

Densification, microstructure and microwave dielectric properties of ultra-low fire BaTe₄O₉–TiTe₃O₈ ceramic composites

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Abstract

In this study, BaTe₄O₉–TiTe₃O₈ ceramic composites with various amounts of TiTe₃O₈ were prepared, and the densification, microstructural evolution, and dielectric properties of the ultra-low fire ceramic composites were characterized. With the addition of TiTe₃O₈, the ceramic composites were densified at 575 °C with the maximum densities ranging from 93% to 96% of theoretical density. Except the BaTe₄O₉ and TiTe₃O₈ phases, no other second phase was observed in the XRD results. The change in the microstructures caused by the increase of TiTe₃O₈ content appeared to be insignificant. Wide grain size distributions with angular grains in the range of 1–4 μm were observed for all cases. The best dielectric properties – ϵ_r value of 25, $Q \times f$ value of 19,340 GHz, and τ_f value of –2.7 ppm/°C – were obtained for BaTe₄O₉–40 wt% TiTe₃O₈ ceramic composite sintered at 575 °C, qualifying the ultra-low fire composites for use in the application of ceramic resonators.
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1. Introduction

Dielectric ceramics for use in resonators at microwave frequency have received increasing attention due to the rapid growth of mobile communication devices such as cellular phone, global positioning systems and personal communication systems. For applications in microwave devices, a high dielectric constant, a high dielectric loss quality ($Q > 2000$), and a near-zero temperature coefficient of resonant frequency τ_f (0–10 ppm/°C) are required. High dielectric constant makes it possible to cut the size of the material by a factor of $1/\epsilon_r^{1/2}$ so that the size of circuit can be reduced considerably. The high Q value enables low insertion loss and low bandwidth of the resonance frequency, both necessary for achieving high frequency selectivity and stability in the microwave transmitter components. A near-zero τ_f is also required to stabilize the frequency against temperature.

The sintering temperatures of common dielectric ceramics fall in the range between 1200 °C and 1500 °C, which

are much higher than the melting temperature of Ag (961 °C) or Cu (1064 °C). For instance, the sintering temperatures of BaO–Nd₂O₃–TiO₂–Nb₂O₅, Ba_{6–x}Ln_{8+2x/3}Ti₁₈O₅₄ and (Zr,Sn)TiO₄ systems are around 1325 °C, 1350 °C and 1400 °C, respectively.^{1–3} There is a considerable interest in the development of new materials with a low sintering temperature. One approach involves the investigation of the glass-forming additives on the properties of established microwave materials. For example, the BaO–La₂O₃–4.7TiO₂ ceramic with the addition of 20 wt% PbO–B₂O₃–SiO₂ can reduce the sintering temperature down to 900 °C; this, however, has been observed to trigger degradation of the microwave properties.⁴ Another way is the use of new material systems with a lower sintering temperature, such as Bi₂O₃- and TeO₂-based compounds.⁵ The sintering temperature of Bi₁₂MO_{20–8} (M = Si, Ge, Ti, Pb, Mn, B_{1/2}P_{1/2}), TiO₂–TeO₂, and Bi₂O₃–ZnO–Nb₂O₅ are respectively around 680–850 °C, 720 °C, and 950 °C.^{6–8}

TeO₂, with a melting point of 733 °C, is well known as a network glass former in the glass industry.¹⁰ TeO₂ with ≈20% porosity has been shown to display a relative permittivity of 19.3, a $Q \times f$ value of 30,000 GHz, and a temperature coefficient of –119 ppm/°C. Recent researches have further discovered that TeO₂-based ceramics, including the TiO₂–TeO₂, Bi₂O₃–TeO₂,

