

Low sintering BaNd₂Ti₄O₁₂ microwave ceramics prepared by CuO thin layer coated powder

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Abstract

Recently, BaO–Nd₂O₃–TiO₂ systems are widely studied for microwave applications because of their high dielectric constant and high quality factor. However, pure BaNd₂Ti₄O₁₂ ceramics without additives have to be sintered above 1300 °C to achieve densification. Copper oxide has been known as a good sintering aid for electronic ceramics and less reactive toward silver. We have introduced the CuO into BaNd₂Ti₄O₁₂ by modifying the surface of BaNd₂Ti₄O₁₂ by CuO thin layer on the calcined powder instead of mixing CuO directly with BaNd₂Ti₄O₁₂ powder. The process reduces the amount of sintering aid and minimized the negative impact of sintering aid on dielectric properties such as quality factor. The CuO precursor solution of Cu(CH₃COO)₂, Cu(NO₃)₂ and CuSO₄, were used to prepare CuO thin layer. They were investigated individually to determine their effects on the densification, crystalline structure, microstructure and microwave dielectric properties of BaNd₂Ti₄O₁₂. The CuSO₄ coated BaNd₂Ti₄O₁₂ sintered at 1150 °C has exhibited better dielectric properties than those of CuO doped BaNd₂Ti₄O₁₂ (k , 62.5 versus 61.2; $Q \times f$, 11,500 GHz versus 10,500 GHz). The thin layer dopant coating process has been found to be a very effective way to lower ceramic sintering temperature without scarifying its dielectric properties.

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1. Introduction

Low temperature co-firable ceramics (LTCC) possessing good microwave dielectric properties have been widely investigated due to the necessity for miniaturization of devices in order to reduce the size of wireless communication system. Because of the high sintering temperature, Ag–Pd electrode is the only choice for multilayer ceramic components (MLCCs). Thus, it is desirable to replace the poor conductivity and high cost Ag–Pd electrode with the better properties and lower cost of silver or copper electrodes.

BaO–Nd₂O₃–TiO₂ series materials possess marvelous microwave dielectric properties such as high dielectric constant and high quality factor, and were extensively investigated for the applications in microwave devices.^{1–8} Recently, the chemical

composition of BaNd₂Ti₄O₁₂ has emerged as a good microwave material because it exhibits high dielectric constant ($k \sim 84$) and high quality factor ($Q \times f \sim 7800$ GHz), but its high sintering temperature (>1350 °C) is difficult for LTCC process.⁸ Oxide dopants (B₂O₃, Bi₂O₃, V₂O₅, etc.) and glasses (low temperature melting glasses) have been used as sintering aids. However, some studies have reported that oxide dopants and the glasses exhibited pronounced effects on the microstructure and microwave dielectric properties of the materials. Large and interconnected pores were observed due to the agglomeration of dopants during cofiring process.^{9–13}

Copper oxide has been known as a good sintering aid and less reactive toward silver.^{14–16} We propose to introduce the CuO into BaNd₂Ti₄O₁₂ by modifying the surface of BaNd₂Ti₄O₁₂ by CuO thin layer on the calcined powder instead of mixing CuO directly with BaNd₂Ti₄O₁₂ powder. The process will reduce the amount of sintering aid and eliminate the negative impact of sintering aid on dielectric properties such as quality factor. The CuO layer was prepared from three kinds of Cu precursors: Cu(CH₃COO)₂, Cu(NO₃)₂ and CuSO₄, respectively. We

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have investigated each precursor individually in determining its effects on the densification, crystal structure, microstructure and microwave dielectric properties of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$.

2. Experimental

Reagent grade oxide powders with an appropriate molar ratio of BaCO_3 , Nd_2O_3 and TiO_2 (99.9% purity each, Alfa Chemicals, USA) were used for preparing $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ by conventional mixed solid method. The samples were calcined at 1150°C for 4 h. The crystalline phases of calcined $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ powders were confirmed according to the literature data. The $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ powders were characterized by light scattering (Mastersizer 2000, Malvern Instruments, UK) for particle size, electronic probe micro-analyzer (EPMA, Joel, JXA-8600SX, Japan) equipped with WDS for chemical composition and X-ray diffractometer (XRD, PW 1830, Philips, The Netherlands) for the crystalline structure.

The calcined powder of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ was coated with different type and different concentration of CuO precursor solutions. The $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ powder (20 g) was put into CuO precursor solutions (50 ml) (0.165–1.316 M CuSO_4 , 0.028–0.221 M $\text{Cu}(\text{CH}_3\text{COO})_2$ and 0.685–5.48 M $\text{Cu}(\text{NO}_3)_2$). After stirring for 5 min, standing for 5 min, the coated powder was filtrated by aspirator and dried at 120°C for 12 h. The CuO precursor modified $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ powders were pressed under 500 kg/cm^2 to form tablets (10 mm diameter), and sintered at different temperature for 4 h.

