

$A_2B_2O_7$ ($A = \text{Ln}^{3+}$, $B = \text{Zr}^{4+}$, Hf^{4+} , Ti^{4+} , Ce^{4+}) 型透明陶瓷研究进展

赖扬群¹, 陶世旭¹, 麻朝阳¹, 曹永革^{1,2}

(1. 松山湖材料实验室, 广东 东莞 523808; 2. 中国科学院物理研究所, 北京 100190)

摘 要: $A_2B_2O_7$ 型化合物具有高熔点、高密度和高折射率等特点, 在照明材料、航空材料、医疗成像、磁光材料等领域具有潜在应用价值。随着陶瓷制备工艺的进步, 透明陶瓷的光学、力学和热学等性能不断提升使 $A_2B_2O_7$ 型透明陶瓷受到越来越多研究者的关注, 本文介绍了一些 $A_2B_2O_7$ 型透明陶瓷的制备工艺、性能参数和其潜在的应用价值。

关键词: 透明陶瓷; 烧绿石; 萤石

中图分类号: TQ175 文献标志码: A 文章编号: 0454-5648(2024)03-1157-14

网络出版时间: 2024-02-08



透明陶瓷是一种多晶材料, 一般由无机粉末经过成型和烧结等工艺制成。根据材料体系分类, 可以将透明陶瓷分为氧化物、氮化物、氟化物、氮氧化物、氧硫化物、硫化物、硒化物和碲化物等透明陶瓷^[1]。近年来 $A_2B_2O_7$ 透明陶瓷受到广泛关注, 因为 $A_2B_2O_7$ 透明陶瓷具有耐腐蚀、耐高温、高强度、高密度、高折射率等特点, 在磁光材料、激光材料、高温窗口、闪烁体材料和光学测温材料等领域具有很好的应用前景^[2-8]。

$A_2B_2O_7$ 型化合物中 A 位一般为三价稀土元素, B 位一般为四价过渡金属元素。 $A_2B_2O_7$ 型化合物的晶体结构受到温度、压强和 A 位 B 位原子的半径比等因素影响^[9-11], 其中, A 位和 B 位原子的半径比为主导因素。当 $1.46 < r_A/r_B < 1.78$ 时, 呈有序烧绿石结构(图 1a), 当 $r_A/r_B < 1.46$ 时, 为萤石结构(图 1b); 当 $r_A/r_B > 1.78$ 时, 一般为单斜结构^[1, 12]。萤石结构中 A 位和 B 位原子呈无序排列, 烧绿石结构中 A 位和 B 位原子有序排列。

本文结合近年来 $A_2B_2O_7$ 型透明陶瓷的研究结果, 对 $A_2B_2O_7$ 型透明陶瓷粉体的制备方法、 $A_2B_2O_7$ 型透明陶瓷的烧结工艺和 $A_2B_2O_7$ 型透明陶瓷的应用领域进行了介绍。其中选择了一类双相共存的

$A_2B_2O_7$ 型透明陶瓷进行了详细介绍, 讨论了双相 $A_2B_2O_7$ 型透明陶瓷高透过率的原因和 $A_2B_2O_7$ 型透明陶瓷相变的影响因素。

1 $A_2B_2O_7$ 透明陶瓷的制备

1.1 粉体的制备

透明陶瓷一般由原料粉体经过成型和烧结等工艺制成, 原料粉体的纯度、颗粒尺寸、分散性和烧结活性都会影响陶瓷的光学性能^[13]。目前, 制备 $A_2B_2O_7$ 透明陶瓷粉体的常用方法有: 固相反应法、燃烧法、溶胶凝胶法、化学共沉淀法、水热法和溶剂热法等^[14]。2023 年, Li 等使用 Sm_2O_3 和 ZrO_2 为原料, 通过固相反应法制备了粒径约 200 nm 的 $\text{Sm}_2\text{Zr}_2\text{O}_7$ 粉体^[15]。2023 年, Tan 等采用聚丙烯酰胺凝胶法制备了无团聚的高熵($\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2}$) $_2\text{Zr}_2\text{O}_7$ 和($\text{La}_{0.2}\text{Nd}_{0.2}\text{Y}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2}$) $_2\text{Zr}_2\text{O}_7$ 粉体^[16], 粉体的粒径分别为 25 nm 和 23 nm 左右。研究表明, 当丙烯酸胺和 Zr^{4+} 的比例为 80/1 时, 可以使前驱体粉末在较低的温度(700 °C)得到单相萤石结构的粉体。2013 年, 王正娟等通过燃烧法制备了 $\text{LaGdZr}_2\text{O}_7$ 粉体^[17], 燃烧法制备的 $\text{LaGdZr}_2\text{O}_7$ 粉体容易产生团聚, 王正娟将燃烧法制备的前驱体在 800 °C 煅烧 2 h

收稿日期: 2023-08-25。 修订日期: 2023-12-05。

基金项目: 广东省珠江人才引进行计划创新创业团队(2019ZT08C321)资助。

第一作者: 赖扬群(1995—), 男, 硕士, 助理工程师。

通信作者: 麻朝阳(1985—), 男, 博士, 副研究员。

Received date: 2023-08-25. Revised date: 2023-12-05.

First author: LAI Yangqun (1995—), male, Master, Assistant Engineer.

E-mail: laiyangqun@sslslab.org.cn

Correspondent author: MA Chaoyang (1985—), male, PhD, Associate Professor.

E-mail: machaoyang@sslslab.org.cn

后,再放入球磨罐中球磨 20 h,得到平均粒径 69 nm、比表面积 $13.1 \text{ m}^2/\text{g}$ 的原料粉体。2015 年, Saif 等利用溶胶凝胶法制备了 $\text{Eu}^{3+}:\text{Y}_2\text{Ti}_2\text{O}_7$ 粉体^[18], 通过 Scherrer 公式计算出的平均晶粒尺寸在 90~144 nm 左右。2021 年, Zhang 等使用化学共沉淀法制备了 $\text{Tb}_2\text{Ti}_2\text{O}_7$ 粉体^[19], 通过 Scherrer 公式计算出的平均晶粒尺寸在 61~157 nm 左右。2011 年 Gao 等通过水热法制备了 $\text{Gd}_2\text{Zr}_2\text{O}_7:\text{Tb}^{3+}$ 粉体^[20], SEM 结果显示粉体约为直径 30 nm 长度 150~300 nm 的纳米棒。2020 年 Tang 等通过固相反应法结合微波烧结工艺制备了 $\text{Y}_2\text{Zr}_2\text{O}_7:\text{U}$ 原料粉体^[21], Tang 将球磨后的原料粉体分成 2 份: 一份使用传统的方法在炉子中加热煅烧; 另一份使用微波烧结工艺煅烧。2 份样品的 SEM 照片显示常规加热煅烧的粉体团聚现象更严重, 颗粒之间互相粘结形成更大的团聚物; 微波烧结工艺得到的粉体大部分呈椭圆形, 分散性良好、烧结活性高。2018 年, Huang 等通过溶剂热法制备了粒径分布窄、分散性好的 $\text{Gd}_2\text{Zr}_2\text{O}_7$ 粉体^[22], 平均晶粒尺寸小于 3.5 nm, 比表面积为 $162 \text{ m}^2/\text{g}$ 。

高温固相法成本低、操作简单, 但是固相反应的高温可能导致粉体的烧结活性降低。燃烧法反应迅速, 得到的粉体纯度高、粒径小, 但是燃烧法制备的粉体普遍存在团聚现象。溶胶凝胶法制备的粉体化学均匀性好、纯度高, 但是溶胶凝胶法原料成本较高, 溶胶干燥后会形成严重的团聚, 制备的粉体烧结活性较差。化学共沉淀法可以制备成分和尺寸均匀、高分散性、高纯度和高烧结活性的粉体, 但是制备多组分体系粉体时, 化学共沉淀法很难使各个组分同时完全沉淀。不同的制备方法有各自的优缺点, 选择时需要根据实际粉体的特性使用合适的方法, 得到最佳性能的粉体。

1.2 陶瓷的烧结工艺

烧结是陶瓷素胚致密化的过程, 陶瓷制备工艺

的核心环节^[13]。陶瓷素胚在高温下烧结实现气体排出、体积收缩(致密化)和晶粒长大等过程, 制备 $\text{A}_2\text{B}_2\text{O}_7$ 透明陶瓷常用的烧结方法有真空烧结、放电等离子烧结和热等静压烧结等^[14]。2013 年, 王正娟等通过真空烧结工艺制备了 $\text{La}_{2-x}\text{Gd}_x\text{Zr}_2\text{O}_7$ 系列透明陶瓷^[23], 其中, $\text{La}_{1.6}\text{Gd}_{0.4}\text{Zr}_2\text{O}_7$ 陶瓷平均晶粒尺寸 12 μm 左右, 在 1 100 nm 处的透过率达到 73.6%。2019 年, Aung 等将真空预烧结和热等静压烧结工艺结合制备了 $\text{Tb}_2\text{Hf}_2\text{O}_7$ 透明陶瓷^[24], 陶瓷的平均晶粒为 3~5 μm , 在 600~1 400 nm 范围的透过率均高于 75%。2021 年, An 等通过放电等离子烧结工艺制备了 $\text{Lu}_2(\text{Ti}_{1-x}\text{Hf}_x)_2\text{O}_7$ ($x=0\sim0.5$) 系列透明陶瓷^[25], 陶瓷的平均晶粒为 2~9 μm , $\text{Lu}_2(\text{Ti}_{0.8}\text{Hf}_{0.2})_2\text{O}_7$ 透明陶瓷在 550 nm 的透过率接近 57%。因为成本低、效率高优点, 真空烧结工艺广泛应用于 $\text{A}_2\text{B}_2\text{O}_7$ 透明陶瓷制备中。热等静压烧结工艺可以有效去除陶瓷内部的气孔, 相应的生产成本较高; 放电等离子烧结工艺具有升温速率快、保温时间短和烧结温度低等优点, 但是 SPS 烧结使用石墨坩埚, 烧结后的陶瓷容易渗碳, 影响陶瓷的透过率。

目前, 已报道的 $\text{A}_2\text{B}_2\text{O}_7$ 透明陶瓷中, 根据 B 位元素的种类可以分为: 钨酸盐($\text{Re}_2\text{Hf}_2\text{O}_7$)、钛酸盐($\text{Re}_2\text{Ti}_2\text{O}_7$)、铈酸盐($\text{Re}_2\text{Ce}_2\text{O}_7$)和锆酸盐($\text{Re}_2\text{Zr}_2\text{O}_7$)。2005 年, 吉亚明通过燃烧法制备原料粉体, 在氢气气氛中烧结得到了 $\text{La}_2\text{Hf}_2\text{O}_7$ 透明陶瓷^[26], 在可见光范围内的透过率保持在 70% 左右。目前, 已报道的 $\text{Re}_2\text{Hf}_2\text{O}_7$ 系列透明陶瓷有 $\text{La}_2\text{Hf}_2\text{O}_7$ ^[26]、 $\text{Gd}_2\text{Hf}_2\text{O}_7$ ^[27]、 $\text{Y}_2\text{Hf}_2\text{O}_7$ ^[28]、 $\text{Lu}_2\text{Hf}_2\text{O}_7$ ^[29]、 $\text{La}_{2-x}\text{Gd}_x\text{Hf}_2\text{O}_7$ ^[30]、 $\text{Eu}^{3+}:\text{La}_{0.2}\text{Gd}_{1.8}\text{Hf}_2\text{O}_7$ ^[31]和 $\text{Tb}_2\text{Hf}_2\text{O}_7$ ^[32]等。2018 年, 王正娟等使用球磨后的 Y_2O_3 和 TiO_2 粉体作为原料通过真空烧结制备了 $\text{Y}_{2+x}\text{Ti}_2\text{O}_{7+3x/2}$ 系列透明陶瓷^[33], 在 1 100 nm 处的透过率达到 49.9%。2019 年, 王正娟等使用化学共沉淀法制备 $\text{Y}_2\text{Ti}_2\text{O}_7$ 粉体^[34], 结合

