

微波毫米波用低介电常数低温共烧陶瓷研究进展

王 威¹, 张 玲^{1,2}, 吴亚光³, 乔 峰^{1,2}, 史忠旗⁴, 刘文凤⁵, 周 迪¹

(1. 西安交通大学电信学部电子科学与工程学院, 西安 710049; 2. 成都宏科电子科技有限公司, 成都 610101; 3. 河北半导体研究所, 石家庄 050051; 4. 西安交通大学材料科学与工程学院, 西安 710049; 5. 西安交通大学电气工程学院, 西安 710049)

摘 要: 在新一代高速无线通信技术推动下, 低温共烧陶瓷技术(LTCC)正处于重大变革时期。采用低介电常数(K)、低损耗、谐振频率温度稳定型 LTCC 作为高频基板材料, 可以满足无线技术高速率、低延时、高可靠的需求, 是当前热点研究之一。因此商用基板材料的现状和一些候选材料的研究工作被主要评述, 重点对玻璃/陶瓷体系、氧化物助烧体系、氟化物助烧体系、本征低温烧结体系等低 K 值 LTCC 材料的组成、结构特征、介电性能、热膨胀系数等具体指标及相应优缺点进行了讨论。同时介绍了一些热门体系的改性工作及其毫米波适用性, 最后对未来低 K 值 LTCC 材料的发展进行展望。

关键词: 微波/毫米波; 高频基板; 低介电常数; 低温共烧陶瓷技术; 介电性能

中图分类号: TQ174 文献标志码: A 文章编号: 0454-5648(2023)04-0934-15

网络出版时间: 2023-03-07



Recent Progress on Low-Permittivity LTCC for Microwave/Millimeter Wave Applications

WANG Wei¹, ZHANG Ling^{1,2}, WU Yaguang³, QIAO Feng^{1,2}, SHI Zhongqi⁴, LIU Wenfeng⁵, ZHOU Di¹

(1. School of Electronic and Information Engineering, Faculty of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, China; 2. Chengdu Hongke Electronic Technology Company Limited, Chengdu 610101, China; 3. Hebei Institute of Semiconductor, Shijiazhuang 050051, China; 4. School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China; 5. School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, China)

Abstract: With the development of a high-speed wireless technology, low-temperature co-fired ceramics (LTCC) technology becomes popular. The high-speed, low-delay and high-reliable wireless transmission could be achieved by using LTCC substrates with a low-permittivity (K), a low-loss and a stable-temperature of resonant frequency, as one of functional materials. This review introduced the current situation of commercial substrate materials and alternative LTCCs reported, i.e., ceramic/glass, oxide-assisted sintering, fluoride-assisted sintering and intrinsic low-sintering ceramic systems. The composition, structural characteristics, dielectric properties, coefficient of thermal expansion of low- K LTCCs, as well as the advantages and disadvantages, were also discussed. Some studies of commercial substrates were further described, and their performances in millimeter-wave application were represented. In addition, the development trend of low- K LTCCs was also proposed.

Keywords: microwave/millimeter wave; ceramic substrate; low-permittivity; low temperature co-fired ceramics; dielectric properties

当今高速发展的无线技术, 离不开无源器件的支持。低温共烧陶瓷(LTCC)技术是无源集成的主流技术, 通过将电极材料、基板和电子元件等封装于一体, 制成三维电路基板, 可实现多种微波无源

器件的集成^[1-2]。利用 LTCC 技术, 不仅可以制造天线、滤波器、巴伦等功能元器件, 还可以整合无源/有源器件, 极大地实现电子产品的小型化、集成化、低成本和高可靠性^[3-4]。

收稿日期: 2022-08-23。 修订日期: 2022-09-29。

基金项目: 国家自然科学基金项目(51972260, 52072295); 陕西省重点研发计划国际合作项目(2021KWZ-10); 中央高校基本科研业务费。

第一作者: 王 威(1994—), 男, 博士。

通信作者: 周 迪(1983—), 男, 博士, 教授。

Received date: 2022-08-23. Revised date: 2022-09-29.

First author: WANG Wei (1994—), male, Doctoral candidate.

E-mail: wangwei666@stu.xjtu.edu.cn

Correspondent author: ZHOU Di (1983—), male, Ph.D., Professor.

E-mail: zhoudi1220@xjtu.edu.cn

5G/6G 通信、车载网络、虚拟/增强现实、可穿戴设备等一些热门的应用场景具有高速大容量的网络需求,因此新一代高速无线网络需要向具有大带宽和高速率的毫米波发展。随着无线频谱的使用覆盖微波、毫米波甚至更高频段,以 LTCC 技术为平台的无源集成和无源/有源集成及模块化技术将迎来更大的发展空间,而在相关材料和器件方面同样存在着重大的机遇和挑战,特别是解决适应更高频应用的 LTCC 粉体的基础性需求。

LTCC 材料中高介陶瓷一般用于制备谐振器、滤波器和电容器等,有利于小型化,低介陶瓷可用作基板材料,以减小信号传输延时^[5]。而对于毫米波应用,随着波长和电路尺寸的缩小,小型化不再是难点,材料的低介和低损显得更加重要。低介和低损能降低高频下的噪声和电感串扰,明显提高传输速率,增强选频特性^[6]。因此,低介电常数 LTCC 材料是毫米波应用的关键材料。尽管低介电常数 LTCC 材料的研究工作已大量开展,但具有良好高频特性并且适用于工业化推广的材料很少。因此,本文综述介电常数小于 10.00 的 LTCC 研究进展情况,包括技术成熟度较高的体系和热点研究体系,并透过对微波毫米波应用下的性能要求及商用基板材料的现状分析,综合探讨一些有希望的微波毫米波用低介电常数 LTCC 材料,同时提出一些合理的改性策略,以期为高频 LTCC 材料的开发和国产化推进提供重要的参考价值。

1 微波毫米波应用下的性能要求

通常,LTCC 材料的微波介电性能被首要考虑,主要包括 3 个性能参数:相对介电常数(ϵ_r 或 K)、损耗角正切($\tan\delta$)或品质因数($Q \times f$)、谐振频率温度系数(TCF)。以介质谐振器为例,圆柱状样品的谐振频率 f_0 、介电常数 ϵ_r 、直径 d 间的关系可以简化为下式^[7]:

$$f_0 = \frac{c}{d\sqrt{\epsilon_r}} \quad (1)$$

其中: c 为光速。因此中高 K 材料常用于微波低频段,低 K 材料具有高的谐振频率,更适合毫米波频段。而高 $Q \times f$ 可以减小信号的传输损耗和提高器件工作频率的可选择性。同时需要 TCF 值近零,以保证器件工作时的稳定性。

微波低频到毫米波应用有不同的性能指标要求,主要体现在:1) 毫米波下需要更低 K 值的介质基板;尽管 LTCC 材料的 K 值大小取决于其工作的

频率范围,但要提高传输速率,介质基板的 K 值要尽可能的小,微波低频段用基板材料的 K 值一般小于 10.00,而 K 值小于 5.00 才能满足毫米波应用的低延时需求;2) 适用于微波低频的材料,在毫米波下损耗会明显增加,毫米波应用需要更加低损的材料($\tan\delta < 0.001$);3) 毫米波下更加需要小型化、集成化,所以对材料力学性能和热学性能要求更高;一方面基板材料在封装结构起到支撑作用,面对毫米波应用下高负荷的封装环境,应具备一定的抗弯强度和抗压强度;另一方面基于微波单片集成电路与多芯片组件技术的毫米波有源、无源器件的集成设计,基板材料的热膨胀系数(CTE)和热导率(λ)是重要考虑的热参数,与半导体材料相匹配的 CTE ($3.0 \times 10^{-6} \sim 5.0 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$) 和良好的热导率 [$\lambda > 2.0 \text{ W}/(\text{m} \cdot \text{K})$]能够提高功率和封装密度,保证封装组件的高效和高可靠运行^[8]。

2 典型的商用低 K 值 LTCC 体系

表 1 总结了几种典型的商用 LTCC 基板材料,它们主要分为微晶玻璃、陶瓷/玻璃、低烧陶瓷 3 大类。微晶玻璃体系是用适当组成的玻璃控制析晶成分来制成基板材料,其具有低介电损耗、良好高频性能等特点,但制备难度较大,对结晶相的选择和控制要求较高,以硅灰石相 CaSiO_3 (Ferro A6M)和堇青石相 $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ (IBM)体系最具代表性。陶瓷/玻璃类则以 Dupont 951、9k7 等系列最为典型,其采用结晶 Al_2O_3 作为玻璃的填充相制备而成基板材料;填充相的加入可实现体系介电性能的灵活调节,改善陶瓷的力学和热学性能,该类基板材料相比微晶玻璃表现出更高的抗弯强度、更好的 CTE 匹配性。

目前商用低 K 值 LTCC 基板材料的 K 值大多在 5.00~8.00,极少数具有更低 K 值(< 5.00),同时它们大多数基于微波低频应用开发,很少涉及到毫米波段下的性能评估。据 Ferro 公司公布的 A6M 数据显示,在 10.0~100.0 GHz 下其 K 值在 6.00 附近, $\tan\delta < 0.002$,具有十分稳定的高频性能;另一款产品 Ferro L4 的 K 值为 4.10(@ 10.0 GHz),拥有低 K 值的 L4 作为基板是十分理想的,但其在更高频下的表现仍未知。日本电气硝子公司有 2 款适用于毫米波的低 K (< 5.00)产品,其中 MLS-23 在 28.0~40.0 GHz 下, K 值和损耗分别保持 3.80 和 0.001 6,但抗弯强度仅有 130 MPa,难以用于高负载的运行环境。国产 LTCC 基板材料主要对标 Ferro A6M 和 Dupont 951,如顺

络电子、电子科大和南工大等单位已经成功研制出性能相媲美的产品。国产超低 K 值(<5.00)材料也逐渐走进商用, 如嘉兴佳利电子、汇聚新材料等公司均有相关产品介绍, 该体系产品主要是以 SiO_2 和

$\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{TiO}_2$ 等作为填充相的陶瓷/玻璃复合体系。可以看出, 商用毫米波 LTCC 基板材料处于初步阶段, 开发综合性能优异的超低 K 值 LTCC 瓷粉仍然是当前的紧要任务。

表 1 几种典型的商用 LTCC 基板材料
Table 1 Several typical LTCC materials for commercial substrate

LTCCs (main compositions)	Supplier	ε_r (K)	$\tan\delta$	CTE / $^{\circ}\text{C}^{-1}$	Flexural strength / MPa
A6M ($\text{CaO}-\text{B}_2\text{O}_3-\text{SiO}_2$)	Ferro	5.90	$<0.002 @ 10.0 \text{ GHz}$	7.0×10^{-6}	170
L4 ($\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$)	Ferro	4.10	$<0.003 @ 10.0 \text{ GHz}$	6.9×10^{-6}	120
L5 ($\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$)	Ferro	5.40	$<0.004 @ 10.0 \text{ GHz}$	5.0×10^{-6}	120
951 ($\text{Al}_2\text{O}_3+\text{CaZrO}_3+\text{glass}$)	Dupont	7.80	$0.006 @ 3.0 \text{ GHz}$	5.8×10^{-6}	320
943	Dupont	7.40	$0.002 @ 40.0 \text{ GHz}$	6.0×10^{-6}	230
9k7 ($\text{Al}_2\text{O}_3+\text{La}-\text{B glass}$)	Dupont	7.10	$0.001 5 @ 40.0 \text{ GHz}$	4.4×10^{-6}	230
CT700	Heraeus	7.00	$<0.002 @ 1 \text{ MHz}$	6.7×10^{-6}	240
502K08	Heraeus	7.70–8.70	$<0.001 @ 1 \text{ MHz}$	5.1×10^{-6}	
HL2000	Heraeus	7.30	$<0.002 6 @ 2.5 \text{ GHz}$	6.1×10^{-6}	>200
MLS-23 ($\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$)	NEG	3.80	$0.001 6 @ 40.0 \text{ GHz}$	6.1×10^{-6}	130
MLS-25 ($\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$)	NEG	4.80	$0.004 7 @ 15.0 \text{ GHz}$	4.2×10^{-6}	157
GL952	Kyocera	7.90	$0.001 5 @ 2.0 \text{ GHz}$	8.3×10^{-6}	250
GL570	Kyocera	5.70	$0.000 7 @ 2.0 \text{ GHz}$	3.4×10^{-6}	200
C0-720 ($\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$)	Kyocera	4.90	$0.000 85 @ 1 \text{ MHz}$	$(1.5-2.1) \times 10^{-6}$	200
$\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Li}_2\text{O}$	IBM	5.30–5.70		$(2.5-5.6) \times 10^{-6}$	
$\text{BaO}-\text{SnO}_2-\text{TiO}_2-\text{B}_2\text{O}_3$	Toshiba	7.00–13.00	$0.000 5-0.000 8$		
MG80	Shanghai miracle	7.80	$<0.000 4$		
MG60	Shanghai miracle	5.90	<0.002		
$\text{SiO}_2+\text{TiO}_2+\text{Zn}-\text{Si}-\text{B}-\text{Li}-\text{K glass}$	Glead Electronics	4.39	$0.0022 @ 10.0 \text{ GHz}$	3.3×10^{-6}	
$\text{SiO}_2+\text{ZrO}_2+\text{Zn}-\text{Si}-\text{B}-\text{Li}-\text{Al}-\text{Na glass}$	Glead Electronics	5.70	$0.00185 @ 10.0 \text{ GHz}$	5.6×10^{-6}	176
$\text{CaO}-\text{B}_2\text{O}_3-\text{SiO}_2$	Shenzhen Sunlord	5.70–6.20	$\leq 0.002 5 @ 10.0 \text{ GHz}$		190
$\text{SiO}_2+\text{Al}_2\text{O}_3+\text{Sr}-\text{Ca}-\text{Al}-\text{B}-\text{Si glass}$	Nanjing Synergy	4.10	$0.000 8$		204
L8	Chengdu Hongke	7.80	$0.004 @ 15.0 \text{ GHz}$		320
SC-06L	UESTC	5.90	$<0.002 @ 10.0 \text{ GHz}$	7.0×10^{-6}	>200
SC-08L	UESTC	7.80	$<0.005 @ 10.0 \text{ GHz}$		>200
$\text{CaO}-\text{B}_2\text{O}_3-\text{SiO}_2$	NJTU	5.90	$\leq 0.002 @ 10.0 \text{ GHz}$	$<7.0 \times 10^{-6}$	≥ 170

