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Credit Author Statement

Junqing Ren: Investigation, Materials synthesis, Writing - Original Draft

Ke Bi: Testing

Xiuli Fu: Theoretical guidance, Writing - Review & Editing

Zhijian Peng: Theoretical guidance, Writing - Review & Editing

Novel Bi_2O_3-added $Al_2Mo_3O_{12}$ composite microwave dielectric ceramics for ULTCC applications

Junqing Ren[a,b], Ke Bi[a], Xiuli Fu[*a], Zhijian Peng[*b]

[a] *State Key Laboratory of Information Photonics and Optical Communications, and School of Science, Beijing University of Posts and Telecommunications, Beijing 100876, P. R. China*

[b] *School of Science, China University of Geosciences, Beijing 100083, P. R. China*

[a] *xiulifu@bupt.edu.cn;* [b] *pengzhijian@cugb.edu.cn*

Abstract: Ultra-low temperature co-fired ceramics (ULTCC) technology has been extensively developed in modern microwave communications, for which microwave dielectric ceramics with ultra-low sintering temperature play a crucial role. Among them, $Al_2Mo_3O_{12}$ is a promising candidate with excellent microwave dielectric properties, but its sintering temperature (roughly 790 °C) is still too high for ULTCC. In this work, novel Bi_2O_3-added $Al_2Mo_3O_{12}$ composite microwave dielectric ceramics were designed and prepared by conventional solid-state sintering reaction. The addition effects of Bi_2O_3 on the phase composition, microstructure and microwave dielectric properties of the obtained composite ceramics were investigated. The added Bi_2O_3 will react with $Al_2Mo_3O_{12}$ to form a new $Bi_2Mo_3O_{12}$ phase with an even lower melting point than Bi_2O_3, effectively reducing the sintering temperature of the composite ceramics to below 660 °C. As the extra addition amount of Bi_2O_3 increases from 0 to 5 wt.%, for the composite ceramics sintered at the designed different temperatures (620-710 °C) for 12 h, the dielectric constant (ε_r) increases from 5.5 to 5.98, quality factor ($Q\times f$) could be effectively enhanced, reaching a maximum of 49900 GHz, and temperature coefficient of the resonant frequency (τ_f) changes from -36.4 to -42.8 ppm/ºC. With 4 wt.% Bi_2O_3, the composite ceramics sintered at 650 ºC for 12 h present good microwave dielectric properties of ε_r = 5.91, $Q\times f$ = 49600 GHz and τ_f = -41.2 ppm/ºC, and excellent chemical stability with the electrode metal Al, indicating that it is a promising candidate for ULTCC applications.

Keywords: $Al_2Mo_3O_{12}$; Bi_2O_3; Composite; Ultra-low temperature co-fired ceramics (ULTCC); Microwave

dielectric properties

1. Introduction

The development of wireless communications raises the requirements on electronic information equipment and advanced materials. In recent decades, ultra-low temperature co-fired ceramics (ULTCC) technology has been extensively developed in modern microwave communications, for which microwave dielectric ceramics with ultra-low sintering temperature play a crucial role in preparing a variety of wireless communication devices. In particular, the fabrication of devices with high frequency, miniaturization and multi-function requires high-precision and complicated electronic packaging, where many ULTCC techniques have been developed and applied in integrated circuits.[1-6] As a result, conventional microwave dielectric ceramics with high sintering temperature are no longer suitable for such applications, because the high sintering temperature can not match their co-firing with metal electrodes. Generally speaking, for ULTCC technology, in addition to the requirements that the applied microwave dielectric ceramics have appropriate dielectric constants (ε_r) to adapt for different sizes of devices, high quality factors ($Q\times f$) to satisfy applications at higher frequencies, and a near-zero temperature coefficient of the resonant frequency (τ_f) to ensure the temperature stability of the devices, the sintering temperature of the ceramics should be lower than the melting point of the commonly applied Al electrode (660 °C). Therefore, extensive studies have currently been performed on dielectric ceramics with low sintering temperature so as to accommodate for ULTCC application.[7-12]

However, among the already-reported microwave dielectric ceramics, the ones with ultra-low sintering temperature are still scarce, which can not meet the requirements for various ULTCC devices. Moreover, although the sintering temperature of some ceramics is lower than the melting point of metal Al, the poor chemical stability with the electrode will also limit their practical applications. Therefore, exploring high-performance microwave dielectric ceramics with very low sintering temperature (below 660 °C) and good chemical stability with metal Al

has become a hot topic.

