

光固化成型制备钛酸钡基 1-3 型压电复合材料

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摘 要: 1-3 型压电复合材料作为一种新型的功能材料, 具有低介电常数, 低声阻抗和高机电耦合系数的优点, 常用于制备高灵敏度宽带超声换能器。采用光固化成型技术打印钛酸钡微柱状结构作为 1-3 型复合材料的压电相, 通过优化浆料配方, 坯体的平面尺寸精度可达到 $\pm 10\ \mu\text{m}$, 烧结后压电微柱的宽度和高度分别为 120、330 μm , 将环氧树脂填充于压电微柱的间隙制备 1-3 型压电复合材料, 研究了不同压电相体积分数(20%~45%)对 1-3 型压电复合材料电学性能的影响。当压电相体积分数为 45%时, 压电复合材料的压电常数 d_{33} 为 74 pC/N, 机电耦合系数 k_t 为 0.48, 介电常数 ϵ_r 为 1 167, 介电损耗 $\tan\delta$ 为 0.023, 声阻抗 Z 为 10.43 MRayl (1 Rayl=1 Pa·s/m= 10^{-6} MRayl), 与钛酸钡陶瓷相比(k_t 约为 0.37, Z 为 31.64 MRayl), 其机电耦合系数提高了 30%, 声阻抗降低 67%。研究表明, 光固化成型技术制备的压电复合材料兼具高机电耦合系数和低声阻抗的优势, 为压电复合材料在高性能超声换能器的应用提供了一种高效、低成本的制备方法。

关键词: 光固化成型; 钛酸钡; 1-3 型; 压电复合材料

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锆钛酸铅(PZT), 铌镁酸铅-钛酸铅(PMN-PT), 钛酸钡(BTO)等压电陶瓷具有高能量转换效率, 被广泛用于制备压力传感器、滤波器、谐振器、超声换能器等各种压电器件, 但脆性大、声阻抗高以及厚度振动模式不纯等问题, 一定程度上限制了其在水听器 and 医用超声换能器等方面的应用^[1-3]。压电复合材料由压电陶瓷和聚合物通过不同的连通方式组成, 既保留了压电陶瓷良好的压电性, 同时也降低了压电材料的声阻抗, 易于实现与水 and 生物组织的匹配; 且提高了材料的柔韧性, 避免振动过程中材料发生断裂。其中, 1-3 型压电复合材料采用聚合物在 3 个方向上连通的方式将压电柱分开, 从而抑制了压电材料的横向振动模式, 增强了厚度振动模式, 使得厚度模式机电耦合系数 k_t 增加^[1,4-6]。

1-3 型复合材料的制备工艺有切割-灌胶法^[7-9]、排列-浇注法^[10-11]、注模成型法^[12-13]以及激光切割法^[14]等, 随着检测场景的多样化, 所要求的压电材料结构越来越复杂。目前, 工业上最常用的是切割-灌胶法, 该方法所切割的压电阵列图案单一; 而激

光切割的切割精度高, 对材料损伤小, 可以满足阵列多形态的需求, 但仪器价格昂贵。光数字处理技术属于光固化成型技术中的一种, 该技术基于面曝光成型, 具有固化速率快, 几何复杂度高, 分辨率高, 成本低等优势^[15]。目前, 该技术广泛应用于各种结构压电陶瓷的制备^[16-20]。本工作基于光固化成型技术制备了钛酸钡基 1-3 型压电复合材料, 研究了不同压电体积分数对压电复合材料性能的影响, 对其微观形貌和电学性能进行表征, 为 3D 打印在复合压电材料的研究与应用奠定基础。

1 实验

1.1 钛酸钡压电微柱的制备

为了使浆料具有良好的流动性和光固化性能, 陶瓷粉体质量分数选定为 84%, 以钛酸钡粉体(500 nm)、光敏树脂和分散剂(粉体质量的 2.5%)为原料加入黑色聚乙烯塑料罐中, 在均质机(深圳中毅科技有限公司, ZYMC-180V)中 2 000 r/min 混合 90 s。在陶瓷数字光处理(DLP)光固化 3D 打印机(浙江迅实科技