3 低 K 值 LTCC 材料研究进展

3.1 玻璃/陶瓷 LTCC 体系

玻璃/陶瓷 LTCC 体系主要包括微晶玻璃和陶瓷/玻璃复合 2 类, 作为商用 LTCC 的主流技术方案, 玻璃/陶瓷 LTCC 体系已经具有很高的技术成熟度。

3.1.1 微晶玻璃 有控制的析晶(结晶相的种类、析晶程度等)是制造微晶玻璃的基础, 如结晶相的种类往往决定着该微晶玻璃体系的 K 值、TCF、CTE 等一系列性能。常见的结晶相有堇青石/印度石、硅灰石、莫来石、锂辉石和钙/钡长石, 它们都属于硅酸盐基, 一些相关性能可见表 2。

$\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ 系是重要的微晶玻璃体系之一, 通常期望析出性能优良的堇青石相。良好析晶控制具体从热处理制度、玻璃成分调控和成核剂等方面把握。据 Ohsato 等^[9]报道, 在烧结温度达到 946°C , 开始生成中间相印度石, 随着烧结温度增加($>1\ 200^{\circ}\text{C}$), 印度石会逐渐转变为稳定的堇青石相。正常化学计量比下该体系烧结温区很窄, 经过适当调节 $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ 三相配比后能有效改善烧结性能。同时合理选择成核剂(如 TiO_2 、 ZrO_2)来促进成核和析晶, 而不改变析出的晶型^[10-11]。固相法制备堇青石陶瓷的微波介电性能为 $K=6.20$, $Q \times f=40\ 000 \text{ GHz}$, $\text{TCF}=-24.0 \times 10^{-6} \cdot ^{\circ}\text{C}^{-1}$ ^[12]; 而堇青石微

晶玻璃介电性能为 $K=4.70$, $Q \times f > 200\,000\text{ GHz}^{[13]}$ 。

$\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ (CBS)系因 Ferro A6M 而备受关注, 以 CaSiO_3 为主要结晶相的技术路线相对成熟, 而对配方及工艺的改进成为近期研究热点。Zhu 等^[14]研究了 $\text{BaO-CaO-B}_2\text{O}_3\text{-SiO}_2$ 微晶玻璃体系, 发现低含量 BaO 体系仍以 $\beta\text{-CaSiO}_3$ 和 $\alpha\text{-CaSiO}_3$ 相结晶为主; 5% BaO 的加入将玻璃转化温度(T_g)降低到 $682\text{ }^\circ\text{C}$, 但对 CTE 影响不大, $800\text{ }^\circ\text{C}$ 烧结下的介电性能为 $5.90 < K < 6.63$, $0.001\,1 < \tan\delta < 0.003\,15$ 。Xia 等^[15]以硅烷偶联剂改性 CBS 微晶玻璃粉体来获得性能优良的生瓷带, $820\text{ }^\circ\text{C}$ 烧结下可获得陶瓷性能: $K=5.93$, $\tan\delta=0.000\,81@12.0\text{ GHz}$, 这已经与 Ferro A6M 性能相匹。据 Matjaz^[16]报道, 单相 CaSiO_3 的 K 值为 $8.40@10.0\text{ GHz}$, 显然以 CaSiO_3 为主要析晶相难以获得更低 K 值(<5.00)。Wang 等^[17]采用熔融法制备了析晶 SiO_2 相的 CBS 微晶玻璃, 具体性能

如下: $K=4.04$, $\tan\delta=0.002\,9@60.0\text{ GHz}$, $\text{CTE}=3.2 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$, $\lambda=2.4\text{ W}/(\text{m} \cdot \text{K})$; 样品的毫米波性能优异, 并且 CTE 与 Si 相匹配。进一步改变 CBS 微晶玻璃的制备工艺为溶胶凝胶法, 发现此时 CBS 微晶玻璃仅有 CaB_2O_4 相析出; $14.5\text{CaO-}22.2\text{B}_2\text{O}_3\text{-}63.3\text{SiO}_2$ 组分经过 $950\text{ }^\circ\text{C}$ 烧结后性能具有低 $K(4.33)$ 、低 $\tan\delta(0.001\,2@60.0\text{ GHz})$ 和良好的 CTE ($4.1 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$), 同样展现出良好的毫米波应用前景^[18]。因此面对毫米波应用不同场景的需求, 微晶玻璃体系研究的关键是通过合理设计和控制获得恰当的结晶相。

其它微晶玻璃体系同样具有一些典型的特征, 值得被关注, 像 $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ 系会析出锂霞石相, 具有低 K 和负 CTE 的特点^[19]; $\text{BaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ 系析出钡长石相或硅钡石相, 而钡长石相的 CTE 值与 Si 相匹配^[20-21]。

表 2 玻璃组分和结晶相及其性能

Table 2 Crystalline phases and their properties considered for glass-ceramics

Composition	Crystalline phase	$\epsilon_r(K)$	CTE / $^\circ\text{C}^{-1}$	Reference
$\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$	$\beta\text{-eucryptite}$	4.80	-10.0×10^{-6}	[5]
$\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$	$\beta\text{-spodumene}$	6.40	0.9×10^{-6}	[5]
$\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$	Cordierite	4.80–6.00	1.0×10^{-6}	[5]
$\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$	Celsian	7.00	2.7×10^{-6}	[5]
$\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$	Anorthite	7.40	4.7×10^{-6}	[5]
$\text{CaO-B}_2\text{O}_3\text{-SiO}_2$	Wollastonite	6.80	9.4×10^{-6}	[5]
$\text{MgO-B}_2\text{O}_3\text{-SiO}_2$	Forsterite	6.90	9.4×10^{-6}	[5]
SiO_2	Quartz	3.81	11.2×10^{-6}	[5]
$\text{Al}_2\text{O}_3\text{-SiO}_2$	Mullite	6.00–7.20	4.5×10^{-6}	[22]
$\text{MgO-B}_2\text{O}_3\text{-SiO}_2$	Enstatite	6.70	7.8×10^{-6}	[23]
CaO-MgO-SiO_2	Diopside	7.60	7.3×10^{-6}	[24]

CTE is thermal expansion coefficient.

3.1.2 陶瓷/玻璃复合 一些低 K 、高 $Q \times f$ 的硅酸盐、铝酸盐和硼酸盐等通常被选作为陶瓷填充相, 如 SiO_2 、 Mg_2SiO_4 、 $\text{BaAl}_2\text{Si}_2\text{O}_8$ 、 $\text{CaMgSi}_2\text{O}_6$ 、 Al_2O_3 、 AlN 、 ZnAl_2O_4 和 $\text{Mg}_3\text{B}_2\text{O}_6$ 等^[25-33]。其中, 使用频率较高的陶瓷填充相为 Al_2O_3 、 Mg_2SiO_4 、 SiO_2 和 AlN 。 Al_2O_3 的选择源于其高抗弯强度(约 400 MPa)、超高的 $Q \times f$ 值($680\,000\text{ GHz}$)和成本优势^[34-35]。 AlN 具有接近 Al_2O_3 的 K 值(8.80)和抗弯强度($300\sim 400\text{ MPa}$), 有数倍于 Al_2O_3 的热导率[约为 $180\text{ W}/(\text{m} \cdot \text{K})$], CTE ($4.5 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$)接近 Si 和 GaAs 等半导体材料, 缺点是造价昂贵^[36-37]。 SiO_2 是理想的低 K 基体材料, 结晶 SiO_2 的烧结温度为 $1\,650\text{ }^\circ\text{C}$, K 值为 3.81 , $Q \times f=80\,400@22.0\text{ GHz}$, TCF 为 $-16.0 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$ ^[38];

无定型 SiO_2 的性能更优, K 值为 3.83 , $Q \times f=122\,100@21.0\text{ GHz}$, TCF 仅为 $-8.2 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$ ^[39]。 SiO_2 系陶瓷需要注意由晶型转变导致的微裂纹或开裂等系列问题。

玻璃相的选择通常从软化温度、流动性、对陶瓷颗粒的润湿性和微波介电性能等方面考虑, 以便收获合适烧结区间、良好烧结行为和介电性能的陶瓷/玻璃复合材料。以 $\text{B}_2\text{O}_3\text{-SiO}_2$ 基玻璃的使用最为常见, 主要为一系列添加碱金属和碱土金属的硼硅玻璃, 如 Ba/Ca/Zn/Mg-B-Si 、 Li-Al-B-Si 等^[40-41]。Renjini 等^[42-45]报道了 1 种 Li-Mg-Zn-B-Si (LMZBS) 玻璃并成功改性 $\text{Sm}_2\text{Si}_2\text{O}_7$ 、 Mg_2SiO_4 、 $\text{Li}_2\text{MgSiO}_4$ 和 $\text{SrCuSi}_4\text{O}_{10}$ 等硅酸盐陶瓷; 通过验证 $\text{SrCuSi}_4\text{O}_{10}$ —

LMZBS 复合陶瓷对流延工艺的适用性及 Ag 电极的兼容性, 流延片样品在 900 °C 烧结后表现出不错的高频性能: $K=4.70$, $\tan\delta=0.0019$ @15 GHz。Wang 等^[27, 30]使用 LMZBS 玻璃分别改性 $\text{BaAl}_2\text{Si}_2\text{O}_8$ 和 ZnAl_2O_4 , 同样获得了良好的降温 and 性能优化效果, 烧结温度可以降低到 950 °C 以下, 而 $Q \times f$ 值分别为 48 926 GHz 和 34 100 GHz。Chen 等^[46]报道了 1 种具有良好降温效率的 Li–B–Si–Ca–Al(LBSCA)玻璃, 2% LBSCA 可实现 $\text{Zn}_{1-x}\text{Co}_x\text{SiO}_4$ 在 850~950 °C 致密烧结; 采用 3% LBSCA 复合 LiAlO_2 可以在 900 °C 获得 $K=4.48$, $Q \times f=35\,540$ GHz, $\text{TCF}=-53.0 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$ 的介电性能^[47]。LBSCA 不与 LiAlO_2 反应, 对 TCF 值影响很小, 同 Ag 电极兼容。Jo 等^[48]报道了一系列低软化温度 (630~700 °C) 硼酸镧玻璃, 包括 La–B–Ca、La–B–Zn 和 La–B–Mg。Chen 等^[49–51]研究了 La–B–Ca+ LaBO_3 、La–B–Zn+ Al_2O_3 和 La–B–Ca+P+堇青石相等陶瓷/硼酸镧玻璃复合材料; 其中 La–B–Ca+P+堇青石复合陶瓷具有超低 K 值 (4.52 @ 12.8 GHz), 合适的 CTE ($4.1 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$) 和 Ag 兼容性, 是潜在毫米波 LTCC 基板材料。Xi 等^[52]报道了 1 种近零 TCF 值的 Li–Cu–B–Zn(LCBZ)无硅微晶玻璃, 620 °C 烧结下有最佳介电性能: $K=3.33$, $Q \times f=17\,724$ GHz, $\text{TCF} \approx 0.0 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$ 。通过填充 10% Al_2O_3 相优化了体系热导率和高频性能, LCBZ+ Al_2O_3 复合陶瓷可实现低 K (3.79)、高 $Q \times f$ (38 557 @16.6 GHz)、近零 TCF 的良好综合性能^[53]。Gui 等^[54–55]采用 2 种 Li–Cu–B 基玻璃分别助烧 BaSi_2O_5 和 BaWO_4 , 取得了良好的效果, 如 BaWO_4 添加 1% Li–Cu–B–Ba 可实现 850 °C 下致密烧结, 介电性能为 $K=8.33$, $Q \times f=58\,855$ GHz, $\text{TCF}=-61.4 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$ 。