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CaO–TeO₂, BaO–TeO₂, ZnO–TeO₂, and Bi₂O₃–TiO₂–TeO₂ systems, possess very low sintering temperatures ranging from 650 °C to 800 °C and excellent microwave dielectric characteristics.^{7,11–19} Single phase TiTe₃O₈ sintered at 720 °C to ≈95% of theoretical density exhibits a relative permittivity of 50, a $Q \times f$ value of 30,600 GHz, and a temperature coefficient of +133 ppm/°C. On the other hand, the BaTe₄O₉ compound can be densified at 550 °C and possesses the microwave dielectric properties of $\epsilon_r = 17.5$, $Q \times f = 54,700$ GHz, and $\tau_f = -90$ ppm/°C.²⁰ Though both compounds report excellent dielectric constants and $Q \times f$, their τ_f values remain far away from the acceptable level (≤ 10 ppm/°C). In order to obtain a ceramic with a nearly zero temperature coefficient of resonant frequency, ceramic composites of BaTe₄O₉–TiTe₃O₈ with various amounts of TiTe₃O₈ were prepared in this study. The effects of TiTe₃O₈ content on the densification, microstructural evolution and dielectric properties of BaTe₄O₉–TiTe₃O₈ ceramic composites are discussed through X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal analysis, and dielectric characterization.

2. Experimental procedure

Pre-calcined TiTe₃O₈ and BaTe₄O₉ powders were prepared using the solid-state reaction technique. Highly pure (>99.9% purity) TiO₂ (Toho, Reagent grade), BaCO₃ (Nippon, Reagent grade), and TeO₂ (Acros, Reagent grade) were used as raw materials. Oxides and carbonate based on the compositions of TiTe₃O₈ and BaTe₄O₉ were mixed and milled in methyl alcohol solution using polyethylene jars and zirconia balls for 24 h and then dried at 80 °C in an oven for overnight. After drying, the powders for BaTe₄O₉ and TiTe₃O₈ were calcined at 500 °C and 700 °C, respectively for 10 h. Phase identification on the calcined powders was performed using X-ray diffraction (XRD, Rigaku D/max-B). Different ratios of TiTe₃O₈ and BaTe₄O₉ powders were then mixed and re-milled in methyl alcohol for 24 h. The powders were added with a 4 wt% of 15%-PVA solution and pressed into disc-shaped compacts using uniaxial pressure of 1 tons/cm². The samples were then heat treated at 400 °C for 6 h to eliminate the PVA, followed by sintering at 500–585 °C for 2 h (heating rate = 5 °C/min). Bulk densities of the sintered samples were measured using the Archimedes method with de-ionized water. Phase identification on the calcined powders as well as the sintered bulk ceramics was performed using X-ray diffraction. Differential thermal analysis (DTA) was then conducted in a Pt crucible with a heating rate of 10 °C/min using a PerkinElmer Calorimeter, Series 1700 DTA, on mixtures to evaluate the melting reactions. The microstructures of the sintered samples were observed using scanning electron microscopy (SEM, HITACHI S-4700) with an energy-dispersive spectroscopy (EDS). The densified cylindrical samples were polished to have an exact thickness of 5 mm for measuring microwave properties. The dielectric constant (ϵ_r) and quality factor ($Q \times f$) were evaluated, based on the cylindrical cavity method (cavity 1005CIRC and software CAVITY, Damaskos, Inc.), using a HP 8722D network analyzer. Detailed measurement procedures have been described elsewhere.⁹ The temperature coefficient of resonant frequency

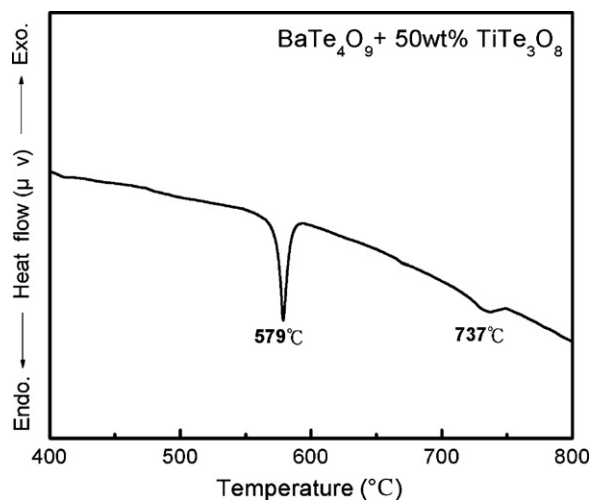


Fig. 1. DTA result of BaTe₄O₉ powders with the addition of 40 wt% TiTe₃O₈.

(τ_f) was measured within the range of 25–80 °C. The τ_f was defined by $(f_T - f_{25})/f_{25}(T - 25$ °C) in Damaskos cavity.