In literature, many Mo-based ceramics have attracted wide attention, because their sintering temperatures are generally low (some are even lower than 700 °C), which provides a new possibility for ULTCC application.[13-22] In our previous work, $Al_2Mo_3O_{12}$-based microwave dielectric ceramics with excellent microwave dielectric performance were reported (ε_r = 5.67, $Q \times f$ = 73900 GHz, and τ_f = -32.3 ppm/ºC), which could be sintered at only 790 °C.[23] By introducing proper sintering aids into $Al_2Mo_3O_{12}$ ceramics, the sintering temperature might be further reduced to below the melting of Al electrodes, and hopefully, ULTCC ceramics would be obtained. In particular, Bi_2O_3 possesses low melting point (825 °C), which has successfully been used to reduce the sintering temperature of many ceramics.[24-28] And in Mo-based ceramic systems, various Bi-Mo-O compounds have exhibited low melting point or low sintering temperature below 700 °C.[29-31]

Taking all these factors into account, in this work, novel Bi_2O_3-added $Al_2Mo_3O_{12}$ composite microwave dielectric ceramics were designed and prepared by conventional solid-state sintering reaction. And the addition effects of Bi_2O_3 on the phase composition, microstructure and microwave dielectric properties of the obtained composite ceramics were investigated. As expected, composite ceramics with excellent microwave dielectric performance can be obtained by sintering the ceramics at a temperature below 660 °C.

2. Experimental section

2.1 Samples preparation

The specimens were designed in a nominal composition of $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 (x = 0, 1, 2, 3, 4 and 5) and prepared by using a conventional solid-state reaction sintering method. During the processing, analytical-grade Al_2O_3 and MoO_3 powders were first weighted according to the stoichiometry of $Al_2Mo_3O_{12}$. The powders were then mixed and ball-milled for 12 h with absolute ethanol as the dispersive media and high-resistance zirconia balls as the grinding media. After milling, the powder slurries were dried at 90 °C for 24 h

in an open oven, and then calcined at 750 °C for 4 h in a Muffle oven. After calcination, the resultant powder chunks were crushed into fine powder and re-milled with Bi_2O_3 for 12 h as done in the first ball-milling for the preparation of $Al_2Mo_3O_{12}$. After drying again, the resultant powder chunks were crushed and grinded with 5 wt.% polyvinyl alcohol as binder, and finally sieved into fine powders. Afterwards, the obtained powders were pressed into cylinders (10 mm in diameter and 5 mm in height). All the green bodies were then sintered in a Muffle oven at 620-710 °C for 12 h.

2.2 Materials characterization

The crystallographic analysis of the as-sintered samples was performed on a X-ray diffractometer (XRD, D/max-RB, Cu Kα, λ = 1.5418 Å). The scanning 2θ angle was in the range of 20-60°, and the scanning rate was 6 °/min. The microstructure was examined by scanning electron microscopy (FE-SEM, S4800) attached with an energy dispersive X-ray (EDX) spectroscope. From the obtained SEM images, the grain size was evaluated by using a software Nano Measurer 1.2 PC. The displayed grain size for each sample was the mean value of all the grains identified from the whole image. The apparent density was measured by Archimedes method. The theoretical density of the obtained ceramics was obtained from the mixture rule as expressed by,

$$\rho = \frac{\rho_1 \times \nu_1 + \rho_2 \times \nu_2}{\nu_1 + \nu_2}, \quad (1)$$

where ρ_1 and ρ_2 are the theoretical density of each phase, and v_1 and v_2 represent their volume, respectively. The relative density of the samples is defined as the percentage of the apparent density to their corresponding theoretical density. The microwave dielectric properties were measured by using a $TE_{01\delta}$ mode cavity method (E5063A Vector Network Analyzer). In addition, the temperature coefficient of resonant frequency (τ_f) was calculated by the following equation:

$$\tau_f = \frac{f_{t2} - f_{t1}}{f_{t1}(t_2 - t_1)}, \quad (2)$$

where f_{t1} and f_{t2} are the resonant frequencies at the measuring temperature t_1 (25 °C) and t_2 (85 °C), respectively.

3. Results and discussion

3.1 Compositional and microstructural properties

Figure 1 shows the XRD patterns of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 composite ceramic samples with different addition amounts of Bi_2O_3 (x = 0-5). Here the samples were sintered at a typical temperature of 650 °C for 12 h. From the recorded XRD patterns, $Al_2Mo_3O_{12}$ with monoclinic structure (JCPDS card no. 84-1652) could be identified in all the samples. After the addition of Bi_2O_3, no second phase could be identified from the samples with x = 1 and 2, but a new $Bi_2Mo_3O_{12}$ phase could be discerned from the ones with x = 3, 4 and 5. This phenomenon can be explained as follows. For the samples with x = 1 and 2, because the added amount of Bi_2O_3 is small, the contents of any Bi-containing compounds in the samples are low, which are lower than the detection limit of XRD. Therefore, none of them could be identified by XRD analysis. When more Bi_2O_3 is added, the reaction of the added Bi_2O_3 with the $Al_2Mo_3O_{12}$ matrix would generate more of the second $Bi_2Mo_3O_{12}$ phase. Resultantly, $Bi_2Mo_3O_{12}$, which also has a monoclinic structure (JCPDS card no. 21-0103), could be discerned from the samples by XRD analysis, and the intensities of its diffraction peaks would increase with increasing addition amount of Bi_2O_3. Meanwhile, a new product Al_2O_3 would be generated due to the decomposition of the $Al_2Mo_3O_{12}$ matrix. However, even if 5 wt.% Bi_2O_3 (the designed maximum addition amount among all the samples in this work) was applied, the content of the produced Al_2O_3 was calculated as only 1.09 wt.%, which is too low to be identified from the samples by XRD analysis. More importantly, the newly formed $Bi_2Mo_3O_{12}$ has a low melting point of 640 °C, which is significantly lower than those of all the other components ($Al_2Mo_3O_{12}$ and Al_2O_3) in the samples. As a result, with an appropriate amount of $Bi_2Mo_3O_{12}$ generated in the samples, it could promote the densification of the composites at a sintering temperature lower than 660 °C.