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有限公司, TC-II型)料盘中加入适量的浆料并铺平, 将三维模型保存为.stl 格式导入控制电脑, 压电微柱的模型尺寸为 $150\ \mu\text{m}$, 打印模型的切片厚度设置为 $7\ \mu\text{m}$ 。打印完成后, 将坯体浸泡在酒精中, 结合超声波清洗将残余在坯体中的浆料清理干净后放入烘箱烘干。坯体后续的热处理包括脱脂和烧结 2 个步骤, 脱脂温度设置为 $800\ ^\circ\text{C}$, 保温 $4\ \text{h}$; 随后, 将其放入马弗炉中烧结, 在 $1290\ ^\circ\text{C}$ 保温 $2\ \text{h}$ 获得钛酸钡压电陶瓷微柱, 微柱的宽度为 $120\ \mu\text{m}$, 高度为 $330\ \mu\text{m}$ 。

1.2 复合材料的制备

将环氧树脂(EPO-TEK 301)进行 2 次抽真空处理, 真空压力小于 $-100\ \text{kPa}$, 抽真空时长分别为 10 、 $20\ \text{min}$ 。环氧树脂混合均匀后进行第 1 次真空除气, 其目的是减少混合过程中产生的气泡, 随后将树脂灌入装有压电陶瓷微柱的容器中, 进行第 2 次真空除气, 目的是将转移过程中产生的气泡以及第 1 次真空处理残留的气泡尽数排出。对压电柱浇注环氧后, 将其置于 $60\ ^\circ\text{C}$ 烘箱中固化 $12\ \text{h}$ 。随后, 在经过打磨的样品上下表面镀金电极, 并在常温硅油中以 $4\ \text{kV/mm}$ 的电场进行极化。图 1 为制备 1-3 压电复合材料的工艺流程示意图。

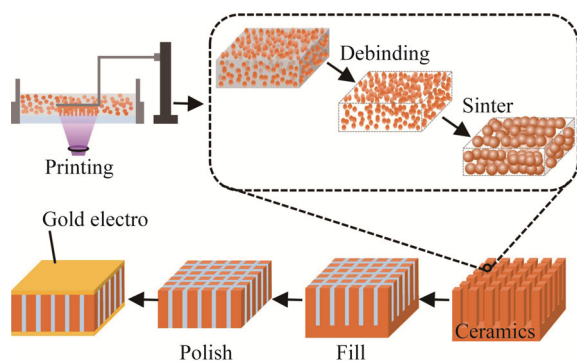


图 1 样品制备工艺流程图
Fig. 1 Processing of sample manufacture

1.3 材料的测试与表征

采用日本日立高新技术公司 TM4000Plus 型台式扫描电子显微镜观察样品形貌。采用英国 Wayne Kerr 公司 6500B 型精密阻抗分析仪表征样品的电容、介电损耗、谐振频率和反谐振频率等参数。采用中科院声学研究所 ZJ-3AN 型准静态 d_{33} 测量仪测量压电常数 d_{33} 。采用德国 aixACCT 公司 2000E 型铁电分析仪测量电滞回线, 分析钛酸钡基 1-3 复合材料的铁电性能。

2 结果与讨论

2.1 显微结构分析

图 2 为光固化成型压电复合材料的 SEM 照片, DLP 技术的平面分辨率高, 本工作中经过优化的浆料配方成型出压电微柱的尺寸为 $(150\pm 10)\ \mu\text{m}$, 可分辨压电微柱的最小间距为 $100\ \mu\text{m}$ 。由于陶瓷粉体与树脂之间存在折射率差, 使得光在界面之间产生散射, 从而降低打印精度^[11, 15], 目前研究报道的陶瓷成型尺寸较大($\geq 500\ \mu\text{m}$)^[17, 21]。图 2a 为钛酸钡压电微柱坯体(45%, 体积分数)的形貌照片。由图 2a 可见, 压电微柱坯体分布均匀, 其宽度约为 $150\ \mu\text{m}$, 压电柱坯体结构完整, 成型质量高。图 2b 为图 2a 中红色方框内压电微柱坯体表面放大照片。从图 2b 可见, 打印平面的浆料固化均匀, 无气孔产生。图 2c 和图 2d 中红色箭头为压电材料的成型方向, 图 2c 为压电微柱坯体侧面的 SEM 照片, 该技术层层叠加的成型方式使得压电柱沿打印方向呈现明显的层状结构; 图 2d 为烧结后压电柱的整体形貌, 压电微柱的弯曲变形较小, 宽度为 $120\ \mu\text{m}$, 横向收缩率约为 20%, 陶瓷的收缩以及晶粒的生长使得层状间隙被填充, 使得烧结后的陶瓷分层现象减少。图 2e 为烧结后陶瓷的晶粒形貌照片, 陶瓷的晶粒尺寸均匀, 无明显的孔隙和裂纹。图 2f 为 1-3 复合材料的形貌照片。从图 2 可见, 压电微柱均匀地分布在环氧树脂中, 环氧树脂内未观察到气泡残留。