The dielectric properties of sintered $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ tablets were evaluated by network analyzer (Hewlett Packard, 8722ES Network Analyzer, USA). The microstructures of sintered samples were evaluated by scanning electron microscopy (SEM) equipped with EDS (Philips, XL-30, The Netherlands).

3. Results and discussion

The solid oxide mixing method prepared $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ was used as our control sample which was sintered at 1150°C for 4 h. The $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramic powder calcined at different temperatures for 4 h was investigated with XRD as shown in Fig. 1. The chemical composition of calcined $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ powder was analyzed by EPMA-WDS. The amount of element remained the same before and after the calcination.

The CuO modified $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramics with different dopant concentrations were sintered at different temperature for 4 h and results are shown in Fig. 2. The density of CuO doped $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ is increased with increasing dopant concentration and temperature (Fig. 2(a)). For the purpose of comparison, we have selected the sintering conditions to be 1150°C for 4 h which provides optimal density for all samples. The density of copper acetate precursor coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ is increased with increasing dopant concentration and increasing sintering temperature (Fig. 2(b)). At 0.22 M copper acetate concentration, a dense $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ($d = 4.70\text{ g/cm}^3$) can be obtained when the sample was sintered at 1150°C . The density of copper nitrated precursor coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ is increased with increasing sintering temperature (Fig. 2(c)). However, by increasing the concentra-

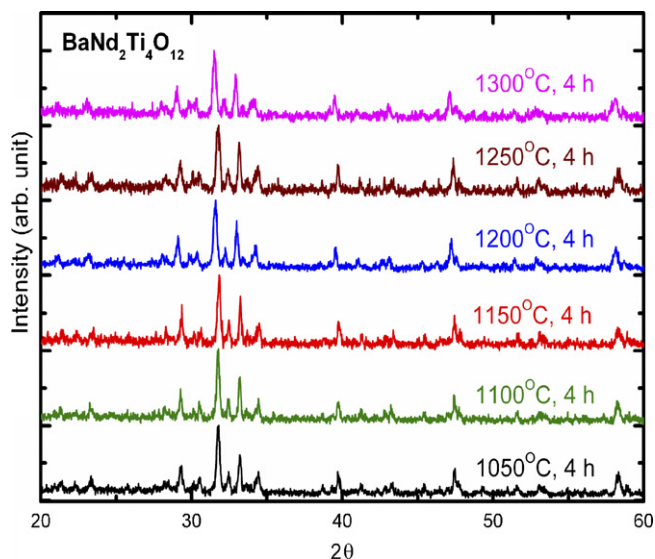


Fig. 1. XRD patterns of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ powders calcined at different temperature for 4 h.

tion of copper nitrate, the density of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ is increased initially, and then decreased at the concentration greater than 1.37 M. The nitrate compound usually exhibits spontaneous combustion reaction in sintering process which involves volatile vapor and reduces the density of samples.¹⁷ At 1.37 M copper nitrate concentration, a dense $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ($d = 5.47\text{ g/cm}^3$) can be obtained when the sample was sintered at 1150°C . At low concentration of copper sulfate precursor ($\leq 0.17\text{ M}$), the density of copper sulfate precursor coated BNT is increased with increase in sintering temperature (Fig. 2(d)). However, the density of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ is decreased with increasing in sintering temperature when the copper sulfate concentration is greater than 0.33 M. At 0.33 M copper sulfate concentration, the highest density $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ($d = 5.52\text{ g/cm}^3$) was obtained among copper precursor coated samples sintered at 1150°C .

The crystalline structure of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ series sintered at 1150°C were investigated by XRD and the results are shown in Fig. 3. The $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ crystalline structure is very stable either with CuO dopant or precursor dopant. The XRD peaks of CuO are found in the 3.0 wt% CuO doped $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ sample. However, the CuO peaks are not observed in the precursor coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ due to their CuO concentration is an order less than the CuO doped samples (Table 1).

