

YAG 透明陶瓷的制备及其在深海领域的应用

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摘 要: 以商业高纯 Al_2O_3 粉和自制纳米 Y_2O_3 粉为原料, 采用真空固相反应烧结法成功制备出了高透光的钇铝石榴石(YAG)透明陶瓷。研究了反应烧结过程中物相演变和显微结构变化, 烧结温度和保温时间对 YAG 透明陶瓷光学透过率的影响以及 YAG 透明陶瓷在深海装备领域的应用性能等。结果表明: 高温条件下, Al_2O_3 和 Y_2O_3 反应先依次形成中间相 YAM 和 YAP, 最终在 $1500\text{ }^\circ\text{C}$ 完全形成 YAG; 随着烧结温度的升高, YAG 陶瓷内气孔不断排出且晶粒不断长大, 光学透率先增加后降低, 在 $1780\text{ }^\circ\text{C}$ 透过率达到最高; 随着保温时间的延长, YAG 陶瓷的透过率逐渐提高, 但超过 6 h 后, 再延长保温时间, 对提高透过率的效果不显著。采用优化工艺制备的 YAG 透明陶瓷球罩经受住 127 MPa 抗压模拟试验, 并成功应用在深海领域装备大功率 LED 照明灯和摄像机保护罩上, 为拍摄“奋斗者”号万米海底作业以及央视现场直播做出了贡献。

关键词: 钇铝石榴石; 透明陶瓷; 固相反应; 烧结; 深海应用

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深海装备是开展深海资源探测、开发和保护的重要保障, 包括各种类型的深海潜水器、着陆器、滑翔机及其附属装备等。在中国“863”专项的支持下, 中国首台 7000 m 级“蛟龙”号载人潜水器于 2012 年成功下潜至 7062 m ^[1]。2017 年 10 月中国再次研发出可靠性更高、国产化率达到 95% 的 4500 m 级“深海勇士”号载人潜水器^[2], 现已完成多次海试。另外, 全海深(11000 m)深海载人潜水器于 2016 年 10 月得到科技部重大研发计划的立项^[3], 并在 2020 年 11 月, “奋斗者”号载人潜水器成功下潜到万米海底, 取得了举世瞩目的成就。在以上深海装备中, 观察窗口以及摄像机和照明灯的透明保护罩必须要用到高强度透明材料。目前所使用的透明材料主要是超厚有机玻璃(观察窗)、无机玻璃和蓝宝石(单晶氧化铝)。由于钇铝石榴石(YAG)透明陶瓷具有和单晶一样良好的透光性, 并且具有光学各向同性、强度大、热导率高、物理和化学性能稳定等特点, 使其应用在深海装备上成为可能。

自 1995 年日本科学家 IKESUE 等制备出高透明

的 $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG)和 Nd:YAG 陶瓷并成功实现激光输出以来^[4-5], 透明陶瓷的研究获得了空前的关注, 并得到了飞速的发展^[6-9]。传统的单晶材料主要采用提拉法生长, 难以获得大尺寸和高浓度掺杂, 而且生产周期长、成本高。透明陶瓷的问世, 正好克服了以上缺点, 从而使其成为现代材料科学发展较为活跃的领域之一。目前透明陶瓷的种类主要有氧化铝透明陶瓷^[10-11]、氧化镁透明陶瓷^[12-13]、氧化钇透明陶瓷^[14-15]、钇铝石榴石(YAG)透明陶瓷^[16-18]、镁铝尖晶石透明陶瓷^[19-20]、氮氧化铝透明陶瓷^[21-23]、透明 PLZT 电光陶瓷^[24-25]等等。高质量的透明陶瓷不仅具有和单晶一样优良的光学性能, 在力学性能上甚至超过单晶, 使其在照明技术、光学、激光、特种仪器制造以及高温技术上都具有潜在的应用。在所有种类的透明陶瓷中, YAG 透明陶瓷是其中最具代表性的一类, 目前研究的最为成熟, 光学质量也达到最高。以往 YAG 透明陶瓷的研究主要偏向于掺杂稀土实现光功能应用, 如激光输出^[5-9]、白光 LED 发光^[26]等, 对大尺寸和复杂形状 YAG 透明陶瓷研究报道的较少。