3. Results and discussion

Fig. 1 shows the DTA result of the BaTe₄O₉ powders with the addition of 50 wt% TiTe₃O₈ up to 800 °C. It indicates that there are two endothermic reactions located at 579 °C and 737 °C during heating. The first one corresponds to the melting temperature of BaTe₄O₉ powders while the latter small one is related to the peritectic reaction between BaTe₄O₉ and TiTe₃O₈, since it is lower than the melting temperature of TiTe₃O₈ (821 °C). Fig. 2 shows the sintered densities of the BaTe₄O₉–TiTe₃O₈ ceramic composites with various amounts of TiTe₃O₈ after sintering at different temperatures. Pure BaTe₄O₉ ceramic reached maximum theoretical density of 96% (5.34 g/cm³) at 550 °C and then significantly declined as the sintering temperature rose toward the melting point of BaTe₄O₉. With the addition of TiTe₃O₈, the sintering temperature for obtaining maximum sintered density

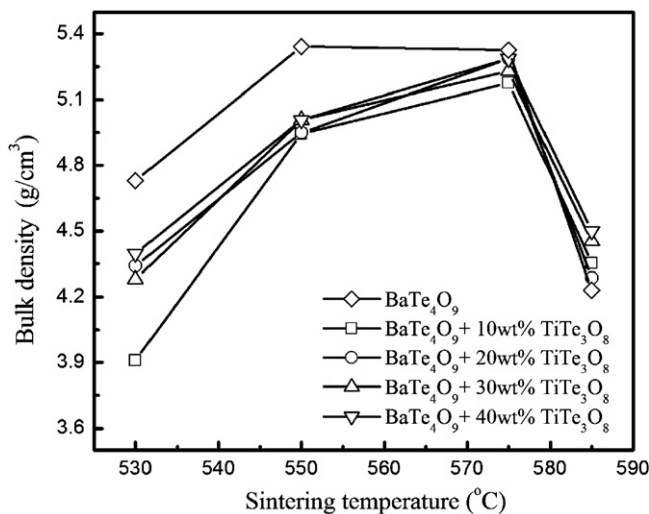


Fig. 2. Sintered density of BaTe₄O₉ ceramics with various amounts of TiTe₃O₈ sintered at different temperatures.

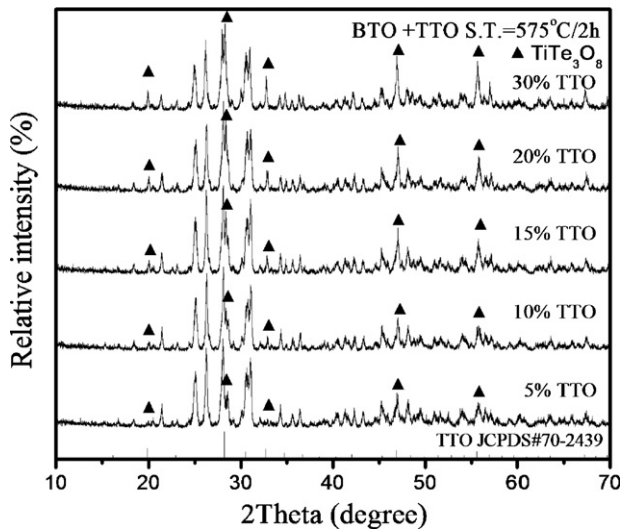


Fig. 3. XRD results of BaTe_4O_9 ceramics with various amounts of TiTe_3O_8 sintered at 575°C .

appeared to slightly increase to 575°C , due to the high melting temperature of TiTe_3O_8 (821°C).¹⁹ The maximum densities for all systems ranged from 93% to 96% of theoretical density. Over 98% sintered density was not obtained because of its volatile nature. The sintered densities of BaTe_4O_9 – TiTe_3O_8 ceramic composites were lower than that of the BaTe_4O_9 ceramic for all sintering temperatures due to the trapped porosity, although the theoretical density of TiTe_3O_8 (5.64 g/cm^3) was slightly higher than that of BaTe_4O_9 (5.56 g/cm^3). The difference in the sintered densities of the BaTe_4O_9 – TiTe_3O_8 ceramic composites with various extent of TiTe_3O_8 was insignificant.

