^{\mu}} \tag{6}$$

where d^{μ} is the bond length, and 33200 is constant. The lattice energy is calculated from formulas proposed by Jenkins [10]:

$$U = AI(2I/V_m)^{\frac{1}{3}} \tag{7}$$

$$2I = \sum_i n_i Z_i^2 \tag{8}$$

$$V_m = V_{cell} / Z \tag{9}$$

where A = 121.39 kJ mol^{-1} nm, I is the ionic strength and V_m is the volume per formula unit.

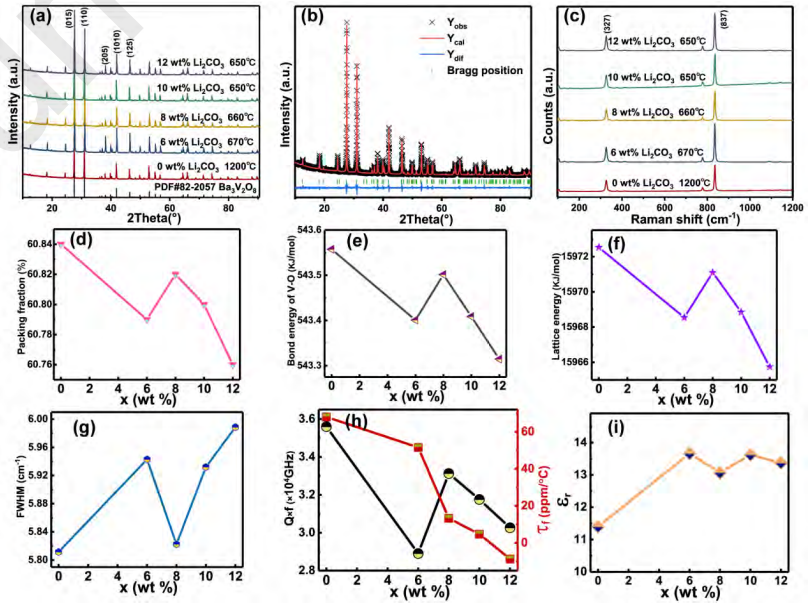

Fig. 1 (a) XRD patterns of $Ba_3V_2O_8$ + x wt.% Li_2CO_3 ($0 \le x \le 12$) ceramics; (b) Rietveld refinement patterns of $Ba_3V_2O_8$ + 8 wt.% Li_2CO_3 ceramic; (c) Raman spectra of $Ba_3V_2O_8$ + x wt.% Li_2CO_3 ($0 \le x \le 12$) ceramics; (d) packing fraction; (e) bond energy of V-O; (f) lattice energy; (g) FWHM; (h) Q × f and τ_f; (i) ε_r value for Li_2CO_3 - added $Ba_3V_2O_8$ ceramics sintered at optimal temperatures (x=0, at 1200℃; x = 6, at 670 ℃; x = 8, at 660 ℃; x = 10 and 12, at 650 ℃) as a function of x value.

Table 1. Rietveld results of $Ba_3V_2O_8$ + x wt.% Li_2CO_3 ($0 \le x \le 12$) ceramics sintered at optimal temperatures.

x	Lattice parameters a = b = c (Å)	Bond length (Å) $2 \times d_{V-O}$	V_{cell} (Å^3)	R_{wp} (%)	R_p (%)	χ^2
0	7.8489	1.69995	205.632	6.77	5.07	1.947
6	7.8511	1.70039	205.786	6.89	5.19	2.134
8	7.8494	1.70008	205.687	7.83	5.74	2.653
10	7.8510	1.70037	205.774	7.30	5.50	2.217
12	7.8521	1.70066	205.894	6.78	5.12	1.994

R_{wp}: reliability factor of weighted patterns; R_p: reliability factor of patterns; χ^2: goodness of fit