Typical SEM images of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 (x = 0-5) composite ceramic samples sintered

at 650 °C for 12 h are exhibited in Fig. 2. As is seen, without the addition of Bi_2O_3, the obtained pure $Al_2Mo_3O_{12}$ ceramics present small grains with average size of 2.38 μm, and many pores could distinctly be observed (see Fig. 2a), revealing that it is not easy for such samples to be sintered. However, after the addition of Bi_2O_3, the samples exhibit bigger sizes of $Al_2Mo_3O_{12}$ grains (see Fig. 2b-2f). With increasing addition amount of Bi_2O_3, the calculated average grain size increases from 2.38 to 4.24 μm, indicating that the addition of Bi_2O_3 promotes the growth of $Al_2Mo_3O_{12}$ grains. Moreover, the pores in the sample gradually disappear, revealing that the densification of ceramics is improved. In addition, with the increase in the added Bi_2O_3, more and more liquid phase (see the dotted areas as shown in Fig. 2f) could be clearly observed around the $Al_2Mo_3O_{12}$ grains (see the areas marked with triangle in Fig. 2f). Through EDX analysis (see Fig. 2g), it was revealed that the elemental composition of the liquid phase was close to the stoichiometry of $Bi_2Mo_3O_{12}$, which is consistent with the result of XRD examination as presented in Fig. 1. Since the melting point of the newly formed $Bi_2Mo_3O_{12}$ phase is 640 °C, at the presently applied sintering temperature of 650 °C it would be of liquid, which will fill in and connect with the $Al_2Mo_3O_{12}$ grains, thereby contributing to the growth of $Al_2Mo_3O_{12}$ grains and densification of the ceramics. This result is also in accordance with the density change of the samples (see Fig. 3).

Figure 3 presents the relative density of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 (x = 0-5) composite ceramic samples sintered at 620-710 °C for 12 h. As is seen, when sintering at 620 °C, all the prepared samples exhibit a low relative density (no more than 95%), indicating a low densification. This phenomenon is easily understood. Because the melting temperature of $Bi_2Mo_3O_{12}$ is about 640 °C, under the present condition, liquid phase will be seldom formed. Resultantly, it is difficult for the samples to be sintered. However, the relative density of the samples sintered at this temperature will increase somewhat with increasing addition amount of Bi_2O_3, which might be attributed to the increased amount of the newly formed second phase of $Bi_2Mo_3O_{12}$ during sintering. Moreover, when sintering at a temperature higher than 640 °C (650, 680 and 710 °C in this work), the relative

density of the samples increases promptly as the addition amount of Bi_2O_3 increases, reaching a constant over 96.5 % when x > 3. This is because at such high sintering temperatures the $Bi_2Mo_3O_{12}$ liquid phase would be easily formed, which will assist the densification of the ceramic samples. However, with the increase in the addition amount of Bi_2O_3, the excessively produced liquid phase would be of no contribution to further promote the densification of the samples, because the samples have been already sintered. For the same reason, with the same addition amount of Bi_2O_3, a relatively higher sintering temperature will result in a higher densification of the samples.

3.2 Microwave dielectric properties

The dielectric constants (ε_r) of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 (x = 0-5) composite ceramic samples sintered at different temperatures (620-710 °C) for 12 h are shown in Fig. 4. As is known, ε_r is mainly determined by the ionic polarizabilities, second phases and pores (relative density) in microwave dielectric ceramics.[32,33] In the present composites, the change of the ε_r value would not be affected by the ionic polarizabilities because ionic substitution does not occur. The contributions to the change of the ε_r value involve in the formation of second phases and the sample densification. Firstly, the ε_r value of each composition of the composite ceramics increases with increasing sintering temperature, due to the improved densification of the samples. Secondly, when sintering at the same temperature, the ε_r value of the composites increases as the adding amount of Bi_2O_3 increases. This phenomenon should be attributed to the formation of the $Bi_2Mo_3O_{12}$ second phase, because it has a larger ε_r value (ε_r = 19) than $Al_2Mo_3O_{12}$ (ε_r = 5.69),[23, 31] and due to its formation, the densification of the samples is also improved.