材料的密度和声阻抗可通过式(1)和式(2)计算得到^[22-23]:

$$\rho = v\rho_1 + (1-v)\rho_2 \quad (1)$$

$$Z = 2t\rho f_a \quad (2)$$

其中: ρ 为复合材料的密度; ρ_1 为压电相材料的密度; ρ_2 为聚合物材料的密度; v 为压电相体积分数, 复合材料的压电相体积分数通过调整压电微柱排列的间距实现; Z 为复合材料的声阻抗; t 为复合材料的厚度; f_a 为复合材料的反谐振频率, 可通过阻抗分析仪测得。表 1 为不同压电相体积分数 1-3 复合材料的密度和声阻抗, 随着压电相体积分数的增大, 压电复合材料的密度和声阻抗也随之增大。当压电相体积分数为 45% 时, 材料的声阻抗为 $10.43\ \text{MRayl}$ ($1\ \text{Rayl} = 1\ \text{Pa}\cdot\text{s/m} = 10^{-6}\ \text{MRayl}$), 与钛酸钡陶瓷($31.64\ \text{MRayl}$)相比大幅降低, 更容易实现与水或生物组织的声学匹配。

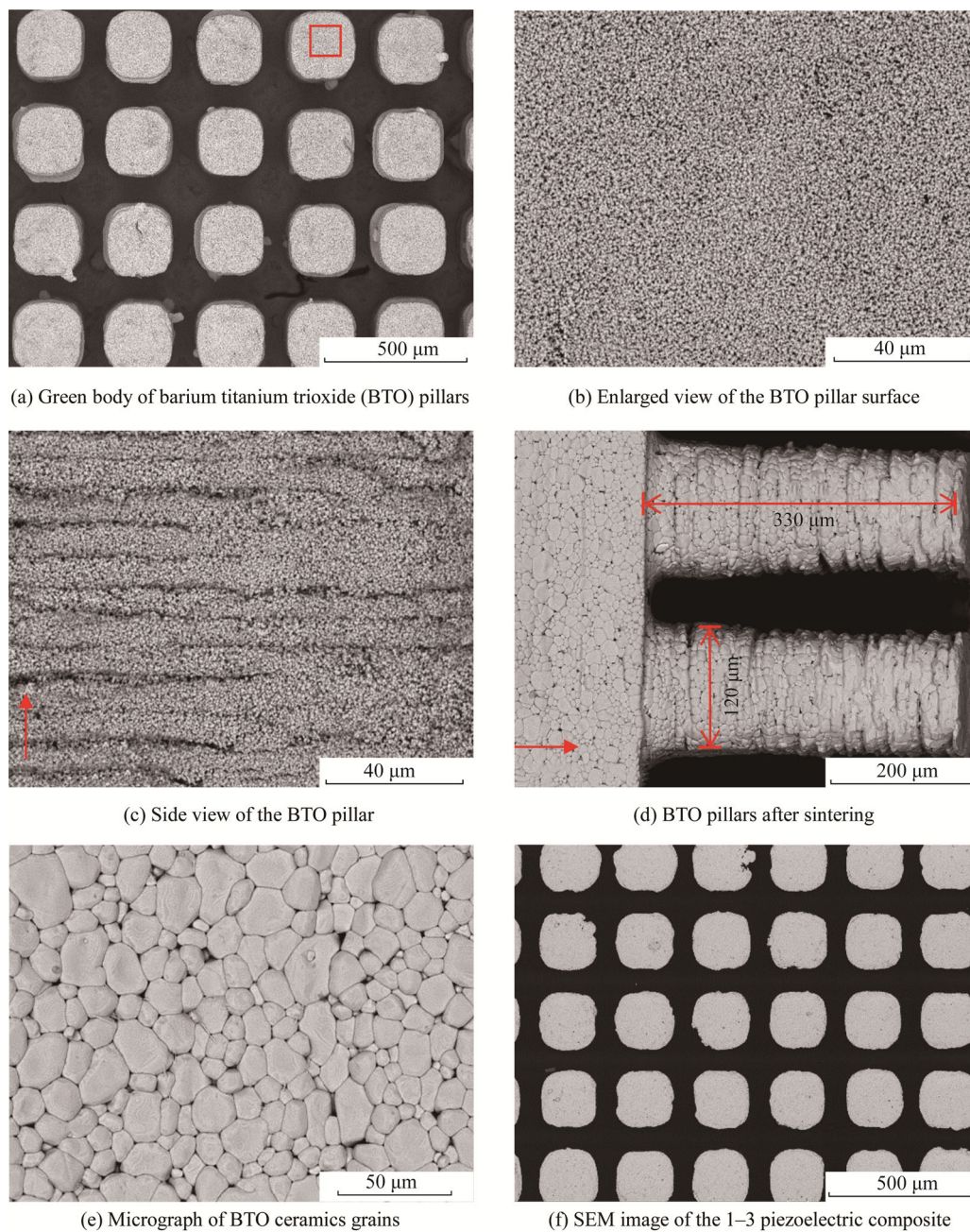


图2 光固化成型压电复合材料(45%)的 SEM 照片

Fig. 2 SEM images of piezoelectric composites (45%) based on digital light processing (DLP)

表1 不同压电相体积分数 1-3 复合材料的密度和声阻抗
Table 1 Density and acoustic impedance of 1-3 piezoelectric composites with different piezoelectric phrase volume fraction

Material	Density/(g·cm ⁻³)	Acoustic impedance/MRayl
Polymer	1.15	2.52
20% piezoelectric phrase	2.06	4.42
30% piezoelectric phrase	2.52	6.40
45% piezoelectric phrase	3.20	10.43
