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Industrial potential of additive manufacturing of transparent ceramics: A review

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ABSTRACT

Transparent ceramics is a unique class of materials, with performance comparable to single crystals, but a high process flexibility given by ceramic technology. Currently, traditional ceramic shaping technologies reliably produce components but are limited in terms of shapes and the use of multiple compositions in a single component. The presented review aims to illustrate how the introduction of additive manufacturing (AM) technology in the production of transparent ceramic components opens new possibilities, both thanks to the high variability of shapes and thanks to the high precision in producing parts with a controlled variation of composition. Within this review, several AM techniques and their current state of the art are analysed, with focus on their advantages in producing transparent ceramics, along with the associated challenges and limitations. The future perspective and possibilities for an industrial production are discussed, with emphasis on the most promising AM techniques, direct ink writing and vat photopolymerisation, pointing out the future scenario for the transparent ceramics market.

1. Introduction

1.1. *Transparent ceramics, applications*

Transparent polycrystalline ceramics have attracted significant interest as versatile and high-performance materials. This is thanks to their combination of optical properties and high thermal and mechanical performance, given their crystalline structure and flexibility of ceramic production technology.

The principal main markets for translucent-to-transparent ceramics are those of.

- optics and photonics [1–3], viz. laser materials (solid state laser gain media, active and passive optical elements), lighting (phosphors, light converters) or scintillating detectors;
- protective windows and domes for defence, aerospace [4,5];
- chemically and temperature resistant transparent windows or envelopes for discharge lamps [6].
- decorative products and jewellery [7].

To a certain extent, these markets are currently served by single crystals or glasses and in some cases by ceramics produced with other shaping processes. Each market has specific requirements on the optical quality, dimensions of components and degree of freedom in shape. The general specifications are listed in Table 1.

Commercial translucent-to-transparent ceramics have been produced for decades for lamp envelopes, but the industrialization of highly transparent ceramics in general is still relatively limited, because it is very challenging to produce defect-free materials at an industrial scale.

Transparency is a material quality, and in ceramics, it depends on the phase composition and microstructure. A material may reflect or absorb light of a certain wavelength based on the interaction between the light and the material – its electronic structure, band gap energy, electronic transitions and impurities. The microstructural features (pores, other phases, or, in some cases, the single grains), determine the level of scattering of light inside the material. The degree of transparency is quantified by transmittance. The maximum theoretical transmittance $T_{\max}$ of a homogeneous, non-absorbing material depends on the refractive index n, as given by eq.

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Table 1
Performance parameters and typical geometries and sizes of components required for the most common applications of transparent ceramics.

Application	Quality requirements	Typical shape	Typical size range
Laser gain media, optical elements for lasers	The highest optical quality and homogeneity, negligible scattering of light	Rods, discs, slabs	mm up to more than 10 cm in one or two dimensions
Protective windows and domes	Good mechanical properties, good optical quality, transparency in visible and IR	Flat slabs, domes	cm to tens of cm in two dimensions
Scintillators	Good control of composition; limited scattering may be acceptable, depending on the specific application	usually simple shapes, plates or elongated cuboids, but with a potential for the use of complex tailored geometries, e.g., for pixelated detectors	mm to several cm
Phosphors	Good control of composition and of the level of scattering; high transparency is often not required (for diffuse light sources controlled light scattering is requested)	small components, generally thin; shape may vary e.g., from platelets and discs to more freeform ones, based on the application	mm to cm
Lamp envelopes	Thermal and chemical resistance, translucency to transparency	Tubes, bulbs	cm
Jewellery	Good optical quality, control of colour	From simple to complex shapes	mm to cm

$$T_{\max} = \frac{2n}{1+n^2}. \tag{1}$$

The maximum theoretical transmittance is therefore specific to individual materials, which has to be taken into account when comparing measured data along with the thickness of the tested sample. A detailed discussion of the transparency of ceramics, mechanisms of transmittance losses, and related calculations can be found in Refs. [8,9]. The effect of scattering is noticeable already at low concentrations of defects, particularly because their dimensions are often similar to the wavelength of interest, therefore significantly contributing to scattering efficiency.

The most challenging are components for lasers, where a few defects or even a single one may compromise the material, especially when high-power lasers are concerned. Therefore, there are only few companies that produce and commercialise transparent ceramics for laser applications, producing them mostly in small series or on demand; the most known being Konoshima Chemical Co. Ltd.

A slightly lesser challenge in terms of optical quality is presented by protective windows and domes, where the transmittance (the quantification of transparency) does not have to reach theoretical values: i.e., some optical defects may be present. This application requires excellent mechanical properties and wear resistance, and no large defects should be present for defence or aerospace applications. But even this market has a limited number of players, and the challenge here is often the size of the required components (e.g., for large protective windows), in particular when the production process requires the use of hot-pressing equipment, that has to be scaled for the size of the components [10].

The shape of components for scintillating detectors may range from elongated cuboids for applications in PET detectors to thin sheets for imaging screens [11]. The flexibility in shape and in the internal structuring may be of interest for example in pixelated scintillation arrays [12]. The optical quality requirements are less stringent, compared to those for laser-grade materials.

Within the lighting market, transparent (or translucent) ceramics are along with single crystals the materials of choice for high-intensity light sources (e.g., for searchlights, projectors, stage lighting or laser headlights), where the thermal properties and stability of crystalline materials are fundamental. For these applications, a full optical transmittance is often not required, and may even be counterproductive, when a diffused light source is requested. In such cases, a controlled scattering may be achieved by the introduction of a secondary phase (e.g., Al_2O_3, which has a high thermal conductivity [13]). One example of components for lighting may be small parts with a precise geometry (e.g., hemispherical or other curved shapes). Currently, these components could be produced from larger single crystals by subtractive manufacturing, with a significant cost per piece due to the machining process and a high amount of scrap from production.