The quality factors ($Q\times f$) of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 (x = 0-5) composite ceramic samples sintered at different temperatures (620-710 °C) for 12 h are illustrated in Fig. 5. It is well known that the factors influencing the $Q\times f$ value of microwave ceramics include the intrinsic ones mainly contributing to the lattice

vibration mode, as well as the extrinsic ones such as the second phases in the samples, grains morphology and sample densification.[34] For the present composite ceramics, the extrinsic factors play a major role in the change of $Q\times f$ value. When the sintering temperature is lower than the melting point of $Bi_2Mo_3O_{12}$, the $Q\times f$ value increases with the increase in the x value because the sample density plays the major role. Thus the $Q\times f$ value presents a similar change trend with the density as shown in Fig. 3. However, when the sintering temperature is higher than the melting point of $Bi_2Mo_3O_{12}$, the $Q\times f$ value of the samples increases firstly and then decreases with the increase in the x value, implying that the formation of the $Bi_2Mo_3O_{12}$ second phase could promote the densification of the present composite ceramics, thus enhancing their $Q\times f$ value. However, the excessively formed $Bi_2Mo_3O_{12}$ might also lead to a decrease in the $Q\times f$ value of the samples, because the $Q\times f$ value of $Bi_2Mo_3O_{12}$ (21800 GHz) is much lower than that of the $Al_2Mo_3O_{12}$ matrix.[31] In particular, for the sample with x = 2, the maximum value of $Q\times f$ (49900 GHz) was reached when the sample was sintered at 710 °C. More interestingly, when the samples were sintered at 650 °C, a near-maximum value of $Q\times f$ (49600 GHz) could still be obtained when x = 4, indicating that an appropriate addition of Bi_2O_3 could effectively reduce the sintering temperature of the samples to below 660 °C without substantially degrading their quality factor.

Fiugre 6 presents the temperature coefficient of resonate frequency of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 (x = 0-5) composite ceramic samples sintered at different temperatures (620-710 °C) for 12 h. As is seen, the variation of τ_f would not be affected by the sintering temperature evidently. Generally speaking, the τ_f value of microwave dielectric ceramics is determined by their composition including the matrix and second phases. In this work, although Al_2O_3 will be generated in samples, its effect on τ_f variation could be neglected because its content is very low (see Section 3.1). Accordingly, the τ_f value should obey the following mixing rule:

$$\tau_f = v_1\tau_{f1} + v_2\tau_{f2}, \quad (3)$$

where v_1 and v_2 represent the volume fraction of the components $Al_2Mo_3O_{12}$ and $Bi_2Mo_3O_{12}$, while τ_{f1} and τ_{f2} are

their temperature coefficient of resonant frequency, respectively. Here the τ_f value of the newly formed $Bi_2Mo_3O_{12}$ second phase (-215 ppm/ºC) is lower than that of the $Al_2Mo_3O_{12}$ matrix. Thus, with the increase of x value, the τ_f value of the samples will further deviate from zero.[31]

In summary, the $Al_2Mo_3O_{12}$ - 4 wt.% Bi_2O_3 composite ceramics sintered at 650 ℃ exhibit good microwave dielectric properties of ε_r = 5.91, $Q \times f$ = 49600 GHz and τ_f = -41.2 ppm/ºC.

3.3 Chemical stability with metal Al

To investigate the chemical stability of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 composite ceramics with the commonly applied metal Al electrode in ULTCC, the $Al_2Mo_3O_{12}$ - 4 wt.% Bi_2O_3 composite is chosen as an example to be mixed with 20 wt.% Al powders and then co-fired at 650 ℃ for 12 h. After that, the prepared samples were first characterized by XRD, and the result is shown in Fig. 7. As is seen in this figure, only $Al_2Mo_3O_{12}$, $Bi_2Mo_3O_{12}$ and Al phases without any other phases are identified from this sample, indicating that no chemical reaction happens between the present composite ceramics and metal Al electrode, implying good chemical stability of the present composite with metal Al.

Moreover, a cylindrical green body prepared with the $Al_2Mo_3O_{12}$ - 4 wt.% Bi_2O_3 composite and brushed with metal Al slurry on the surface was co-fired at 650 ℃ for 12 h. Afterwards, the polished cross-section of the sample was examined by SEM-EDX linear scanning analysis, and the result is displayed in Fig. 8. As can be seen in Fig. 8a, the boundary between the composite and Al electrode is clear-cut and easily distinguished. And the EDX linear scanning analysis revealed that the two regions of metal Al and $Al_2Mo_3O_{12}$-Bi_2O_3 composite present almost no diffusion across their interface (see Fig. 8b-8e). These results indicate that there is no chemical reaction between the present composite ceramics and metal Al electrode, which is consistent with the result of XRD analysis.

In a word, the present $Al_2Mo_3O_{12}$ - 4 wt.% Bi_2O_3 composite ceramics are stable with metal Al, which can be

applied in co-firing processes at a low sintering temperature of 650 °C. In combination with their good microwave dielectric properties and excellent chemical stability with metal Al, it is convinced that the $Al_2Mo_3O_{12}$-Bi_2O_3 composite ceramics are a promising candidate for ULTCC applications.