BTO	5.70	31.64

1 Rayl=1 Pa·s/m=10⁻⁶ MRayl

2.2 压电性能分析

图3为钛酸钡/环氧树脂 1-3 压电复合材料的压电常数 d_{33} 和机电耦合系数 k_t 随压电相体积分数的变化曲线。压电复合材料的压电常数的大小不仅与压电相相关,也和环氧树脂的弹性性能有关,压电相含量越高,复合材料的压电常数越大。从图3可见,压电常数 d_{33} 均随着压电相体积分数的增大而增大,当压电相体积分数为 20%、30%和 45%时,压电常数 d_{33} 分别为 37, 54 pC/N 和 74 pC/N。

1-3 型压电复合材料中压电柱的振动模式是纵

向长度模态, 该振动模态下纵向长度机电耦合系数大于陶瓷块体厚度模态机电耦合系数 k_t 。因此, 当压电相体积分数较小时, 复合材料 k_t 随着压电相体积分数的增加快速上升, 到达一定体积分后, k_t 基本保持不变, 当压电相体积分继续增大, 横向振动模态被增强, k_t 下降^[24]。如图 3 所示, 机电耦合系数 k_t 随着体积分(≤45%)的增大而增大, 当体积分 45% 时为 0.48, 相对于纯钛酸钡陶瓷(k_t 约为 0.37)增加了 30%。图 4 所示为压电复合材料(45%)的频率阻抗谱。从图 4 可见, 压电复合材料为单一的厚度振动模态, 说明 1-3 型复合材料可以有效抑制横向振动模态, 增强厚度振动模态, 其作为超声换能器的压电元件能有效改善器件的脉冲回波响应从而提高成像分辨率。

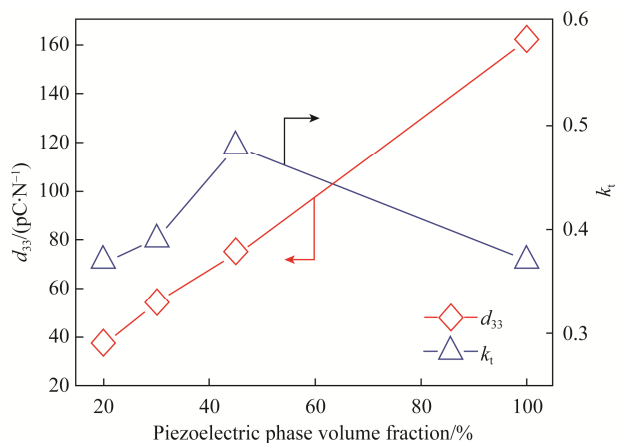


图 3 钛酸钡/环氧树脂 1-3 压电复合材料的压电常数 d_{33} 和机电耦合系数 k_t 随压电相体积分数的变化曲线

Fig. 3 Curves of effects of piezoelectric phase volume fraction on the piezoelectric constant (d_{33}) and thickness electromechanical coupling coefficient (k_t) of BTO/epoxy piezoelectric composites