The physical properties and microwave dielectric properties of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ series ceramics sintered at 1150°C for 4 h are shown in Table 1. The copper amount of Cu precursor coated BNT was measured by SEM-EDS as shown in Table 1. The $Q \times f$ value of Cu precursor coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ ceramics are degraded with an increasing in copper concentration of the Cu precursor. The 0.22 M $\text{Cu}(\text{CH}_3\text{COO})_2$ coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ with the lowest copper concentration (0.2 wt%) exhibits the highest $Q \times f$ value ($\sim 12,500\text{ GHz}$) among tested samples. However, the dielectric constant ($k \sim 47.6$) of the 0.22 M $\text{Cu}(\text{CH}_3\text{COO})_2$ coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ is not as good as the other tested samples. The 0.33 M CuSO_4 coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ containing 0.3 wt% copper exhibits the best microwave properties

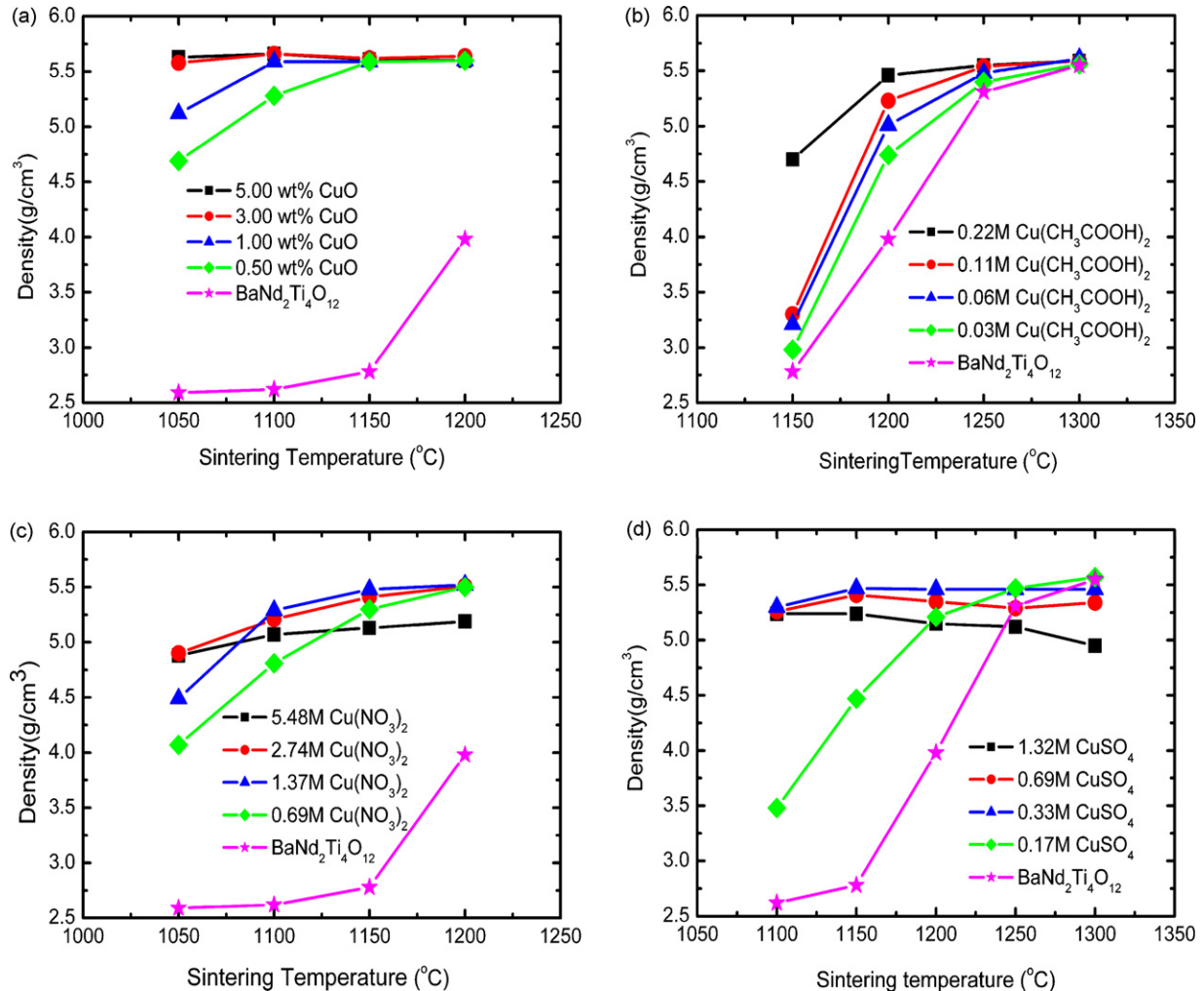


Fig. 2. Densities of: (a) CuO doped BaNd₂Ti₄O₁₂, (b) Cu(CH₃COO)₂ coated BaNd₂Ti₄O₁₂, (c) Cu(NO₃)₂ coated BaNd₂Ti₄O₁₂ and (d) CuSO₄ coated BaNd₂Ti₄O₁₂ ceramics sintered at different temperature for 4 h.