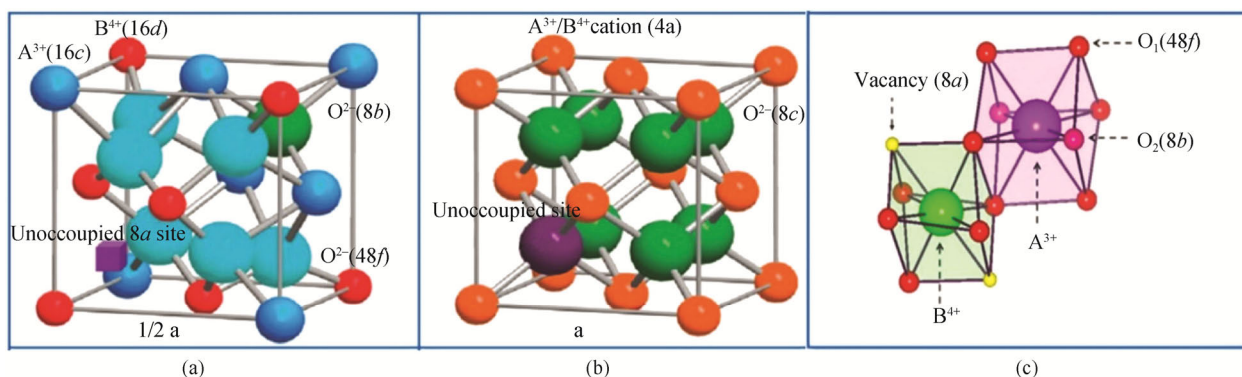


图 1 (a)烧绿石结构, (b)萤石型结构, (c)烧绿石结构中 A、B 位离子的配位结构^[1,12]

Fig. 1 (a) Pyrochlore structure (b) Fluorite structure (c) Coordination structure of A^{3+} and B^{4+} in pyrochlore^[1,12]

真空烧结工艺制备了高透过率的 $Y_2Ti_2O_7$ 透明陶瓷。该陶瓷在可见光范围内具有较高的折射率(大于 2.25), 在 1000 nm 的透过率为 73%, 达到了理论透过率的 98.1%。目前, 已报道的 $Re_2Ti_2O_7$ 系列透明陶瓷有 $Y_2Ti_2O_7$ ^[34]、 $Yb_2Ti_2O_7$ ^[35]、 $Lu_2Ti_2O_7$ ^[36]、 $Tb_2Ti_2O_7$ ^[19]等。2021 年, Kim 等通过固相反应法、无压烧结和热等静压烧结等工艺制备了 $La_2Ce_2O_7$ 透明陶瓷^[37], 在 6~7 μm 范围内的透过率接近 40%。2013 年, 王正娟等使用燃烧法制备原料粉体, 通过真空烧结制备了 $La_{2-x}Gd_xZr_2O_7$ 系列透明陶瓷^[38], $La_{1.6}Gd_{0.4}Zr_2O_7$ 透明陶瓷在 632.8 nm 的折射率为 2.08, 在 1100 nm 处的透过率达到 73.6%, 达到了理论透过率的 94.1%, 是一种很有潜力的光学透镜材料。2023 年, Han 等使用球磨法制备 $(Y_{0.2}La_{0.2}Gd_{0.2}Yb_{0.2}Dy_{0.2})_2Zr_2O_7$ 粉体, 经过真空烧结之后制备了高透过率的高熵 $(Y_{0.2}La_{0.2}Gd_{0.2}Yb_{0.2}Dy_{0.2})_2Zr_2O_7$ 透明陶瓷^[39], 该透明陶瓷的晶粒约 200 μm , 在可见光和近红外区域的透过率接近 74%。粉末在 900 $^{\circ}C$ 煅烧得到的粉末为混合相, 1400 $^{\circ}C$ 煅烧得到的粉末为萤石相, 烧结后陶瓷晶相表现为缺陷萤石相。目前已报

道的 $Re_2Zr_2O_7$ 系列透明陶瓷有 $La_{2-x}Lu_xZr_2O_7$ ^[40]、 $Y_2Zr_2O_7$ ^[8]、 $La_{2-x}Gd_xZr_2O_7$ ^[41]、 $La_{1.28}Er_{1.28}Zr_2O_7$ ^[42]、 $La_{1.28}Yb_{1.28}Zr_2O_7$ ^[43]、 $Gd_2Zr_2O_7$ ^[44]、 $(Y_{0.2}La_{0.2}Gd_{0.2}Yb_{0.2}Dy_{0.2})_2Zr_2O_7$ ^[39]、 $Ho^{3+}:Y_2Zr_2O_7$ ^[45]、 $Er^{3+}/Yb^{3+}:Y_2Zr_2O_7$ ^[5]、 $Er^{3+}:Y_2Zr_2O_7$ ^[46]、 $Sm^{3+}:Gd_2Zr_2O_7$ ^[47]等。

2 烧绿石与萤石双相共存 $A_2B_2O_7$ 透明陶瓷

目前, 已报道的 $A_2B_2O_7$ 透明陶瓷主要有 3 种相结构: 烧绿石、萤石和烧绿石与萤石双相共存。烧绿石和萤石结构的 $A_2B_2O_7$ 透明陶瓷已有文献报道^[48-49], 本文对烧绿石与萤石双相共存的 $A_2B_2O_7$ 透明陶瓷进行详细介绍。2014 年, 王正娟等使用溶胶凝胶燃烧法制备 $LaLuZr_2O_7$ 粉体, 通过真空烧结工艺成功制备了 $LaLuZr_2O_7$ 透明陶瓷^[50], 陶瓷的 XRD 谱(图 2a)可以看出, $LaLuZr_2O_7$ 透明陶瓷为烧绿石与萤石双相共存结构。

双相结构的 $LaLuZr_2O_7$ 陶瓷在 1100 nm 处的透过率为 73.4%, 比单相结构的 $LaGdZr_2O_7$ (70.7%

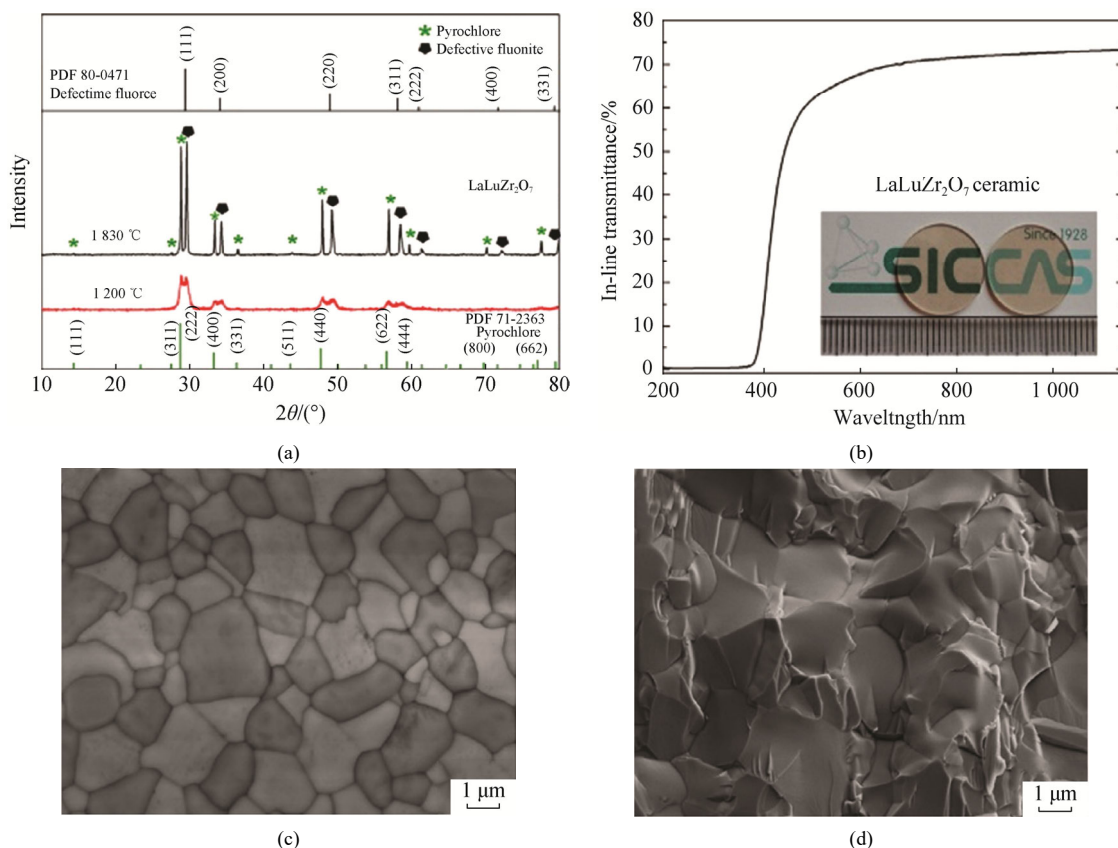


图 2 (a) $LaLuZr_2O_7$ 粉末和陶瓷的 XRD 谱, (b) $LaLuZr_2O_7$ 陶瓷的照片和透过率曲线, (c) 陶瓷的热腐蚀显微结构; (d) 陶瓷的断面显微结构^[50]

Fig. 2 (a) X-ray diffraction patterns of $LaLuZr_2O_7$ powder and ceramic, (b) Photo and transmittance curve of $LaLuZr_2O_7$ ceramic, Thermal etched surface (c) and ceramic fracture morphology (d) of $LaLuZr_2O_7$ ceramic^[50]

@1 100 nm)透过率更高。为了制备高透过率的透明陶瓷, 研究者们都追求制备单相结构的陶瓷。因为双相或者多相陶瓷中不同相之间的折射率不同, 如果相与相之间的折射率相差过大, 光束穿过陶瓷片后在相界面会发生严重的散射降低陶瓷的透过率。王正娟等认为, 烧绿石和萤石相的折射率相差非常小, 所以光束穿过 $\text{LaGdZr}_2\text{O}_7$ 陶瓷双相界面时造成的散射可以忽略, 对陶瓷透过率的影响很小。

随后, 王正娟采用球磨法制备原料粉体, 通过真空烧结工艺制备了 $\text{La}_{2-x}\text{Lu}_x\text{Zr}_2\text{O}_7$ ($x=0\sim 2$) 系列陶瓷^[51], XRD 谱结果(图 3b)表明, 在 $\text{La}_{2-x}\text{Lu}_x\text{Zr}_2\text{O}_7$

系列陶瓷中随着 Lu 含量的增加, 陶瓷逐渐由烧绿石转变为萤石结构。

当 $x<0.4$ 时陶瓷为烧绿石相, $0.4<x<1.4$ 时烧绿石与萤石双相共存, $x>1.4$, 呈萤石相。烧绿石相的陶瓷一般晶粒大小为 $11\sim 14\ \mu\text{m}$, 双相共存的陶瓷晶粒更小, 一般小于 $3\ \mu\text{m}$, 萤石相陶瓷的晶粒更大一般在 $60\sim 82\ \mu\text{m}$ 左右。 $\text{La}_{2-x}\text{Lu}_x\text{Zr}_2\text{O}_7$ ($x=0\sim 2$) 系列陶瓷中双相结构的陶瓷透过率最高。图 4 为 $\text{La}_{2-x}\text{Lu}_x\text{Zr}_2\text{O}_7$ ($x=0.6\sim 1.2$) 系列陶瓷的热腐蚀表面背散射照片。由图 4 可以看出, $x=0.6\sim 1.2$ 的样品都为烧绿石与萤石双相共存结构, 与 XRD 结果一

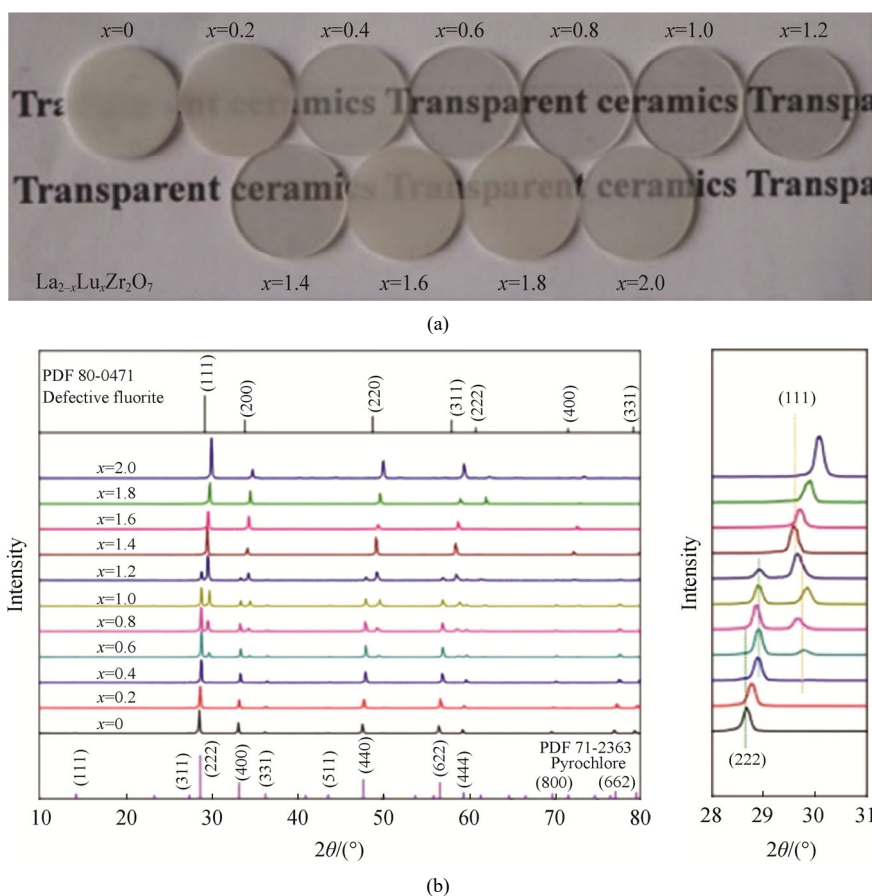


图 3 $\text{La}_{2-x}\text{Lu}_x\text{Zr}_2\text{O}_7$ ($x=0\sim 2$) 陶瓷照片(a)和 XRD 谱(b)^[51]