In the case of windows or domes the materials of choice need to offer superior mechanical properties and often also a wide range of transparency towards IR. The most commonly used are $MgAl_2O_4$, spinel, AlON, Y_2O_3, MgO, and for some applications also translucent Al_2O_3. Another growing field of applications for dopant-free transparent ceramics is that of lenses, and in particular microlenses that could be printed directly without the need of further machining [14].

Material-wise, the typical composition for the aforementioned applications (lasers, scintillators and lighting) is similar, or belongs to the same group of materials (synthetic garnets), only with different functional doping ions.

1.2. Materials processing

The typical materials used include garnets (e.g., yttrium aluminium garnet $Y_3Al_5O_{12}$ – YAG, lutetium aluminium garnet $Lu_3Al_5O_{12}$ – LuAG), spinel $MgAl_2O_4$, sesquioxides (Y_2O_3, Lu_2O_3), AlON or Al_2O_3. Note that Al_2O_3 has limited transparency due to its non-cubic crystalline structure. For applications in photonics, these ceramics are typically doped with rare earth or transition metal ions [15].

These ceramics are often produced in near-net shapes using various shaping techniques, which marks a significant advancement over traditionally used inorganic transparent materials. Single crystals, while possessing superior properties, face significant production limitations, e.g., high melting temperatures, size limitations, optical non-uniformity within the crystal boule, segregation from melt, or in some cases phase transitions or incongruent melting. In contrast, glasses are widely used but have properties inferior to crystalline materials [16]. Achieving good transparency requires ceramics to be as free as possible from light-scattering sources: the material should be optically isotropic (i.e. shall not be birefringent) and free of pores or secondary phases. Optical isotropy depends directly on the selection of material, on its crystalline structure. The presence of secondary phases can be mostly controlled by stoichiometry, the use of high-purity raw materials and good mixing when a mixture of different powders is used, but the presence of pores remains a major challenge [6,8,17].

On the practical side, obtaining such material is not trivial. A key role in achieving this material is played by the forming method of the ceramic body, but the process leading to transparency of ceramics has multiple critical points, all of which need to be addressed in the optimisation.

- **raw materials**: high-purity powders with a good sinterability, preferably spherical to avoid the presence of voids and improve packing density of the green part [18,19]. The current ceramic processes used in the production of transparent ceramics often use fine, even nanometric powders [13];
- **use of sintering aids**: often, the full densification requires the introduction of an agent that promotes densification, favours the

removal of pores and allows to control the microstructure of sintered parts [20];

- **shaping**: the main requirement is in obtaining a compact with a uniform microstructure, free of voids and defects and possibly with a high relative density before sintering. The shaping methods like uniaxial and cold isostatic pressing (CIP) [21], gel casting [22], slip casting [23] or tape casting [24] have provided good results. The shaping step is logically the most important one for the present article and will be discussed more in detail;
- **sintering**: the selection of a suitable sintering process is fundamental for the removal of pores and therefore for reaching transparency. For most materials, the traditional pressureless sintering in air does not provide a sufficient driving force to fully close porosity. The most commonly used approaches could be divided into vacuum sintering [25], pressure-assisted sintering techniques that use uniaxial pressing in a die (hot pressing, HP [26], or at a more experimental level spark plasma sintering, SPS [27]), sintering under chemically controlled atmosphere (e.g. in hydrogen, oxygen) or a combination of a pre-sintering step followed by hot isostatic pressing [18,28]. In the case of transparent windows and domes, the method of choice is usually hot pressing (HP) or SPS, combining the shaping and sintering steps. The selection of the sintering process is correlated with the specific material, or a combination of a material and a sintering aid. On the other hand, apart from pressure-assisted methods that use dies, and thus also shape the material, it is generally independent of the shaping technology.

Traditional methods for producing transparent ceramics have been extensively reviewed in several publications: [3,18,29–31].

The results obtained are promising and the data presented in the literature can even surpass the performance of single crystals, while being produced by a less energy- and material-consuming process. Nevertheless, the traditional techniques are hardly suitable for producing complex geometries and customized parts, which are becoming more relevant in the current industry. Examples include micro lenses [32], advanced pixelated scintillators [12] or internally structured composite laser gain media [33].

In contrast to the traditional shaping methods, additive manufacturing (AM) offers almost unlimited design freedom and customisation capability in the production of ceramics [34].

A great advantage of ceramic processing techniques in the field of transparent inorganic materials is the possibility of producing composite structures. These macroscopic composites are multimaterial structures, which may consist of parts of mm-to-cm size of different compositions, produced as a single component, as described by Tian et al. [35]. The production of such components is challenging, but promising results from AM processes start to appear. In transparent ceramics, such composites are promising for laser gain media, particularly for the use in pulsed and high-power lasers, or in compact laser devices. These composite structures may consist of parts with relatively small compositional differences, e.g. different dopants, different dopant concentration, providing additional functionalities, enhancing thermal management, or allowing for miniaturisation of laser devices. In the case of laser components, the standard materials of choice are single crystals, where a composite structure can be obtained only with very limited geometries by bonding. Ceramic technology as already provided very good results in this direction, and ceramic laser components composed of a core with one doping ion and an external cladding doped with another ion have been successfully commercialized and implemented in high-power lasers [35,36]. The implementation of AM in the production of such components would provide an unprecedented freedom of design and has the potential to revolutionize different parts of the photonics sector, integrating waveguides or a precise thermal management through variation of composition.

With respect to the specific AM method, the importance of the steps mentioned above may vary (e.g., in the direct energy deposition approaches the considerations are different, as is shown later), and some aspects may become problematic (the use of very fine powders with a high specific surface area for liquid feedstocks). In the presented review we are mostly addressing the AM techniques as the shaping process, that is then combined with the selection of a suitable raw materials and the use of an efficient sintering process.