Fig. 3 shows the XRD results of the BaTe_4O_9 – TiTe_3O_8 ceramic composites with various amounts of TiTe_3O_8 sintered at 575°C . Peak intensities located at 19.5° , 28° , and 33° in the XRD results corresponding to the TiTe_3O_8 phase increased with the TiTe_3O_8 content in the composites. Except the BaTe_4O_9 and TiTe_3O_8 phases, no other second phase was observed in the XRD results. BaTe_4O_9 having a monoclinic structure and TiTe_3O_8 with a cubic structure demonstrated no visible solubility in each other when sintered at temperatures ranging from 500°C to 585°C . It appeared that there was no possibility for the formation of other phases, because only one compound TiTe_3O_8 reported a

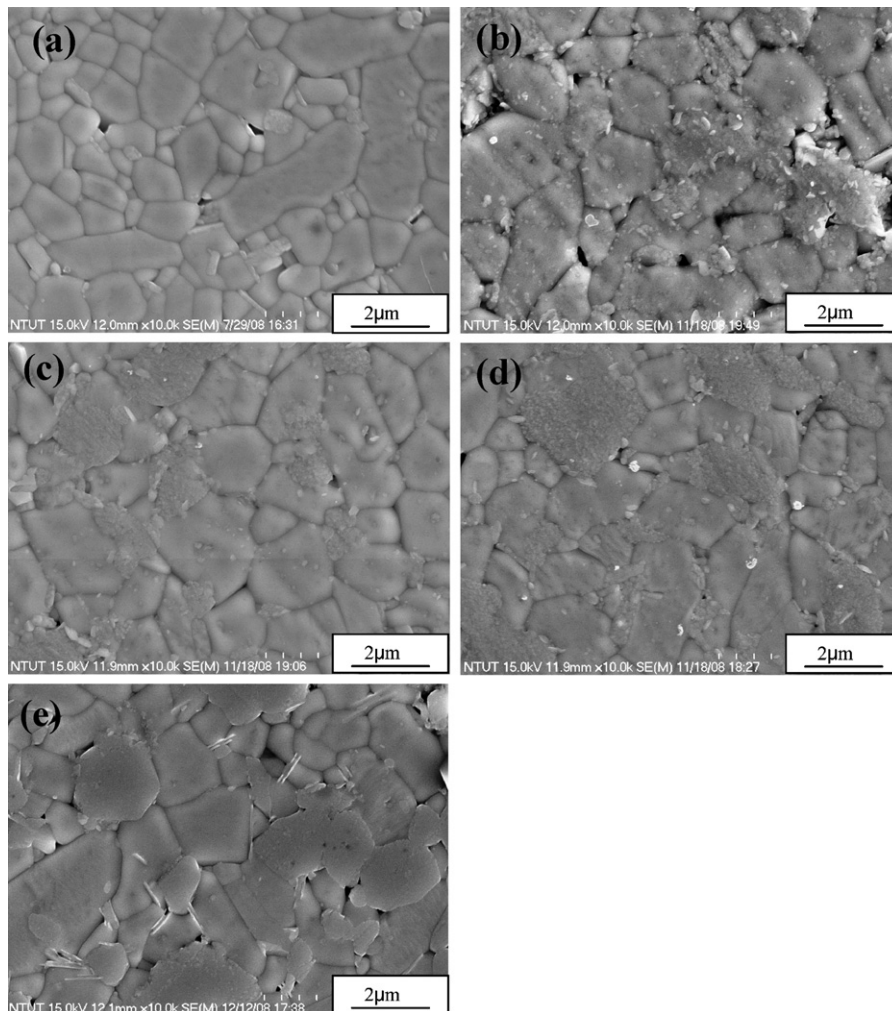


Fig. 4. SEM micrographs of BaTe_4O_9 ceramics with (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 30 wt%, and (e) 40 wt% of TiTe_3O_8 sintered at 575°C .