3.2 无玻璃相 LTCC 体系

无玻璃相 LTCC 体系通常是以低熔点氧化物或者氟化物作为烧结助剂, 甚至是一些本征低烧或超低温烧结的陶瓷材料体系。因为微结构中玻璃相含量极少甚至为零, 该类体系可以在满足低温共烧的需求下最大程度地保留原始的微波介电性能。因此, 低玻璃相或者无玻璃相的特点决定该体系良好的高频特性, 虽然目前商用很少, 仍是微波毫米波高频应用最有希望的候选体系。

3.2.1 氧化物助烧体系 硅酸盐、锆酸盐、锡酸盐、铝酸盐和镓酸盐等陶瓷家族普遍具有低 K 值 (<10.00) 和高 $Q \times f$ 值的特点, 展现出高频基板应用的潜力, 相关微波介电性能见表 3, 考虑选用氧化物助烧从而保留良好高频特性是可行的策略。Li₂O、CuO、

B_2O_3 、 V_2O_5 、 Bi_2O_3 和 BaCuB_2O_5 (BCB)等^[56–64]氧化物是常见的烧结助剂, 助烧机理包括液相(生成液相润湿陶瓷相晶粒)和固相(产生缺陷来活化晶格)2 种。Xiang 等^[65]采用 5% B_2O_3 复合 CaMgGeO_4 , 将烧结温度从 1 300 °C 降低到 940 °C, 同时获得陶瓷性能为 $Q \times f=102\,000$ GHz, $K=5.80$, $\text{TCF}=-64.7 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$, B_2O_3 的加入没有过多损失 CaMgGeO_4 微波介电性能。Kim 等^[56]报道了 BCB 的微波介电性能 ($K=7.40$, $Q \times f=50\,000$ GHz, $\text{TCF}=-32.0 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$), 同时约 850 °C 的熔点使其成为一种理想的烧结助剂。Weng 等^[66–67]使用 BCB 分别实现 $\text{Zn}_{1.8}\text{SiO}_{3.8}$ 和 CaSiO_3 低于 950 °C 致密烧结, 同时确认了与 Ag 共烧的可行性, 其中 CaSiO_3 –BCB 复合陶瓷获得了兼具低烧低 K 的良好性能: $Q \times f=34\,807$ GHz, $K=4.70$, $\text{TCF}=-21.5 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$ 。除了单一氧化物作为助烧剂, 采用复合氧化物添加的策略, 可以获得更多的协同效果, 如 $\text{Li}_2\text{O}/\text{CuO}$ 、 $\text{Li}_2\text{O}/\text{Bi}_2\text{O}_3$ 、 $\text{B}_2\text{O}_3/\text{CuO}$ 和 $\text{ZnO}/\text{B}_2\text{O}_3$ 等^[7, 68]。

硅酸盐家族单相陶瓷的介电性能汇总见图 1, 可以发现大多数硅酸盐的 K 值很低 (<10), 部分岛状、架状硅酸盐的 K 值更是低于 5; 岛状和链状整体具有超高 $Q \times f$ 值 (图 1 超高 $Q \times f$ 区); 同时许多单相硅酸盐的 TCF 处于合适的区间 ($\pm 30 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$), 所以硅酸盐基陶瓷作为毫米波用 LTCC 基板的路线具备可行性, 下面以岛状硅酸盐为例讨论。Roshni 等^[117]以 Mg_2SiO_4 为基板, 设计和制备了一款中心频率为 2.4 GHz 的微带贴片天线, 其有着大的回波损耗 (20.6 dB), 较高的增益 (3.2 dB), 性能可与许多商用天线媲美 (像以 FR4、RO3003 为基板), 这得益于 Mg_2SiO_4 陶瓷的低 K 高 $Q \times f$ 值的特性, 极大地提高了贴片天线的增益和匹配性。通过 Li^+ 、 Cu^{2+} 等离子取代的岛状硅酸盐往往具有中温烧结的温度和一些良好的特性, 如 $\text{Mg}_{1.92}\text{Cu}_{0.08}\text{SiO}_4$ 和 $\text{Li}_2\text{MgSiO}_4$ 可分别在 1 250 °C 和 1 175 °C 致密烧结^[118–119], $\text{Zn}_{1.92}\text{Cu}_{0.08}\text{SiO}_4$ 的 TCF 改善为 $-28.0 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$ ^[120], $\text{Li}_2\text{SrSiO}_4$ 兼具低烧结温度 (880 °C) 和高 $Q \times f$ 值 (100 700 GHz)^[89], LiYbSiO_4 表现出低 K (7.30) 和近零 TCF ($4.52 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$)^[87]。而以氧化物助烧的硅酸盐展现出诱人的毫米波应用潜力, Szwagierczak 等^[121]报道了低烧的 Zn_2SiO_4 – $\text{Zn}_4\text{B}_6\text{O}_{13}$ 复合陶瓷体系, 0.15~1.10 THz 毫米波下, K 值为 5.80, $\tan\delta$ 为 0.006。Weng 等^[59]报道了低烧硅酸盐 $\text{Bi}_4(\text{SiO}_4)_3$ 复合改性 $\text{Zn}_{1.8}\text{SiO}_{3.8}$, 15.7 GHz 下测得性能: $K=6.78$, $Q \times f=28\,742$ GHz, $\text{TCF}=-22.6 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$ 。

表 3 硅、锗、镓、锡、铝酸盐体系的微波介电性能和烧结温度汇总

Table 3 A summary of reported single-phase dielectric properties and sintering conditions for silicate, germanate, gallate, stannate and aluminate

Composition	Sintering temperature/ $^{\circ}\text{C}$	$\epsilon_r(K)$	f_0/GHz	$Q \times f/\text{GHz}$	$\text{TCF}/^{\circ}\text{C}^{-1}$	Reference
SiO_2 (cristobalite)	1 650	3.81	22.0	80 400	-16.1×10^{-6}	[38]
SiO_2 (amorphous)	>1 700	3.83	21.0	122 100	-8.3×10^{-6}	[39]
Al_2SiO_5	1 525	4.43		41 800	-17.0×10^{-6}	[6]
LiAlSiO_4	1 350	4.80		36 000	8.0×10^{-6}	[7]
$\text{Li}_2\text{MgSiO}_4$	1 250	5.10	8.0	15 385		[7]
LiAlO_2	1 250	5.45	10.0–12.0	14 748	-190.0×10^{-6}	[69]
Mg_2GeO_4	1 450	5.48		11 037	-27.6×10^{-6}	[70]
$\text{NaAlSi}_3\text{O}_8$	1 025	5.50	10.5	11 200	-5.0×10^{-6}	[41]
$\text{Li}_2\text{CaSiO}_4$	1 000	5.60	8.0	4 210.5		[71]
$\text{CaCuSi}_4\text{O}_{10}$	1 045	5.75	13.0	20 210	-38.9×10^{-6}	[72]
$\text{SrCuSi}_4\text{O}_{10}$	1 025	5.77	13.0	48 790	-46.3×10^{-6}	[72]
$\text{SrCuSi}_4\text{O}_{10}$	1 100	5.59	14.0–16.0	82 252	-41.3×10^{-6}	[73]
$\text{BaCuSi}_4\text{O}_{10}$	1 100	6.03	14.0–16.0	49 952	-18.0×10^{-6}	[73]
$\text{Li}_2\text{ZnSiO}_4$	1 250	5.80		14 700	-96.6×10^{-6}	[74]
$\text{CaCoSi}_2\text{O}_6$	1 175	6.04	5.0–15.0	12 457	-18.9×10^{-6}	[6]
$\text{Li}_2\text{MgGeO}_4$	1 250	6.10		28 500	-74.7×10^{-6}	[75]
$\text{SrZnSi}_3\text{O}_8$	1 150	6.12	12.0–14.0	78 064	-33.2×10^{-6}	[6]
$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	1 440	6.20		40 000	-24.0×10^{-6}	[12]
LiBGeO_4	820	6.28		21 620	-88.7×10^{-6}	[76]
$\text{BaAl}_2\text{Si}_2\text{O}_8$	1 450	6.36		44 800	-46.9×10^{-6}	[7]
Li_2GeO_3	1 080	6.36	14.5	29 000	-72.0×10^{-6}	[77]
$\text{Li}_2\text{ZnGeO}_4$	1 220	6.50		35 400	-60.6×10^{-6}	[75]
Zn_2SiO_4	1 340	6.60		219 000	-61.0×10^{-6}	[6]
$\text{BaZnSi}_3\text{O}_8$	1 100	6.60	15.4	52 400	-24.5×10^{-6}	[6]
BaSi_2O_5	1 250	6.70	12.6	59 500	-28.0×10^{-6}	[78]
$\text{SrMgSi}_2\text{O}_6$	1 125	6.70		25 800	-46.0×10^{-6}	[79]
MgSiO_3	1 380	6.70		121 200	-17.0×10^{-6}	[23]
CaMgGeO_4	1 300	6.71	15.5	124 900	-73.7×10^{-6}	[65]
Ca_2GeO_4	1 420	6.76		82 400	-67.0×10^{-6}	[80]
CaSiO_3	1 500	6.80		42 200	-19.0×10^{-6}	[81]
SrSiO_3	1 500	6.80		13 100	-66.0×10^{-6}	[81]
Mg_2SiO_4	1 550	6.80		270 000	-70.0×10^{-6}	[82]
MgGeO_3	1 200	6.80		65 200	-45.0×10^{-6}	[83]
Zn_2GeO_4	1 300	6.87		102 700	-32.4×10^{-6}	[84]
Li_4GeO_4	720	6.99	15.5	47 813	-159.2×10^{-6}	[85]
HfSiO_4	1 600	7.00	10.0	25 000	-44.0×10^{-6}	[7]
$\text{Ba}_2\text{MgSi}_2\text{O}_7$	1 350	7.00		30 000	-62.0×10^{-6}	[41]
CaMgSiO_4	1 350	7.05	9.0–13.0	62 500	-62.9×10^{-6}	[86]
$\text{Sr}_2\text{Al}_2\text{SiO}_7$	1 525	7.20	12.0–16.0	33 000	-37.0×10^{-6}	[7]
LiYbSiO_4	1 140	7.30		25 276	$(4.5-8.0) \times 10^{-6}$	[87]
$\text{Ba}_5\text{Si}_8\text{O}_{21}$	1 200	7.30	12.4	16 700	25.0×10^{-6}	[78]
$\text{CaMnSi}_2\text{O}_6$	1 220	7.39	14.0	34 100	-25.6×10^{-6}	[88]
$\text{Li}_2\text{SrSiO}_4$	880	7.40		100 700	-85.4×10^{-6}	[89]
ZrSiO_4	1 570	7.40	5.2	8 583		[7]
$\text{CaAl}_2\text{Si}_2\text{O}_8$	1 525	7.40	10.5	12 000	-130.0×10^{-6}	[41]