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本研究采用真空固相反应烧结法制备出了大尺寸和复杂形状 YAG 透明陶瓷, 并成功应用于万米深海装备上, 详细研究了陶瓷的物相演变过程以及显微结构变化, 烧结温度和保温时间对 YAG 透明陶瓷光学透过率的影响, 最后研究了 YAG 透明陶瓷在深海装备领域的应用性能。

1 实验

1.1 样品制备

采用商业 Al_2O_3 粉(日本大明, 纯度 99.99%)和共沉淀法自制纳米 Y_2O_3 粉为原料, 以 $\text{Y}_3\text{Al}_5\text{O}_{12}$ 的化学计量比配料, 加入 0.5% (质量分数)正硅酸乙酯 (TEOS, 99.99%)和 0.05% 的 MgO 粉(分析纯)作烧结助剂, 以无水乙醇(分析纯)为介质, 用行星式球磨机进行混料和研磨处理, 球磨机转速为 200 转/分, 球磨时间为 12 h。球磨后的浆料在 60 °C 的烘箱中干燥 24 h, 然后过 200 目筛 (筛孔尺寸为 74 μm), 一部分粉体在 900~1 500 °C 煅烧; 另一部分粉体用钢模在 30 MPa 压强下压制成直径为 20 mm 的圆片, 再用 200 MPa 的压强冷等静压处理得到陶瓷素坯。将素坯置于真空钨丝炉中进行烧结, 升温速率为 2 °C/min, 烧结温度为 1 200~1 800 °C, 保温时间为 2~20 h, 降温速率为 10 °C/min, 保温时炉内真空度小于 5×10^{-3} Pa。将烧结得到的 YAG 透明陶瓷样品在 1 450 °C 保温 10 h 空气气氛中作退火处理, 然后双面抛光。

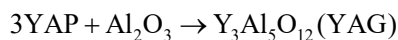
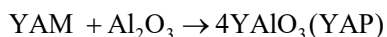
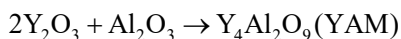
1.2 样品表征

采用日本 Rigaku 公司的高分辨率 X 射线衍射仪(D/Max-2550V)进行物相分析。采用美国 Varian 公司的 Carry-5000 型 UV-VIS-FIR 分光光度计测试各组样品的透过率。采用日本 JEOL 公司的 JSM-6360 型扫描电子显微镜观察各组样品热腐蚀后的表面显微结构变化。

2 结果与讨论

2.1 固相反应烧结法合成 YAG 透明陶瓷物相演变分析

固相反应烧结法作为一种制备 YAG 透明陶瓷的有效途径, 具有工艺简单、成本低廉且工艺重复性好等众多优点。高温条件下, Al_2O_3 和 Y_2O_3 反应先依次形成中间相 YAM 和 YAP, 最终形成 YAG。反应过程如下:



将商业 Al_2O_3 (日本大明, 纯度 99.99%)和共沉淀法制备纳米 Y_2O_3 粉混合均匀后在不同温度下保温 3 h 煅烧, 然后将煅烧后的粉末进行物相分析, XRD 分析结果如图 1 所示。从图 1 可以看出, 经过 900 °C 煅烧后, 粉体中的物相仍为原料 Al_2O_3 和 Y_2O_3 ; 经过 1 000 °C 煅烧后, 除了 Al_2O_3 和 Y_2O_3 外, 开始出现少量 YAM 新相; 经过 1 100 °C 煅烧后, 粉体中物相仍为 Al_2O_3 、 Y_2O_3 和 YAM 三相, 但 YAM 占主要成分; 经过 1 200 °C 煅烧后, 粉体中开始大量生成 YAP 相, YAM、 Al_2O_3 和 Y_2O_3 逐渐减少, 粉体中四相共存; 经过 1 300 °C 煅烧后, 粉体中 YAP 相占主要部分, 并开始生成少量 YAG 相, Y_2O_3 相消失, 粉体中 YAP、 Al_2O_3 和 YAG 三相共存; 经过 1 400 °C 煅烧后, 粉体中主要成分则为 YAG 相, 另外还残余少量 YAP 相; 经过 1 500 °C 煅烧后, 粉体则为纯 YAG 相。