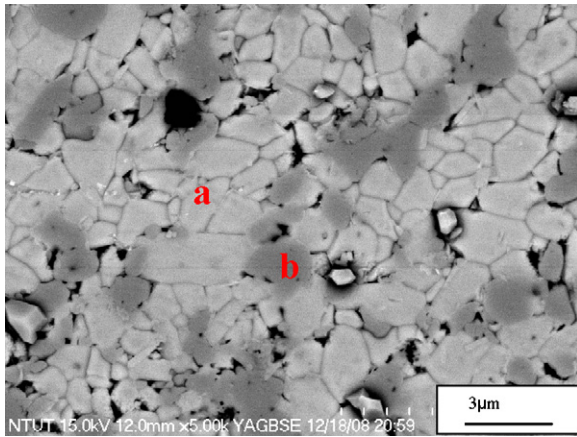


Fig. 5. Backscattering electron image (BEI) of $\text{BaTe}_4\text{O}_9 + 10 \text{ wt}\% \text{ TiTe}_3\text{O}_8$ ceramic sintered at 575°C .

thermodynamically stable single phase in the $\text{TiO}_2\text{--TeO}_2$ binary system,²¹ and the formation of BaTe_4O_9 , BaTe_2O_5 , BaTe_2O_6 , and BaTeO_3 required input of additional Ba contents.^{12,20}

SEM microstructures for the polished and thermal etched surfaces of $\text{BaTe}_4\text{O}_9\text{--TiTe}_3\text{O}_8$ ceramic composites with various amounts of TiTe_3O_8 sintered at 575°C are shown in Fig. 4. The change in the microstructures caused by the increase of the TiTe_3O_8 content seemed insignificant. A wide grain size distribution was observed for all cases, with the grain sizes of angular grains in the range of $1\text{--}4 \mu\text{m}$. In order to obtain detailed information of the structure, the $\text{BaTe}_4\text{O}_9\text{--}10 \text{ wt}\% \text{ TiTe}_3\text{O}_8$ ceramic composite was carefully examined by backscattering electron image (BEI) with the results shown in Fig. 5 and the corresponding EDS results listed in Table 1. The lighter color grains of area a in the BEI image were recognized as pure BaTe_4O_9 , and the darker grains of area b were identified as the TiTe_3O_8 phase, according to the EDS results. Based on the above observation, it is evident that the TiTe_3O_8 phase could not react with the BaTe_4O_9 , a finding further verified by the XRD results in Fig. 3. Some plate-like species were observed and identified as the TeO_2 phase resulting from the vaporization of TeO_2 during thermal etching. There was no other detectable second phase in the $\text{BaTe}_4\text{O}_9\text{--TiTe}_3\text{O}_8$ ceramic composites after sintering. Apparently, solubility of the TiTe_3O_8 in BaTe_4O_9 ceramics was limited.

Fig. 6 shows the microwave dielectric properties of the $\text{BaTe}_4\text{O}_9\text{--TiTe}_3\text{O}_8$ ceramic composites with various amounts

Table 1
EDS results of the bright and dark grains shown in Fig. 5 for $\text{BaTe}_4\text{O}_9 + 10 \text{ wt}\% \text{ TiTe}_3\text{O}_8$ ceramic sintered at 575°C .

Grain structure	Element	wt%	m (%)
Bright grains	O	16.04	60.49
	Ti	0.52	0.66
	Te	66.04	31.22
	Ba	17.39	7.64
Dark grains	O	18.83	61.47
	Ti	7.79	8.49
	Te	73.38	30.04

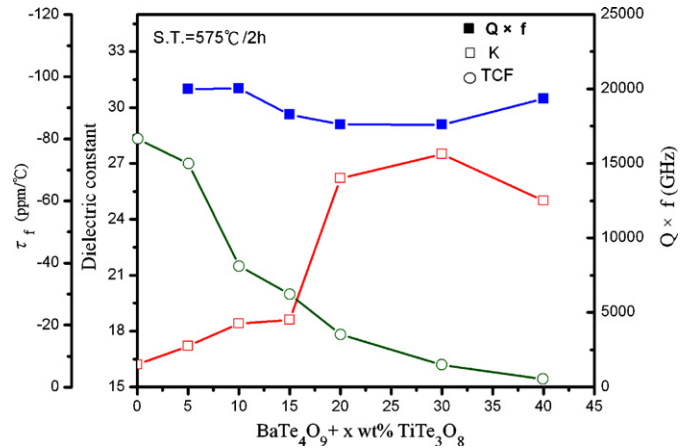


Fig. 6. Dielectric properties of BaTe_4O_9 ceramics with various amounts of $40 \text{ wt}\% \text{ TiTe}_3\text{O}_8$ sintered at 575°C .