Mg ₂ SnO ₄	1 600	7.40	12.3	59 500	-61.2×10^{-6}	[90]
CaMgSi ₂ O ₆	1 290	7.46		59 640	-46.0×10^{-6}	[6]
Ba ₂ MgGe ₂ O ₇	1 280	7.76		20 700	-55.0×10^{-6}	[91]
Ca ₃ Si ₂ O ₇	1 300	7.80	10.0	28 400		[16]
Nd ₂ SiO ₅	1 500	7.94	17.6	38 800	-53.0×10^{-6}	[7]
Ba ₂ ZnSi ₂ O ₇	1 200	8.09	10.0	26 634	-51.5×10^{-6}	[6]
LiInSiO ₄	1 150	8.20		12 600	-55.0×10^{-6}	[92]
Ba ₂ Si ₃ O ₈	1 300	8.20	13.1	29 800	-37.0×10^{-6}	[78]
MgAl ₂ O ₄	1 550	8.20		110 510	-74.1×10^{-6}	[93]
BaCu ₂ Si ₂ O ₇	1 025	8.29	12.0–14.0	46 085	-27.5×10^{-6}	[61]
Sr ₂ MgSi ₂ O ₇	1 550	8.30	10.0–18.0	55 000	-47.5×10^{-6}	[6]
CaSiO ₃	1 300	8.40	10.0	16 000		[16]
Sr ₂ ZnSi ₂ O ₇	1 475	8.40	12.6	105 000	-51.5×10^{-6}	[6]
SrCaAlSiO ₇	1 475	8.40	12.0–16.0	25 000	-42.0×10^{-6}	[6]
Ca ₃ SnSi ₂ O ₉	1 500	8.40	15.1	92 000	-60.0×10^{-6}	[41]
LiAl ₅ O ₈	1 600	8.43		51 700	-38.0×10^{-6}	[94]
Sm ₂ SiO ₅	1 500	8.44	14.4	64 000	-37.0×10^{-6}	[7]
BaCuSi ₂ O ₆	1 050	8.45	12.0–14.0	31 424	0.4×10^{-6}	[6]
CaAl ₄ O ₇	1 575	8.45		25 500	-98.0×10^{-6}	[95]
ZnAl ₂ O ₄	1 380	8.50	12.3	56 000	-79.0×10^{-6}	[41]
Mn ₂ SiO ₄	1 100/N ₂	8.52		50 000	-90.0×10^{-6}	[41]
Sr ₂ MgGe ₂ O ₇	1 330	8.56		28 800	-70.5×10^{-6}	[96]
Ca ₂ SiO ₄	1 450	8.60	4.0–6.0	26 100	-89.0×10^{-6}	[7]
Li ₂ NiGe ₃ O ₈	940	8.60	12.2	42 200	-78.2×10^{-6}	[97]
BaZnSiO ₄	1 275	8.80		34 000	-58.0×10^{-6}	[98]
Li ₂ Mg ₃ SnO ₆	1 360	8.80	10.7	123 000	-32.0×10^{-6}	[99]
Sr ₂ ZnGe ₂ O ₇	1 290	8.81		35 700	-84.4×10^{-6}	[96]
Sr ₂ CoSi ₂ O ₇	1 375	8.90	10.0–18.0	34 000	-56.7×10^{-6}	[6]
CaGeO ₃	1 200	8.90	10.0	32 200		[16]
CaAl ₂ O ₄	1 450	8.90		91 350	-55.0×10^{-6}	[100]
Ca ₃ Al ₂ Ge ₃ O ₁₂	1 325	8.97	14.0	114 871	-54.6×10^{-6}	[101]
Ba ₂ ZnGe ₂ O ₇	1 180	9.00		13 950	-75.0×10^{-6}	[91]
Li ₂ CoGe ₃ O ₈	950	9.00	12.6	40 500	-42.0×10^{-6}	[97]
CaSnSiO ₅	1 525	9.08		61 000	35.0×10^{-6}	[6]
CaGa ₄ O ₇	1 275	9.10	12.4	40 600	-86.3×10^{-6}	[102]
SrGa ₄ O ₇	1 300	9.20	14.6	62 400	-63.4×10^{-6}	[102]
SrGa ₂ O ₄	1 275	9.20		66 000	-85.0×10^{-6}	[103]
Sr ₃ Ho ₂ Ge ₃ O ₁₂	1 260	9.23	15.7	104 600	-26.0×10^{-6}	[104]
BaCo ₂ Si ₂ O ₇	1 350	9.26	12.0–14.0	31 135	-92.1×10^{-6}	[105]
Sr ₃ Yb ₂ Ge ₃ O ₁₂	1 240	9.30	15.4	129 360	-42.0×10^{-6}	[104]
Ca ₂ Al ₂ SiO ₇	1 500	9.30	12.0–17.0	31 000	-34.0×10^{-6}	[6]
SrY ₂ Si ₃ O ₁₀	1 425	9.30		64 100	-31.0×10^{-6}	[106]
Li ₂ TiGeO ₅	1 140	9.43	14.7	65 300	24.3×10^{-6}	[107]
Sr ₂ SiO ₄	1 575	9.50	4.0–6.0	19 100	-205.0×10^{-6}	[7]
BaY ₂ Si ₃ O ₁₀	1 400	9.50		65 600	-28.0×10^{-6}	[106]
MgGa ₂ O ₄	1 410	9.54	14.7	117 000	-4.0×10^{-6}	[7]
Ca ₃ Ga ₂ Ge ₃ O ₁₂	1 320	9.79	14.3	129 356	-50.2×10^{-6}	[101]
BaGe ₄ O ₉	1 060	9.80		78 400	-44.2×10^{-6}	[108]

ZnGa ₂ O ₄	1 400	9.85	9.9	85 824	-64.0×10 ⁻⁶	[109]
Ca ₂ MgSi ₂ O ₇	1 300	9.86	7.9	8 016	-42.0×10 ⁻⁶	[6]
Li ₂ TiSiO ₅	1 180	9.89	14.2	38 100	50.1×10 ⁻⁶	[107]
Sm ₂ Si ₂ O ₇	1 375	10.00	10.0	1 670		[42]
Al ₂ O ₃	1 550	10.05		680 000	-60.0×10 ⁻⁶	[34]
Ca ₂ SnO ₄	1 450	10.10	10.0–12.0	84 600	-42.5×10 ⁻⁶	[110]
Zn ₂ SnO ₄	1 225	10.20		39 000	-84.3×10 ⁻⁶	[111]
Li ₂ ZnGe ₃ O ₈	945	10.30	13.3	47 400	-63.9×10 ⁻⁶	[112]
LiGa ₃ O ₈	1 280	10.50	13.3	127 040	-60.2×10 ⁻⁶	[113]
Y ₃ Al ₅ O ₁₂	1 780	10.53	7.4	95 270	-51.7×10 ⁻⁶	[114]
Ca ₃ ZrSi ₂ O ₉	1 400	10.60	12.0–15.0	54 791	-76.8×10 ⁻⁶	[6]
CaGa ₂ O ₄	1 275	10.60		15 400	-58.0×10 ⁻⁶	[103]
Ca ₄ ZrGe ₃ O ₁₂	1 340	10.68		76 900	-41.3×10 ⁻⁶	[115]
Ca ₃ Y ₂ Ge ₃ O ₁₂	1340	10.80	13.2	97 126	-40.6×10 ⁻⁶	[116]
CaGe ₂ O ₅	1 180	10.90	10.0	39 000		[16]
Ca ₂ ZnSi ₂ O ₇	1 300	11.00	10.0–18.0	13 500	-64.3×10 ⁻⁶	[6]
BaSiO ₃	1 200	11.10	11.7	6 600	-35.0×10 ⁻⁶	[78]
SrGe ₄ O ₉	1 100	11.20		62 500	-11.7×10 ⁻⁶	[108]

TCF is temperature coefficient of resonant frequency.

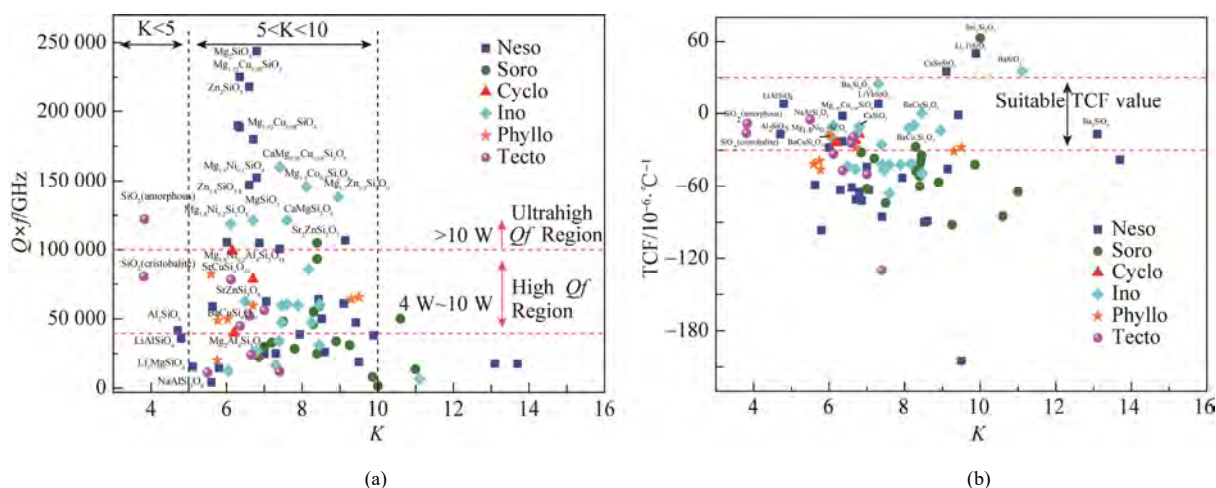


图1 硅酸盐家族的(a)品质因数 $Q \times f$ 、(b)谐振频率温度系数 TCF 与介电常数 K 相互关系

Fig. 1 Variation of (a) $Q \times f$ and (b) TCF as a function of K values in silicate family

3.2.2 氟化物助烧体系 氟化物是一类低烧结温度的微波介质陶瓷。相对氧化物，氟化物的助烧效率更高，少量掺杂即可实现良好的降温效果。Zhang 等^[122]使用 2% LiF 助烧 Mg_2SiO_4 实现了在 800 °C 的良好烧结。Lai 等^[123]同样以 2% LiF 降温 $\text{CaMgSi}_2\text{O}_6$ 获得低温烧成的高 $Q \times f$ 值陶瓷样品。Song 等^[124]报道了一系列氟化物陶瓷块的微波介电性能，他们发现混合氟化物比单相氟化物的熔点更低，采用混合氟化物改性的 $\text{BaCuSi}_2\text{O}_6 + 0.36\text{LiF} - 0.39\text{MgF}_2 - 0.25\text{SrF}_2$ 陶瓷兼具低温烧成和近零 TCF。有报道研究了氟化物助烧体系同 Ag 电极的兼容性，成功验证的陶瓷相包括 $\text{SrCuSi}_4\text{O}_{10}$ 、 $\text{Li}_2\text{Mg}_3\text{SnO}_6$ 和 $\text{BaAl}_2\text{Si}_2\text{O}_8$ 等^[125-127]。

3.2.3 本征低温烧结陶瓷体系 通常认为单相陶瓷的烧结温度小于 950 °C 是本征低温烧结陶瓷，烧结温度低于 700 °C 是超低温烧结陶瓷，这时电极材料可以考虑 Al 电极^[128-129]。这些陶瓷体系往往来自本征烧结温度低的氧化物的盐类，氧化物包括 MoO_3 (熔点 795 °C)、 TeO_2 (733 °C)、 V_2O_5 (690 °C)、 Bi_2O_3 (817 °C)、 P_2O_5 (340 °C) 和 B_2O_3 (450 °C)^[130-131]。

图 2 汇总了各本征低温烧结陶瓷体系的介电性能。碲基陶瓷普遍为中 K 值材料，不适合用于毫米波基板。研究较多的钨酸盐多为 AWO_4 ，其中 A 位离子半径大的形成白钨矿 (Ba、Sr、Ca)，较小的形成黑钨矿 (Mg、Zn、Li)^[132]。大部分的钨酸盐烧结温度为中温， K 值在 7.00~18.00。只有含碱金属的钨

酸盐烧结温度低, 如 Li_2WO_4 、 Na_2WO_4 。Zhou 等^[133]报道了 Li_2WO_4 的介电性能, $Q \times f$ 高达 62 000 GHz, K 只有 5.50, TCF 为 $-146.0 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$ 仍需要优化。通过使用 Bi、Y、Nd 等取代 Li_2WO_4 的 A 位, TCF 值会不同程度的增加, 但 $Q \times f$ 会明显减小^[134–135]。 Na_2WO_4 陶瓷性能十分亮眼, 565 $^\circ\text{C}$ 超低温烧结下 K 为 5.60, $Q \times f$ 达到 124 200 GHz, TCF 为 $-63.0 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$ ^[136]。目前已开发的钼酸盐陶瓷体系主要有 AMoO_4 (A=Li、Mg、K/Bi 等)、 $\text{A}_2\text{Mo}_2\text{O}_7$ (A=Na、Ag 等)、 AMoO_6 (A=Ln)、 $\text{AB}(\text{MoO}_4)_3$ (A=Li、Al、Sc; B=Zn、Ca 等) 和 $\text{AB}(\text{MoO}_4)_9$ (A=Ln; B=Zr) 等^[137–150]。 K 值小于 10.00 的主要为 AMoO_4 结构, $Q \times f$ 较高 (10 000~100 000 GHz), 但 TCF 大多数过于负 (图 2b 虚线以下)。整体来说, 钼酸盐的介电性能较优, 但存在吸湿性和 TCF 过大等问题。

磷酸盐的烧结温度在 700~1 200 $^\circ\text{C}$, 具有低 K 和较高 $Q \times f$ 的性能 ($5.00 < K < 9.00$, $17\ 000 \leq Q \times f \leq 100\ 000$ GHz), 但 TCF 值也多为负。主要结构有 LnPO_4 、 LiMPO_4 (M=Mg、Ni、Zn、Mn、Co、Ca)、 $\text{A}_2\text{P}_2\text{O}_7$ (A=Co、Zn、Ca、Sr) 和 $\text{AZn}_2(\text{PO}_4)_2$ (A=Ba、Sr)^[151–156]。 LiMPO_4 结构是热门的低 K 值 LTCC 材料, 如 LiMgPO_4 和 LiZnPO_4 的 K 值分别为 6.60 和 5.50, 并同 Ag 化学兼容。钨酸盐研究较多的结构主

要有 AVO_4 (A=Bi、Ln、Ba、Mg、Sr)、 LiMVO_6 (M=Mo、W)、 AV_2O_6 (A=Ba、Ca、Na)、 $\text{A}_2\text{V}_2\text{O}_7$ (A=Ba、Zn、Mg、Sr)、钒基石榴石 $\text{A}_3\text{B}_2\text{V}_3\text{O}_{12}$ (B=Zn、Mg、Ca) 和 $\text{NaB}_4\text{V}_5\text{O}_{17}$ (B=Ca、Sr) 等^[157–166], 大部分 K 值大于 8.00, 仅少数 K 值较小。值得注意的是许多钨酸盐有着正 TCF 值 (图 2b 虚线以上), 是为数不多的低/中 K 值 TCF 调节剂。