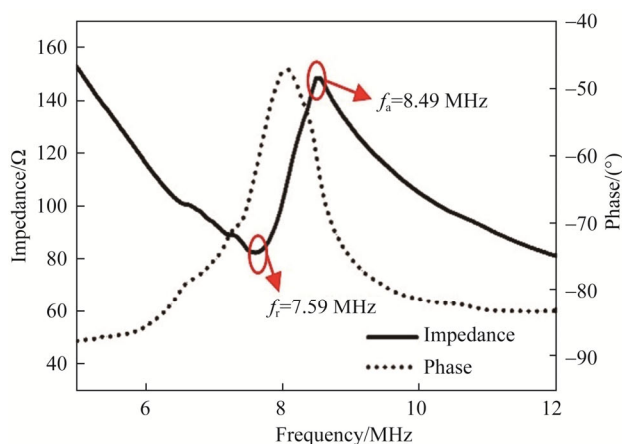


图 4 压电复合材料(体积分 45%)的频率阻抗谱

Fig. 4 Frequency impedance resonance for piezoelectric composites (45%, in volume)

2.3 介电性能分析

图 5 为 1 kHz 条件下测定的不同压电相体积分数复合材料的介电性能, 由于钛酸钡陶瓷的介电常数(2580)远大于环氧树脂的介电常数(3.8), 1-3 型压电复合材料的相对介电常数几乎随着压电相含量的增加而线性增大。压电复合材料的介电损耗比纯陶瓷的介电损耗略大, 但整体变化不大, 压电复合材料的介电损耗均小于 3%。当压电相体积分 45% 时, 压电复合材料的介电常数 ϵ_r 为 1167, 介电损耗 $\tan\delta$ 为 2.3%。较低的介电损耗可以减少能量消耗, 提高换能器的接收灵敏度。

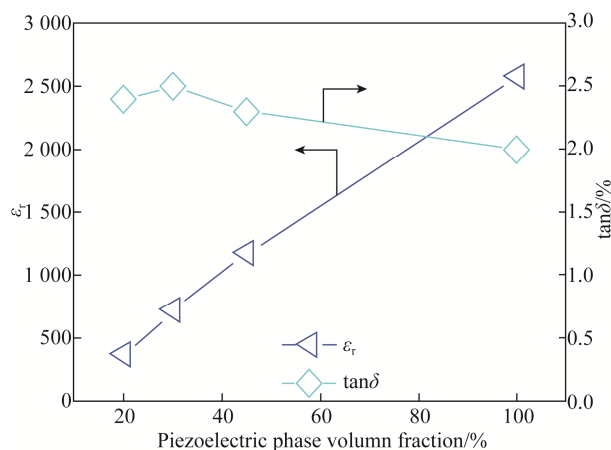


图 5 压电复合材料的介电常数(ϵ_r)和介电损耗($\tan\delta$)与压电相体积分数的关系曲线

Fig. 5 Relationship between dielectric properties of piezoelectric composites and piezoelectric phase volume fraction

2.4 铁电性能分析

1-3 压电复合材料的铁电性是由压电相引起的, 因此, 压电复合材料的剩余极化强度与压电相的体积含量相关且比纯压电陶瓷的剩余极化强度低。图 6 为在频率 100 Hz, 外电场 4 kV/mm 的条件

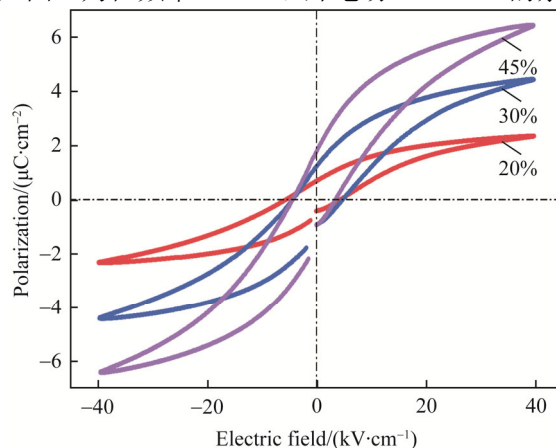


图 6 不同压电相体积分压电复合材料的电滞回线

Fig. 6 Ferroelectric hysteresis loop of piezoelectric composites with different piezoelectric phase volume fraction