of TiTe_3O_8 sintered at 575°C . Both the microwave dielectric properties and the sintered density exhibited the same trend of increasing with the sintering temperatures and reaching best performance at 575°C . The dielectric constants of the dense $\text{BaTe}_4\text{O}_9\text{--TiTe}_3\text{O}_8$ ceramic composites ranged from 16.2 to 26.2 and increased with the content of TiTe_3O_8 , since the dielectric constant of BaTe_4O_9 is 16.2 and that of TiTe_3O_8 is 48. As TiTe_3O_8 addition increased, the dielectric constant was partly degraded by the trapped porosity. It was observed that the $Q \times f$ value of the BaTe_4O_9 ceramic was 45,000 GHz and lowered by the addition of TiTe_3O_8 . The $Q \times f$ values of the $\text{BaTe}_4\text{O}_9\text{--TiTe}_3\text{O}_8$ ceramic composites, ranging from 17,600 GHz to 20,020 GHz, reported no significant difference. As there was no interaction between BaTe_4O_9 and TiTe_3O_8 during sintering and the grain microstructure seemed to experience no change with the TiTe_3O_8 addition, the decline in the $Q \times f$ values as compared to that of pure BaTe_4O_9 ceramic was mainly due to the existence of the trapped porosities and thus the lower sintered densities for the ceramic composites as shown in Fig. 2. The τ_f value of the $\text{BaTe}_4\text{O}_9\text{--TiTe}_3\text{O}_8$ ceramic composites ranged from $-80 \text{ ppm}/^\circ\text{C}$ for the pure BaTe_4O_9 to $-2.7 \text{ ppm}/^\circ\text{C}$ for the $\text{BaTe}_4\text{O}_9\text{--}40 \text{ wt}\% \text{ TiTe}_3\text{O}_8$ composites, which was quite consistent with the calculated value according to the mixing rule. Taking the τ_f values of the pure BaTe_4O_9 and TiTe_3O_8 ceramics as $-80 \text{ ppm}/^\circ\text{C}$ and $+133 \text{ ppm}/^\circ\text{C}$, respectively, and having them substituted into the equation of $\tau_{f,\text{composite}} = V_1 \tau_{f,1} + V_2 \tau_{f,2}$, a τ_f value of $-3.3 \text{ ppm}/^\circ\text{C}$ was obtained for the $\text{BaTe}_4\text{O}_9\text{--}40 \text{ wt}\% \text{ TiTe}_3\text{O}_8$ ceramic composite. The best dielectric properties – ϵ_r value of 25, $Q \times f$ value of 19,340 GHz, and τ_f value of $-2.7 \text{ ppm}/^\circ\text{C}$ – were obtained for the $\text{BaTe}_4\text{O}_9\text{--}40 \text{ wt}\% \text{ TiTe}_3\text{O}_8$ ceramic composite sintered at 575°C , qualifying the composites for use in the application of ceramic resonators.

4. Conclusion

With the addition of TiTe_3O_8 , the $\text{BaTe}_4\text{O}_9\text{--TiTe}_3\text{O}_8$ ceramic composites were densified at 575°C . The variation in the sintered densities of the $\text{BaTe}_4\text{O}_9\text{--TiTe}_3\text{O}_8$ ceramic composites with various extent of TiTe_3O_8 was insignificant. The sintered

densities of the BaTe₄O₉–TiTe₃O₈ ceramic composites were lower than that of the BaTe₄O₉ ceramic for all sintering temperatures due to the trapped porosity. Only the BaTe₄O₉ and TiTe₃O₈ phases were observed in the XRD results. There was no interaction between BaTe₄O₉ and TiTe₃O₈ during sintering. The dielectric constants of the dense BaTe₄O₉–TiTe₃O₈ ceramic composites ranged from 16.2 to 26.2, the $Q \times f$ value from 17,600 GHz to 20,020 GHz, and the τ_f values from -80 ppm/°C to -2.7 ppm/°C.