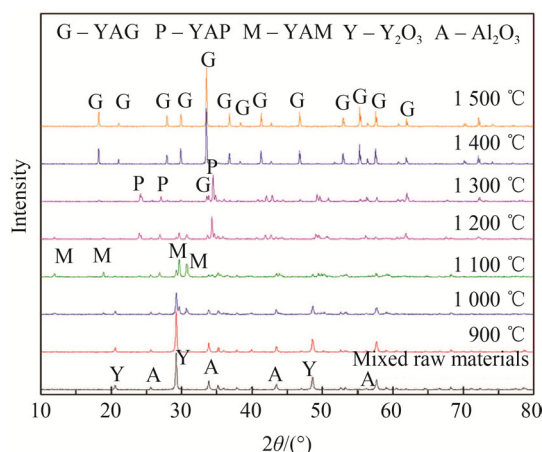


图 1 Al_2O_3 和 Y_2O_3 混合粉体在不同温度下煅烧后的 XRD 谱
Fig. 1 XRD patterns of Al_2O_3 and Y_2O_3 mixed powders calcined at different temperatures

2.2 固相反应烧结法合成 YAG 透明陶瓷显微结构分析

为了进一步观察固相反应法合成 YAG 晶粒长大的情况, 对不同温度煅烧的样品抛光表面形貌进行了分析, 结果如图 2 所示。

从图 2 可以清楚地看到 YAG 的形成和晶粒不断长大的情况, 1 400 °C 以前, 仍然以混合粉体的形式存在; 1 400 °C 陶瓷开始烧结, 陶瓷中含有大量气孔; 1 600 °C 烧结后, 晶粒明显长大, 气孔也最大量地被排出, YAG 晶粒发育成形; 1 700 °C 烧结后, 晶粒进一步长大, 达到 7~8 μm , 样品中的气孔也基本上被全部排出。因此, 1 400 °C 到 1 700 °C 是样品中