硼酸盐陶瓷的研究工作包括: 氧化硼复合①碱金属/碱土金属/过渡金属等氧化物: $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ 、 $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ 、 $\text{B}_2\text{O}_3-\text{MgO}$ 体系、 $\text{B}_2\text{O}_3-\text{ZnO}$ 体系、 $\text{BaTi}(\text{BO}_3)_2$ 、 $\text{BaCu}(\text{B}_2\text{O}_5)$ 、 $\text{Li}_3\text{AlB}_2\text{O}_6$ 、 $\text{CaAl}_{2x}\text{B}_2\text{O}_{4+3x}$; ②稀土氧化物: LnBO_3 (Ln=La、Y、Sm、Nd); ③其它金属氧化物: $\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3$ 、 BaSnB_2O_6 等^[167–173]。由于硼原子具有绝对低的极化率, 以硼为主要元素构成的硼基陶瓷在毫米波用低 K 值 LTCC 方面极具潜力。硼酸盐陶瓷 K 值普遍小于 8.00, 一些超低 K 值硼酸盐已有报道, 如 $\text{Li}_3\text{AlB}_2\text{O}_6$ ($K=4.20$)、 Li_3BO_3 ($K=5.00$) 和 CaAlB_2O_4 ($K=5.80$)。硼酸盐陶瓷基本结构单元是 $[\text{BO}_3]$ 和 $[\text{BO}_4]$, 它们可以相互孤立构造, 也能通过顶角等方式联结成各种配阴离子^[174], 这种构造形式与硅酸盐具有相似性, 很多硼酸盐也表现出了类似高 $Q \times f$ 的介电性能, 如岛状 $\text{Mg}_3\text{B}_2\text{O}_6$ 的 $Q \times f$ 值为 230 000 GHz^[168]。

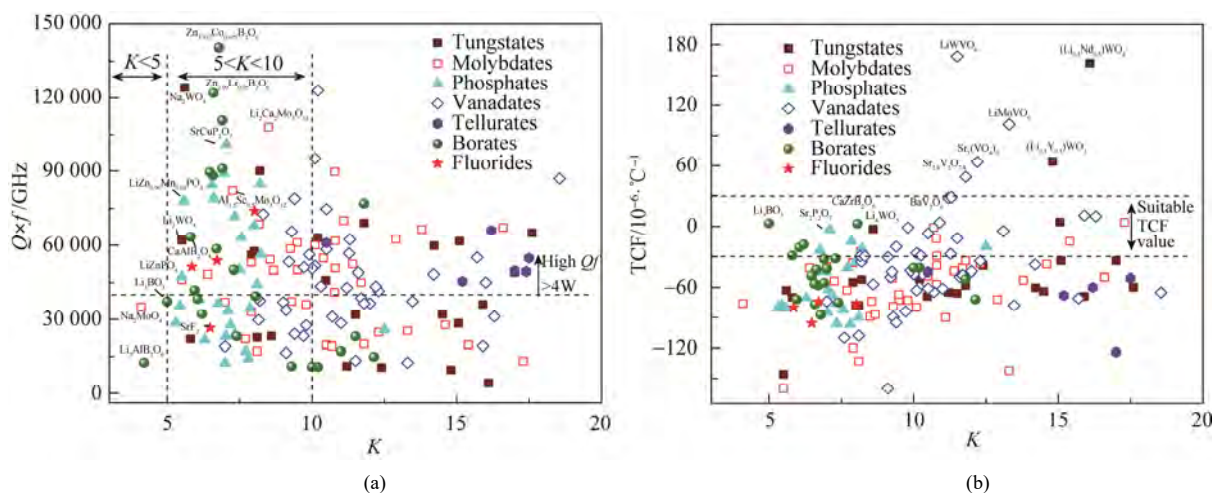


图2 本征低温烧结陶瓷体系的(a)品质因数 $Q \times f$ 、(b)谐振频率温度系数 TCF 与介电常数 K 相互关系

Fig. 2 Variation of (a) $Q \times f$ and (b) TCF as a function of K values of intrinsic low-sintering ceramic systems

4 总结和展望

具有低 K 值和良好高频特性的 LTCC 材料是未来毫米波应用的基础性需求。当前商用低 K 值瓷粉多以微波低频应用开发, 正处于微波低频向毫米波过渡的关键时期, 开发超低 K 值瓷粉仍十分必要。玻

璃/陶瓷作为商用 LTCC 的主流技术方案, 在毫米波使用中仍有着不俗的表现。而包括低熔点氧化物/氟化物助烧、本征低烧和超低烧在内的低 K 值 LTCC 体系, 透露出更多的高频应用潜力, 有希望成为下一代商用 LTCC 基板材料。硅酸盐体系具备廉价、高性能等综合优势, 正逐渐在毫米波应用中崭露头角。

未来毫米波用 LTCC 材料的发展趋势: 在高频下具有更低的 K 值 1.00~5.00, 合适的 $\tan\delta < 0.001$, 近零的 TCF 值, 高抗弯强度 ≥ 200 MPa, 良好的热导率 ≥ 3.0 W/(m·K)。陶瓷材料无论是实现超低 K 值, 还是同时兼具上述性能特性, 都具有很高的难度。探究性能更优的毫米波用基板材料, 要合理利用非晶及气孔(如采用玻璃微球和泡沫陶瓷)等方法来降低陶瓷体系 K 值, 合理选择助烧剂种类和陶瓷基体收获良好的电学、热学和力学性能, 可结合计算机深度学习进行材料预测和设计, 最终做好协调低烧、低 K 和良好性能特性的难题。毫米波段性能测试是 LTCC 材料毫米波应用研究的先导, 准确的测试对于低 K 瓷粉的开发、高频基板的设计起到关键性作用。随着测试频率的提高, 用于微波频段的测试方法逐渐不能适用, 需要精确高、普适性强的毫米波介电性能测试方法。同时, 应制定合理的毫米波性能评估标准, 以便于对毫米波性能进行统一的对比判断。另外, 可结合软件仿真进行毫米波段原型器件设计, 验证材料毫米波应用可行性。推进低 K 值 LTCC 材料的国产化, 除了关注瓷粉的高频介电性能、力学和热学性能; 还需考虑瓷粉其它方面的问题, 包括瓷粉和电极共烧匹配、与流延工艺的适配、同电极浆料的线膨胀匹配, 甚至瓷粉的成本控制, 这需要企业、高校和科研工作者的共同努力。

参考文献:

- [1] IMANAKA Y. Multilayered low temperature cofired ceramic technology[J]. *Ceram Jpn*, 2010, 45: 350–362.
- [2] SOBOCINSKI M, PUTAALA J, JANTUNEN H. Multilayer low-temperature co-fired ceramic systems incorporating a thick-film printing process[M]. *Printed Films*, 2012: 134–164.
- [3] 王睿, 王悦辉, 周济, 等. 低温共烧陶瓷技术及其应用[J]. *硅酸盐学报*, 2007, 35(S1): 125–130.
WANG Rui, WANG Yuehui, ZHOU Ji, et al. *J Chin Ceram Soc*, 2007, 35(S1): 125–130.
- [4] 杨邦朝, 胡永达. LTCC 技术的现状和发展[J]. *电子元件与材料*, 2014, 33(11): 5–9.
YANG Bangchao, HU Yongda. *Electron Comp Mater (in Chinese)*, 2014, 33(11): 5–9.
- [5] SEBASTIAN M T, JANTUNEN H. Low loss dielectric materials for LTCC applications: A review[J]. *Int Mater Rev*, 2013, 53(2): 57–90.
- [6] KAMUTZKI F, SCHNEIDER S, BAROWSKI J, et al. Silicate dielectric ceramics for millimetre wave applications[J]. *J Eur Ceram Soc*, 2021, 41(7): 3879–3894.
- [7] SEBASTIAN M T, UBIC R, JANTUNEN H. Low-loss dielectric ceramic materials and their properties[J]. *Inter Mater Rev*, 2015, 60(7): 392–412.
- [8] 李建辉, 丁小聪. LTCC 封装技术研究现状与发展趋势[J]. *电子与封装*, 2022, 22(3): 030205.
LI Jianhui, DING Xiacong. *Electron Packag (in Chinese)*, 2022, 22(3): 030205.
- [9] OHSATO H, KIM J S, CHEON C I, et al. Crystallization of indialite/cordierite glass ceramics for millimeter-wave dielectrics[J]. *Ceram Int*, 2015, 41: S588–S593.
- [10] ANDO M, OHSATO H, IGIMI D, et al. Low-temperature sintering of silica-boric acid-doped willemite and microwave dielectric properties[J]. *Jpn J Appl Phys*, 2015, 54(10S): 10NE03.
- [11] OHSATO H, VARGHESE J, KAN A, et al. Volume crystallization and microwave dielectric properties of indialite/cordierite glass by TiO_2 addition[J]. *Ceram Int*, 2021, 47(2): 2735–2742.
- [12] OHSATO H, TERADA M. Sintering conditions of cordierite for microwave/millimeterwave dielectrics[J]. *IEEE Trans Ultrason Ferroelectr Freq Control*, 2008, 55(5): 503–505.
- [13] OHSATO H, KIM J S, CHEON C I, et al. Millimeter-wave dielectrics of indialite/cordierite glass ceramics: Estimating Si/Al ordering by volume and covalency of Si/Al octahedron[J]. *J Ceram Soc Jpn*, 2013, 121(1416): 649–654.
- [14] ZHU H, FU R, AGATHOPOULOS S, et al. Crystallization behaviour and properties of $\text{BaO-CaO-B}_2\text{O}_3\text{-SiO}_2$ glasses and glass-ceramics for LTCC applications[J]. *Ceram Int*, 2018, 44(9): 10147–10153.
- [15] XIA Y, HU Y, REN L, et al. Manufacturing a high performance film of $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ glass-ceramic powder with surface modification for LTCC application[J]. *J Eur Ceram Soc*, 2018, 38(1): 253–261.
- [16] VALANT M, SUVOROV D. Glass-free low-temperature cofired ceramics: Calcium germanates, silicates and tellurates[J]. *J Eur Ceram Soc*, 2004, 24(6): 1715–1719.
- [17] WANG S F, LAI B C, HSU Y F, et al. Dielectric properties of $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ glass-ceramic systems in the millimeter-wave frequency range of 20–60 GHz[J]. *Ceram Int*, 2021, 47(16): 22627–22635.
- [18] WANG S F, LAI B C, HSU Y F, et al. Physical and structural characteristics of sol-gel derived $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ glass-ceramics and their dielectric properties in the 5G millimeter-wave bands[J]. *Ceram Int*, 2022, 48(7): 9030–9037.
- [19] VENKATESWARAN C, SREEMOOLANADHAN H, VAISH R. Lithium aluminosilicate (LAS) glass-ceramics: A review of recent progress[J]. *Int Mater Rev*, 2021, 67(6): 620–657.
- [20] LI B, LI W, ZHENG J. Effect of SiO_2 content on the sintering kinetics, microstructures and properties of $\text{BaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ glass-ceramics for LTCC application[J]. *J Alloys Compd*, 2017, 725: 1091–1097.
- [21] LIN S E, CHENG Y R, WEI W C J. $\text{BaO-B}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ sealing glass for intermediate temperature solid oxide fuel cell[J]. *J Non-Cryst Solids*, 2012, 358(2): 174–181.
- [22] SZWAGIERCZAK D, SYNKIEWICZ B, KULAWIK J. Low dielectric constant composites based on B_2O_3 and SiO_2 rich glasses, cordierite and mullite[J]. *Ceram Int*, 2018, 44(12): 14495–14501.
- [23] SONG M E, KIM J S, JOUNG M R, et al. Synthesis and microwave dielectric properties of MgSiO_3 ceramics[J]. *J Am Ceram Soc*, 2008, 91(8): 2747–2750.