Table 1 reveals that some Li^+ enter into the $Ba_3V_2O_8$ structure. Accordingly, as shown in Figures 1(d-f), Q × f values possess a close correlation with the packing fraction, the bond energy of V-O, and the lattice energy as a function of Li_2CO_3 content. The probable principle is that the lattice vibration is affected by the packing fraction, the bond energy of V-O, and the lattice energy. Therefore, the enlargement of them results in intrinsic loss reducing, and then improves the Q × f values further. Comparing Figure 1g with Figure 1h, the FWHM of the peak 837 cm^{-1} in Raman spectra demonstrate inversely trending with the Q × f value. This phenomenon can be attributed to the that the low FWHM value means a high ordering degree of cations, which result in the dielectric loss reduction. Moreover,

the τ_f values are calculated from the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \tag{10}$$

where f_{25} and f_{85} are the resonant frequencies at 25 °C and 85 °C. As illustrated in Figure 1h, with the augment of Li_2CO_3 content, the τ_f value reduces from 67 to -8 ppm/°C. The $Ba_3V_2O_8$ + 10 wt.% Li_2CO_3 ceramic sintered at 650 °C possess τ_f values of 4.7 ppm/°C. As depicted in Figure 1i, the addition of Li_2CO_3 increases the ε_r value.

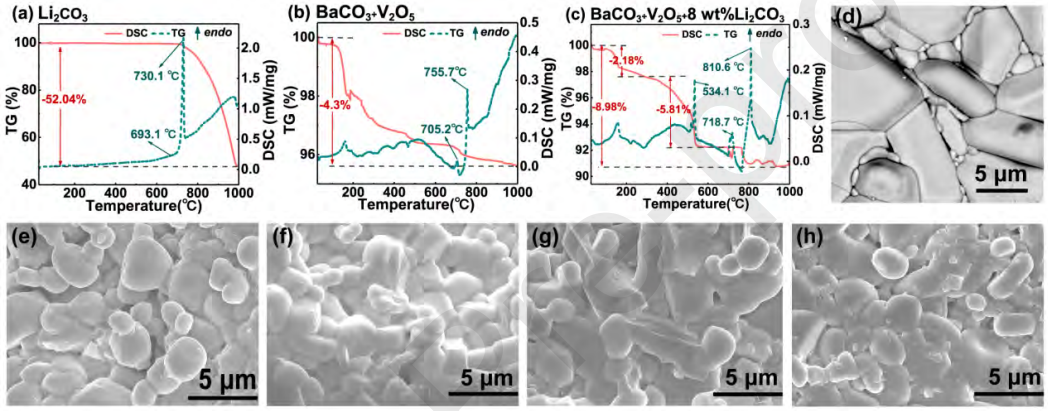

Fig. 2 TG-DSC curves of (a) pure Li_2CO_3 powder; (b) mixed powder of $BaCO_3$ and V_2O_5; (c) mixed powder of $BaCO_3$, V_2O_5 and 8 wt.% Li_2CO_3; SEM images of $Ba_3V_2O_8$ + x wt.% Li_2CO_3 ceramics: (d) x=0, at 1200 ℃; (e) x = 6, at 670 ℃; (f) x = 8, at 660 ℃; (g) x = 10 and (h) x = 12, at 650 ℃.

In order to study the principle of Li_2CO_3 lowered the sintering temperature of samples, thermal analyses are carried on the pure Li_2CO_3 powder (Figure 2a), the mixed powder of $BaCO_3$ and V_2O_5 (Figure 2b), and the mixed powder of $BaCO_3$, V_2O_5, and 8 wt.% Li_2CO_3 (Figure 2c). Comparing the TG-DSC curves, it is found that pure Li_2CO_3 hardly decomposes when the sintering temperature below 730 ℃ (Figure 2a), and the endothermal peak at 755.7 ℃ corresponds to the decomposition of $BaCO_3$ (Figure 2b) meaning no reaction happens between $BaCO_3$ and V_2O_5 under such low-temperature condition. However, the decomposition temperature of $BaCO_3$ or Li_2CO_3 is greatly reduced and the

reaction of $BaCO_3$ and V_2O_5 is promoted in Figure 2c. Obviously, it proves that some second phase with a low melting temperature is formed, which is conducive to lower the reaction temperature of $BaCO_3$ and V_2O_5. In further, Figures 2d-h show the SEM images of 0~12 wt.% Li_2CO_3 doped $Ba_3V_2O_8$ ceramics sintered at optimal temperatures. It can be seen that the shape and size of grains changed with the addition of Li_2CO_3, and some white particles deposited on the surface of the grains, which is considered as the second phase formed as a liquid.