Fig. 3 Photograph (a) and X-ray diffraction patterns (b) of $\text{La}_{2-x}\text{Lu}_x\text{Zr}_2\text{O}_7$ ($x=0\sim 2$) ceramics^[51]

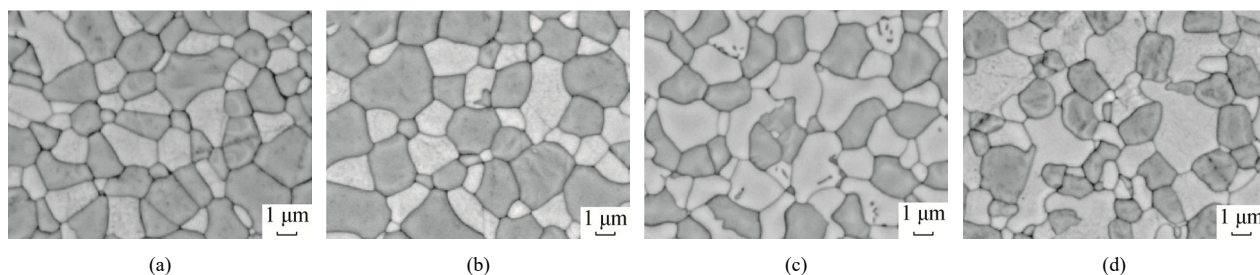


图 4 $\text{La}_{2-x}\text{Lu}_x\text{Zr}_2\text{O}_7$ 陶瓷的热腐蚀微观结构: (a) $x=0.6$, (b) $x=0.8$, (c) $x=1.0$, (d) $x=1.2$ ^[51]

Fig. 4 Thermal-etched surfaces of $\text{La}_{2-x}\text{Lu}_x\text{Zr}_2\text{O}_7$ ceramics: (a) $x=0.6$, (b) $x=0.8$, (c) $x=1.0$, (d) $x=1.2$ ^[51]

致。图 4 中深色的晶粒为烧绿石相, 浅色晶粒为萤石相, 随着 x 从 0.6 逐渐增加到 1.2 浅色晶粒的比例增大, 说明 Lu 元素含量的增加让陶瓷中的烧绿石相减少, 萤石相增多, 到 $x=1.4$ 时, 陶瓷变成了单相萤石结构。

2019 年, 赵文文等使用燃烧法制备原料粉体, 使用真空烧结工艺制备了 $\text{La}_{2-x}\text{Er}_x\text{Zr}_2\text{O}_7$ ($x = 0.1 \sim 2.0$) 系列透明陶瓷^[52]。陶瓷的 XRD 谱结果(图 5)表明: Er 的掺杂量 $x > 1.4$, 该体系的陶瓷为缺陷萤石

结构; $x < 1.4$ 时候为烧绿石结构; 在 $x = 0.4 \sim 1.2$ 范围内的陶瓷烧绿石和萤石两相共存结构; $x = 1.6 \sim 2.0$ 的陶瓷为单相萤石结构。由陶瓷的透过率曲线(图 6)可以看出, $x=0$ 的 $\text{Er}_2\text{Zr}_2\text{O}_7$ 陶瓷透过率最高, 在可见光范围内接近 45%。从陶瓷的热腐蚀显微结构(图 7)可以看出, $x = 0.4 \sim 1.2$ 的陶瓷存在两相共存区, 和 XRD 谱结果一致。图 7a~图 7d 中烧绿石和萤石相的晶粒的尺寸差距较大, 可能与真空烧结过程中的升温速率、烧结温度和保温时间有关。

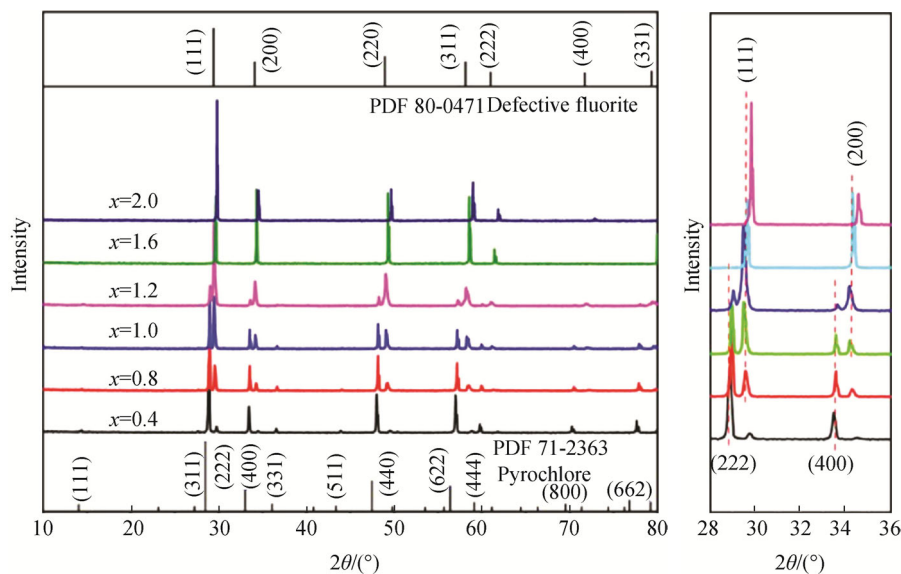


图 5 $\text{La}_{2-x}\text{Er}_x\text{Zr}_2\text{O}_7$ 陶瓷的 XRD 谱^[52]

Fig. 5 X-ray diffraction patterns of $\text{La}_{2-x}\text{Er}_x\text{Zr}_2\text{O}_7$ ceramics^[52]

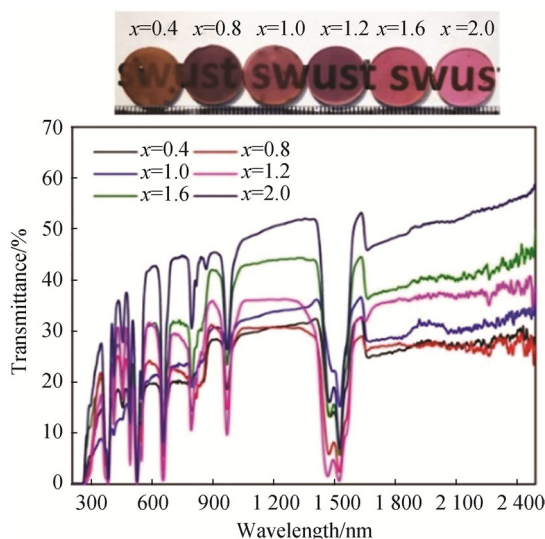


图 6 $\text{La}_{2-x}\text{Er}_x\text{Zr}_2\text{O}_7$ 透明陶瓷照片和透过率曲线^[52]

Fig. 6 Transmittance curve and photo of $\text{La}_{2-x}\text{Er}_x\text{Zr}_2\text{O}_7$ transparent ceramic^[52]

赵文文等对 $\text{LaErZr}_2\text{O}_7$ 中 Er 和 La 元素过量的体系进行了研究, 使用类似 $\text{La}_{2-x}\text{Er}_x\text{Zr}_2\text{O}_7$ ($x = 0.1 \sim 2.0$)

系列透明陶瓷的制备工艺, 成功制备了 $\text{La}_{1.28}\text{Er}_{1.28}\text{Zr}_2\text{O}_{7.84}$ 透明陶瓷^[43]。XRD 结果(图 8)表明, 制备的 $\text{La}_{1.28}\text{Er}_{1.28}\text{Zr}_2\text{O}_{7.84}$ 粉末为单相烧绿石结构, 经过高温烧结之后陶瓷变成了烧绿石与萤石双相共存的结构, 陶瓷在 1100 nm 处的透过率达到 81% (图 9a)。

陶瓷的热腐蚀表面显微结构照片(图 9c 和图 9d)中深色的区域应该是萤石相, 浅色区域应该是烧绿石相, 平均尺寸为 3 μm 左右, 在陶瓷的热腐蚀表面显微结构和断面显微结构图中都未观察到气孔和杂质。

赵文文等对 $\text{LaYbZr}_2\text{O}_7$ 中 Er 和 La 元素过量的体系进行了探索, 使用燃烧法制备了 $\text{La}_{1.28}\text{Yb}_{1.28}\text{Zr}_2\text{O}_{7.84}$ 粉体, 通过真空烧结工艺制备了 $\text{La}_{1.28}\text{Yb}_{1.28}\text{Zr}_2\text{O}_{7.84}$ 透明陶瓷^[43]。XRD 谱结果(图 10a)表明, 烧结后的陶瓷为烧绿石和萤石两相共存的结构。该陶瓷在 1100~2500 nm 之间的透过率稳定在 83.9% 左右(图 10b)。图 10c 中较亮的晶粒为(富 Yb)缺陷萤石相, 较暗的晶粒应该是(富 La)烧绿石相。平均晶粒为 3 μm 左右。

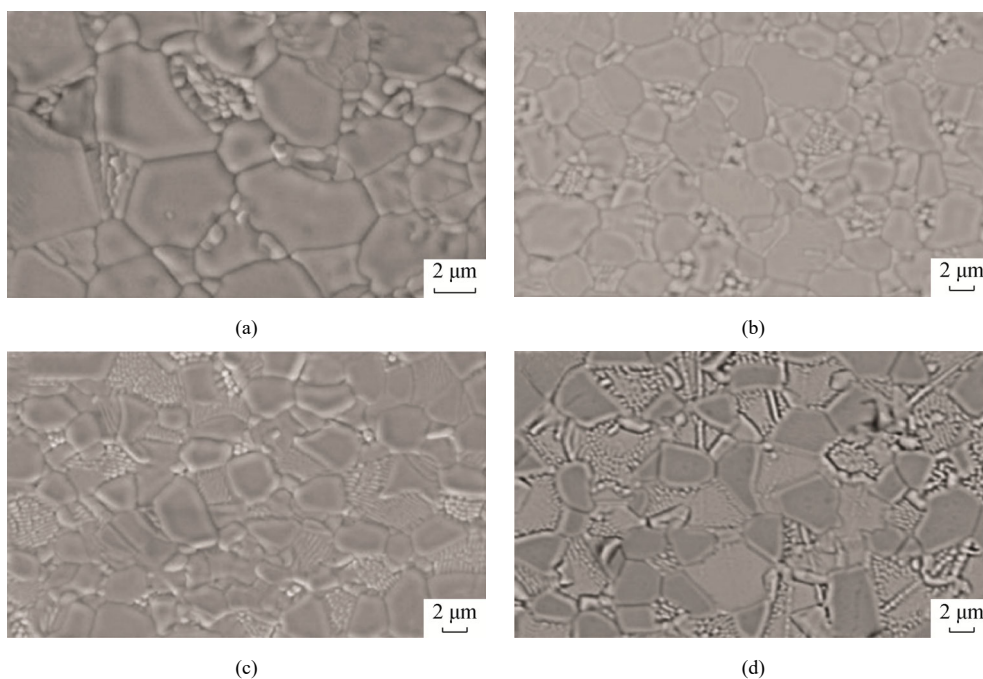


图 7 $\text{La}_{2-x}\text{Er}_x\text{Zr}_2\text{O}_7$ 透明陶瓷的热腐蚀表面: (a) $x=0.4$, (b) $x=0.8$, (c) $x=1.0$, (d) $x=1.2$ ^[52]
Fig. 7 Thermal etched surface of $\text{La}_{2-x}\text{Er}_x\text{Zr}_2\text{O}_7$ transparent ceramics: (a) $x=0.4$, (b) $x=0.8$, (c) $x=1.0$, (d) $x=1.2$ ^[52]