This review focusses on the advantages and the still unsolved issues of AM techniques in the production of transparent ceramic components. The future perspectives of transparent ceramics made by AM are also discussed.

2. AM technologies for transparent ceramics

Additive Manufacturing (AM) techniques offer promising advancements in the production of high-performance transparent ceramics. These techniques allow for improved shaping possibilities while maintaining or enhancing the quality of the produced material. This review focuses on the successful applications of AM in the fabrication of transparent ceramics.

Among the various AM technologies, several have been identified as particularly suitable for the production of transparent ceramics: Direct Ink Writing (DIW), Vat Photopolymerisation Techniques (VPP), Direct Energy Deposition (DED), Binder Jetting Technology (BJT), Material Jetting (MJ), and hybrid approaches combining different methods. This review will focus on the AM techniques that have been successfully applied to the production of transparent ceramics, omitting those that have not demonstrated efficacy in this area.

In the case of transparent ceramics, the maturity is at an earlier stage, and currently, there are no commercially available products at the market produced by any AM technique. In this section, we thus present the state of the art, described by scientific publications and patents, of the techniques that were successfully applied for the fabrication of transparent ceramics at the research and development level.

2.1. Direct ink writing (DIW)

Direct ink writing (DIW), also known as Robocasting, is a solid-based AM technique that allows the production of 3D parts by extrusion. More specifically, for ceramic applications, a ceramic paste (semi-solid feedstock) with a considerably high solid loading is extruded through a controllable nozzle into precise two-dimensional designs, building the desired shape layer by layer.

DIW has been used for several applications, the ceramic field included, due to its many advantages: the overall process is easy, with low costs and sustainable. Moreover, DIW can produce large parts with a relatively high resolution, and the high solid loading of the extruded paste allows to print off a green body with a fairly high level of density, limiting thus shrinkage during the following thermal treatments, mainly sintering [37]. The low-to-medium costs associated with DIW make it economically interesting and viable for producing custom, small-batch parts.

This set of properties makes DIW a very interesting technique also from the perspective of transparent ceramics. Nevertheless, it also has some drawbacks: mainly the anisotropic properties (e.g., mechanical, due to anisotropy of the microstructure derived from the extrusion and the layer-wise printing process) of the final product, and the printed surfaces, which are not perfectly smooth, presenting bumps and staircase effects. Furthermore, using a highly viscous paste is beneficial to the quality of the material, but it can also cause a nozzle clog. The process optimisation is thus a result of trade-offs.

As stated, the advantages of DIW make it suitable for the production of transparent ceramics. Indeed, it is one of the most explored techniques in this sense. Jones et al. were the first to report the production of transparent ceramics by DIW [38]. In this work, a YAG (yttrium aluminium garnet, $Y_3Al_5O_{12}$) cylinder with a core of Nd:YAG has been produced, showing the feasibility of a multi-material component by DIW (see Fig. 1), where the optical properties may vary within a single component according to requirements. The process used two syringes with nozzles, each filled with an ink of different composition, to produce the green body by extrusion (Fig. 1a). The inks were prepared from very fine spherical single-phase powders with the desired composition (YAG, Nd:YAG) using an organic binder system. To obtain a transparent component, the green body was dried, cold isostatically pressed, treated in air to remove the organic binder system, sintered under vacuum at 1750 °C and hot isostatically pressed at the same temperature at 200 MPa.

Subsequently, the same group from Lawrence Livermore National Laboratory (LLNL, USA) explored more complex doping profiles to have a better result in terms of thermal profile, using two syringes for inks [39] and working also on other dopants such as Er and Lu [40] (see Fig. 2). In the last work, optical scatter levels as low as 0.5 %/cm at 543 nm were achieved. However, the authors were facing some issues with ink penetration and, consequently, a distorted dopant concentration profile, depending on the orientation of the component.

Despite these issues, the production of a multimaterial transparent ceramic component, a transparent ceramic composite, represents a major leap forward in the potential of AM in this field. In the field of laser components, which is the case of the work demonstrated above, this is a great advantage in comparison to the currently used single crystals. To produce single crystalline components with a simple structure, a planar interface between two compositions has to be produced by high-quality polishing and bonding. More complex structures, including that with a doped core shown in Fig. 2, are thus very difficult, if feasible at all.

All the results mentioned have been obtained from slurries where the solvent was an organic system. Another possible approach is to start from aqueous slurries. The advantage here is the chance of reaching higher solid loadings compared to organic-based slurries, decreasing the possibility of cracking and deformation during thermal treatments. Zhang et al. opted for this approach for producing YAG [41], reaching a transmittance around 70 % (the theoretical maximum is about 84.5 %) in the visible wavelength range, with a sample 1.45 mm thick. Ji et al. improved that result with more tests on solid loading [42], with a transmittance at the wavelength of 1 μm around 81 % for a sample 1.2 mm thick. Further studies on ink rheology and printability have been published by the same research group [43], which reported the production of Nd:YAG part with transmittance values higher than 80 % for a sample 1.8 mm thick.

A third way is presented by Chen et al., and it consists in making a slurry UV-curable, combining DIW with UV light curing [44]. A transmittance value of around 84 % at the wavelength of 1 μm is reported for a sample 1.2 mm thick. The mentioned value is very close to the theoretical limit and confirms DIW as one of the most promising techniques for transparent ceramics. Furthermore, this work shows again, as in the case of [42], the beneficial effect of higher solid loading (here at 76 wt% for the best result).