下测定的不同压电相体积分数的 1–3 型钛酸钡/环氧树脂压电复合材料的电滞回线,其剩余极化强度和矫顽场如表 2 所示。由表 2 可知,剩余极化强度随着压电相体积分数的增加而增加,在外加电场为 4 kV/mm 时,体积分数为 45%压电复合材料的最大剩余极化强度达到最大为 $1.77 \mu\text{C}/\text{cm}^2$ 。

表 2 压电复合材料的铁电性能参数

Table 2 Ferroelectric parameters of piezoelectric composites

Piezoelectric phase volume fraction/%	Polarization/ $(\mu\text{C}\cdot\text{cm}^{-2})$	Electric field/ $(\text{kV}\cdot\text{cm}^{-1})$
20	0.68	5.55
30	1.20	4.30
45	1.77	4.32

3 结论

采用光固化成型技术制备了 1–3 型钛酸钡/环氧树脂压电复合材料,研究了不同压电相体积分数对复合材料电学性能的影响,得出主要结论:

1) 随着压电相体积分数($\leq 45\%$)的增加,1–3 型压电复合材料的介电常数、压电常数、机电耦合系数和剩余极化强度也逐渐增大;

2) 聚合物相可以有效降低压电材料的声阻抗,更易于实现超声换能器压电层与待测组织之间的声匹配,减少声波传播过程中的损耗;

3) 相对于纯钛酸钡陶瓷而言,1–3 型复合材料能有效地抑制了材料的横向振动,增强了厚度振动模态;

4) 光固化成型技术的平面分辨率高,成型速率快,可制备复杂结构,为压电复合材料在超声换能器方向的应用提供了一种新的制备方法。

参考文献:

- JIANG L M, CHEN R M, XING J E, et al. Fabrication of a (K, Na)NbO₃-based lead-free 1-3 piezocomposite for high-sensitivity ultrasonic transducers application[J]. J Appl Phys, 2019, 125(21): 214501.
- SHUNG K K, CANNATA J M, ZHOU Q F. Piezoelectric materials for high frequency medical imaging applications: A review[J]. J Electroceram, 2007, 19(1): 141–147.
- GUO R, WANG C G, YANG A K. Effects of pore size and orientation on dielectric and piezoelectric properties of 1-3 type porous PZT ceramics[J]. J Eur Ceram Soc, 2011, 31(4): 605–609.
- SMITH W A, AULD B A. Modeling 1-3 composite piezoelectrics: Thickness-mode oscillations[J]. IEEE Trans Ultrason Ferroelectr Freq Control, 1991, 38(1): 40–47.
- LEE H J, ZHANG S J. Design of low-loss 1-3 piezoelectric composites for high-power transducer applications[J]. IEEE Trans Ultrason Ferroelectr Freq Control, 2012, 59(9): 1969–1975.
- GENG X C, ZHANG Q M. Resonance modes and losses in 1-3