4. Conclusions

Novel $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 (x=0-5) composite ceramics were designed and prepared by a conventional two-step solid-state reaction sintering method. The effects of Bi_2O_3 addition on the phase composition, microstructure and microwave dielectric properties of the obtained ceramics were investigated. During sintering, Bi_2O_3 would react with the matrix $Al_2Mo_3O_{12}$, producing a second phase $Bi_2Mo_3O_{12}$. Because of its low melting point of 640 ºC, the newly formed $Bi_2Mo_3O_{12}$ could decrease the sintering temperature of the samples, promoting the densification of the composite ceramics effectively. Therefore, the microwave dielectric properties of the obtained $Al_2Mo_3O_{12}$-Bi_2O_3 composite ceramics have a close relationship with the addition amount of Bi_2O_3 and sintering temperature. As the x value increases from 0 to 5, for the composite ceramics sintered at the designed different temperatures (620-710 °C) for 12 h, the ε_r value increases from 5.5 to 5.98, $Q\times f$ could be effectively enhanced, reaching a maximum of 49900 GHz, and τ_f changes from -36.4 to -42.8 ppm/ºC. With x = 4, the $Al_2Mo_3O_{12}$-Bi_2O_3 composite ceramics sintered at 650 ºC possess good microwave dielectric properties of ε_r = 5.91, $Q\times f$ = 49600 GHz and τ_f = -41.2 ppm/ºC, and exhibit excellent chemical stability with Al. Thus, the $Al_2Mo_3O_{12}$ - 4 wt.% Bi_2O_3 composite ceramics are a promising candidate for ULTCC applications.

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Figure captions:

Fig. 1 XRD patterns of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 composite ceramic samples sintered at 650 °C for 12 h.

Fig. 2 Typical SEM images of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 composite ceramic samples sintered at 650 °C for 12 h with different addition amounts of Bi_2O_3: (a) 0 wt.%, (b) 1 wt.%, (c) 2 wt.%, (d) 3 wt.%, (e) 4 wt.% and (f) 5 wt.%. (g) Typical EDX data on the dotted areas in (f).

Fig. 3 Relative densities of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 (x = 0-5) composite ceramic samples sintering at 620-710 °C for 12 h.

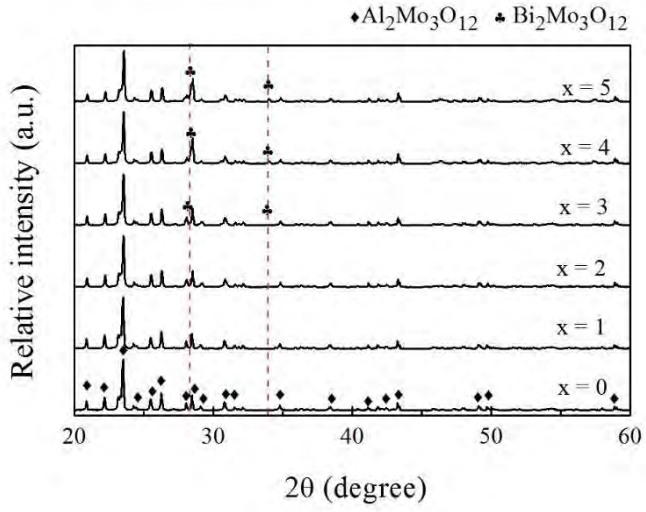
Fig. 4 Dielectric constants of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 (x = 0-5) composite ceramic samples sintered at 620-710 ℃ for 12 h.

Fig. 5 Quality factors of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 (x = 0-5) composite ceramic samples sintered at 620-710 ℃ for 12 h.

Fig. 6 Temperature coefficients of resonate frequency of the obtained $Al_2Mo_3O_{12}$ - x wt.% Bi_2O_3 (x = 0-5) composite ceramic samples sintered at 620-710 ℃ for 12 h.

Fig. 7 XRD pattern of the sample from $Al_2Mo_3O_{12}$ added with 4 wt.% Bi_2O_3 and mixed with 20 wt.% Al powder, which was co-fired at 650 ℃ for 12 h.

Fig. 8 EDX mapping images on the cross-section of the sample prepared from the $Al_2Mo_3O_{12}$ - 4 wt.% Bi_2O_3 composite and brushed with metal Al slurry on the surface. The sample was co-fired at 650 ℃ for 12 h.