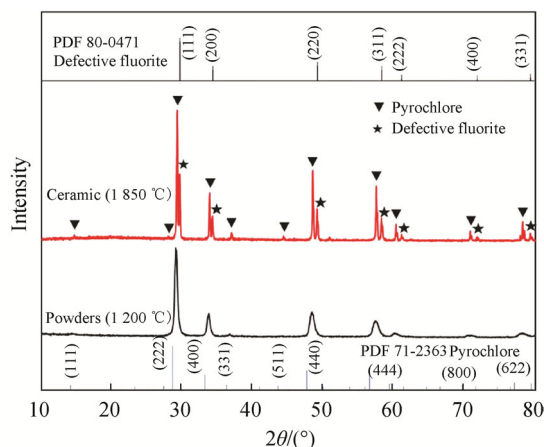


图 8 $\text{La}_{1.28}\text{Er}_{1.28}\text{Zr}_2\text{O}_{7.84}$ 粉末和陶瓷的 XRD 谱^[42]
Fig. 8 X-ray diffraction patterns of $\text{La}_{1.28}\text{Er}_{1.28}\text{Zr}_2\text{O}_{7.84}$ powder and ceramic^[42]

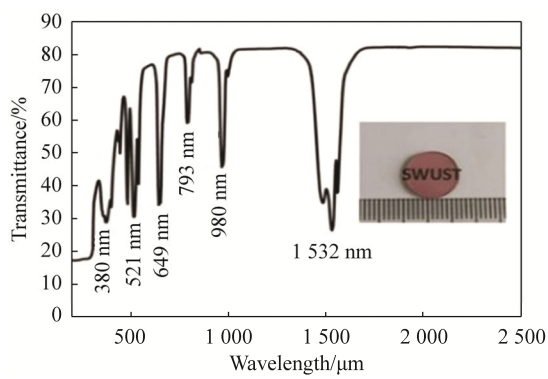
2021 年, 邓婷等通过燃烧法制备 $\text{La}_{1+x}\text{Yb}_{1+y}\text{Zr}_2\text{O}_7$ ($x=0.1\sim0.5$) 系列粉体, 通过真空烧结工艺制备了 $\text{La}_{1+x}\text{Yb}_{1+y}\text{Zr}_2\text{O}_7$ ($x=0.1\sim0.5$) 系列透明陶瓷^[53]。图 11 为 $\text{La}_{1+x}\text{Yb}_{1+y}\text{Zr}_2\text{O}_7$ 系列陶瓷的 XRD 谱。由图 11 可以看出, $\text{La}_{1+x}\text{Yb}_{1+y}\text{Zr}_2\text{O}_7$ ($x=0.1\sim0.5$) 系列陶瓷均为烧绿石与萤石双相共存结构, $y=0.1\sim0.3$ 系列的 $\text{LaYb}_{1+y}\text{Zr}_2\text{O}_7$ 陶瓷均为烧绿石与萤石双相共存结构, 当 Yb 的含量增加到 0.4 和 0.5 时陶瓷逐渐从双相结构转变为单相萤石结构, 这一现象和王正娟之前研究的 $\text{La}_{2-x}\text{Lu}_x\text{Zr}_2\text{O}_7$ 系列陶瓷中 Lu 含量增加陶瓷逐渐由双相结构转变为单相萤石结构的结果

类似, 所有陶瓷都是烧绿石与萤石双相共存结构。图 12a~图 12c 分别为 $\text{La}_{1+x}\text{YbZr}_2\text{O}_7$ 、 $\text{LaYb}_{1+y}\text{Zr}_2\text{O}_7$ 和 $\text{La}_{1+x}\text{Yb}_{1+y}\text{Zr}_2\text{O}_7$ ($x=0.1\sim0.5$) 系列透明陶瓷的样品图和透过率曲线。 $\text{La}_{1.3}\text{Yb}_{1.3}\text{Zr}_2\text{O}_7$ 陶瓷在 1100 nm 处的透过率接近 84.1%

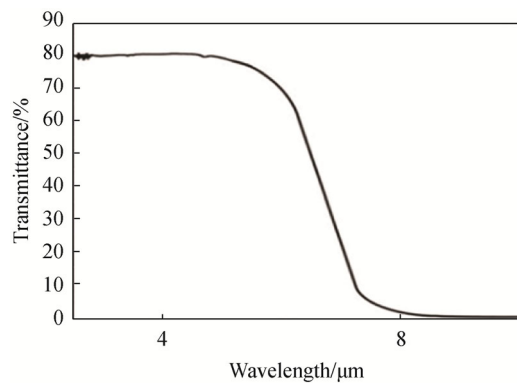
2019 年, 张奎宝等通过燃烧法结合球磨工艺制备了 $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ 纳米粉体, 然后通过真空烧结工艺制备了 $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ 透明陶瓷^[54]。

陶瓷的 XRD 谱(图 13a)中有微弱的(331)和(511)的衍射峰, 陶瓷的 Raman 光谱(图 13c)中有 2 个 F_{2g} Raman 峰, 烧绿石结构一般为 4 个 F_{2g} 键, 萤石结构一般为 1 个 F_{2g} 键^[54], 所以 $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ 陶瓷应为烧绿石与萤石双相共存结构。

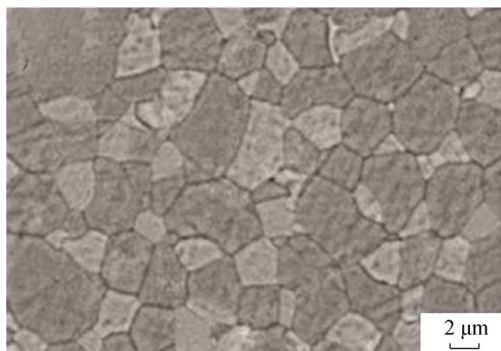
2022 年, Chen 等通过球磨法制备原料粉体, 通过真空烧结工艺制备了 $\text{La}_x\text{Gd}_{2-x}\text{Zr}_{1.92}\text{U}_{0.04}\text{Ca}_{0.04}\text{O}_7$ ($x=0.4, 1, 1.6, 2$) 系列透明陶瓷^[55], 700~2000 nm 范围 U: $\text{La}_{1.6}\text{Gd}_{0.4}\text{Zr}_2\text{O}_7$ 的透过率接近 80% (图 15a), Chen 等认为, U: $\text{La}_{1.6}\text{Gd}_{0.4}\text{Zr}_2\text{O}_7$ 的高透过率归因于它的烧绿石与萤石双相共存的结构, 双相共存抑制了陶瓷晶粒的长大。从 U: $\text{La}_{1.6}\text{Gd}_{0.4}\text{Zr}_2\text{O}_7$ 陶瓷的热腐蚀表面显微结构和断面显微结构(图 15c 和图 16d)可以看出, 陶瓷的晶界清晰可见, 晶粒尺寸均匀, 没有异常长大的晶粒, 晶内和晶界没有观察到明显的气孔。



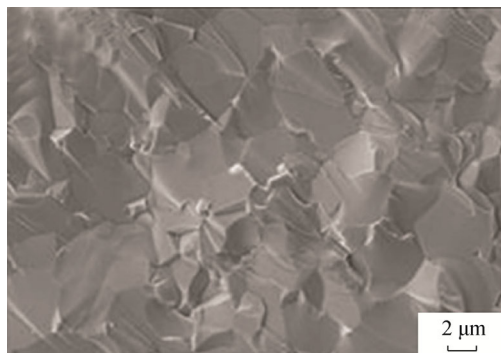
(a)



(b)



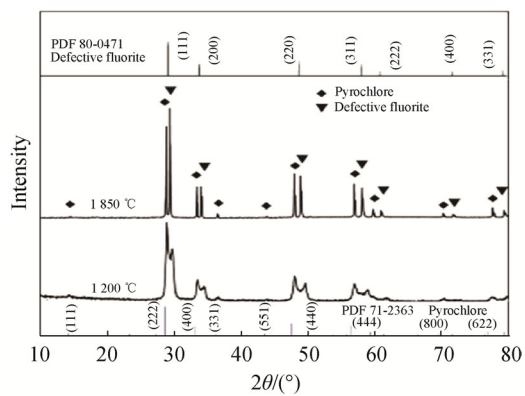
(c)



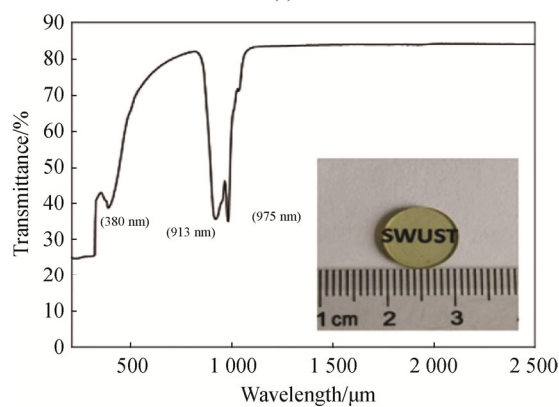
(d)

图 9 $\text{La}_{1.28}\text{Er}_{1.28}\text{Zr}_2\text{O}_{7.84}$ 陶瓷的透射率曲线 (a) 250~2500 nm (b) 2.5~10 μm , (c) 陶瓷的热腐蚀表面, 和(d) 断面显微结构^[42]

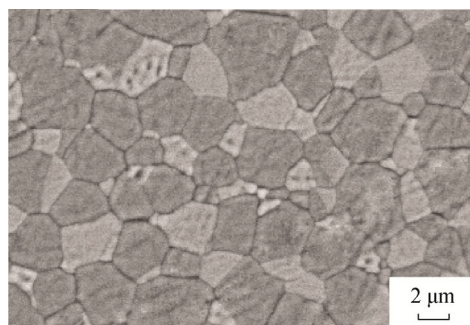
Fig. 9 Transmittance curve of $\text{La}_{1.28}\text{Er}_{1.28}\text{Zr}_2\text{O}_{7.84}$ ceramic: (a) 250–2500 nm (b) 2.5–10.0 μm , thermal etched surface (c) and ceramic fracture morphology (d) of $\text{La}_{1.28}\text{Er}_{1.28}\text{Zr}_2\text{O}_{7.84}$ ceramic^[42]



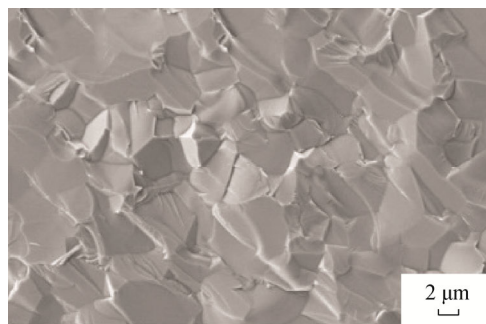
(a)



(b)



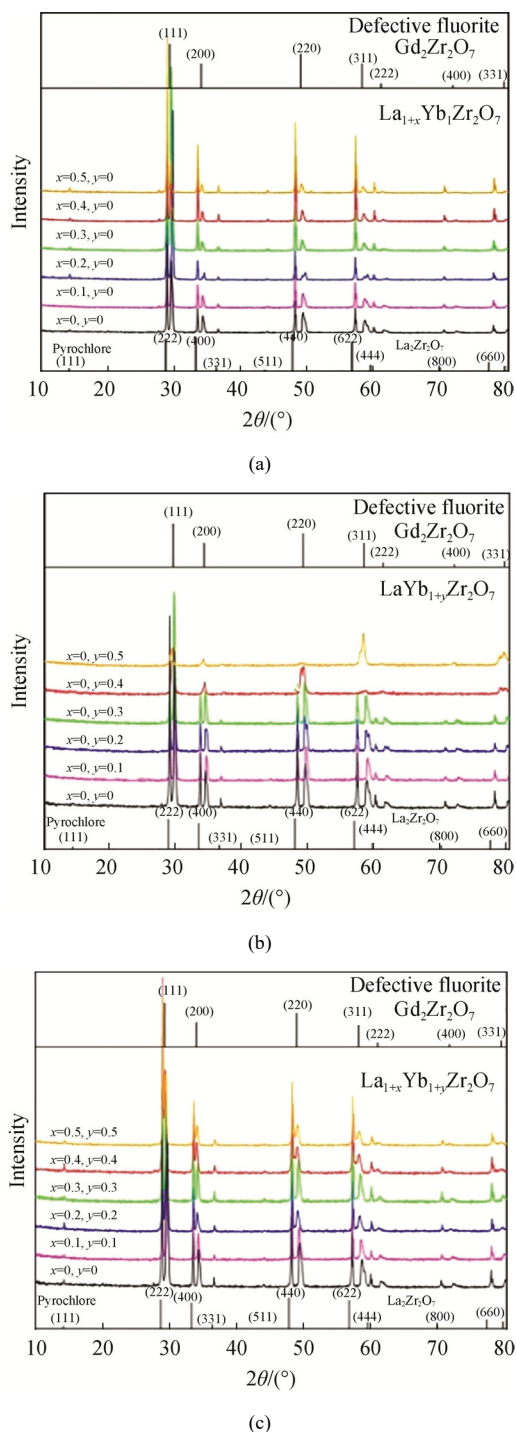
(c)