- piezocomposites for ultrasonic transducer applications[J]. J Appl Phys, 1999, 85(3): 1342–1350.
- CHENG K C, CHAN H L W, CHOY C L, et al. Single crystal PMN-0.33PT/epoxy 1-3 composites for ultrasonic transducer applications[J]. IEEE Trans Ultrason Ferroelectr Freq Control, 2003, 50(9): 1177–1183.
- CUI M T, GUO R B, XUE S, et al. The finite element simulation and design of a 50 MHz spherical ultrasonic transducer[C]//2015 Symposium on Piezoelectricity, Acoustic Waves, and Device Applications (SPAWDA). Jinan, China. IEEE, 2015: 290–294.
- ZHOU D, LAM K H, CHEN Y, et al. Lead-free piezoelectric single crystal based 1-3 composites for ultrasonic transducer applications[J]. Sens Actuat A Phys, 2012, 182: 95–100.
- PRAMANIK R, AROCKIARAJAN A. Effective properties and nonlinearities in 1-3 piezocomposites: A comprehensive review[J]. Smart Mater Struct, 2019, 28(10): 103001.
- ELTOUBY P, SHYHA I, LI C C, et al. Factors affecting the piezoelectric performance of ceramic-polymer composites: A comprehensive review[J]. Ceram Int, 2021, 47(13): 17813–17825.
- LEE H J, ZHANG S J, BAR-COHEN Y, et al. High temperature, high power piezoelectric composite transducers[J]. Sensors, 2014, 14(8): 14526–14552.
- HAN J S, GAL C W, KIM J H, et al. Fabrication of high-aspect-ratio micro piezoelectric array by powder injection molding[J]. Ceram Int, 2016, 42(8): 9475–9481.
- JIAN X H, LIU P B, LI Z J, et al. Development of self-focusing piezoelectric composite ultrasound transducer using laser engraving technology[J]. IEEE Trans Ultrason Ferroelectr Freq Control, 2019, 66(12): 1866–1873.
- CHAUDHARY R, FABBRI P, LEONI E, et al. Additive manufacturing by digital light processing: A review[J]. Prog Addit Manuf, 2023, 8(2): 331–351.
- CHENG J, CHEN Y, WU J W, et al. 3D printing of BaTiO₃ piezoelectric ceramics for a focused ultrasonic array[J]. Sensors, 2019, 19(19): 4078.
- CHEN Z Y, SONG X, LEI L W, et al. 3D printing of piezoelectric element for energy focusing and ultrasonic sensing[J]. Nano Energy, 2016, 27: 78–86.
- CHEN Y, BAO X L, WONG C M, et al. PZT ceramics fabricated based on stereolithography for an ultrasound transducer array application[J]. Ceram Int, 2018, 44(18): 22725–22730.
- ZHENG K, DING D F, QUAN Y, et al. 3D printing orientation controlled PMN-PT piezoelectric ceramics[J]. J Eur Ceram Soc, 2023, 43(6): 2408–2416.
- DU Q P, ZHANG C, LIU C L, et al. Highly-textured BaTiO₃ ceramics with high piezoelectric performance prepared by vat photopolymerization[J]. Addit Manuf, 2023, 66: 103454.
- HUANG W F, WU Y C, CHEN W W, et al. Reinforcement effect in printing precision and sintering performance for liquid crystal display stereolithography additive manufacturing of alumina ceramics[J]. Ceram Int, 2022, 48(22): 33809–33818.
- 徐玲芳, 陈文, 周静, 等. 锆钛酸铅钨纤维 1–3 压电复合材料的制备及性能[J]. 硅酸盐学报, 2007, 35(9): 1152–1156.
- XU Lingfang, CHEN Wen, ZHOU Jing, et al. J Chin Ceram Soc, 2007, 35(9): 1152–1156.
- 甄玉花, 李敬峰. 微细 1–3 型 PZT/环氧树脂压电复合材料的制备及其性能[J]. 硅酸盐学报, 2006, 34(3): 381–384.
- ZHEN Yuhua, LI Jingfeng. J Chin Ceram Soc, 2006, 34(3): 381–384.

[24] CHAN H W, UNSWORTH J. Simple model for piezoelectric ceramic/polymer 1-3 composites used in ultrasonic transducer

applications[J]. IEEE Trans Ultrason Ferroelectr Freq Control, 1989, 36(4): 434-441.

Fabrication and Characterization of Barium Titanate Based 1-3 Piezoelectric Composites by Stereolithography Technology

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Extended Abstract

Introduction 1-3 type piezoelectric composites are widely used to fabricate high-sensitivity and broadband ultrasonic transducers due to the advantages like a low dielectric constant, a low acoustic impedance, and a high electromechanical coupling coefficient. However, some conventional manufacturing methods such as the cut-and-fill method, the arrangement-casting process, and the injection molding method have challenges to emanate from geometric complexity and structural integrity. Stereolithography technology based on the mask projection approach is an alternative method for manufacturing piezoelectric ceramics with a rapid prototyping and a high precision. Lead-free barium titanate BaTiO_3 (BTO) ceramics are widely investigated for piezoelectric sensors and dielectric capacitors applications because of their high dielectric constant, good piezoelectric coefficient, and favorable electromechanical coupling coefficient. In this work, digital light processing (DLP) technology was used to manufacture barium titanate based 1-3 type piezoelectric composites. The influence of piezoelectric phase volume fraction (*i.e.*, 20%–45%) on the micrograph, acoustic impedance and electrical properties of BTO 1-3 composites was investigated.