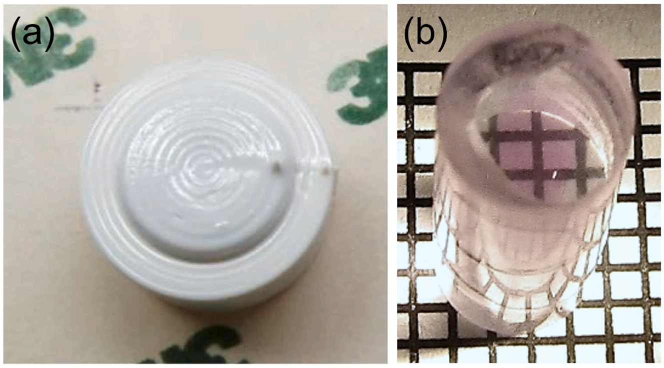

Fig. 1. *YAG/Nd:YAG multicomponent cylinder produced by DIW; reprinted from* Ref. [38]*, with permission from Elsevier.*

The market for transparent ceramics does not refer only to YAG, and the same goes for DIW. The technique has been explored also for the production of Al_2O_3 [45] and AlON [46] transparent components. Both works use aqueous slurries for printing. Carloni et al. reported a transmittance of 70 % at 800 nm (1.5 mm sample thickness) [45], showing the feasibility of DIW for transparent Al_2O_3 parts. Ji et al. worked on AlON components [46]: a transmittance of about 82 % was obtained for a 0.9 mm thick sample.

Li et al. produced by DIW 3Y-TZP (3 mol% yttria-stabilized tetragonal zirconia), which is transparent in the infrared region [47]. The group reported a transmittance value higher than 70 % at 3–5 μm region, with a sample of 1 mm thickness.

Compared to other techniques like stereolithography and digital light processing, DIW has not yet been used to produce transparent ceramics with complex shapes, although Carloni et al. [45] showed a cogwheel-designed transparent alumina components. In the case of long vertically printed rods, an external support was required during the printing to prevent the green bodies from falling over [39]. The implementation of UV-curable slurries may represent an enabling factor in this direction.

Nonetheless, even if the current state of the art is not mature enough, it seems that the way for passing to an industrial level for the production of transparent ceramic with this process is by now traced. In the last few years several patents concerning DIW of transparent ceramics were filed for this purpose: describing the production process of different materials [48], different shapes (e.g. rod [49]) and different applications [50–52]. Several approaches towards products and processes have been explored and patented ([53,54], or [55] where a gel is used as feedstock material), showcasing once again the potential and the interest in DIW for applications in transparent ceramics.

2.2. *Vat photopolymerisation (VPP)*

Vat photopolymerisation techniques are a set of liquid-based AM techniques, based on a selective photopolymerisation of the feedstock. More specifically, a ceramic suspension is put into a vat and selectively cured by a light source (usually in the ultraviolet range). This process is made possible by using a slurry with organic components such as specific light-sensitive monomers and photoinitiators, which react when exposed to the light source and create a solid body. This category of techniques is represented mostly by stereolithography (SLA), digital light processing (DLP) and two-photon polymerisation (TPP). VPP techniques offer high resolution printing with a high surface smoothness. In the case of TPP, the resolution is unmatched among the AM and traditional ceramic production techniques. The photopolymerisation approaches share a requirement on the optical properties of the powders used in the feedstock: the material should not absorb light in the wavelength used for curing. In the case of transparent ceramics, this is generally not an issue, as these materials are transparent in the indicated range, and thus do not absorb light. Exceptions may occur in the case of specific doping with ions that would introduce new absorption bands.

2.2.1. *Stereolithography (SLA)*

The specificity of SLA is that the vat is exposed using a two-dimensional scanner system. The advantages of SLA are many, and they allow this technique to be used at an industrial level for non -transparent ceramic applications (see Section 3): this technique can produce parts with very high resolution, smooth surfaces, fully dense, and without needing post-processing (apart from thermal treatments). Moreover, the overall printing process is fast [56].

However, this technique also has some disadvantages: the material selection is limited, and the wall thickness of the printed parts is also limited since the debinding process has strict requirements, posing dimension restrictions.

The properties of SLA make it suitable for the production of

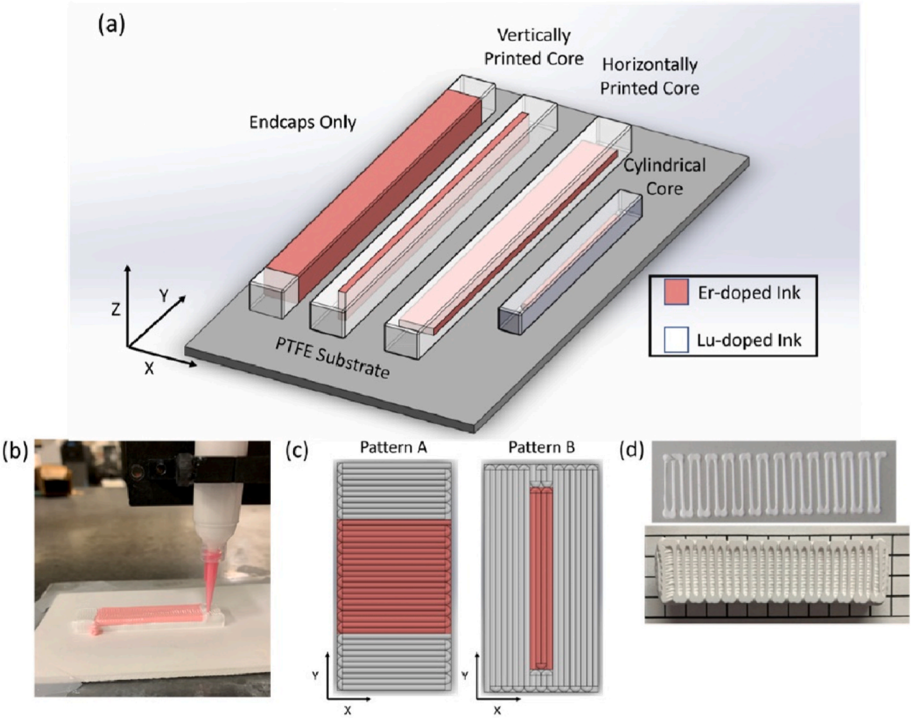

Fig. 2. *Direct ink writing of YAG-based composite structure presented in* Ref. [40]*: (a) illustration of doping profiles, the two colours indicate different dopants, (b) printing a rod with a horizontally printed Er-doped core, (c) two printing patterns, A and B, were used in the same work to investigate variations due to the printing orientation, (d) (top) a single sacrificial drying layer, as was used for printing on glass substrates, (bottom) a dried green body flipped over, showing the sacrificial drying layer; reprinted from* Ref. [40]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

transparent ceramics, but the state of the art is still quite limited. Dosovitskiy et al. first reported the production of complex-shaped Ce:YAG by SLA [57]. The component works as scintillator and was translucent, not transparent, but this is also related to the sintering conditions used, which were not enough severe to allow the closing of all porosity and, hence, the obtainment of a transparent component.