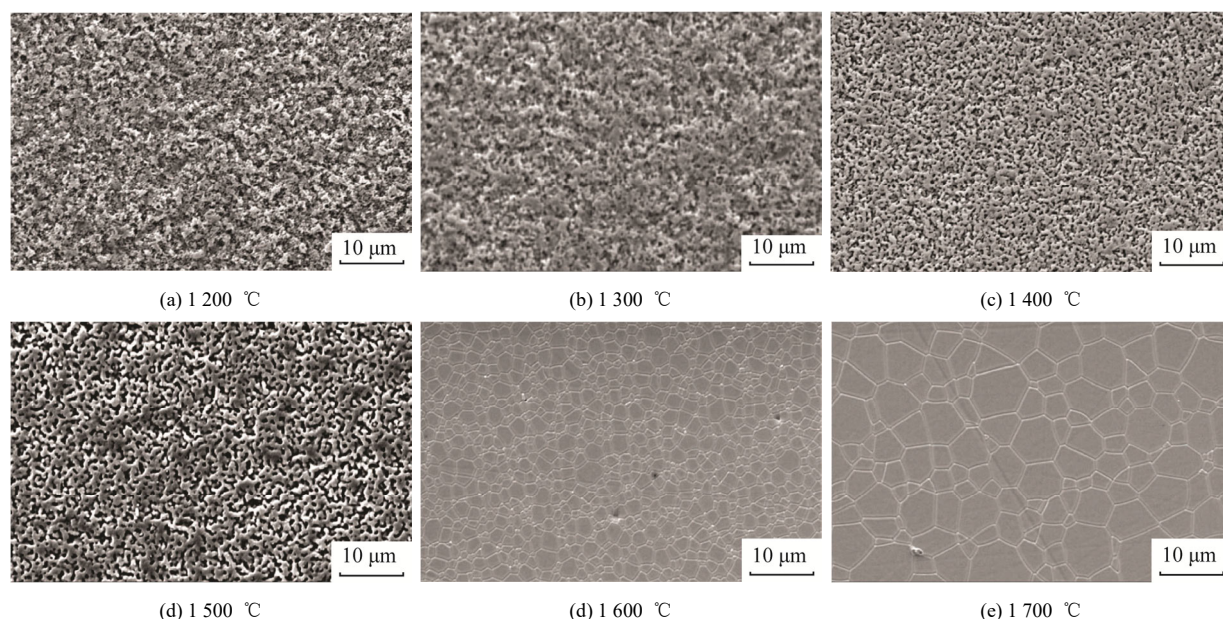


图 2 不同温度下真空烧结 2 h 后的陶瓷抛光表面形貌

Fig. 2 Micrographs of the mirror-polished and thermal etched surfaces of ceramics sintered at different temperature with 2 h in vacuum

气孔大量排出和晶粒不断长大的关键阶段, 这个过程的升温速度要比较慢, 以利于气孔有充足的时间被排出。

2.3 烧结温度和保温时间对 YAG 透明陶瓷光学透过率的影响

图 3 是采用固相反应烧结法制备得到的 YAG 透明陶瓷照片和不同温度烧结得到的透明陶瓷透过率曲线。从图 3 可以看出, 1780 °C 保温 6 h 真空烧结后的 YAG 陶瓷非常透明, 陶瓷下面的字迹清晰可见, 肉眼看不到陶瓷中任何白点和雾状物, 光学均匀性良好。经过 1780 °C 烧后, YAG 陶瓷在 1100 nm 处的透过率达到 83.4%, 在 400 nm 处的透过率达到 82.2%, 更加接近理论透过率数值 84.8% (1064 nm 处), 这也和文献[27–28]报道的高水平研究结果相当。另外, 从透过率曲线还可以看出, 随着温度的升高, YAG 陶瓷的透过率变化是先升高, 然后再降低, 这可能是由于纳米级 Y_2O_3 粉的烧结活性高, 在过高温下烧结速度和晶粒长大速度过快导致陶瓷中晶粒异常长大并残留了更多的气孔, 从而使 YAG 陶瓷的透过率下降。

图 4 是 YAG 透明陶瓷在 1780 °C 保温不同时间的透过率曲线。从图 4 可以看出, 随着保温时间从 2 h 延长到 6 h, 透过率有非常明显的提高, 这是由于延长保温时间可以使气孔进一步排除, 继续延长保温时间, 透过率提高不大。可见, 延长时间可以提高陶瓷的透过率, 但也不是越长越好。1780 °C 保

温 20 h 的 YAG 陶瓷样品的透过率在 1100 nm 处已达 84.7%, 在 400 nm 处达到 82.8%, 说明陶瓷样品的透过率已经非常之高, 几乎和理论值一样。

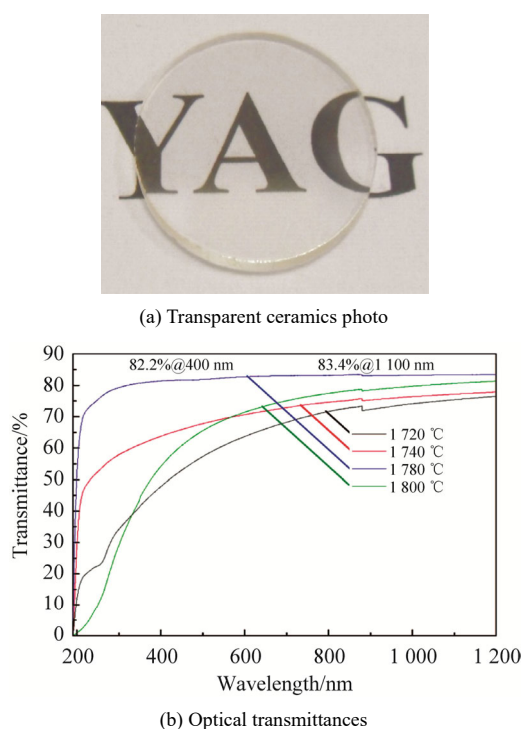


图 3 1780 °C 保温 6 h 烧结 YAG 透明陶瓷照片和不同温度烧结得到的 YAG 透明陶瓷的透过率曲线(1 mm 厚)