(d)

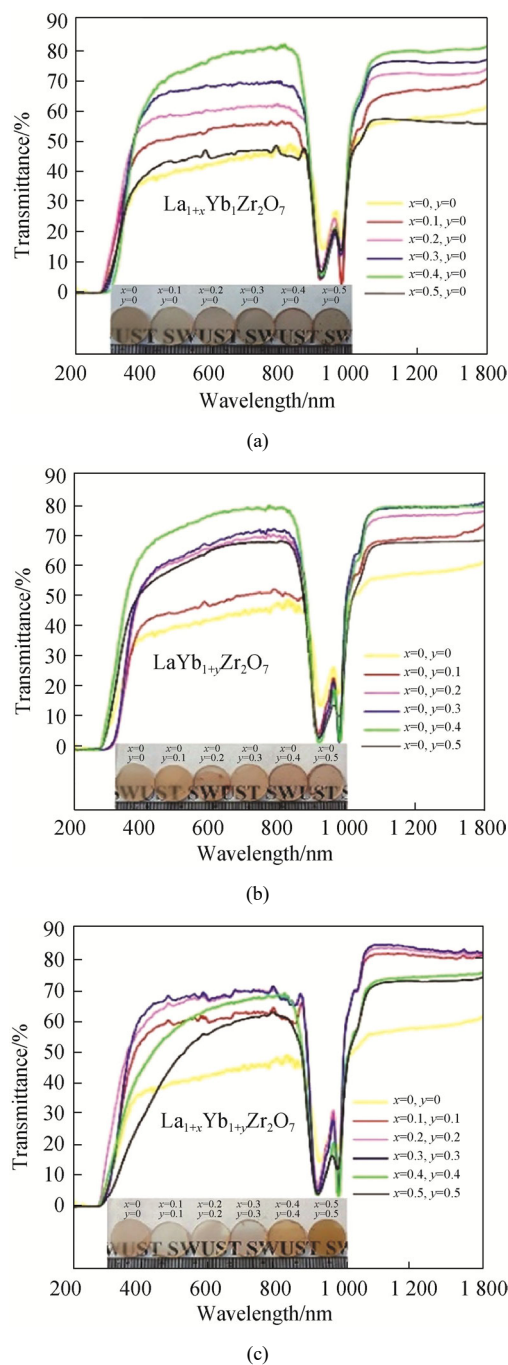
图 10 (a) $\text{La}_{1.28}\text{Yb}_{1.28}\text{Zr}_2\text{O}_{7.84}$ 粉末和陶瓷的 XRD 谱, (b) $\text{La}_{1.28}\text{Yb}_{1.28}\text{Zr}_2\text{O}_{7.84}$ 陶瓷的透射率曲线(b), 热腐蚀显微结构(c), 断面显微结构(d)^[43]

Fig. 10 (a) X-ray diffraction patterns of $\text{La}_{1.28}\text{Yb}_{1.28}\text{Zr}_2\text{O}_{7.84}$ powder and ceramic, Transmittance curve (b), ceramic thermal etched surface (c), ceramic fracture morphology (d) of $\text{La}_{1.28}\text{Yb}_{1.28}\text{Zr}_2\text{O}_{7.84}$ ceramic

图 11 $\text{La}_{1+x}\text{Yb}_{1+y}\text{Zr}_2\text{O}_7$ 系列陶瓷的 XRD 谱^[53]Fig. 11 X-ray diffraction patterns of $\text{La}_{1+x}\text{Yb}_{1+y}\text{Zr}_2\text{O}_7$ ceramics^[53]

与传统的单相 $\text{A}_2\text{B}_2\text{O}_7$ 透明陶瓷相比, 双相结构的 $\text{A}_2\text{B}_2\text{O}_7$ 透明陶瓷可以达到更高的透过率, 具有较好的研究价值, 但是制备高透过率的双相 $\text{A}_2\text{B}_2\text{O}_7$ 透明陶瓷并不容易, $\text{La}_{2-x}\text{Er}_x\text{Zr}_2\text{O}_7$ 系列透明陶瓷中部分双相共存的陶瓷透过率很低, 甚至低于单相结构的 $\text{A}_2\text{B}_2\text{O}_7$ 陶瓷。可能是萤石相晶粒和烧绿石相晶粒生长速率不一致, 导致陶瓷的晶粒大小不均匀,

陶瓷残留孔隙较多。高透过率的双相 $\text{A}_2\text{B}_2\text{O}_7$ 透明陶瓷一般烧绿石相和萤石相的晶粒大小接近, 在 $1 \sim 3 \mu\text{m}$ 左右。要制备高透过率的双相 $\text{A}_2\text{B}_2\text{O}_7$ 透明陶瓷, 首先需要选择合适的 A 位和 B 位元素, 通过计算 A 位和 B 位元素的离子半径比来预测产物的相结构, 这些双相共存的 $\text{A}_2\text{B}_2\text{O}_7$ 透明陶瓷都是 A 位掺杂 2 种元素的锆酸盐($\text{A}_2\text{Zr}_2\text{O}_7$)。其次陶瓷原料粉体的性能对陶瓷的透过率影响很大, 颗粒尺寸均匀、

图 12 $\text{La}_{1+x}\text{Yb}_{1+y}\text{Zr}_2\text{O}_7$ 系列陶瓷的样品图和透过率曲线^[53]Fig. 12 Photo and Transmittance curve of $\text{La}_{1+x}\text{Yb}_{1+y}\text{Zr}_2\text{O}_7$ ceramics^[53]

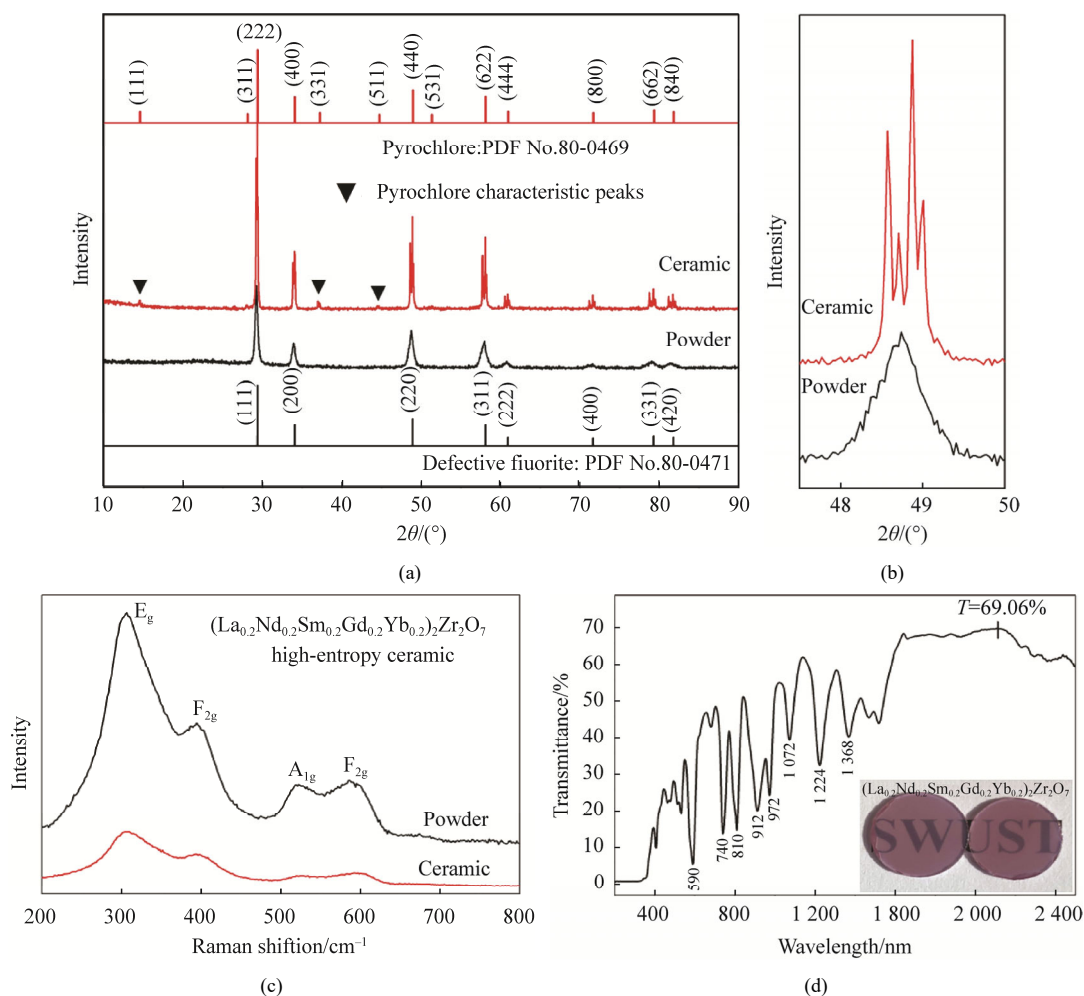


图 13 (a) (b) $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ 粉末和陶瓷的 XRD 谱, (c) $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ 粉末和陶瓷的 Raman 光谱, (d) $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ 陶瓷的照片和透过率曲线^[54]

Fig. 13 X-ray diffraction patterns of the synthesized $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ powder and ceramic (a) (b), Raman spectra of the as-prepared $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ powder and final ceramic (c), Ultraviolet-visible spectrum and outside view of the ceramic (d)^[54]

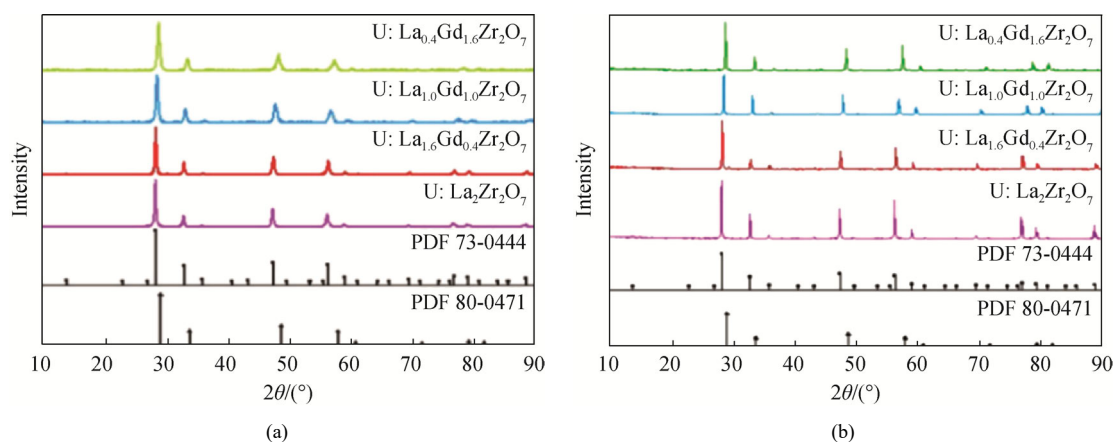
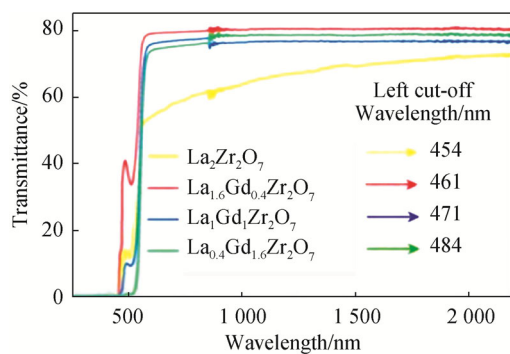