Wang et al. worked on $MgAl_2O_4$ spinel [58], managing to produce a highly transparent part with a transmittance value of 84.7 % at 1550 nm (about 97 % of the theoretical value), with a sample 1.2 mm thick. The authors used a submicron-sized spinel powder and a trimethylolpropane triacrylate resin to prepare the slurry. Within the same work, the group demonstrated that SLA can also be suitable for the production of complex shapes (see Fig. 3).

2.2.2. *Digital light processing (DLP)*

Another technique that falls into the vat photopolymerisation

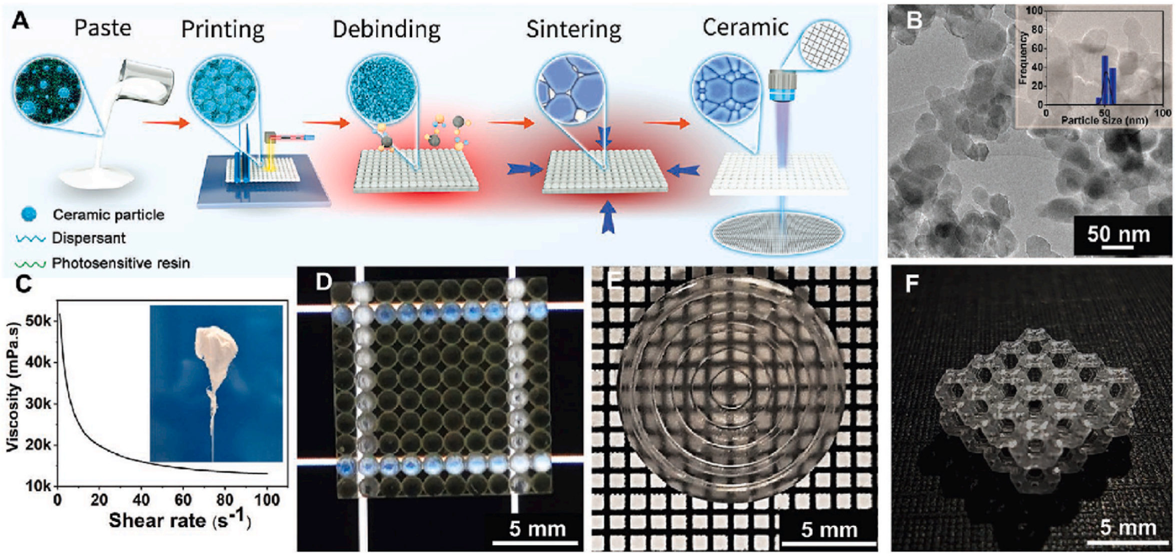

Fig. 3. *Illustration of the spinel ceramics produced in* Ref. [58] *by stereolithography: A) schematic illustration of the 3D printing and post heat treatment process, B) TEM image of spinel nanoparticles and particle size distribution (inset), C) the rheological behaviour of printable spinel ceramic paste with 55 wt% solid load and 3 wt% dispersant, inset showing the photo of spinel ceramic paste with good self-holding ability, D–F) photos of printed spinel transparent prototypes: lens array (D), Fresnel lens (E), Kelvin cell microlattice (F); reprinted from* Ref. [58], *with permission from John Wiley and Sons.*

category is digital light processing (DLP). This technique can be considered a variation of stereolithography, where the difference consists in the presence of a digital micromirror device through which the light is projected on the whole layer at once instead of scanning with a laser beam during SLA. Since DLP and SLA are very similar and share the same principles, most of the advantages and disadvantages are shared either. Compared to SLA, DLP offers generally a lower printing resolution, but a faster printing speed.

Like in the case of SLA, also DLP has attracted the interest of researchers in the transparent ceramics field. Among them, Hu et al. reported for the first time the production of Ce:YAG/Al_2O_3 by DLP [59]. The component was intended to be a phosphor and it was not transparent (the presence of another phase, Al_2O_3, is an important source of scattering). Later, Hostaša et al. [60] obtained a Yb:YAG component with transmittance around 50 %–60 % in the visible range (for a sample 1.2 mm thick) starting from a mixture of oxide powders that react into the YAG phase during reactive sintering under vacuum. The authors demonstrated laser emission, showing the possibility of using DLP for laser gain media components. The YAG system was investigated also by other research groups: Zhang et al. worked on Nd:YAG [61], achieving a value of transmittance close to 80 % in the visible range with a sample 2.64 mm thick (see Fig. 4) using also a mixture of oxide powders for the slurry preparation, exploring different thermal treatments for transparency. The investigation of debinding and sintering profiles was continued by Shen et al., which reported a maximum in-line transmittance of 77 % at 1064 nm for pure YAG parts 0.8 mm thick [62].

As in the case of DIW, there has been an effort in producing transparent ceramic parts with a controlled distribution of dopant. The major technological challenge in the production of multimaterial components by DLP, and also by SLA, lies in avoiding cross-contamination between the different materials, mostly connected to the need to clean the single layers. A DLP-based process for the production of multimaterial transparent ceramics has been patented [63], and one of the outcomes is shown in Fig. 5.