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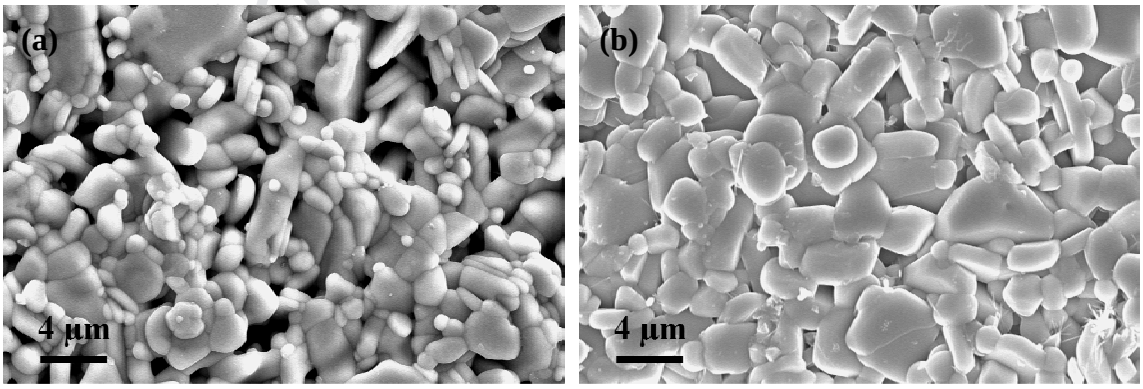
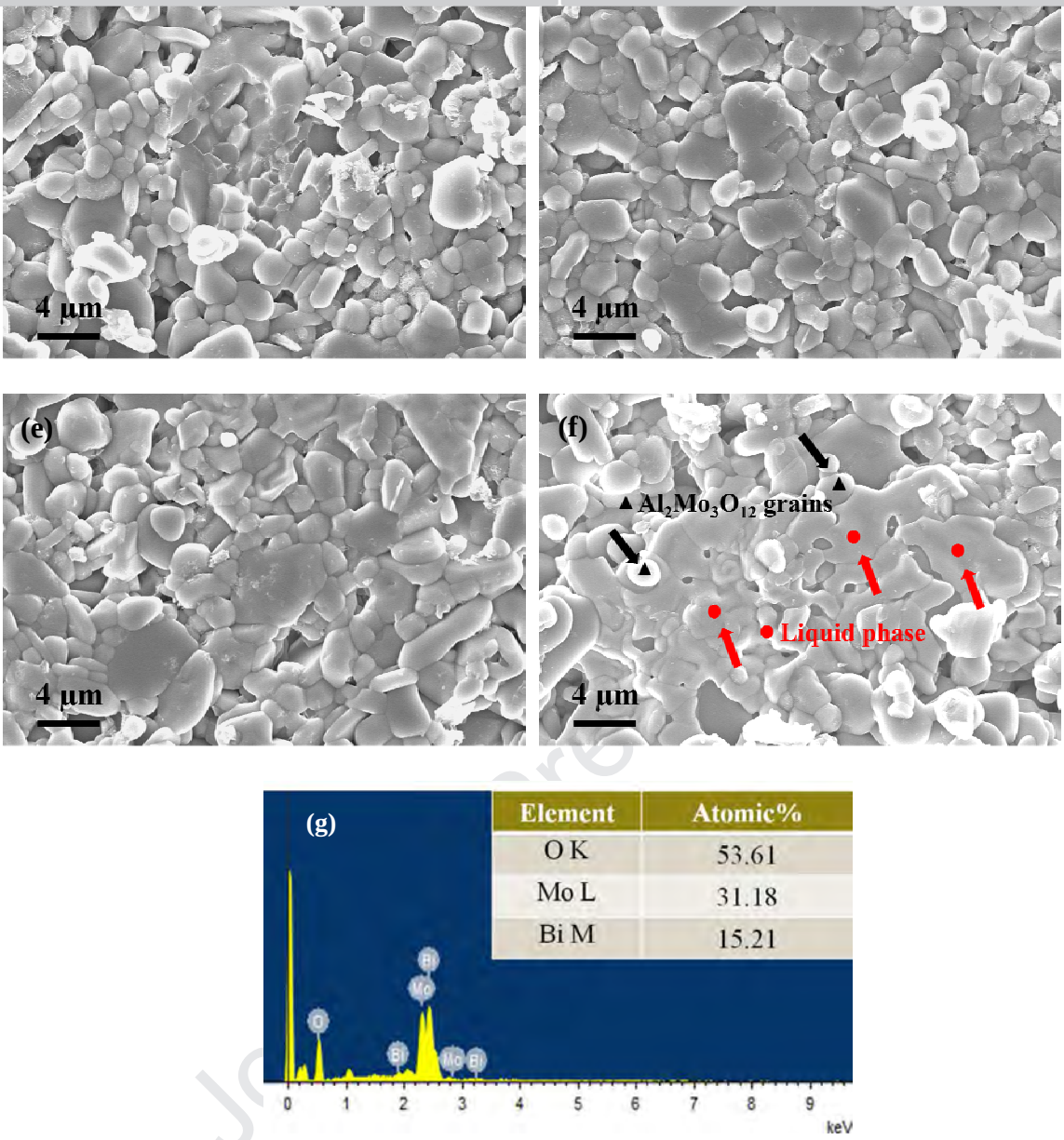