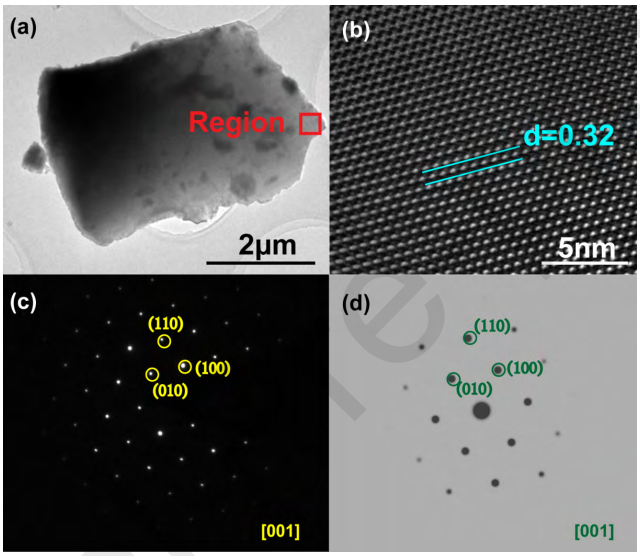

Fig. 3 (a) The bright-filed TEM image of $Ba_3V_2O_8$ + 8 wt.% Li_2CO_3 ceramic; (b) the HRTEM image and the amplifying HRTEM image for the region, (c) the SAED image for the region; (d) the TEM diffraction simulations of the $Ba_3V_2O_8$ hexagonal single crystal in the R-3 m space group taken along the [001] zone-axis.

The crystal structure and morphology of $Ba_3V_2O_8$ + 8 wt.% Li_2CO_3 ceramic were confirm by HRTEM further. As demonstrated in Figure 3a, the bright-field TEM micrograph exhibits the detail of the morphology. The HRTEM image from the thin region is depicted in Figure 3b, which illustrates the appearance of a regular atomic arrangement. Moreover, the TEM diffraction simulation of $Ba_3V_2O_8$ (R-3 m (166)) crystal with the hexagonal structure is implemented via Single Crystal. The selected area electronic diffraction (SAED) pattern of the same area through the [001] zone-axis is depicted in Figure

3c, revealing that the grains are well crystallized and the experimental diffraction pattern is in good agreement with the simulated pattern shown in Figure 3d.

4. Conclusions

Novel Li_2CO_3 doped $Ba_3V_2O_8$ ceramic was developed for ULTCC applications. XRD and SAED analysis verified the crystal structure of $Ba_3V_2O_8$ + x wt.% Li_2CO_3 ($0 \leq x \leq 12$) ceramics keep the hexagonal system. The Q × f values were proved to behave inversely tendency with the FWHM values, while having a positive correlation with packing fraction, bond energy of V-O and lattice energy. By adding Li_2CO_3 into $Ba_3V_2O_8$, near-zero τ_f was achieved when x = 10. The 8 wt.% Li_2CO_3 added $Ba_3V_2O_8$ ceramics sintered at 660 °C behaved superior microwave performance: ε_r = 13.07, Q × f = 33,000 GHz, and τ_f =13.0 ppm/°C.