Another material explored in the literature is alumina. Sun et al. obtained slightly transparent alumina ceramics with a complex shape [64], while Moshkovitz et al. produced components with optical transmittance of above 80 % at 600 nm (sample thickness was not specified though) with a combination of Sol-Gel method and DLP [65]. In the case of alumina, it is much more difficult to achieve transparency due to birefringence caused by the non-cubic crystalline structure and the random orientation of the crystalline grains. One possible solution is to keep the grain size very low, so that light is not scattered at grain boundaries. Another is the use of texturing, where the grains are oriented in the same direction. This has been recently tested by Nečina et al. [66] who combined DLP of Al_2O_3 slurry containing a limited amount of high-aspect-ration alumina template particles and SPS to promote texturing via a templated grain growth. In-line transmittance of 54.6 % at 550 nm was obtained for a 0.8 mm thick sample.

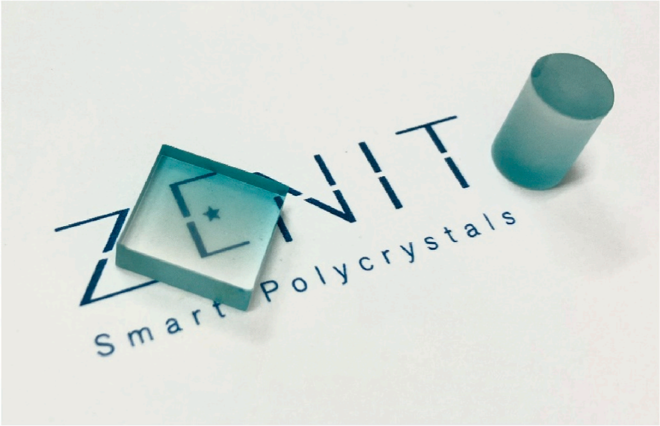

Fig. 5. Photograph of transparent Yb:YAG ceramic component with Yb concentration gradient produced by DLP; courtesy Zenit Smart Polycrystals.

From the industrial point of view, both SLA and DLP have been patented and adopted by companies as shaping methods. Some companies like Lithoz, 3DCeram Sinto or Admatec and others (see Section 3) based their market around ceramic applications on such techniques. Up to now, a number of patents have been filed: they describe the

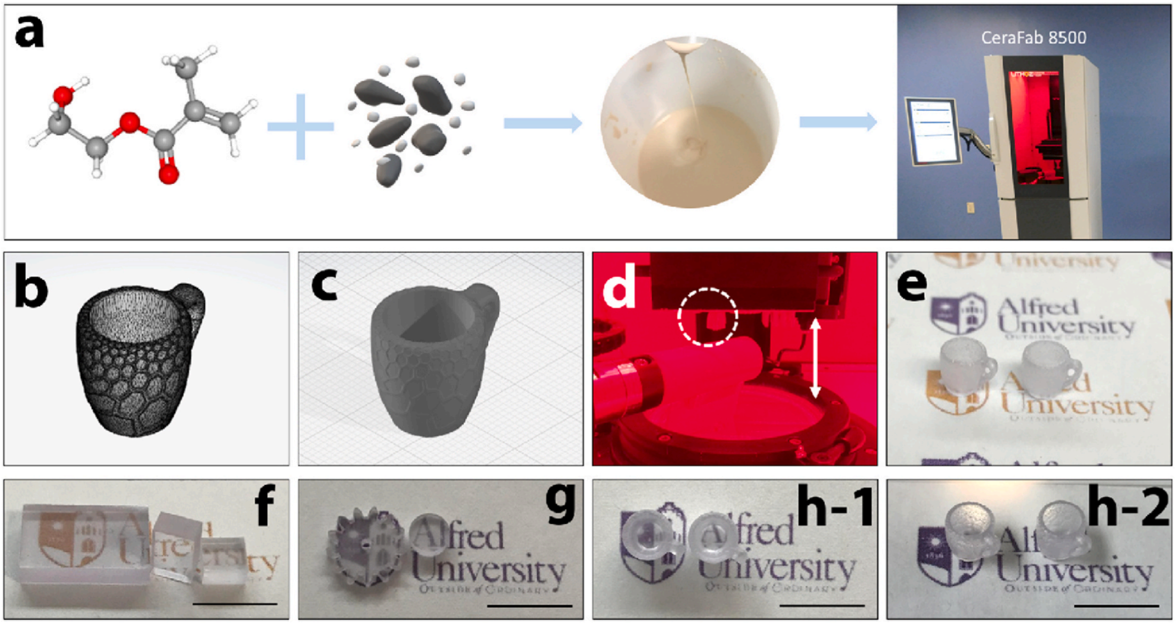

Fig. 4. *Schematic demonstration of fabricating transparent Nd: YAG ceramics as produced in Ref. [61] by digital light processing: (a) printing slurry prepared by mixing Nd_2O_3, Al_2O_3, and Y_2O_3 ceramic powders with acrylate monomer-based resin and a photoinitiator, ceramic printing conducted by a CeraFab 8500 ceramic printer, (b) creation of a CAD model, (c) loading of the 3D model to the printer for printing program generation, (d) actual 3D printing scene with the printing part constructed upside-down on the printing platform, as indicated in the white dashed circle, (e) final transparent Nd:YAG ceramic synthesis from the printed part by multiple thermal treatment steps, (f–h) examples of printed and sintered transparent Nd: YAG ceramics with different sizes and geometries (scale bar:* 10 mm*); reprinted from* Ref. [61]*, with permission from Elsevier.*

production process of uniform [67] and multimaterial bodies [63], focusing on complex shaping [68]. The patents can be referred to a specific part of the printing process, like slurry preparation [69], or to the overall process [70,71]. There are still some advancements needed for the commercialisation of transparent ceramics produced through vat polymerisation 3D printing, but the techniques look promising, at least for smaller parts, and the reported patents highlight the growing interest in this field of application. The machine costs and feedstock costs may represent limits for some of the applications.