(c) **(d)**



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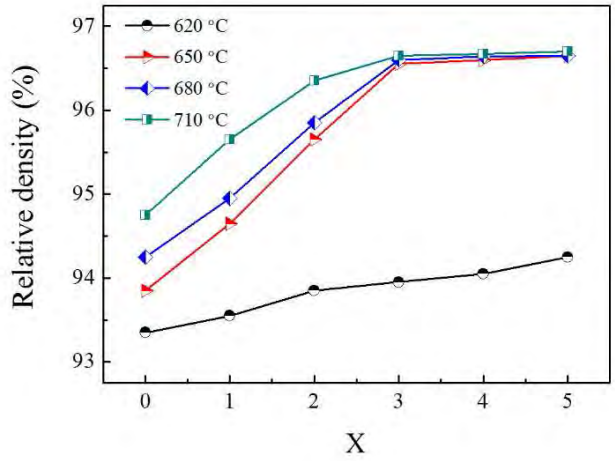

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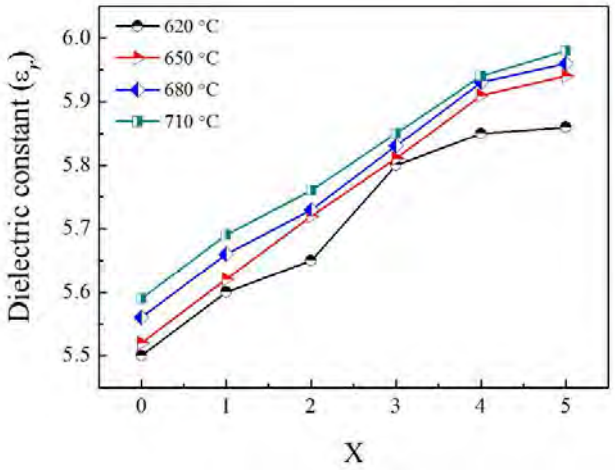

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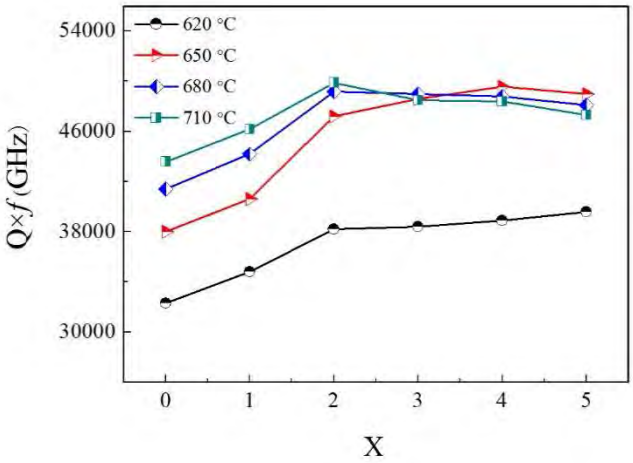

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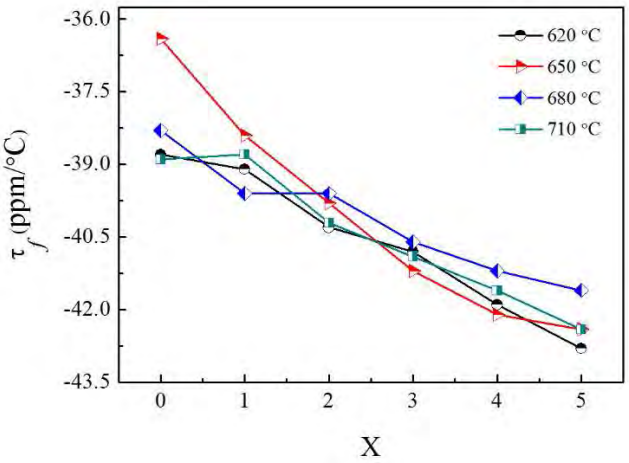

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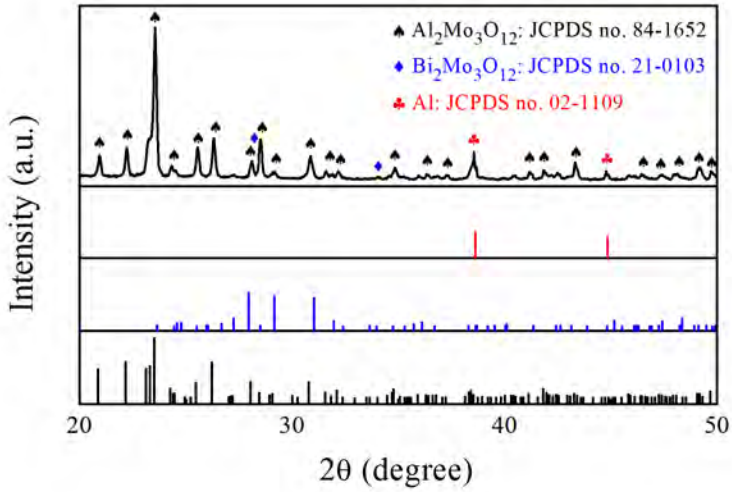