References

- Zheng XH, Chen XM. Dielectric ceramics with Tungsten–Bronze structure in the BaO–Nd₂O₃–TiO₂–Nb₂O₅ System. *J Mater Res* 2002;**17**:1664.
- Yebin Xu, Yanyan He. Polymeric precursor synthesis of Ba_{6–3x}Sm_{8+2x}Ti₁₈O₅₄ ceramic powder. *Ceram Int* 2002;**28**:75.
- Wolfram G, Gobel HE. Existence range, structural and dielectric properties of Zr_xTi_ySn_zO₄ ceramics ($x + y + z = 2$). *Mater Res Bull* 1952;**16**:1455.
- Lee CC, Lin P. Effect of glass addition on microwave properties of BaO–La₂O₃·4.7TiO₂. *Jpn J Appl Phys* 1998;**37**:6048.
- Borisevich A, Davies PK. Microwave dielectric properties of Li_{1+x-y}M_{1-x-3y}Ti_{x+4y}O₃ (M=Nb⁵⁺, Ta⁵⁺) solid solutions. *J Eur Ceram Soc* 2001;**21**:1719.
- Valant M, Suvorov D. Processing and dielectric properties of sillenite compounds Bi₁₂MO₂₀–(M=Si, Ge, Ti, Pb, Mn, B1/2P1/2). *J Am Ceram Soc* 2001;**12**:2900.
- Udovic M, Valant M, Suvorov D. Dielectric characterization of ceramics from the TiO₂–TeO₂ system. *J Euro Ceram Soc* 2001;**21**:1735–8.
- Wang H, Yao X. Structure and dielectric properties of pyrochlore-fluorite biphasic ceramics in the Bi₂O₃–ZnO–Nb₂O₅ system. *J Mater Res* 2001;**16**(1):83.
- Damaskos NJ, Kelsall BJ. Measuring dielectric constants of low loss materials using a broadband cavity technique. *Microwave J* 1995;**38**:140.
- Turky G, Dawy M. Spectral and electrical properties of ternary (TeO₂–V₂O₅–Sm₂O₃) glasses. *Mater Chem Phys* 2002;**77**:48–59.
- Kwon DK, Lanagan MT, Shrout TR. Synthesis of BaTiTe₃O₉ ceramics for LTCC application and its dielectric properties. *J Ceram Soc Jpn* 2005;**113**(3):216–9.
- Kwon DK, Lanagan MT, Shrout TR. Microwave dielectric properties of BaO–TeO₂ binary compounds. *Mater Lett* 2007;**61**:1827–31.
- Udovic M, Valant M, Suvorov D. Phase formation and dielectric characterization of the Bi₃O₃–TeO₂ system prepared in an oxygen atmosphere. *J Am Ceram Soc* 2004;**87**(4):591–7.
- Valant M, Suvorov D. Glass-free low-temperature cofired ceramics: calcium germanates, silicates and tellurates. *J Eur Ceram Soc* 2004;**24**(6):1715–9.
- Udovic M, Valant M, Suvorov D. Formation and decomposition of Bi₂TeO₆ compound. *J Euro Am Ceram Soc* 2004;**24**:953–8.
- Udovic M, Valant M, Suvorov D. Formation and crystal-structure determination in the Bi₂O₃–TiO₂–TeO₂ system prepared in an oxygen atmosphere. *J Am Ceram Soc* 2006;**89**(11):2462–9.
- Udovic M, Suvorov D. Sintering and dielectric characterization of pseudoternary compounds from the Bi₂O₃–TiO₂–TeO₂ system. *J Am Ceram Soc* 2007;**90**(8):2404–8.
- Subodh G, Sebastian MT. Glass-free Zn₂Te₃O₈ microwave ceramic for LTCC applications. *J Am Ceram Soc* 2007;**90**(7):2266–8.
- Wang SF, Wang YR, Wang SJ, Hsu YF, Chen LY, Tsai JS. Effect of SiO₂ addition on the microstructure and microwave dielectric properties of ultra-low fire TiTe₃O₈ ceramics. *Ceram Int* 2009;**35**:1813–7.
- Kwon DK, Lanagan MT, Shrout TR. Microwave dielectric properties and low-temperature cofiring of BaTe₄O₉ with aluminum metal electrode. *J Am Ceram Soc* 2005;**88**(12):3419–22.
- Yamanaka S, Miyaka M. Study of the ternary Ti–Te–O system. *J Less-Common Metal* 1990;**159**:179–89.