Methods The printed ceramic slurries with 84% (in mass fraction) BTO content, including BTO powders ($d_{50}=500$ nm), dispersant, and liquid photopolymers, were mixed by a model ZYMC-180V homogenizer (ZYE) at 2 000 r/min for 90 s. The printed models were built by a software named Computer-Aided Design (CAD) and sliced to a thickness of 7 μm . The piezoelectric pillars (150 μm) with a support were printed layer by layer to form the physical models (*i.e.*, Soon solid, TC-II). The printed samples were washed in alcohol by ultrasonic cleaner to remove the residual slurry. Afterwards, the green bodies were treated by a two-step heating treatment, *i.e.*, a debonding process and a sintering process, to obtain the piezoelectric phase structures. Two-time vacuum treatments below -100 kPa were introduced to remove air bubbles in epoxy resin (EPO-TEK301) that filled in the kerfs between piezoelectric pillars (width of 120 μm , height of 330 μm). The samples filled with epoxy resin were heat treated at 60 $^{\circ}\text{C}$ for 12 h and then coated with gold electrodes. The BTO 1-3 composites were polarized in an electric field of 4 kV/mm in silicone oil. The microstructures of samples were characterized by a model TM4 000 Plus scanning electron microscope (Hitachi Co., Ltd., Japan). The dielectric constant ϵ_r , dielectric loss δ , and frequency impedance spectrum were measured by a model 6500B precision impedance analyzer (Wayne Kerr Co., Ltd., UK). Piezoelectric constant d_{33} was determined by a model ZJ-3A piezo- d_{33} meter (Institute of Acoustics, Chinese Academy of Sciences, China). The ferroelectric hysteresis loop was measured by a model 2000E ferroelectric analyzer (aixACCT Co., Germany).

Results and discussion The uniform piezoelectric pillars with a width of (150 ± 10) μm are printed through optimizing the slurry formula, and the minimum distance between pillars is approximately 100 μm . The bending deformation of BTO pillars is negligible, and the lateral shrinkage rate is 20%. The forming mechanism of DLP technology results in a clear lamination of the piezoelectric pillar along the printing direction. The shrinkage of ceramics and the growth of grains fill the gap between interlayers, thus reducing the lamination after sintering. There are no residual bubbles in the epoxy resin after vacuum treatment. The density and acoustic impedance of the piezoelectric composites increase with the growth of the piezoelectric phase volume proportion. Compared with the acoustic impedance of BTO ceramics (*i.e.*, $Z=31.64$ MRayl, $1\text{Rayl}=1\text{ Pa}\cdot\text{s}/\text{m}=10^{-6}\text{ MRayl}$), the acoustic impedance of composites (45%, in volume fraction) is decreased by 67%.

The piezoelectric constant d_{33} and electromechanical coupling coefficient k_t enhance with the piezoelectric phase volume proportion of the composites, meeting their maximum values of 74 pC/N and 0.48, respectively. Compared with the BTO ceramics ($k_t=0.37$), the electromechanical coupling coefficient is improved by 30%. According to the frequency impedance spectra of piezoelectric composites, 1-3 type composites have a pure thickness vibration mode. The dielectric constant ϵ_r increases linearly with increasing the piezoelectric phase volume fraction, reaching its maximum of 1 167. The dielectric loss $\tan\delta$ is lower than 3%, which can enhance the receiving sensitivity of ultrasound transducers. The residual polarization intensity increases with the increase of volume fraction of the piezoelectric phase. The residual polarization intensity of the piezoelectric composite with a volume fraction of 45% reaches a maximum of 1.77 $\mu\text{C}/\text{cm}^2$ at 4 kV/mm.

Conclusions 1-3 type barium titanate/epoxy resin piezoelectric composites were fabricated by the DLP technology. The effect of

volume fraction of piezoelectric phases on the electrical performances of composites was investigated. The electrical properties such as piezoelectric constant d_{33} , electromechanical coupling coefficient k_t , and dielectric constant ϵ_r were optimized as the volume fraction of the piezoelectric phase ($\leq 45\%$) was increased. The polymer phase could effectively reduced the acoustic impedance of piezoelectric materials, thus obtaining an acoustic matching between the piezoelectric materials and tissues or water. Compared to pure barium titanate ceramics, 1-3 type composites as a material of ultrasound transducers could effectively suppress the lateral vibration of the material and enhance the thickness vibration mode, which could improve the pulse echo response. The DLP technology with a high resolution provides an effective and low-cost method for fabricating the piezoelectric composites.

Keywords stereolithography; barium titanate; 1-3 types; piezoelectric composite