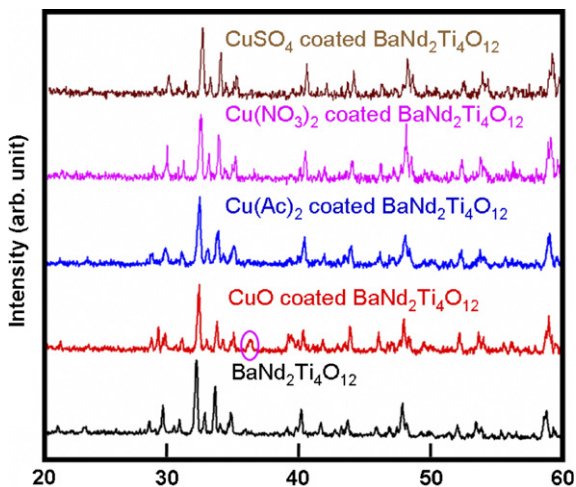


Fig. 3. XRD patterns of different CuO precursors coated on BaNd₂Ti₄O₁₂ powders sintered at 1150 °C for 4 h.

($k \sim 62.5$; $Q \times f \sim 11,500$ GHz) among tested samples. Thus, the CuSO₄ coated BaNd₂Ti₄O₁₂ has potential for microwave applications. These results clearly indicate the dopant addition process by thin layer coating is superior to by solid oxide mixing.

The differences of dielectric property between CuO doped BaNd₂Ti₄O₁₂ and precursor coated BaNd₂Ti₄O₁₂ can be explained by the microstructure study using SEM as shown in Fig. 4. Fig. 4(a) is the microstructure of pure BaNd₂Ti₄O₁₂, and Fig. 4(b) is the microstructure of 3.0 wt% CuO doped BaNd₂Ti₄O₁₂. The Cu(NO₃)₂ coated BaNd₂Ti₄O₁₂ exhibits large pores and defects (Fig. 4(d)) which is due to the spontaneous combustion behavior of nitrate compound. The Cu(CH₃COO)₂ coated BaNd₂Ti₄O₁₂ (Fig. 4(c)) exhibits smaller crystal grains and larger amount of small pores as compared with the CuSO₄ coated BaNd₂Ti₄O₁₂ (Fig. 4(e)).

The spontaneous combustion behavior of Cu(NO₃)₂ coated BaNd₂Ti₄O₁₂ results in a lower dielectric constant and a lower quality factor as compared with that of pure BaNd₂Ti₄O₁₂ even though its density is higher (2.78 g/cm³ versus 5.47 g/cm³). The density of Cu(CH₃COO)₂ coated BaNd₂Ti₄O₁₂ is lower

Table 1
Physical properties and microwave dielectric properties of $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ series ceramics after sintering

Material	Sintering condition	Density (10^3 kg/m^3)	f (GHz)	k	$Q \times f$ (GHz)	Cu content by EDX (wt%)
$\text{BaNd}_2\text{Ti}_4\text{O}_{12}$	1150 °C, 4 h	2.78	4.7	45.2	13,500	0.0
3.0 wt% CuO doped $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$	1150 °C, 4 h	5.62	5.0	61.2	10,500	2.3
0.22 M $\text{Cu}(\text{CH}_3\text{COO})_2$ coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$	1150 °C, 4 h	4.70	4.9	47.6	12,500	0.2
1.37 M $\text{Cu}(\text{NO}_3)_2$ coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$	1150 °C, 4 h	5.47	5.7	44.8	3,600	0.6
0.33 M CuSO_4 coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$	1150 °C, 4 h	5.52	5.0	62.5	11,500	0.3

than that of CuSO_4 coated BNT (4.70 g/cm^3 versus 5.52 g/cm^3) which results in a lower dielectric constant (47.6 versus 62.5). However, the $\text{Cu}(\text{CH}_3\text{COO})_2$ coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ has a higher $Q \times f$ value (12,500 GHz versus 11,500 GHz) due to a lower

Cu concentration (0.2% versus 0.3%) in the $\text{Cu}(\text{CH}_3\text{COO})_2$ coated samples. The CuSO_4 coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ is not as dense as CuO doped BNT (5.52 g/cm^3 versus 5.62 g/cm^3). However, it has a higher dielectric constant (62.5 versus 61.2) and a