图 14 $\text{U:La}_x\text{Gd}_{2-x}\text{Zr}_2\text{O}_7$ 粉末(a)和陶瓷片(b)的 XRD 谱^[55]

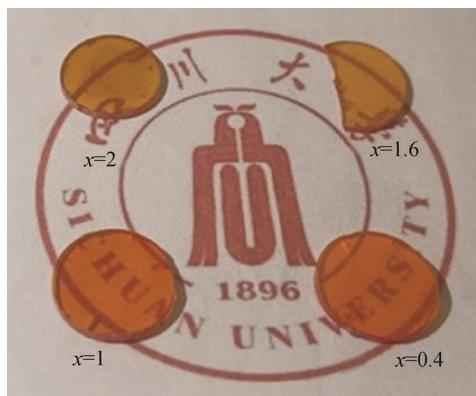
Fig. 14 X-ray diffraction patterns of $\text{U:La}_x\text{Gd}_{2-x}\text{Zr}_2\text{O}_7$ as-prepared powders (a) and transparent ceramic samples (b)^[55]

无硬团聚的粉体烧结活性高, 烧结后的陶瓷气孔少, 透过率高。此外陶瓷的烧结工艺也很重要, 烧结助剂的选择, 以及烧结过程中升温速率、烧结温度和

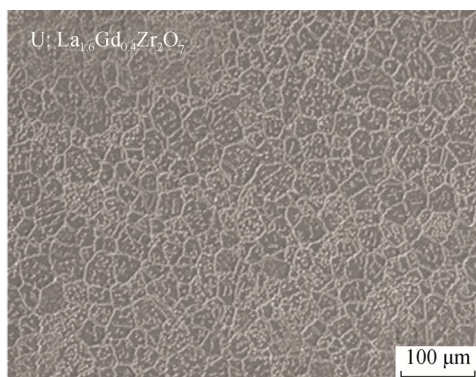
保温时间等参数的控制, 让陶瓷中的萤石相晶粒和烧绿石相晶粒生长速率保持一致, 从而得到晶粒尺寸接近的双相 $A_2B_2O_7$ 透明陶瓷。



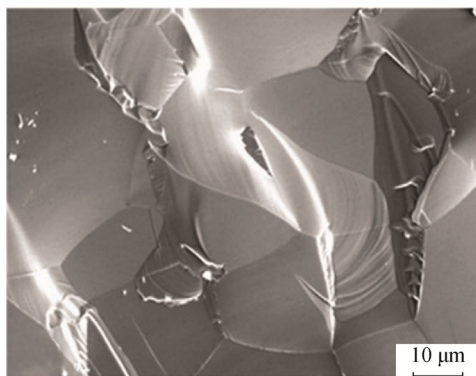
(a)



(b)



(c)



(d)

图 15 (a)陶瓷的透过率曲线(b)陶瓷的样品图, U:La_{1.6}Gd_{0.4}Zr₂O₇陶瓷的热腐蚀显微结构(c)和断面显微结构(d)[55]

Fig. 15 Transmittance curve (a) and photo (b) of ceramics, thermally etched surfaces (c) and fracture surfaces (d) of U:La_{1.6}Gd_{0.4}Zr₂O₇ ceramic [55]

3 A₂B₂O₇透明陶瓷的相变

A₂B₂O₇透明陶瓷可以通过控制 A 位和 B 位离子的半径使其相结构发生转变,除了 A 位和 B 位离子半径之外还有许多因素可以诱导 A₂B₂O₇透明陶瓷发生相变,比如压力和烧结过程中的降温速率。2006 年, Zhang 等研究了烧绿石 Y₂Ti₂O₇陶瓷在压力诱导下的相变^[56],结果表明,压力大于 60 GPa 后 Y₂Ti₂O₇陶瓷由有序的烧绿石相转变为无序缺陷萤石相和少量非晶相。2023 年, Zhang 等发现烧绿石结构的 Tm₂Sn₂O₇陶瓷在 36.7 GPa 压力下由立方晶系变成了正交晶系,并且释放压力之后相变是可逆的^[57]。Shlyakhtina 等使用共沉淀法制备 Lu₂Hf₂O₇粉体,粉体成型之后在 1600 °C 烧结,然后以 130 °C/h 和 5 °C/h 2 种冷却速率降温冷却,这 2 种不同的冷却速率得到了 2 种不同相结构的 Lu₂Hf₂O₇陶瓷,说明烧结过程中降温速率可能会影响陶瓷的相变^[58]。2021 年, An 等通过球磨法制备原料粉体结合放电等离子烧结工艺成功制备了 Lu₂(Ti_{1-x}Hf_x)₂O₇系列透明陶瓷^[59], x=0 时 Lu₂Ti₂O₇陶瓷透过率最高,在 550 nm 处透过率达到 57%。Lu₂(Ti_{1-x}Hf_x)₂O₇系列透明陶瓷在 x=0~0.3 范围内为烧绿石结构,在 0.4~0.5 范围内为缺陷萤石结构。根据 Subramanian 理论^[60],当 1.46<r_A/r_B<1.78 时呈现为烧绿石结构,但是在 Lu₂(Ti_{1-x}Hf_x)₂O₇体系中烧绿石结构向萤石结构的转变发生在 r_A/r_B=1.51 处,而不是在 1.46。2018 年, Lu 等使用放电等离子烧结工艺制备 Gd_{2-x}Nd_xZr₂O₇系列陶瓷时发现, Gd_{2-x}Nd_xZr₂O₇系列陶瓷相转变发生在 r_A/r_B=1.49 处,而不是预期的 r_A/r_B=1.46 处^[61],这是由于 SPS 烧结过程中的压力、烧结温度和降温速率等多种原因导致的。

4 A₂B₂O₇透明陶瓷的潜在应用

2005 年, 吉亚明等通过燃烧法制备原料粉体,通过氢气气氛烧结的方式成功制备了 La₂Hf₂O₇:Ti⁴⁺透明陶瓷^[62]。厚度 1 mm 的 La₂Hf₂O₇:2%Ti⁴⁺陶瓷样品在 800 nm 附近的透过率接近 60%,在 120 kV 的 X 射线激发下陶瓷发出明亮的蓝绿光,光产额是同尺寸 Bi₄Ge₃O₁₂单晶的 1.5 倍,未来 La₂Hf₂O₇:Ti⁴⁺透明陶瓷有可能成为更经济实惠的闪烁体材料。2020 年, Tang 等通过固相反应法和真空烧结工艺制备了 Ln_{0.1}La_{0.9}GdZr₂O₇ (Ln = Nd, Yb)系列透明陶瓷^[63], Nd_{0.1}La_{0.9}GdZr₂O₇陶瓷在 1 100 nm 处的透过率接近 68%,平均粒径为 6~24 μm。Nd_{0.1}La_{0.9}GdZr₂O₇陶

瓷在 808 nm 泵浦激光器激发下发出 1061 nm 波长的近红外光, $Yb_{0.1}La_{0.9}GdZr_2O_7$ 陶瓷在 976 nm 泵浦激光器激发下发出 1032 nm 的近红外光, 这 2 种陶瓷以后在激光材料领域可能有很好的前景。2022 年, Tang 通过固相反应和真空烧结工艺制备了 $Y_2Zr_2O_7: Eu^{3+}/Bi^{3+}$ 透明陶瓷^[64], 在 1200 nm 处的透过率接近 67%。 $Y_2Zr_2O_7: Eu^{3+}/Bi^{3+}$ 透明陶瓷的 PL 光谱显示, 当激发波长从 250~467 nm 范围内变化时, 发光颜色可以从红色到白色再到橙红色, 说明该陶瓷在紫外激发 WLED 材料领域具有很大的潜在价值。2022 年, Zhang 等通过固相反应、真空预烧结和热等静压处理工艺成功制备了 $Tb_{2.45}Hf_2O_{7.68}$ 透明陶瓷^[65], 陶瓷在 1064 nm 处的透过率接近 79.4%。 $Tb_{2.45}Hf_2O_{7.68}$ 透明陶瓷在 633 nm 处的 Verdet 常数为 $-165.6 \text{ rad} \cdot T^{-1} \cdot m^{-1}$ 比商用的 $Tb_3Al_5O_{12}$ 单晶高 23.26% 左右, 说明 $Tb_{2.45}Hf_2O_{7.68}$ 透明陶瓷是一种很有潜力的磁光材料。2023 年, Lu 等通过固相反应和真空烧结工艺制备了 $Y_2Zr_2O_7: xPr$ 系列透明陶瓷^[66], $Y_2Zr_2O_7: Pr$ 陶瓷在 760 nm 的透过率接近 74%, $Y_2Zr_2O_7: 0.5Pr$ 陶瓷具有较好的光学测温性能, 450 nm 激发下绝对灵敏值最大值为 0.008 K^{-1} (663 K), 相对灵敏度最大值为 $0.47\%K^{-1}$ (363 K), 说明 $Y_2Zr_2O_7: 0.5Pr$ 陶瓷在高温视窗、光学测温领域具有很好的应用前景。2023 年, Li 等通过固相反应和真空烧结工艺制备了 $Sm_2Zr_2O_7$ 透明陶瓷^[15], 陶瓷在可见光区域和红外区域的透过率分别为 73% 和 65% 左右。对陶瓷的介电常数进行测试, $Sm_2Zr_2O_7$ 透明陶瓷具有较高的介电常数和较低的介电损耗, 说明 $Sm_2Zr_2O_7$ 透明陶瓷在介电材料领域具有潜在价值。2023 年, Han 等通过固相反应和真空烧结工艺成功制备了 1.5 mm 厚的 $(Y_{0.2}La_{0.2}Gd_{0.2}Yb_{0.2}Dy_{0.2})_2Zr_2O_7$ 透明陶瓷^[39], 在可见光和红外区的透过率接近 74%。在多波长激发下 $(Y_{0.2}La_{0.2}Gd_{0.2}Yb_{0.2}Dy_{0.2})_2Zr_2O_7$ 透明陶瓷的发射光可以从暖白光到冷白光, 说明该高熵陶瓷有望成为一种具有多波长激发和发射特性的新型荧光材料。

5 结论及展望

本文综述了近年来 $A_2B_2O_7$ 透明陶瓷原料粉体的制备方法、 $A_2B_2O_7$ 透明陶瓷的烧结工艺、一些特殊双相共存结构的 $A_2B_2O_7$ 透明陶瓷、 $A_2B_2O_7$ 透明陶瓷的相变和 $A_2B_2O_7$ 透明陶瓷的应用前景。双相结构的 $A_2B_2O_7$ 透明陶瓷比传统的单相 $A_2B_2O_7$ 透明陶瓷晶粒更小、透过率更高, 具有更高的研究价值。

现在关于烧绿石与萤石双相共存结构的 $A_2B_2O_7$ 透明陶瓷研究很少, 烧绿石与萤石双相共存形成的原理值得进一步研究。

$A_2B_2O_7$ 透明陶瓷实现应用还有很多困难需要解决, 透明陶瓷制备过程中容易产生气孔, 大的气孔会影响陶瓷的光学质量。选择尺寸均匀、形状均匀的近球形原料粉体, 可以有效减少陶瓷中气孔的数量^[67-68]。这种粉体可以排列更紧密, 减少粉体颗粒之间的空隙, 在陶瓷素胚烧结过程中更容易致密, 残留气孔更少。当原料粉体存在团聚现象导致陶瓷素胚烧结过程中团聚体内部和外部的烧结速率不一致(差分烧结), 烧结完的陶瓷中会留下大气孔, 所以应该选择无团聚或少团聚的原料粉体^[69]。如果原料粉体中存在大量气孔, 烧结后的陶瓷中容易残余晶粒内包裹气孔, 所以要减少原料粉体的气孔含量^[14]。

$A_2B_2O_7$ 透明陶瓷的热导率较低 [$2 \sim 4 \text{ W}/(\text{m} \cdot \text{K})$], $A_2B_2O_7$ 透明陶瓷作为激光增益介质应用在高功率激光器上时陶瓷的表面可能产生较大的温度梯度, 这可能会导致陶瓷各部分的折射率产生差异、陶瓷的内部产生内应力等, 影响光束传输质量^[70]。目前 $A_2B_2O_7$ 透明陶瓷的制备技术尚不成熟, 无法制备尺寸大、光学质量好的产品, 实现应用仍有许多问题需要解决。

参考文献:

- [1] 王正娟. $Ln_2M_2O_7$ ($M = Zr, Hf$) 透明陶瓷的制备与性能研究[D]. 上海: 中国科学院大学 (中国科学院上海硅酸盐研究所), 2015.
Wang Zhengjuan. Fabrication and properties of $Ln_2M_2O_7$ ($M = Zr, Hf$) transparent ceramics[D]. Shanghai: Shanghai Institute of Ceramics, Chinese Academy of Sciences, 2015.
- [2] 吉亚明. 钨酸盐陶瓷闪烁体的探索及其发光特性研究[D]. 上海: 中国科学院上海硅酸盐研究所, 2006.
JI Yaming. Exploration of hafnate ceramic scintillator and its luminescent characteristics[D]. Shanghai: Shanghai Institute of Ceramics, Chinese Academy of Sciences, 2006.
- [3] 邹小庆, 周国红, 易海兰, 等. 燃烧法合成钨酸钪粉体及其透明陶瓷的制备[J]. 无机材料学报, 2011, 26(9): 929-932.
ZOU Xiaoqing, ZHOU Guohong, YI Hailan, et al. J Inorg Mater, 2011, 26(9): 929-932.
- [4] TROJAN-PIEGZA J, GIERLOTKA S, ZYCH E, et al. Spectroscopic studies of nanopowder and nanoceramics $La_2Hf_2O_7: Pr$ scintillator[J]. J Am Ceram Soc, 2014, 97(5): 1595-1601.
- [5] YE Y C, LU K L, QI J Q. Developing smart temperature sensing window based on highly transparent rare-earth doped yttrium zirconate ceramics[J]. ACS Appl Mater Interfaces, 2022, 14(34): 39072-39080.
- [6] LI Y L, YE Y C, QUAN W K, et al. Investigation of up/down-converted luminescence and related mechanisms in Ho^{3+}/Yb^{3+} co-doped $Y_2Zr_2O_7$ highly transparent ceramics as phosphor material[J]. J Lumin, 2022, 251: 119255.