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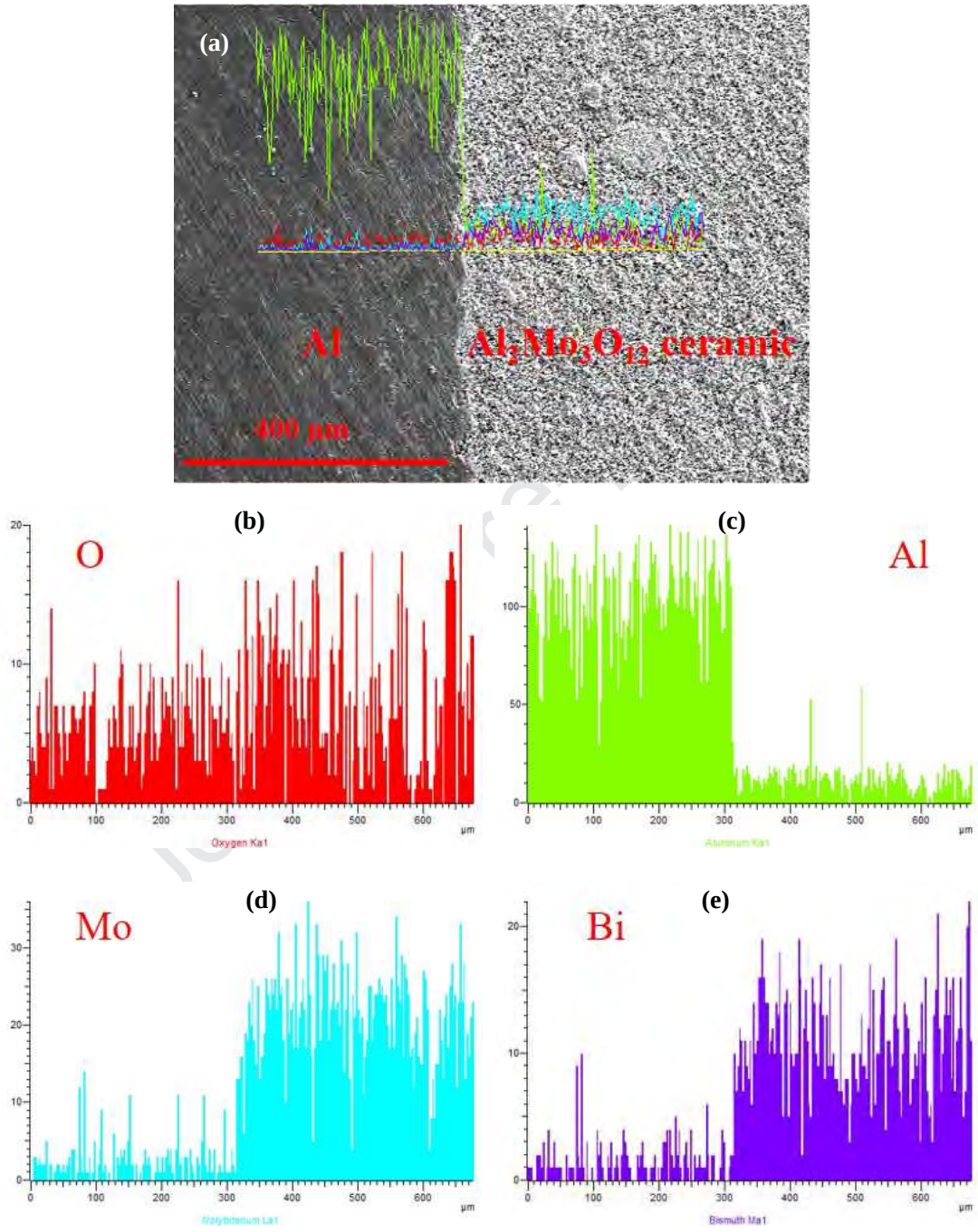

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Highlights (for review)

Highlights:

This article designed the novel Bi_2O_3-added $Al_2Mo_3O_{12}$ composite microwave dielectric ceramics which were prepared by conventional solid-state sintering reaction.

The added Bi_2O_3 will react with $Al_2Mo_3O_{12}$ to form a new $Bi_2Mo_3O_{12}$ phase with low melting point, effectively promoting the densification and reducing the sintering temperature of the composite ceramics to below 660 °C.

The microwave dielectric properties of the obtained $Al_2Mo_3O_{12}$-Bi_2O_3 composite ceramics have a close relationship with the addition amount of Bi_2O_3 and sintering temperature.

With 4 wt.% Bi_2O_3, the composite ceramics sintered at 650 ºC for 12 h present good microwave dielectric properties of ε_r = 5.91, $Q \times f$ = 49600 GHz and τ_f = -41.2 ppm/ºC, and excellent chemical stability with the electrode metal Al, indicating that it is a promising candidate for ULTCC applications.

Declaration of Interest Statement

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.