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Credit author statement

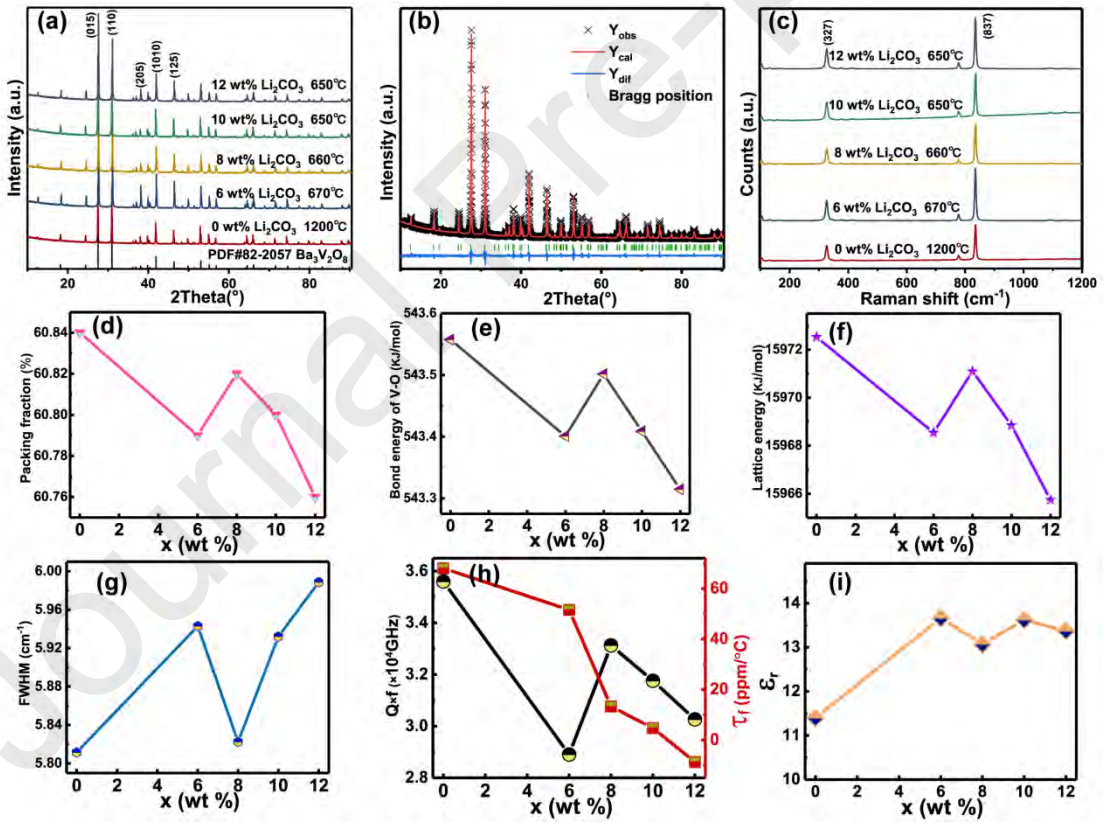
Yaping Deng: Conceptualization, Validation, Formal analysis, Investigation, Writing-original draft.

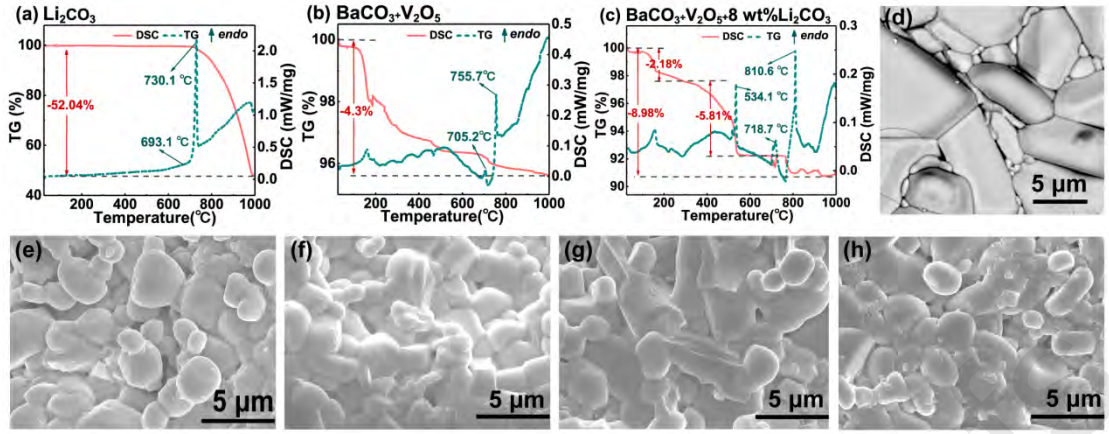
Pengyu Yao: Conceptualization, Vali-dation, Investigation.