- [7] WANG Z J, ZHOU G H, ZHANG J, et al. Luminescence properties of Eu^{3+} -doped Lanthanum gadolinium hafnates transparent ceramics[J]. *Opt Mater*, 2017, 71: 5–8.
- [8] TANG Z, HUANG Z Y, HAN W, et al. Microwave-assisted synthesis of uranium doped $\text{Y}_2\text{Zr}_2\text{O}_7$ transparent ceramics as potential near-infrared optical lens[J]. *Scr Mater*, 2020, 178: 90–93.
- [9] 李伟伟. $\text{Gd}_{2-x}\text{M}_x\text{Zr}_2\text{O}_7$ ($\text{M}=\text{Nd}, \text{Sm}$) 型透明陶瓷的制备及性能研究[D]. 绵阳: 西南科技大学, 2020.
LI Weiwei. Preparation and properties of $\text{Gd}_{2-x}\text{M}_x\text{Zr}_2\text{O}_7$ ($\text{M}=\text{Nd}, \text{Sm}$) transparent ceramics[D]. Mianyang: Southwest University of Science and Technology, 2020.
- [10] 邓婷. 非化学计量比 $\text{A}_2\text{B}_2\text{O}_7$ 透明陶瓷制备与光学性能研究[D]. 绵阳: 西南科技大学, 2021.
DENG Ting. Preparation and optical properties of non-stoichiometric $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics[D]. Mianyang: Southwest University of Science and Technology, 2021.
- [11] AN L Q, ITO A, GOTO T. Effect of calcination temperature on the fabrication of transparent lutetium titanate by spark plasma sintering[J]. *Ceram Int*, 2012, 38(6): 4973–4977.
- [12] WANG Z J, ZHOU G H, JIANG D Y, et al. Recent development of $\text{A}_2\text{B}_2\text{O}_7$ system transparent ceramics[J]. *J Adv Ceram*, 2018, 7(4): 289–306.
- [13] 潘裕柏, 陈昊鸿, 石云. 稀土陶瓷材料[M]. 北京: 冶金工业出版社, 2016.
- [14] 潘裕柏, 李江, 姜本学. 先进光功能透明陶瓷[M]. 北京: 科学出版社, 2013.
- [15] LI S R, HAN W H, LU K L, et al. Highly transparent $\text{Sm}_2\text{Zr}_2\text{O}_7$ ceramics with excellent dielectric performance[J]. *Appl Phys Lett*, 2023, 123(4): 1–5.
- [16] TAN L, SU X H, YANG J X, et al. Facile synthesis of high-entropy zirconate nanopowders and their sintering behaviors[J]. *J Adv Ceram*, 2023, 12(3): 498–509.
- [17] WANG Z J, ZHOU G H, QIN X P, et al. Fabrication of $\text{LaGdZr}_2\text{O}_7$ transparent ceramic[J]. *J Eur Ceram Soc*, 2013, 33(4): 643–646.
- [18] SAIF M, SHEBL M, MBAREK A, et al. Synthesis of non-toxic phosphor material based on pyrochlore-type dititanate ($\text{Eu}^{3+}/\text{Yb}_2\text{Ti}_2\text{O}_7$)[J]. *J Photochem Photobiol A Chem*, 2015, 301: 1–5.
- [19] ZHANG L X, LI X Y, HU D J, et al. Fabrication and properties of transparent $\text{Tb}_2\text{Ti}_2\text{O}_7$ magneto-optical ceramics[J]. *J Eur Ceram Soc*, 2021, 41(14): 7208–7214.
- [20] GAO L, ZHU H, WANG L, et al. Hydrothermal synthesis and photoluminescence properties of $\text{Gd}_2\text{Zr}_2\text{O}_7$: Tb^{3+} phosphors[J]. *MATER LETT*, 2011, 65(9): 1360–1362.
- [21] TANG Z, HUANG Z, HAN W, et al. Microwave-assisted synthesis of uranium doped $\text{Y}_2\text{Zr}_2\text{O}_7$ transparent ceramics as potential near-infrared optical lens[J]. *Scr Mater*, 2020, 178: 90–93.
- [22] HUANG Z, QI J, ZHOU M, et al. A facile solvothermal method for high-quality $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanopowder preparation[J]. *Ceram Int*, 2018, 44(2): 1334–1342.
- [23] WANG Z J, ZHOU G H, QIN X P, et al. Transparent $\text{La}_{2-x}\text{Gd}_x\text{Zr}_2\text{O}_7$ ceramics obtained by combustion method and vacuum sintering[J]. *J Alloys Compd*, 2014, 585: 497–502.
- [24] AUNG Y L, IKESUE A, YASUHARA R, et al. Optical properties of improved $\text{Tb}_2\text{Hf}_2\text{O}_7$ pyrochlore ceramics[J]. *J Alloys Compd*, 2020, 822: 153564.
- [25] AN L Q, WANG L F, FAN R H, et al. Fabrication and electrical conductivity of $\text{Lu}_2(\text{Ti}_{1-x}\text{Hf}_x)_2\text{O}_7$ transparent ceramics prepared by spark plasma sintering[J]. *J Asian Ceram Soc*, 2021, 9(3): 893–901.
- [26] JI Y M, JIANG D Y, FEN T, et al. Fabrication of transparent $\text{La}_2\text{Hf}_2\text{O}_7$ ceramics from combustion synthesized powders[J]. *Mater Res Bull*, 2005, 40(3): 553–559.
- [27] CHEN C F, BRENNECKA G L, SYNOWICKI R A, et al. Transparent polycrystalline $\text{Gd}_2\text{Hf}_2\text{O}_7$ ceramics[J]. *J Am Ceram Soc*, 2018, 101(9): 3797–3807.
- [28] ZOU X Q, ZHOU G H, YI H L, et al. Fabrication of transparent $\text{Y}_2\text{Hf}_2\text{O}_7$ ceramic from combustion synthesized powders[J]. *J Inorg Mater*, 2011, 26(9): 929–932.
- [29] AN L Q, ITO A, GOTO T. Fabrication of transparent $\text{Lu}_2\text{Hf}_2\text{O}_7$ by reactive spark plasma sintering[J]. *Opt Mater*, 2013, 35(4): 817–819.
- [30] WANG Z J, ZHOU G H, ZHANG F, et al. Fabrication and properties of $\text{La}_{2-x}\text{Gd}_x\text{Hf}_2\text{O}_7$ transparent ceramics[J]. *J Lumin*, 2016, 169: 612–615.
- [31] WANG Z J, ZHOU G H, ZHANG J, et al. Luminescence properties of Eu^{3+} -doped Lanthanum gadolinium hafnates transparent ceramics[J]. *Opt Mater*, 2017, 71: 5–8.
- [32] YASUHARA R, IKESUE A. Magneto-optic pyrochlore ceramics of $\text{Tb}_2\text{Hf}_2\text{O}_7$ for faraday rotator[J]. *Opt Express*, 2019, 27(5): 7485–7490.
- [33] WANG X J, XIE J J, WANG Z J, et al. Fabrication and properties of $\text{Y}_2\text{Ti}_2\text{O}_7$ transparent ceramics with excess Y content[J]. *Ceram Int*, 2018, 44(8): 9514–9518.
- [34] WANG Z J, WANG X J, ZHOU G H, et al. Highly transparent yttrium titanate ($\text{Y}_2\text{Ti}_2\text{O}_7$) ceramics from co-precipitated powders[J]. *J Eur Ceram Soc*, 2019, 39(10): 3229–3234.
- [35] SHLYAKHTINA A V, ABRANTES J C C, LARINA L L, et al. Synthesis and conductivity of $\text{Yb}_2\text{Ti}_2\text{O}_7$ nanoceramics[J]. *Solid State Ion*, 2005, 176(17/18): 1653–1656.
- [36] AN L Q, ITO A, GOTO T. Highly transparent lutetium titanium oxide produced by spark plasma sintering[J]. *J Eur Ceram Soc*, 2011, 31(1/2): 237–240.
- [37] KIM H, AKDIM B, PARK J, et al. IR transmission prediction, processing, and characterization of dense $\text{La}_2\text{Ce}_2\text{O}_7$ [J]. *J Am Ceram Soc*, 2021, 104(11): 5659–5670.
- [38] WANG Z J, ZHOU G H, QIN X P, et al. Transparent $\text{La}_{2-x}\text{Gd}_x\text{Zr}_2\text{O}_7$ ceramics obtained by combustion method and vacuum sintering[J]. *J Alloys Compd*, 2014, 585: 497–502.
- [39] HAN W H, YE Y C, LU K L, et al. High-entropy transparent ($\text{Y}_{0.2}\text{La}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2}\text{Dy}_{0.2}$) Zr_2O_7 ceramics as novel phosphor materials with multi-wavelength excitation and emission properties[J]. *J Eur Ceram Soc*, 2023, 43(1): 143–149.
- [40] WANG Z J, ZHOU G H, QIN X P, et al. Fabrication and phase transition of $\text{La}_{2-x}\text{Lu}_x\text{Zr}_2\text{O}_7$ transparent ceramics[J]. *J Eur Ceram Soc*, 2014, 34(15): 3951–3958.
- [41] WANG Z J, ZHOU G H, QIN X P, et al. Transparent $\text{La}_{2-x}\text{Gd}_x\text{Zr}_2\text{O}_7$ ceramics obtained by combustion method and vacuum sintering[J]. *J Alloys Compd*, 2014, 585: 497–502.
- [42] ZHAO W W, ZHANG K B, LI W W, et al. Fabrication and optical properties of transparent $\text{LaErZr}_2\text{O}_7$ ceramic with high excess contents of La and Er[J]. *Ceram Int*, 2019, 45(9): 11717–11722.
- [43] ZHAO W W, ZHANG K B, HE Z S, et al. Vacuum sintering of highly transparent $\text{La}_{1.28}\text{Yb}_{1.28}\text{Zr}_2\text{O}_{7.84}$ ceramic using nanosized raw powders[J]. *Ceram Int*, 2018, 44(11): 12535–12538.
- [44] LI W W, ZHANG K B, XIE D Y, et al. Characterizations of vacuum