Fig. 3 Photo of the mirror-polished YAG transparent ceramics sintered at 1780 °C for 6 h and optical transmittances of the ceramics sintered at different temperatures (1 mm thick)

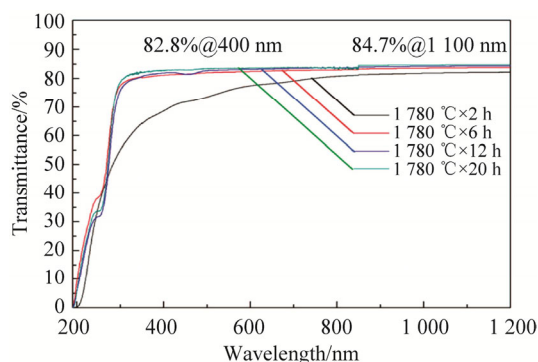


图4 YAG透明陶瓷在1780℃保温不同时间的透过率曲线
Fig. 4 Optical transmittances of YAG ceramics sintered at 1780 °C for different holding times

2.4 YAG透明陶瓷在深海领域的应用研究

深渊11 000 m深度的海水静压可达110 MPa,因此,深海探测设备必须满足全海深设计需要。在设计阶段的窗口结构及支撑壳体的有限元力学分析是十分必要的,初期分析可以预先发现结构问题,合理调整设计参数,节约试制成本,缩短研发周期并提高成功率,为壳体打压验证实验提供技术保障。首先利用有限元分析软件ANSYS对在高压(127 MPa,考虑1.15倍安全系数)使用环境下的光学窗口进行静力分析。图5为系统有限元分析结果。口径120 mm球罩所受最大压应力为773.7 MPa,最大拉应力为21.9 MPa,均小于YAG透明陶瓷材料的最大许用应力(约1 000 MPa)。

根据设计结果,采用特制的橡胶模套和不锈钢半球模具灌粉后等静压成型制备出近净尺寸的YAG陶瓷球罩素坯,然后采用前述优化的工艺真空烧结得到YAG陶瓷球罩。经过双面磨削和抛光,制备出了高透光且口径达到120 mm,厚度达到15 mm的YAG透明陶瓷球罩,如图6所示。从图6可以看出,透过球罩,纸面上的文字仍然清晰可见,几乎和玻璃无异。

将制备得到的YAG透明陶瓷球罩和钛合金筒体进行密封封装,首先进行模拟深海压力试验,在等静压缸体内进行抗压测试。经过127 MPa压力,保压1.5 h打压,拆卸后发现透明陶瓷球罩完整不开裂,无渗漏现象,装配情况良好。然后将YAG透明陶瓷球罩分别封装在深海大功率LED灯和深海摄像机的前端作为保护罩,如图7所示。

采用YAG透明陶瓷作为保护罩的深海大功率LED照明灯和深海摄像机安装在深海系统装备“沧海”号着陆器上,于2020年11月多次在世界海洋最深处马里亚纳海沟下潜到万米海底,录制了大量

珍贵视频资料,并为拍摄“奋斗者”号万米海底作业以及央视现场直播做出了贡献。图8为“奋斗者”号载人潜水器在马里亚纳海沟下潜过程中的照片。

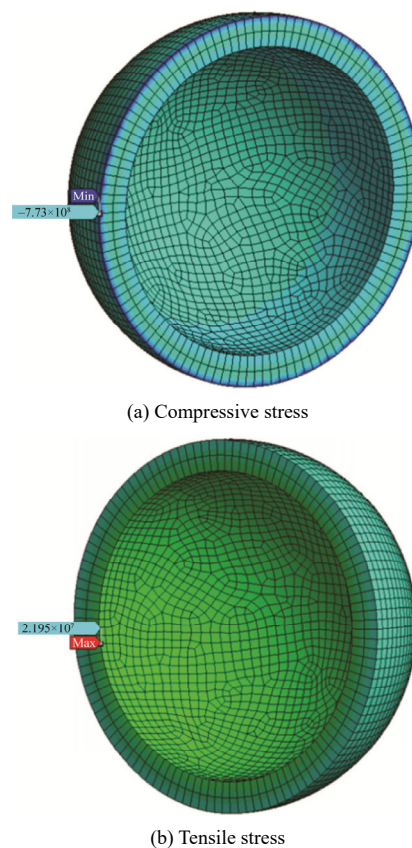


图5 透明陶瓷保护罩在127 MPa外压下的应力分布
Fig. 5 Stress distribution of transparent ceramic dome under 127 MPa