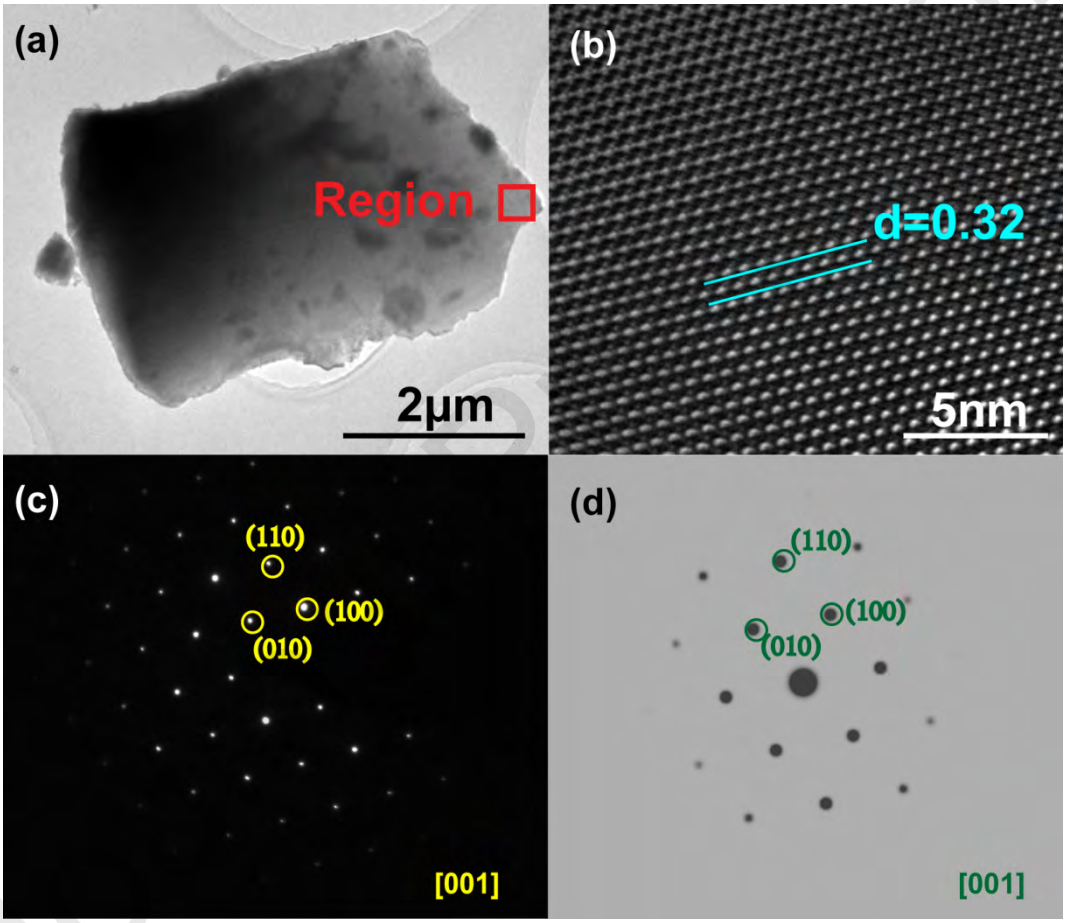
Bo Li: Data curation, Writing-review&editing, Supervision.

Declaration of Interest Statement

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







1. An appropriate amount of Li_2CO_3 dramatically lowers the sintering temperature of $Ba_3V_2O_8$ ceramics.

2. Q × f values have correlation with ordering degree of cation, packing fraction, bond energy of V-O and lattice energy.

3. The τ_f value of $Ba_3V_2O_8$ shifts to near zero along with the augment of

Li_2CO_3.

4. Novel $Ba_3V_2O_8$ - 8 wt.% Li_2CO_3 ceramics sintered at 660 ℃ exhibits optimum microwave properties.