- sintered $\text{Gd}_2\text{Zr}_2\text{O}_7$ transparent ceramics using combustion synthesized nanopowder[J]. *J Eur Ceram Soc*, 2020, 40(4): 1665–1670.
- [45] YE Y, TANG Z, JI Z, et al. Fabrication and luminescent properties of holmium doped $\text{Y}_2\text{Zr}_2\text{O}_7$ transparent ceramics as new type laser material[J]. *OPT MATER*, 2021, 121: 111643.
- [46] LI S, MA K, YE Y, et al. Effect of annealing temperature on optical properties of Erbium doped $\text{Y}_2\text{Zr}_2\text{O}_7$ transparent ceramics[J]. *Ceram Int*, 2022, 48(24): 37180–37185.
- [47] YU L, ZHANG K, LI W, et al. Fabrication and luminescent properties of Sm-doped $\text{Gd}_2\text{Zr}_2\text{O}_7$ transparent ceramics[J]. *J LUMIN*, 2022, 243: 118674.
- [48] An L L, Wang Z J, Ito A, et al. Transparent ceramics based on pyrochlores[M]. *Pyrochlore Ceramics*, Elsevier, 2022: 399–432.
- [49] HE Y, LIU K G, XIANG B X, et al. An overview on transparent ceramics with pyrochlore and fluorite structures[J]. *J Adv Dielectr*, 2020(3): 1–32.
- [50] WANG Z J, ZHOU G H, QIN X P, et al. Two-phase $\text{LaLuZr}_2\text{O}_7$ transparent ceramic with high transparency[J]. *J Am Ceram Soc*, 2014, 97(7): 2035–2037.
- [51] WANG Z J, ZHOU G H, QIN X P, et al. Fabrication and phase transition of $\text{La}_{2-x}\text{Lu}_x\text{Zr}_2\text{O}_7$ transparent ceramics[J]. *J Eur Ceram Soc*, 2014, 34(15): 3951–3958.
- [52] 赵文文. $\text{La}_{2-x}\text{M}_x\text{Zr}_2\text{O}_7$ ($M = \text{Pr}$, Er , Yb , Gd) 透明陶瓷的制备与性能研究[D]. 绵阳: 西南科技大学, 2019.
- ZHAO Wenwen. Preparation and properties of $\text{La}_{2-x}\text{M}_x\text{Zr}_2\text{O}_7$ ($M = \text{Pr}$, Er , Yb , Gd) transparent ceramics[D]. Mianyang: Southwest University of Science and Technology, 2019.
- [53] DENG T, ZHANG K B, LIU K, et al. Vacuum sintering of highly transparent $\text{La}_{1+x}\text{Yb}_{1-y}\text{Zr}_2\text{O}_7$ ceramics with excess La and Yb contents[J]. *J Eur Ceram Soc*, 2021, 41(3): 2106–2113.
- [54] ZHANG K B, LI W W, ZENG J J, et al. Preparation of $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ high-entropy transparent ceramic using combustion synthesized nanopowder[J]. *J Alloys Compd*, 2020, 817: 153328.
- [55] Chen Y, Ye Y, Liao W, et al. Fabrication and phase transition of uranium-doped $\text{La}_x\text{Gd}_{2-x}\text{Zr}_2\text{O}_7$ transparent ceramics: A prospective neutron detection material[J]. *J Am Ceram Soc*, 2023, 106(1): 24–31.
- [56] ZHANG F X, MANOUN B, SAXENA S K. Pressure-induced order-disorder transitions in pyrochlore $\text{RE}_2\text{Ti}_2\text{O}_7$ ($\text{RE} = \text{Y}$, Gd)[J]. *Mater Lett*, 2006, 60(21/22): 2773–2776.
- [57] ZHANG F Q, ZHAO Y S, ZHAO X B, et al. Pressure-induced structural transition of pyrochlore $\text{Tm}_2\text{Sn}_2\text{O}_7$ [J]. *J Alloys Compd*, 2023, 963: 171248.
- [58] SHLYAKHTINA A V, BELOV D A, STEFANOVICH S Y, et al. δ -Phase to defect fluorite (order-disorder) transition in the $\text{R}_2\text{O}_3\text{--MO}_2$ ($\text{R} = \text{Sc}$, Tm , Lu ; $\text{M} = \text{Zr}$, Hf) systems[J]. *Mater Res Bull*, 2011, 46(4): 512–517.
- [59] AN L Q, WANG L F, FAN R H, et al. Fabrication and electrical conductivity of $\text{Lu}_2(\text{Ti}_{1-x}\text{Hf}_x)_2\text{O}_7$ transparent ceramics prepared by spark plasma sintering[J]. *J Asian Ceram Soc*, 2021, 9(3): 893–901.
- [60] SUBRAMANIAN M A, ARAVAMUDAN G, SUBBA RAO G V. Oxide pyrochlores—A review[J]. *Prog Solid State Chem*, 1983, 15(2): 55–143.
- [61] LU X R, SHU X Y, WANG L, et al. Microstructure evolution of rapidly fabricated $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) by spark plasma sintering[J]. *Ceram Int*, 2018, 44(2): 2458–2462.
- [62] JI Y M, JIANG D, SHI J L. $\text{La}_2\text{Hf}_2\text{O}_7$: Ti^{4+} ceramic scintillator for x-ray imaging[J]. *J MATER RES*, 2005, 20(3): 567–570.
- [63] TANG Z, HAN W, HUANG Z Y, et al. Near-infrared luminescent properties of Ln: $\text{LaGdZr}_2\text{O}_7$ ($\text{Ln} = \text{Nd}$, Yb) transparent ceramics for solid-state laser applications[J]. *Ceram Int*, 2020, 46(14): 22270–22275.
- [64] TANG Z, QI J Q, HUANG Z Y, et al. Novel multicolor-tunable $\text{Eu}^{3+}/\text{Bi}^{3+}$ co-doped $\text{Y}_2\text{Zr}_2\text{O}_7$ transparent ceramics as potential white-light-emitting materials[J]. *Ceram Int*, 2022, 48(3): 4216–4222.
- [65] ZHANG L X, LI X Y, HU D J, et al. Transparent non-stoichiometric $\text{Tb}_{2.45}\text{Hf}_{2.68}\text{O}_{7.68}$ magneto-optical ceramics with high Verdet constant[J]. *Scr Mater*, 2021, 204: 114158.
- [66] LU K L, YE Y C, HAN W H, et al. Defect elimination to enhance photoluminescence and optical transparency of Pr-doped ceramics for self-calibrated temperature feedback windows[J]. *J Adv Ceram*, 2023, 12(4): 681–694.
- [67] HAN W, TANG Z, MA N, et al. Optimization of ball-to-powder weight ratio toward to highly transparent $\text{LaGdZr}_2\text{O}_7$ ceramics processing by solid reactive sintering[J]. *J ALLOY COMPD*, 2019, 771: 944–950.
- [68] XIAO ZHUOHAO, Yu S, Li Y, et al. Materials development and potential applications of transparent ceramics: A review[J]. *Mater Sci Eng R Rep*, 2020, 139: 100518.
- [69] MING W, JIANG Z, LUO G, et al. Progress in Transparent Nano-Ceramics and Their Potential Applications[J]. *NANOMATERIALS-BASEL* 2022, 12, 1491.
- [70] TIAN F, IKESUE A, LI J. Progress and perspectives on composite laser ceramics: A review[J]. *J EUR CERAM SOC*, 2022, 42(5): 1833–1851.

Research Progress on $A_2B_2O_7$ ($A = \text{Ln}^{3+}$, $B = \text{Zr}^{4+}$, Hf^{4+} , Ti^{4+} , Ce^{4+}) Transparent Ceramics

LAI Yangqun¹, TAO Shixu¹, MA Chaoyang¹, CAO yongge^{1,2}

(1. Songshan Lake Materials Laboratory, Dongguan 523808, Guangdong, China; 2. Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China)

Extended Abstract

Conventional transparent materials can be primarily divided into four categories, i.e., glasses, polymers, single crystals, and transparent ceramics. Growing large single crystals with high melting points is difficult, and glass and polymers have poor mechanical and chemical stability. These shortcomings limit their applications. Transparent ceramics are favored because of their

high refractive index, high hardness, high strength, high thermal conductivity, and high chemical stability. In 2005, $\text{La}_2\text{Hf}_2\text{O}_7$ was fabricated into transparent ceramics with a high density and a high atomic number, having a great potential in the detection field of scintillators. Since then, $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics has attracted much attention. The structure of $\text{A}_2\text{B}_2\text{O}_7$ ceramics is mainly determined by the radius ratio of A-site and B-site ions (r_A/r_B), and includes three structures (i.e., fluorite structure ($r_A/r_B < 1.46$), pyrochlore structure ($1.46 < r_A/r_B < 1.78$) and monoclinic structure ($r_A/r_B > 1.78$)). While, only the fluorite- and pyrochlore-structure $\text{A}_2\text{B}_2\text{O}_7$ ceramics could be transparent monolith when sintered at proper temperature and pressure.

$\text{A}_2\text{B}_2\text{O}_7$ ceramics with fluorite and pyrochlore two-phase coexisting structures have the advantage of smaller grains, compared with conventional $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics with single-phase structures. The mechanical properties of two-phase coexisting structures ceramics can be improved due to the smaller grains. $\text{LaLuZr}_2\text{O}_7$ transparent ceramics with two phases of fluorite and pyrochlore were fabricated in 2014. Two phases are uniformly distributed in the ceramic and the average grain size of the ceramic is only 2–3 μm . The in-line transmittance of $\text{LaLuZr}_2\text{O}_7$ transparent ceramic is 73.4% at 1 100 nm due to the close refractive index between the two phases of fluorite and pyrochlore, and the scattering of light across the interface between the two phases is negligible. In 2019, $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ was fabricated into transparent ceramics with a fluorite and pyrochlore two-phase coexisting structure. Compared with conventional transparent ceramics, high-entropy transparent ceramics may have better mechanical properties, corrosion resistance, and high-temperature resistance. The enhanced atomic disorder due to multi-element doping in high-entropy ceramics makes it a promising material for high-temperature windows with a lower thermal conductivity. However, there are some challenges in the preparation of two-phase coexistence transparent $\text{A}_2\text{B}_2\text{O}_7$ ceramics. In some previous reports on $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics with two-phase coexistence, the transmittance of the ceramics was severely reduced when there was a large difference in the grain sizes of the fluorite and pyrochlore phases. It is necessary to ensure that the grain growth rates of the pyrochlore and fluorite phases are similar during sintering.

Transparent ceramic scintillators of $\text{La}_2\text{Hf}_2\text{O}_7:\text{Ti}^{4+}$ were fabricated in 2005. The transmittance of $\text{La}_2\text{Hf}_2\text{O}_7:\text{Ti}^{4+}$ transparent ceramics at 600–800 nm is close to 60%. $\text{La}_2\text{Hf}_2\text{O}_7:\text{Ti}^{4+}$ transparent ceramics gain a high X-ray stopping power due to its high density and high atomic number. The integrated emission intensity of $\text{La}_2\text{Hf}_2\text{O}_7:\text{Ti}^{4+}$ transparent ceramics is 1.5 times greater than that of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ single crystals for the same size and the same excitation conditions. In 2019, $\text{Tb}_2\text{Hf}_2\text{O}_7$ was fabricated into transparent ceramics. $\text{Tb}_2\text{Hf}_2\text{O}_7$ transparent ceramic ceramics perform well in the Faraday magneto-optical effect tests, having higher measured Verdet constants than commercial $\text{Tb}_3\text{Ga}_5\text{O}_{12}$ single crystals and a potential application as an excellent magneto-optical material. It is indicated that the magneto-optical properties of magneto-optical materials are related to the concentration of Tb^{3+} in the materials, and the higher the Tb^{3+} concentration is, the better the magneto-optical properties will be. $\text{Tb}_2\text{Hf}_2\text{O}_7$ transparent ceramics can be doped with higher concentrations of Tb^{3+} due to the structural advantages of $\text{A}_2\text{B}_2\text{O}_7$, thus having better magneto-optical properties rather than garnet-structured $\text{Tb}_3\text{Ga}_5\text{O}_{12}$ single crystal.

Summary and prospects This review represented the preparation methods, performances, and potential applications of $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramic. $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics have the characteristics of a high melting point, a high density, and a high refractive index, which are potentially valuable in the fields of optical material. However, the optical loss and optical homogeneity of $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics are difficult to guarantee, a further study of optical quality improvement for $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics is still needed. At present, the preparation process of $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics is still immature, there are many residual pores in the sintered $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics, affecting the optical quality of the $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics. It is necessary to optimize the raw powder preparation process and add sintering additives to reduce the pores in the sintered $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics.

Although $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics have great application prospects in solid-state lasers, the low thermal conductivity of $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics makes heat dissipation a challenge. If $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics can be used in solid-state lasers, a superior heat dissipation system needs to be designed. In summary, $\text{A}_2\text{B}_2\text{O}_7$ transparent ceramics is a promising transparent material, but there are still many problems to be solved before the application.

Keywords transparent ceramics; pyrochlore; fluorite