- [24] HE L, XIA G, YANG D A. Synthesis and characterization of LTCC composites based on the spodumene/anorthite crystallizable glass[J]. *J Alloys Compd*, 2013, 556: 12–19.
- [25] GUO J F, LIN Y X, ZHOU Z W, et al. Design and preparation of BaO–Al₂O₃–SiO₂–B₂O₃/quartz LTCC composites with tailored coefficient of thermal expansion[J]. *Ceram Int*, 2022, 48(9): 12065–12073.
- [26] XIANG L, ZHONG C, QIN T, et al. Densification, flexural strength and dielectric properties of CaO–MgO–ZnO–SiO₂/Al₂O₃ glass ceramics for LTCC applications[J]. *Ceram Int*, 2021, 47(20): 28904–28912.
- [27] WANG M, ZHONG C, QIN T, et al. Effect of LMZBS glass on the microstructure and microwave dielectric properties of monocelsian ceramics[J]. *Ceram Int*, 2020, 46(8): 12088–12095.
- [28] LIU D, ZHONG C, QIN T, et al. Low-temperature sintering of CaMgSi₂O₆-KBS composites with ultralow dielectric constant [J]. *Ceram Int*, 2020, 46(11): 17818–17824.
- [29] SHANG Y, ZHONG C, XIONG H, et al. Ultralow-permittivity glass /Al₂O₃ composite for LTCC applications[J]. *Ceram Int*, 2019, 45(11): 13711–13718.
- [30] QIN T, ZHONG C, QIN Y, et al. Low-temperature sintering mechanism and microwave dielectric properties of ZnAl₂O₄–LMZBS composites[J]. *J Alloys Compd*, 2019, 797: 744–753.
- [31] KESHAVARZ M, EBADZADEH T, BANIJAMALI S. Preparation of forsterite/MBS (MgO–B₂O₃–SiO₂) glass-ceramic composites via conventional and microwave assisted sintering routes for LTCC application[J]. *Ceram Int*, 2017, 43(12): 9259–9266.
- [32] YUAN L, LIU B, SHEN N, et al. Synthesis and properties of borosilicate/AlN composite for low temperature co-fired ceramics application[J]. *J Alloys Compd*, 2014, 593: 34–40.
- [33] DOU G, GUO M, LI Y, et al. The effect of LMBS glass on the microwave dielectric properties of the Mg₃B₂O₆ for LTCC[J]. *J Mater Sci: Mater El*, 2015, 26(6): 4207–4211.
- [34] OHASTO H, TSUNOOKA T, ANDO M, et al. Millimeter-wave dielectric ceramics of alumina and forsterite with high quality factor and low dielectric constant[J]. *J Kore Ceram Soc*, 2003, 40(4): 350–353.
- [35] 姚义俊, 丘泰, 蒋晓龙, 等. 改性氧化铝陶瓷的抗弯强度和显微结构[J]. *电子元件与材料*, 2009, 28(6): 1–3.
YAO Yijun, QIU Tai, JIANG Xiaolong, et al. *Electron Comp Mater*(in Chinese), 2009, 28(6): 1–3.
- [36] 孟献丰, 朱宏. AlN 基板材料研究进展[J]. *材料导报*, 2003, 17(3): 35–37.
MENG X, LU C, NI Y, et al. *Mater Rev*(in Chinese), 2003, 17(3): 35–37.
- [37] THORP J S, EVANS D, AL-NAIEF M, et al. The dielectric properties of aluminium nitride substrates for microelectronics packaging[J]. *J Mater Sci*, 1990, 25(12): 4965–4971.
- [38] FANG Y, LI L, XIAO Q, et al. Preparation and microwave dielectric properties of cristobalite ceramics[J]. *Ceram Int*, 2012, 38(6): 4511–4515.
- [39] LI L, FANG Y, XIAO Q, et al. Microwave dielectric properties of fused silica prepared by different approaches[J]. *Int J App Ceram Tech*, 2014, 11(1): 193–199.
- [40] CHEN G, LIU Z, MA M, et al. Composites of Li–Al–B–Si–O glass and β -Al₂O₃ for LTCC-silicon heterogeneous integration applications[J]. *Ceram Int*, 2018, 44: S141–S144.
- [41] SEBASTIAN M T. Dielectric materials for wireless communication[M]. Elsevier Sci, 2008.
- [42] RENJINI S N, THOMAS S, SEBASTIAN M T, et al. Microwave dielectric properties and low temperature sintering of Sm₂Si₂O₇ ceramic for substrate applications[J]. *Int J App Ceram Tech*, 2009, 6(2): 286–294.
- [43] SASIKALA T S, PAVITHRAN C, SEBASTIAN M T. Effect of lithium magnesium zinc borosilicate glass addition on densification temperature and dielectric properties of Mg₂SiO₄ ceramics[J]. *J Mater Sci: Mater El*, 2009, 21(2): 141–144.
- [44] GEORGE S, SAJITH V K, SEBASTIAN M T, et al. Synthesis and microwave dielectric properties of Li₂MgSiO₄ ceramics prepared using citrate gel route[J]. *J Adv Dielectr*, 2012, 1(2): 209–213.
- [45] MANU K, SEBASTIAN M T. Tape casting of low permittivity Wesselsite–glass composite for LTCC based microwave applications[J]. *Ceram Int*, 2016, 42(1): 1210–1216.
- [46] CHEN H W, SU H, ZHANG H W, et al. Low-temperature sintering and microwave dielectric properties of (Zn_{1-x}Co_x)₂SiO₄ ceramics[J]. *Ceram Int*, 2014, 40(9): 14655–14659.
- [47] ZUO H, TANG X, ZHANG H, et al. Low-dielectric-constant LiAlO₂ ceramics combined with LBSCA glass for LTCC applications[J]. *Ceram Int*, 2017, 43(12): 8951–8955.
- [48] JO Y H, KANG M S, CHUNG K W, et al. Chemical stability and dielectric properties of RO–La₂O₃–B₂O₃ (R=Ca, Mg, Zn)-based ceramics[J]. *Mater Res Bull*, 2008, 43(2): 361–369.
- [49] WANG F, ZHANG W, CHEN X, et al. Synthesis and characterization of low CTE value La₂O₃–B₂O₃–CaO–P₂O₅ glass/cordierite composites for LTCC application[J]. *Ceram Int*, 2019, 45(6): 7203–7209.
- [50] WANG F, ZHANG W, CHEN X, et al. Low temperature sintering and characterization of La₂O₃–B₂O₃–CaO glass–ceramic/LaBO₃ composites for LTCC application[J]. *J Eur Ceram Soc*, 2020, 40(6): 2382–2389.
- [51] CHEN X, WANG F, GUAN Y, et al. Phase evolution and dielectric properties of La₂O₃–B₂O₃–ZnO glass-ceramics/Al₂O₃ composites for LTCC substrates at high frequencies[J]. *J Mater Sci: Mater El*, 2022, 33(15): 12436–12446.
- [52] XI J, LU B, CHEN J, et al. Ultralow sintering temperature and permittivity with excellent thermal stability in novel borate glass-ceramics[J]. *J Non-Cryst Solids*, 2019, 521: 119527.
- [53] XI J, CHEN G, LIU F, et al. Synthesis, microstructure and characterization of ultra-low permittivity CuO–ZnO–B₂O₃–Li₂O glass/Al₂O₃ composites for ULTCC application[J]. *Ceram Int*, 2019, 45(18): 24431–24436.
- [54] GUI L, YANG H, ZHAO Q, et al. Synthesis of low temperature firing scheelite-type BaWO₄ microwave dielectric ceramics with high performances[J]. *Ceram Int*, 2022, 48(1): 1360–1365.
- [55] WU P, YANG H, YANG H, et al. Synthesis of a low-firing BaSi₂O₅ microwave dielectric ceramics with low dielectric constant[J]. *Ceram Int*, 2022, 48(12): 17289–17297.
- [56] KIM M H, LIM J B, KIM J C, et al. Synthesis of BaCu(B₂O₅) ceramics

- and their effect on the sintering temperature and microwave dielectric properties of $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Ceramics[J]. *J Am Ceram Soc*, 2006, 89(10): 3124–3128.
- [57] ROSE A, MASIN B, SREEMOOLANADHAN H, et al. Synthesis and microwave dielectric studies of pure $\text{Li}_2\text{MgSiO}_4$ and B_2O_3 , MgF_2 , WO_3 added $\text{Li}_2\text{MgSiO}_4$ for substrate applications[J]. *Appl Surf Sci*, 2018, 449: 96–104.
- [58] MA X H, KWEON S H, IM M, et al. Low-temperature sintering and microwave dielectric properties of B_2O_3 -added ZnO -deficient Zn_2GeO_4 ceramics for advanced substrate application[J]. *J Eur Ceram Soc*, 2018, 38(14): 4682–4688.
- [59] WENG Z, AMINIRASTABI H, XIONG Z, et al. Effects of the Bi_2O_3 - SiO_2 addition on the sintering behavior and microwave dielectric properties of $\text{Zn}_{1.8}\text{SiO}_{3.8}$ ceramics[J]. *J Alloys Compd*, 2017, 725: 1063–1068.
- [60] ZHANG P, LIAO J, ZHAO Y, et al. Microstructures and dielectric properties of low permittivity $\text{SrCuSi}_4\text{O}_{10}$ - Bi_2O_3 ceramics for LTCC applications[J]. *J Mater Sci: Mater El*, 2016, 28(6): 4946–4950.
- [61] SONG X Q, LU W Z, LOU Y H, et al. Synthesis, lattice energy and microwave dielectric properties of $\text{BaCu}_{2-x}\text{Co}_x\text{Si}_2\text{O}_7$ ceramics[J]. *J Eur Ceram Soc*, 2020, 40(8): 3035–3041.
- [62] FU Z, MA J, LIU P, et al. Crystal structure and microwave dielectric properties of middle-temperature-sintered $\text{Mg}_2\text{Si}_{(1-x)}\text{V}_x\text{O}_4$ ceramics[J]. *J Electroceram*, 2016, 36(1–4): 82–86.
- [63] KIM JS, SONG ME, JOUNG MR, et al. Effect of B_2O_3 addition on the sintering temperature and microwave dielectric properties of Zn_2SiO_4 ceramics[J]. *J Eur Ceram Soc*, 2010, 30(2): 375–379.
- [64] LV Y, ZUO R. Effect of the B_2O_3 addition on the sintering behavior and microwave dielectric properties of $\text{Ba}_3(\text{VO}_4)_2$ - $\text{Zn}_{1.87}\text{SiO}_{3.87}$ composite ceramics[J]. *Ceram Int*, 2013, 39(3): 2545–2550.
- [65] XIANG H, LI C, JANTUNEN H, et al. Ultralow loss CaMgGeO_4 microwave dielectric ceramic and its chemical compatibility with silver electrodes for low-temperature cofired ceramic applications[J]. *ACS Sustain Chem Eng*, 2018, 6(5): 6458–6466.
- [66] WENG Z, HAN Z, XIAO F, et al. Low temperature sintering and microwave dielectric properties of $\text{Zn}_{1.8}\text{SiO}_{3.8}$ ceramics with $\text{BaCu}(\text{B}_2\text{O}_5)$ additive for LTCC applications[J]. *Ceram Int*, 2018, 44(12): 14145–14150.
- [67] OUYANG L, WANG W, FAN H, et al. Sintering behavior and microwave performance of CaSiO_3 ceramics doped with $\text{BaCu}(\text{B}_2\text{O}_5)$ for LTCC applications[J]. *Ceram Int*, 2019, 45(15): 18937–18942.
- [68] ZHAN Y, LI L, DU M. The simulation for a high-efficiency millimeter wave microstrip antenna by low dielectric loss and wide temperature stable lithium-based microwave dielectric ceramics for LTCC applications[J]. *Ceram Int*, 2021, 47(19): 27462–27468.
- [69] LAN X K, LI J, ZOU Z Y, et al. Lattice structure analysis and optimised microwave dielectric properties of $\text{LiAl}_{1-x}\text{Zn}_{0.5}\text{Si}_{0.5}\text{O}_2$ solid solutions[J]. *J Eur Ceram Soc*, 2019, 39(7): 2360–2364.
- [70] CHEN C X, WU S P, FAN Y X. Synthesis and microwave dielectric properties of B_2O_3 -doped Mg_2GeO_4 ceramics[J]. *J Alloys Compd*, 2013, 578: 153–156.
- [71] GEORGE S, SEBASTIAN M T, RAMAN S, et al. Novel low loss, low permittivity glass-ceramic composites for LTCC applications[J]. *Int J Appl Ceram Tech*, 2011, 8(1): 172–179.
- [72] QIN J, LIU Z, MA M, et al. Structure and microwave dielectric properties of gillespite-type $\text{ACuSi}_4\text{O}_{10}$ ($A=\text{Ca}, \text{Sr}, \text{Ba}$) ceramics and quantitative prediction of the $Q \times f$ value via machine learning[J]. *ACS Appl. Mater*, 2021, 13(15): 17817–17826.
- [73] SONG X Q, LEI W, WANG F, et al. Phase evolution, crystal structure, and microwave dielectric properties of gillespite-type ceramics[J]. *J Am Ceram Soc*, 2020, 104(4): 1740–1749.
- [74] DOU G, ZHOU D, GONG S, et al. Low temperature sintering and microwave dielectric properties of $\text{Li}_2\text{ZnSiO}_4$ ceramics with ZB glass[J]. *J Mater Sci: Mater El*, 2012, 24(5): 1601–1607.
- [75] LI C, XIANG H, XU M, et al. Li_2AGeO_4 ($A=\text{Zn}, \text{Mg}$): Two novel low-permittivity microwave dielectric ceramics with olivine structure[J]. *J Eur Ceram Soc*, 2018, 38(4): 1524–1528.
- [76] XING Z, YIN C, YU Z, et al. Synthesis of LiBGeO_4 using compositional design and its dielectric behaviors at RF and microwave frequencies[J]. *Ceram Int*, 2020, 46(14): 22460–22465.
- [77] YIN C, XIANG H, LI C, et al. Low-temperature sintering and thermal stability of Li_2GeO_3 -based microwave dielectric ceramics with low permittivity[J]. *J Am Ceram Soc*, 2018, 101(10): 4608–4614.
- [78] LEI W, ZOU Z Y, CHEN Z H, et al. Controllable τ_f value of barium silicate microwave dielectric ceramics with different Ba/Si ratios[J]. *J Am Ceram Soc*, 2018, 101(1): 25–30.
- [79] ZHOU X, ZHOU H, HU S, et al. Sintering behavior and microwave dielectric properties of low-permittivity $\text{SrMgSi}_2\text{O}_6$ ceramic[J]. *J Electron Mater*, 2020, 49(10): 5989–5993.
- [80] TANG Y, X U M, DUAN L, et al. Structure, microwave dielectric properties, and infrared reflectivity spectrum of olivine type Ca_2GeO_4 ceramic[J]. *J Eur Ceram Soc*, 2019, 39(7): 2354–2359.
- [81] KAGOMIYA I, SUZUKI I, OHSATO H. Microwave dielectric properties of $(\text{Ca}_{1-x}\text{Sr}_x)\text{SiO}_3$ ring silicate solid solutions[J]. *Jpn J Appl Phys*, 2009, 48(9): 09KE02.
- [82] OHSATO H, TSUNOOKA T, SUGIYAMA T, et al. Forsterite ceramics for millimeterwave dielectrics[J]. *J Electroceram*, 2006, 17(2–4): 445–450.
- [83] FANG W, CHENG K, XIANG H, et al. Phase composition and microwave dielectric properties of low permittivity AGeO_3 ($A=\text{Mg}, \text{Zn}$) ceramics[J]. *J Alloys Compd*, 2019, 799: 495–500.
- [84] WU S, MA Q. Synthesis, characterization and microwave dielectric properties of Zn_2GeO_4 ceramics[J]. *J Alloys Compd*, 2013, 567: 40–46.
- [85] YANG Z, TANG Y, LI J, et al. Crystal structure, Raman spectra and microwave dielectric properties of novel low-temperature cofired ceramic Li_4GeO_4 [J]. *J Alloys Compd*, 2021, 867: 159059.
- [86] ZHOU H, HUANG J, TAN X, et al. Microwave dielectric properties of low-permittivity CaMgSiO_4 ceramic[J]. *J Mater Sci: Mater El*, 2017, 28(20): 15258–15262.
- [87] SU C, AO L, ZHANG Z, et al. Crystal structure, Raman spectra and microwave dielectric properties of novel temperature-stable LiYbSiO_4 ceramics[J]. *Ceram Int*, 2020, 46(12): 19996–20003.
- [88] CHEN X, LI H, ZHANG P, et al. Phase composition, microstructure, and microwave dielectric properties of $\text{CaMnSi}_2\text{O}_6$ ceramics[J]. *Ceram Int*, 2021, 47(3): 4083–4089.
- [89] DU Q, TANG Y, LI J, et al. A low- ϵ_r and high-Q microwave dielectric