2.2.3. Two-photon polymerisation (TPP)

Two-photon polymerisation (TPP) is another vat polymerisation technique operating at a significantly smaller scale compared to the two previously discussed. This technique needs a slurry which is transparent to the wavelength of the laser source, using either liquid precursors or nanometric particles, and its polymerisation occurs by simultaneous absorption of two photons from a pulsed laser source. A set of papers involving transparent YAG ceramics have been published, presenting interesting results [72,73]. The produced parts have a very high resolution, in the micron-range, and size from tens to hundreds of microns. Interestingly, due to the very small grain size and to the low wall thickness, good transparency has been achieved after a low-temperature sintering. More recently, MgAl2O4 spinel transparent ceramic parts have been produced by TTP followed by sintering followed by HIP [74]. A mixture of organic precursor and nanometric spinel particles has been used as feedstock The results are shown in Fig. 6. We can foresee a series of future applications of such components in the micro-optics and photonics fields. Currently, the use of TPP at industrial scale is still limited by process-related technical issues (printing speed, the use of supports) and by the high costs. Considering specialized high-value applications, such as micro-optics, the higher initial investment costs may be justified.

2.3. Direct energy deposition (DED)

Direct energy deposition (DED) is a powder-based single-step process: this means that both shaping and sintering occur during the printing, without the need for subsequent thermal treatment. This technique is based on the creation of a small melt pool by heating the substrate, most often by irradiating the substrate with a laser beam, followed by the injection of powder into the melt pool through a nozzle coupled with the laser beam.

Pappas et al. investigated the possibility of producing $MgAl_2O_4$ spinel ceramics using DED. Within their works, the group managed to produce a translucent spinel [75] and, one year later, a slightly transparent flat cuboid using a mixture of micron-sized powders of MgO and Al_2O_3 [76]. To improve the transparency, they decided to switch the feedstock material, from powder to a dense spinel filament, which itself has been prepared by DED [77]. The produced component was a rod with a reported total optical transmittance at 632.8 nm of 82 % (the sample thickness was about 2 mm; however, the total transmittance measurement does not fully illustrate the effect of scattering in comparison to in-line measurements), but it still suffered from cracking due to high thermal gradients experienced during production. The use of DED is interesting, as it does not require any debinding step. On the other hand, the high temperature gradients can easily cause cracking in many of the transparent ceramic materials.

2.4. Binder Jetting Technology (BJT)

Another technique rarely explored for transparent ceramic applications is binder jetting. Binder jetting technology (BJT) is a powder-based technique where a liquid binder is jetted into a powder layer, and then cured layer by layer.

Ragulya et al. used BJT to obtain $MgAl_2O_4$ domes transparent in the infrared region (around 70 % transmittance in the wavelength range 2.5–5.0 μm; the measurement details were not provided, e.g. the sample thickness, measurement setup and geometry, the absolute measured values) [78]. The authors used granulated spinel nano-sized powder as feedstock to produce components up to 120 mm in diameter in the green state.

While advantageous thanks to the relatively high production speed and larger size of produced components, binder jetting is not suitable for the production of ceramics fully transparent in the visible range due to the presence of residual porosity in the sintered body. In the IR region the effect of small pores as scattering centres is limited, and thus it may

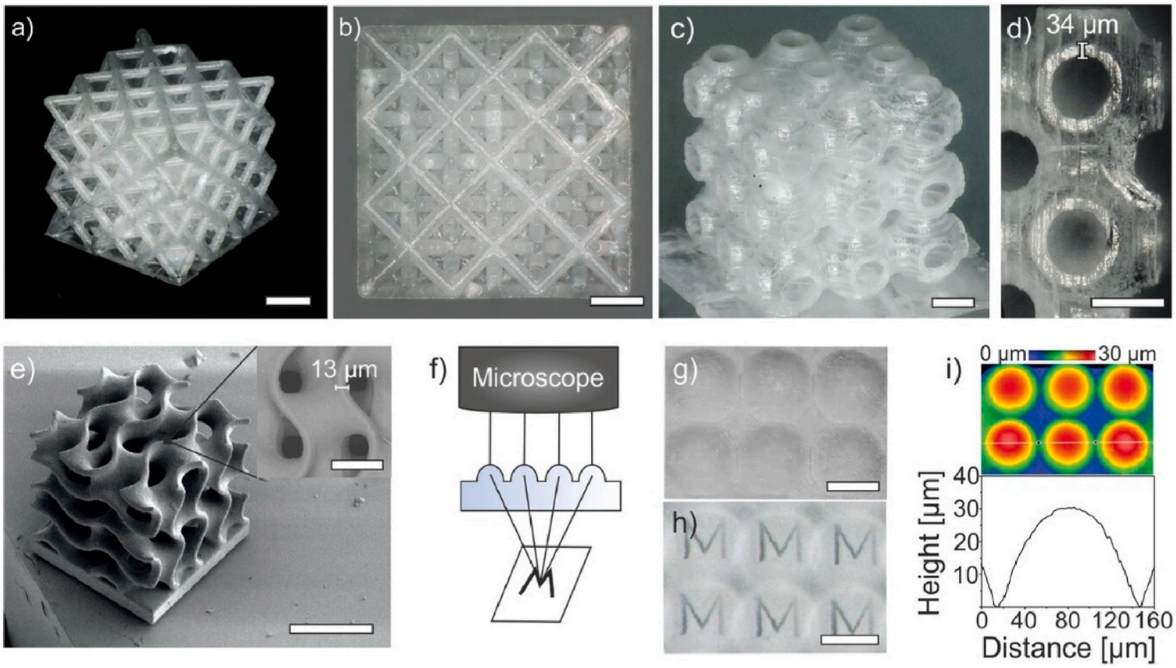

Fig. 6. *$MgAl_2O_4$ spinel transparent ceramics with a complex structure produced by TPP followed by sintering and HIP; scale bar is* 200 μm *in (a)–(e),* 50 μm *in the inset of (e) and* 100 μm *in (g) and (h), reprinted from* Ref. [74].

be possible to use some components that appear opaque to the naked eye, where IR transmittance is requested, e.g. for the protection of IR sensors in harsh environments, in defence or aerospace. A possible improvement in the density of the produced ceramics may be expected for example from approaches like post-infiltration [79], where the printed or pre-sintered body is infiltrated with a suspension, although the challenge of uniformity of microstructure remains.