图6 工艺优化后制备的高质量的大尺寸YAG透明陶瓷球罩
Fig. 6 Photos of the large-size YAG transparent ceramic dome



(a) LED light



(b) Camera

图 7 采用 YAG 透明陶瓷作为保护罩的深海大功率 LED 灯和深海摄像机

Fig. 7 Deep sea high-power LED light and camera using YAG transparent ceramics as protective window

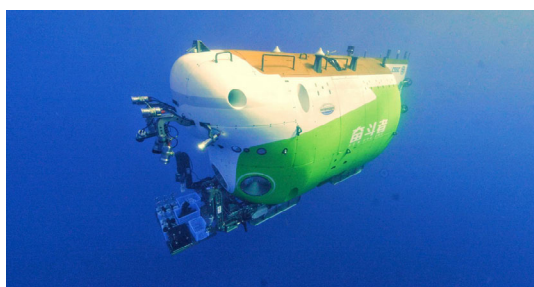


图 8 “奋斗者”号载人潜水器下潜过程中

Fig. 8 Process of diving of the manned submersible “Striver”

3 结论

采用真空固相反应烧结法成功制备出了高透光的 YAG 透明陶瓷。高温条件下, Al_2O_3 和 Y_2O_3 反应先依次形成中间相 YAM 和 YAP, 最终在 $1500\text{ }^\circ\text{C}$ 完全形成 YAG; 随着烧结温度的升高, YAG 陶瓷内气孔不断排出且晶粒不断长大, 光学透率先增加后降低, 在 $1780\text{ }^\circ\text{C}$ 透过率达到最高; 随着保温

时间的延长, YAG 陶瓷的透过率逐渐提高, $1780\text{ }^\circ\text{C}$ 保温 20 h 真空烧结的 YAG 陶瓷样品的透过率在 1100 nm 处达到 84.7% , 在 400 nm 处为 82.8% 。采用优化工艺制备的高透明 YAG 透明陶瓷球罩经受住 127 MPa 抗压模拟试验, 并成功应用在深海领域装备大功率 LED 照明灯和摄像机保护罩上, 为拍摄“奋斗者”号万米海底作业以及央视现场直播做出了贡献, YAG 透明陶瓷球罩在万米深潜科考的应用目前尚未见其他报导。

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Fabrication of YAG Transparent Ceramics and Its Application in Deep-Sea Equipment Field

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Extended Abstract

Introduction Deep sea equipment is an important guarantee for the exploration, development, and protection of deep-sea resources, including various types of deep-sea submersibles, landers, gliders, and their auxiliary equipment. In the deep-sea equipment above, the transparent protective cover for observation windows, cameras, and lighting must use high-strength transparent materials. The main transparent materials currently used are ultra-thick organic glass (observation window), inorganic glass, and sapphire (single crystal aluminum oxide). Their application in deep-sea equipment is possible due to the superior transparency of yttrium aluminum garnet (YAG) transparent ceramics like single crystals, as well as the characteristics of optical isotropy, high strength, high thermal conductivity, and stable physical and chemical properties. At present, there are many kinds of transparent ceramics, among which YAG transparent ceramics are the most representative. The existing researches on YAG transparent ceramics mainly focus on doping rare-earth elements to achieve optical functional applications, such as laser output, white LED luminescence, etc.. There are a few reports on the research of large-sized and complex shaped YAG transparent ceramics. In this paper, large-sized and complex shaped YAG transparent ceramics were prepared by a solid-state reaction sintering method, which could be applied to deep-sea equipment at 10 000 meter.