- ceramic $\text{Li}_2\text{SrSiO}_4$ with abnormally low sintering temperature[J]. *J Eur Ceram Soc*, 2021, 41(15): 7678–7682.
- [90] LI H, TANG B, LI Y, et al. Relationships between Sn substitution for Ti and microwave dielectric properties of $\text{Mg}_2(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_4$ ceramics system[J]. *J Mater Sci: Mater El*, 2014, 26(1): 571–577.
- [91] LI C, YIN C, CHEN J, et al. Crystal structure and dielectric properties of germanate melilites $\text{Ba}_2\text{MGe}_2\text{O}_7$ (M=Mg and Zn) with low permittivity[J]. *J Eur Ceram Soc*, 2018, 38(15): 5246–5251.
- [92] SUNNY A, LAZER K A, MANU K M, et al. Effect of glass fluxing on densification and microwave dielectric properties of LiInSiO_4 ceramic[J]. *J Alloys Compd*, 2013, 552: 83–87.
- [93] DU C, GUO H H, ZHOU D, et al. Dielectric resonator antennas based on high quality factor MgAl_2O_4 transparent dielectric ceramics[J]. *J Mater Chem C*, 2020, 8(42): 14880–14885.
- [94] LAN X K, LI J, LI J P, et al. Phase evolution and microwave dielectric properties of novel $\text{LiAl}_{5-x}\text{Zn}_x\text{O}_{8-0.5x}$ -based ($0 \leq x \leq 0.5$) ceramics[J]. *J Am Ceram Soc*, 2019, 103(2): 1105–1112.
- [95] WU Y, HU C C, LIU B, et al. Crystal structure, vibrational spectroscopy, and microwave dielectric properties of CaAl_4O_7 ceramics with low permittivity[J]. *J Mater Sci: Mater El*, 2020, 31(6): 4520–4526.
- [96] YIN C, TANG Y, CHEN J, et al. Two low-permittivity melilite ceramics in the SrO-MO-GeO_2 (M=Mg, Zn) system and their temperature stability through compositional modifications[J]. *J Eur Ceram Soc*, 2020, 40(4): 1186–1190.
- [97] LUO H, FANG L, XIANG H, et al. Two novel low-firing germanates $\text{Li}_2\text{MGe}_3\text{O}_8$ (M=Ni, Co) microwave dielectric ceramics with spinel structure[J]. *Ceram Int*, 2017, 43(1): 1622–1627.
- [98] JOSEPH T, SEBASTIAN M T. Microwave dielectric properties of $(\text{Sr}_{1-x}\text{A}_x)_2(\text{Zn}_{1-x}\text{B}_x)\text{Si}_2\text{O}_7$ ceramics (A=Ca, Ba and B=Co, Mg, Mn, Ni)[J]. *J Am Ceram Soc*, 2010, 93(1): 147–154.
- [99] FU Z, LIU P, MA J, et al. Novel series of ultra-low loss microwave dielectric ceramics: $\text{Li}_2\text{Mg}_3\text{BO}_6$ (B=Ti, Sn, Zr)[J]. *J Eur Ceram Soc*, 2016, 36(3): 625–629.
- [100] LIU B, HU C C, HUANG Y H, et al. Crystal structure, infrared reflectivity spectra and microwave dielectric properties of CaAl_2O_4 ceramics with low permittivity[J]. *J Alloys Compd*, 2019, 791: 1033–1037.
- [101] ZHAI Y, TANG Y, LI J, et al. Structure, Raman spectra and properties of two low- ϵ_r microwave dielectric ceramics $\text{Ca}_3\text{B}_2\text{Ge}_3\text{O}_{12}$ (B=Al, Ga)[J]. *Ceram Int*, 2020, 46(18): 28710–28715.
- [102] MA J, CHEN J, TANG Y, et al. Chemical bond and microwave dielectric properties of two novel low- ϵ_r AGa_4O_7 (A=Ca, Sr) ceramics[J]. *J Eur Ceram Soc*, 2022, 42(2): 478–484.
- [103] LIU B, SHA K, ZHOU M F, et al. Novel low- ϵ_r MGA_2O_4 (M=Ca, Sr) microwave dielectric ceramics for 5 G antenna applications at the Sub-6 GHz band[J]. *J Eur Ceram Soc*, 2021, 41(10): 5170–5175.
- [104] LI J, TANG Y, ZHANG Z, et al. Two novel garnet $\text{Sr}_3\text{B}_2\text{Ge}_3\text{O}_{12}$ (B=Yb, Ho) microwave dielectric ceramics with low permittivity and high Q[J]. *J Eur Ceram Soc*, 2021, 41(2): 1317–1323.
- [105] SONG X Q, LEI W, XIE M Q, et al. Sintering behaviour, lattice energy and microwave dielectric properties of melilite-type $\text{BaCo}_2\text{Si}_2\text{O}_7$ ceramics[J]. *Mater Res Express*, 2020, 6(12): 126322(9pp).
- [106] LIN Q, SONG K, LIU B, et al. Vibrational spectroscopy and microwave dielectric properties of $\text{AY}_2\text{Si}_3\text{O}_{10}$ (A=Sr, Ba) ceramics for 5G applications[J]. *Ceram Int*, 2020, 46(1): 1171–1177.
- [107] CHENG K, TANG Y, XIANG H, et al. Two novel low permittivity microwave dielectric ceramics Li_2TiMO_5 (M=Ge, Si) with abnormally positive τ_f [J]. *J Eur Ceram Soc*, 2019, 39(8): 2680–2684.
- [108] LI F, TANG Y, LI J, et al. Effect of A-site cation on crystal structure and microwave dielectric properties of AGe_4O_9 (A=Ba, Sr) ceramics[J]. *J Eur Ceram Soc*, 2021, 41(7): 4153–4159.
- [109] LU X, DU Z, QUAN B, et al. Structural dependence of the microwave dielectric properties of Cr^{3+} -substituted ZnGa_2O_4 spinel ceramics: Crystal distortion and vibration mode studies[J]. *J Mater Chem C*, 2019, 7(27): 8261–8268.
- [110] DU K, SONG X Q, LI J, et al. Phase compositions and microwave dielectric properties of Sn-deficient Ca_2SnO_4 ceramics[J]. *J Alloys Compd*, 2019, 802: 488–492.
- [111] CHEN Y C, LIOU J M, WENG M Z, et al. Improvement microwave dielectric properties of Zn_2SnO_4 ceramics by substituting Sn^{4+} with Ti^{4+} [J]. *Ceram Int*, 2014, 40(7): 10337–10342.
- [112] XIANG H, FANG L, FANG W, et al. A novel low-firing microwave dielectric ceramic $\text{Li}_2\text{ZnGe}_3\text{O}_8$ with cubic spinel structure[J]. *J Eur Ceram Soc*, 2017, 37(2): 625–629.
- [113] AO L, TANG Y, LI J, et al. Structure characterization and microwave dielectric properties of LiGa_5O_8 ceramic with low- ϵ_r and low loss[J]. *J Eur Ceram Soc*, 2020, 40(15): 5498–5503.
- [114] DU C, FU M S, ZHOU D, et al. Dielectric resonator antenna with $\text{Y}_3\text{Al}_5\text{O}_{12}$ transparent dielectric ceramics for 5G millimeter-wave applications[J]. *J Am Ceram Soc*, 2021, 104(9): 4659–4668.
- [115] SU C, AO L, ZHAI Y, et al. Novel low-permittivity microwave dielectric ceramics in garnet-type $\text{Ca}_4\text{ZrGe}_3\text{O}_{12}$ [J]. *Mater Lett*, 2020, 275: 128149.
- [116] TANG Y, ZHANG Z, LI J, et al. $\text{A}_3\text{Y}_2\text{Ge}_3\text{O}_{12}$ (A=Ca, Mg): Two novel microwave dielectric ceramics with contrasting τ_f and $Q \times f$ [J]. *J Eur Ceram Soc*, 2020, 40(12): 3989–3995.
- [117] ROSHNI S B, ARUN S, SEBASTIAN M T, et al. Low κ Mg_2SiO_4 ceramic tapes and their role as screen printed microstrip patch antenna substrates[J]. *Mater Sci Eng B*, 2021, 264, Doi: 10.1016/j.mseb.2020.114947.
- [118] LAI Y, TANG X, HUANG X, et al. Phase composition, crystal structure and microwave dielectric properties of $\text{Mg}_{2-x}\text{Cu}_x\text{SiO}_4$ ceramics[J]. *J Eur Ceram Soc*, 2018, 38(4): 1508–1516.
- [119] GEORGE S, ANJANA P S, DEEPU V N, et al. Low-temperature sintering and microwave dielectric properties of $\text{Li}_2\text{MgSiO}_4$ ceramics[J]. *J Am Ceram Soc*, 2009, 92(6): 1244–1249.
- [120] LAI Y, ZENG Y, HAN J, et al. Structure dependence of microwave dielectric properties in $\text{Zn}_{2-x}\text{SiO}_{4-x}\text{CuO}$ ceramics[J]. *J Eur Ceram Soc*, 2021, 41(4): 2602–2609.
- [121] SZWAGIERCZAK D, SYNKIEWICZ-MUSIALSKA B, KULAWIK J, et al. LTCC and bulk $\text{Zn}_4\text{B}_6\text{O}_{13}$ - Zn_2SiO_4 composites for submillimeter wave applications[J]. *Materials*, 2021, 14(4): 1014.
- [122] ZHANG J, YUE Z, LUO Y, et al. Novel low-firing forsterite-based microwave dielectric for LTCC Applications[J]. *J Am Ceram Soc*, 2016, 99(4): 1122–1124.
- [123] LAI Y, SU H, WANG G, et al. Low-temperature sintering of