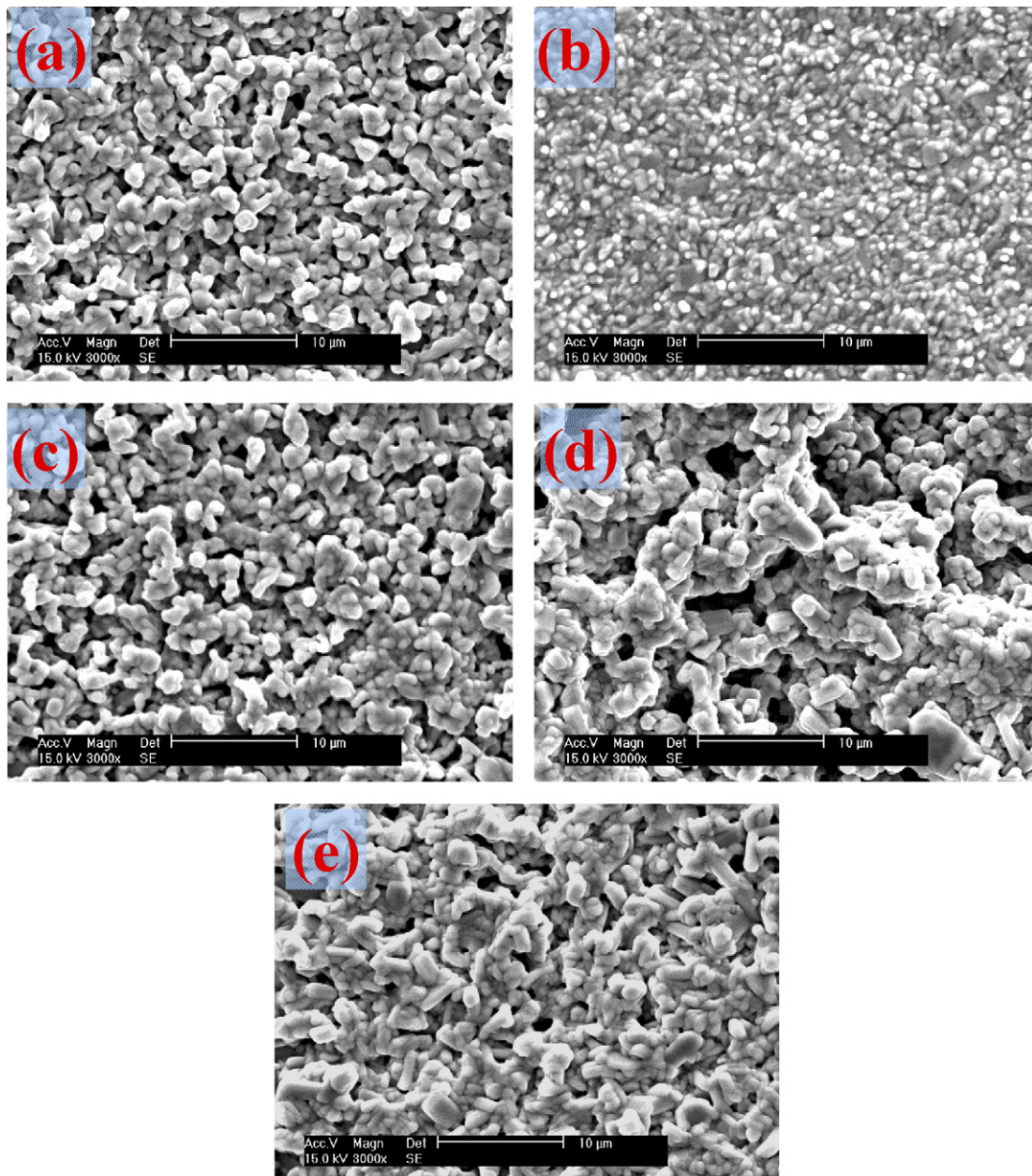


Fig. 4. SEM surface microstructures of: (a) pure $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$, (b) CuO doped $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$, (c) $\text{Cu}(\text{CH}_3\text{COO})_2$ coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$, (d) $\text{Cu}(\text{NO}_3)_2$ coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ and (e) CuSO_4 coated $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ sintered at 1150 °C for 4 h.

higher $Q \times f$ value (11,500 GHz versus 10,500 GHz) due to an order less of Cu concentration (0.3% versus 2.3%) in CuSO_4 coated samples. These results indicate the presence of copper in $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ has a strong influence on the quality factor of the material.

4. Conclusions

We have prepared low sintering $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ by coating the powder with thin layer CuO precursor using CuSO_4 solution instead of conventional CuO oxide solid mixing method. The method reduces the amount sintering aid by an order but provides material with superior dielectric properties as compared with material prepared by conventional method.

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