Methods High-purity powders of α -Al₂O₃ (99.99% purity, Taimei Co., Japan), Y₂O₃ (self-synthesized by co-precipitation method) were used as starting materials. The starting powders were weighed according to a stoichiometric ratio of YAG, and then mixed with 0.5% tetraethyl orthosilicate (TEOS, 99.99%) and 0.05% MgO powder (analytical pure) as a sintering additive in ethanol by ball milling for 12 h. The mixtures were dried in an oven at 60 °C for 24 h and then sieved through 200-mesh screen. A portion of the dried powder was calcined at 900–1 500 °C, and another part of the powder was pressed into circular discs with a diameter of 20 mm using a steel mold at 30 MPa, and then subjected to cold isostatic pressing at 200 MPa to obtain ceramic billets. The green body pellets were then sintered in a vacuum furnace with tungsten meshes as the heating elements under 10⁻³ Pa at 1 200–1 800 °C for 2–20 h. After sintering in vacuum, the pellets were further annealed in air at 1 400 °C for 10 h. Finally, the both surfaces of the as-prepared ceramic samples were mirror-polished with different grade of diamond slurries.

The phase compositions of all the samples were qualitatively identified by a model D/Max-2550V X-ray diffractometer (Rigaku

Co., Japan). The optical transmittances of all the samples of ceramics were measured by a model Carry 5000 UV-VIS-NIR spectrometer (Varian Co., USA). The surface microstructures of each group of samples after hot corrosion were characterized by a model JSM-6360 scanning electron microscope (JEOL Co., Japan).

Results and discussion YAG transparent ceramics were fabricated by a solid-phase reaction sintering method. The phase evolution and microstructural changes during sintering were investigated. At high temperatures, Al_2O_3 and Y_2O_3 react to form intermediate phases YAM and YAP, eventually forming YAG.

The effects of sintering temperature and holding time on the optical transmittance of YAG transparent ceramics were investigated. As the sintering temperature increases, the pores in YAG ceramics continue to discharge and the grains continue to grow. The optical transmittance firstly increases and then decreases, reaching its maximum value at 1 780 °C. As the holding time prolongs, the transmittance of YAG ceramics gradually increases, but after more than 6 h, extending the holding time does not have a significant effect on improving the transmittance.

The YAG ceramic dome is formed using a specially designed rubber mold and a stainless steel hemispherical mold by a cold isostatically press. The YAG ceramic dome is then vacuum sintered in the optimized process. The optical window under 127 MPa was analyzed by finite element analysis (*i.e.*, a software named ANSYS). The analysis results show that the maximum compressive stress of the 120 mm diameter dome is 773.7 MPa and the maximum tensile stress is 21.9 MPa, both of which are less than the maximum allowable stress of YAG transparent ceramic material (*i.e.*, approximately 1 000 MPa). The YAG transparent ceramic dome and titanium alloy cylinder are sealed and packaged. The transparent ceramic dome is undamaged without cracking or leakage at 127 MPa for 1.5 h. The high-power deep-sea LED lighting and deep-sea camera, using YAG transparent ceramics as protective covers, are installed on a deep-sea equipment “Canghai” lander. In November 2020, the lander sank to the depths of 10 000 meters in the Mariana Trench (the deepest part of the oceans) for several times, and a large amount of valuable video data were recorded.

Conclusions Highly transparent YAG transparent ceramics were fabricated in vacuum via solid-state reaction sintering. Under high temperature conditions, Al_2O_3 and Y_2O_3 reacted to form intermediate phases YAM and YAP in sequence, and finally formed YAG at 1 500 °C. As the sintering temperature increased, the pores in YAG ceramics continued to discharge and the grains continued to grow. The optical transmittance firstly increased and then decreased, reaching its maximum value at 1 780 °C. As the holding time prolonged, the transmittance of YAG ceramics gradually increased. The transmittance of YAG ceramic samples sintered in vacuum at 1 780 °C for 20 h was 84.7% at 1 100 nm and 82.8% at 400 nm, respectively. The YAG transparent ceramic dome was prepared via optimization. It could be applied to high-power LED lighting and camera protection covers in the deep-sea equipment at 10 000 meters.

Keywords yttrium aluminum garnet; transparent ceramics; solid-state reaction; sintering; deep-sea application



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