- microwave ceramics with high $Q \times f$ values through LiF addition[J]. *J Am Ceram Soc*, 2019, 102(4): 1893–1903.
- [124] SONG X Q, LEI W, ZHOU Y Y, et al. Ultra-low fired fluoride composite microwave dielectric ceramics and their application for BaCuSi₂O₆-based LTCC[J]. *J Am Ceram Soc*, 2019, 103(2): 1140–1148.
- [125] ZUO R, ZHANG J, SONG J, et al. Liquid-phase sintering, microstructural evolution, and microwave dielectric properties of Li₂Mg₃SnO₆-LiF ceramics[J]. *J Am Ceram Soc*, 2018, 101(2): 569–576.
- [126] SONG X Q, DU K, ZOU Z Y, et al. Temperature-stable BaAl₂Si₂O₈-Ba₅Si₈O₂₁-based low-permittivity microwave dielectric ceramics for LTCC applications[J]. *Ceram Int*, 2017, 43(16): 14453–14456.
- [127] ZHANG P, WU S, ZHAO Y, et al. Effects of LiF on sintering characteristics and dielectric properties of low-loss SrCuSi₄O₁₀ ceramics for LTCC applications[J]. *Mater Chem Phys*, 2019, 222: 246–250.
- [128] WANG D, LI L, JIANG J, et al. Cold sintering of microwave dielectric ceramics and devices[J]. *J Mater Res*, 2021, 36(2): 333–349.
- [129] 张高群, 汪宏. 超低温烧结微波介质陶瓷研究进展[J]. *硅酸盐学报*, 2017, 45(9): 1256–1264.
- ZHANG Gaoqun, WANG Hong. *J Chin Ceram Soc*, 2017, 45(9): 1256–1264.
- [130] ZHOU D, PANG L X, WANG D W, et al. Novel water-assisting low firing MoO₃ microwave dielectric ceramics[J]. *J Eur Ceram Soc*, 2019, 39(7): 2374–2378.
- [131] SEBASTIAN M T, WANG H, JANTUNEN H. Low temperature co-fired ceramics with ultra-low sintering temperature: A review[J]. *Curr Opin Solid State Mater Sci*. 2016, 20(3): 151–170.
- [132] YOON S H, KIM D W, CHO S Y, et al. Investigation of the relations between structure and microwave dielectric properties of divalent metal tungstate compounds[J]. *J Eur Ceram Soc*, 2006, 26(10/11): 2051–2054.
- [133] ZHOU D, RANDALL C A, PANG L X, et al. Microwave dielectric properties of Li₂WO₄ ceramic with ultra-low sintering temperature[J]. *J Am Ceram Soc*, 2011, 94(2): 348–350.
- [134] ZHOU H, WANG H, LI K, et al. Microwave dielectric properties of low temperature firing (Li_{1/2}Nd_{1/2})WO₄ ceramic[J]. *J Mater Sci: Mater El*, 2009, 21(3): 252–255.
- [135] KIM J S, LEE J C, CHEON C I, et al. Crystal structures and low temperature cofiring ceramic property of (1-x)(Li, RE)W₂O₈-xBaWO₄ Ceramics (RE=Y, Yb)[J]. *Jpn J Appl Phys*, 2006, 45(9B): 7397–7400.
- [136] YUAN X, XUE X, WANG H. Preparation of ultra-low temperature sintering ceramics with ultralow dielectric loss in Na₂O-WO₃ binary system[J]. *J Am Ceram Soc*, 2019, 102(7): 4014–4020.
- [137] ZHOU D, RANDALL C A, WANG H, et al. Microwave dielectric ceramics in Li₂O-Bi₂O₃-MoO₃ system with ultra-low sintering temperatures [J]. *J Am Ceram Soc*, 2010, 93(4): 1096–1100.
- [138] ZHOU D, RANDALL C A, PANG L X, et al. Microwave dielectric properties of Li₂(M²⁺)₂Mo₃O₁₂ and Li₃(M³⁺)Mo₃O₁₂ (M=Zn, Ca, Al, and In) lyonsite-related-type ceramics with ultra-low sintering Temperatures[J]. *J Am Ceram Soc*, 2011, 94(3): 802–805.
- [139] ZHOU D, PANG L X, QI Z M, et al. Novel ultra-low temperature co-fired microwave dielectric ceramic at 400 degrees and its chemical compatibility with base metal[J]. *Sci Rep*, 2014, 4: 5980.
- [140] PANG L X, ZHOU D, LIU W G, et al. Low-temperature sintering and microwave dielectric properties of CaMoO₄-Based temperature Stable LTCC Material[J]. *J Am Ceram Soc*, 2014, 97(7): 2032–2034.
- [141] ZHANG G Q, WANG H, GUO J, et al. Ultra-low sintering Temperature microwave dielectric ceramics based on Na₂O-MoO₃ binary system[J]. *J Am Ceram Soc*, 2015, 98(2): 528–533.
- [142] JOSEPH N, VARGHESE J, SIPONKOSKI T, et al. Glass-free CuMoO₄ ceramic with excellent dielectric and thermal properties for ultralow temperature cofired ceramic applications[J]. *ACS Sustain Chem Eng*, 2016, 4(10): 5632–5639.
- [143] PANG L X, ZHOU D, WANG D W, et al. Temperature stable K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO₄ microwave dielectrics ceramics with ultra-low sintering temperature[J]. *J Am Ceram Soc*, 2018, 101(5): 1806–1810.
- [144] ZHOU D, PANG L X, WANG D W, et al. Crystal structure, impedance and broadband dielectric spectra of ordered scheelite-structured Bi(Sc_{1/3}Mo_{2/3})O₄ ceramic[J]. *J Eur Ceram Soc*, 2018, 38(4): 1556–1561.
- [145] HU S, ZHOU H, ZHOU X, et al. Phase structure, sintering behaviour and microwave dielectric properties of Ln₂MoO₆ (Ln=La and Y) ceramics[J]. *Ceram Int*, 2020, 46(15): 24552–24556.
- [146] LYU X, LI Z, JIN J, et al. Sintering behavior, structure, and microwave properties of novel Li_{2x}Cu_{1-x}MoO₄ ceramics[J]. *Ceram Int*, 2022, 48(12): 17225–17233.
- [147] GUO Y B, DU K, YIN C Z, et al. Phase transition and microwave dielectric properties of Al_{2-x}Sc_xMo₃O₁₂ solid solutions[J]. *J Alloys Compd*, 2022, 910: 164940.
- [148] FENG C, ZHOU X, TAO B, et al. Crystal structure and enhanced microwave dielectric properties of the Ce₂[Zr_{1-x}(Al_{1/2}Ta_{1/2})_x]₃(MoO₄)₉ ceramics at microwave frequency[J]. *J Adv Ceram*, 2022, 11(3): 392–402.
- [149] BIAN W, ZHOU G, DONG Y, et al. Structural analysis and microwave dielectric properties of a novel Li₂Mg₂Mo₃O₁₂ ceramic with ultra-low sintering temperature[J]. *Ceram Int*, 2021, 47(5): 7081–7087.
- [150] REN J, BI K, FU X, et al. Novel Al₂Mo₃O₁₂-based temperature-stable microwave dielectric ceramics for LTCC applications[J]. *J Mater Chem C*, 2018, 6(42): 11465–11470.
- [151] BAO J, DU J, LIU L, et al. A new type of microwave dielectric ceramic based on K₂O-SrO-P₂O₅ composition with high quality factor and low sintering temperature[J]. *Ceram Int*, 2022, 48(1): 784–794.
- [152] CHEN X, LI H, ZHANG P, et al. Microwave dielectric properties of Co₂P₂O₇ ceramics[J]. *Ceram Int*, 2021, 47(2): 1980–1985.
- [153] CHEN X Q, LI H, ZHANG P C, et al. A low-permittivity microwave dielectric ceramic BaZnP₂O₇ and its performance modification[J]. *J Am Ceram Soc*, 2021, 104(10): 5214–5223.
- [154] GUO T, LI Y, WAHYUDI O, et al. Microwave dielectric properties of AZn₂(PO₄)₂ (A=Sr, Ba) ceramics[J]. *Ferroelectrics*, 2016, 492(1): 91–102.
- [155] SHI F, XIAO E C. Sintering behavior, crystal structures, phonon characteristics and dielectric properties of LiZnPO₄ microwave dielectric ceramics[J]. *Mater Chem Phys*, 2021, 259: 124139.
- [156] THOMAS D, SEBASTIAN M T. Temperature-compensated LiMgPO₄:

- A new glass-free low-temperature cofired ceramic[J]. J Am Ceram Soc, 2010, 93(11): 3828–3831.
- [157]PIRVARAM A, TAHERI-NASSAJ E, ARMAKI H T, et al. Effects of Mg^{2+} substitution on the structure, microstructure, and microwave dielectric properties of CaV_2O_6 ceramic[J]. J Electron Mater, 2022, 51(4): 1498–1504.
- [158]YAO G, LI Y, YAN J, et al. Structure and microwave dielectric properties of $NaSr_4V_5O_{17}$ ceramics for LTCC applications[J]. Ceram Int, 2021, 47(12): 17147–17152.
- [159]HUANG C L, CHU T M, TSAI M H. A low-loss, low temperature sintering dielectric using $Ba_{1-x}Sr_xMg_2(VO_4)_2$ ceramics and its applications at microwave frequencies[J]. Mater Sci Eng B, 2021, 268: 115114.
- [160]HU H, WANG Y, CAI C, et al. $BaMnV_2O_7$: A novel microwave dielectric ceramic for LTCC applications[J]. Ceram Int, 2021, 47(22): 31506–31511.
- [161]HSU T H, HUANG C L. Low-loss microwave dielectric of novel $Li_{1-2x}M_xVO_3$ ($M=Mg, Zn$) ($x=0-0.09$) ceramics for ULTCC applications[J]. J Eur Ceram Soc, 2021, 41(12): 5918–5923.
- [162]LUO H, FANG W, FANG L, et al. Microwave dielectric properties of novel glass-free low temperature firing $ACa_2Mg_2V_3O_{12}$ ($A=Li, K$) ceramics[J]. Ceram Int, 2016, 42(8): 10506–10510.
- [163]ZHOU D, PANG L X, WANG D W, et al. $BiVO_4$ based high k microwave dielectric materials: A review[J]. J Mater Chem C, 2018, 6(35): 9290–9313.
- [164]YAO P, DENG Y, LI B. Sintering characteristic, microstructure and microwave dielectric properties of the borax-added $Sr_3(VO_4)_2$ ceramics[J]. Ceram Int, 2021, 47(2): 2202–2207.
- [165]YIN C, LI C, YANG G, et al. $NaCa_4V_5O_{17}$: A low-firing microwave dielectric ceramic with low permittivity and chemical compatibility with silver for LTCC applications[J]. J Eur Ceram Soc, 2020, 40(2): 386–390.
- [166]PEI C, LI Y, TAN J, et al. Temperature stable $(1-x)NaCa_4V_5O_{17}-xBaV_2O_6$ microwave dielectric ceramics for ULTCC applications[J]. Ceram Int, 2020, 46(17): 27579–27583.
- [167]ZHOU D, PANG L X, WANG D W, et al. High quality factor, ultralow sintering temperature $Li_6B_4O_9$ microwave dielectric ceramics with ultralow density for antenna substrates[J]. ACS Sustain Chem Eng, 2018, 6(8): 11138–11143.
- [168]DOŠLER U, KRŽMANC M M, SUVOROV D. The synthesis and microwave dielectric properties of $Mg_3B_2O_6$ and $Mg_2B_2O_5$ ceramics[J]. J Eur Ceram Soc, 2010, 30(2): 413–418.
- [169]OHASHI M, OGAWA H, KAN A, et al. Microwave dielectric properties of low-temperature sintered $Li_3AlB_2O_6$ ceramic[J]. J Eur Ceram Soc, 2005, 25(12): 2877–2881.
- [170]GU Y J, DING X B, HU W, et al. Effect of Mg/B ratio and Sr^{2+} substitution for Mg^{2+} on the sintering, phase composition and microwave dielectric properties of $Mg_3B_2O_6$ ceramics[J]. Ceram Int, 2020, 46(16): 25888–25894.
- [171]SZWAGIERCZAK D, SYNKIEWICZ-MUSIALSKA B, KULAWIK J, et al. Low temperature sintering of $Zn_4B_6O_{13}$ based substrates, their microstructure and dielectric properties up to the THz range[J]. J Alloys Compd, 2020, 819: 153025.
- [172]WANG K, ZHOU H, ZHOU X, et al. High relative permittivity $Bi_4B_{2-x}O_{9+3/2}$ ($x=1.5, 2.0, 2.5, 3.0$) microwave ceramics for ULTCC technology[J]. Ceram Int, 2020, 46(9): 13841–13847.
- [173]YANG H, ZHANG S, WEN Q, et al. Synthesis of $CaAl_2B_2O_{4+3x}$: Novel microwave dielectric ceramics with low permittivity and low loss[J]. J Eur Ceram Soc, 2021, 41(4): 2596–2601.
- [174]谢先德, 查福标. 硼酸盐矿物物理学[M]. 地震出版社, 1993.

※ ※ ※ ※ ※ ※ ※ ※ ※ ※ ※



周迪, 西安交通大学电子科学与工程学院教授, 博士生导师。中国电子学会元件分会委员, 中国仪表功能材料学会电子元器件关键材料与技术专业委员会委员, 中国电子学会高级会员, 电气与电子工程师协会高级会员(IEEE Senior Member)。Journal of the American Ceramic Society 副编、International Journal of Applied Ceramic Technology 副编、Materials Research Bulletin 编委、Journal of Advanced Dielectrics 编委、ACS Applied Materials & Interfaces 顾问委员、ACS Applied Electronic Materials 顾问委员。先后主持国家自然科学基金青年/面上/联合基金、陕西省国际合作项目、华为公司横向课题等, 在微波介质结构性能调节分析、LTCC 低温共烧陶瓷技术应用、谐振器滤波器及天线基板应用等方面取得一系列新颖的研究成果, 在国际/国内知名期刊发表科技论文 200 余篇, 总引用次数 10000 余次(H 因子=54)。



王威, 西安交通大学微电子学与固体电子学博士研究生, 研究方向为低温共烧陶瓷材料及器件。所在课题组研究项目包括: 新型微波介质陶瓷材料研究; 低温共烧陶瓷技术研究; 储能电容器材料及多层陶瓷电容器研究; 微波吸收材料的微结构设计及机制研究; 高频/储能/吸波功能复合介质材料研究;