2.5. *Material jetting (MJ) and hybrid approaches*

Material jetting (MJ), also referred as direct inkjet printing in the ceramic field, is a liquid-based technique where layers are built through micrometric droplets.

By the term hybrid approaches we describe techniques that combine AM with a traditional ceramic manufacturing process. This approach is particularly useful for the production of multimaterial parts, in which the internal structure is made by an AM process, providing a good spatial control, while the geometry of the whole part is relatively simple and may be obtained through standard shaping.

This has been applied by Seeley et al. [80], who obtained a planar waveguide of YAG/Yb:YAG by printing the doped part on a pre-pressed YAG powder bed, covering it with more YAG powder and pressing into one piece. Later, the same group expanded the research and came up filing a patent about the production of fully transparent ceramic parts using MJ [81].

In another work, the same group one year later reports another example of combination between dry powder pressing and MJ, producing Yb:YAG/Lu:YAG thin disk laser amplifier with paraboloidal interface, as illustrated in Fig. 7 [33]. Powder pressing is used to produce the final disc shape, while the AM technique serves for the production of the specific internal doping structure.

The mentioned hybrid approach is particularly interesting to overcome the limitations associated with each single technique, expanding the potential application spectra. On the other hand, it makes the overall process more complex, with more variables to consider, adjusting each technique's parameters to be mutually suitable.

While no results have been presented so far, it is very likely only a matter of time. In a recent review of multimaterial ceramic AM, Sun et al. indicated approaches already implemented in the ceramic AM for the production of multimaterial components [82]. Apart from multimaterial approaches using a single technique, as described above for DIW or DLP, hybrid approaches are presented as well.

The combination of SLA/DLP and DIW has been so far used for circuit-type components [83,84], but in the field of transparent ceramics may be considered for example for the production of waveguides or core-cladding structures. Process-wise, SLA/DLP-based techniques for multimaterial AM will generally require a cleaning step to remove the uncured slurry.

As written above, there are numerous other AM techniques that have been successfully used for the production of ceramics in general, however not all are promising candidates for transparent ceramics. The main reason is the requirement of a fully dense sintered body, which is not always achievable (e.g. in binder jetting or selective laser sintering). In some cases, the need for a specific feedstock (e.g. fused deposition modelling) may also be hindering the development, although the method itself could be considered valid.

2.6. *Comparison of AM techniques for transparent ceramics*

When comparing the AM techniques listed above, we can draw conclusions concerning their applicability. Table 2 summarizes the key characteristics of various AM techniques in producing transparent ceramics. The insights into the capabilities and limitations of each technique will help interested readers to identify the most suitable AM process based on the operational and financial constraints. The potential applications refer to those, where no substantial post-processing is be required (surface polishing may be needed, but substantial machining should not), and where the obtained transparency is or can be projected as sufficient.

The assessment of the achievable transparency of the materials was based on the transmittance values provided in the literature and on the optical appearance of the ceramic parts. For practical purposes and considering the state of the art and further potential, the following distinction has been used in Table 2.

- *High transparency* corresponds to transmittance values > 80 % of the theoretical value in the visible wavelength range, or to samples that are visibly transparent;
- *Moderate transparency* corresponds to lower transmittance values and to samples that are optically transparent, but may contain large defects.

In the case of TPP, the transparency of the produced ceramics can be high. However, this is not necessarily just a result of the low number of defects, but also an effect of the very low thickness of the material. Therefore, we cannot directly compare the results obtained by TTP with those produced by other AM techniques, unless the dimensions are similar.

3. From research to production, industrialization foresight

The transition of AM techniques for transparent ceramics from research to industrial-scale production presents both opportunities and challenges. As illustrated in the previous sections, various AM techniques have been successfully tested for producing transparent ceramics. Among these, vat photopolymerisation techniques such as SLA and DLP show the highest potential for industrialization due to their ability to produce components with very high resolution and near-theoretical transparency [58,61]. On the other hand, Direct Ink Writing (DIW) is also promising due to its lower material costs and the capability to produce large components.

The growing industrial interest is reflected in the increasing number of patents related to AM techniques for transparent ceramics, as illustrated in Table 3, with inventors both from academia and from the

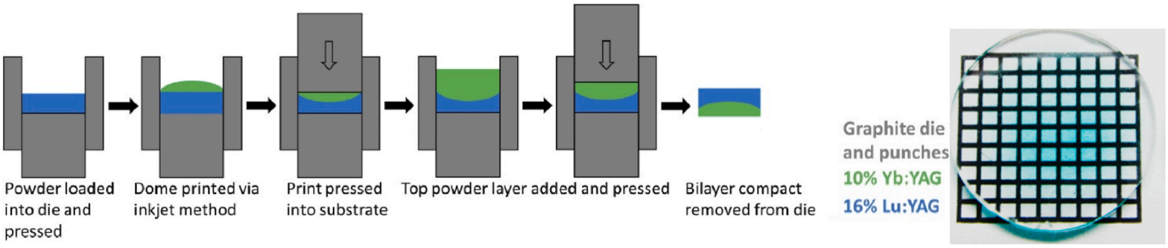

Fig. 7. *Yb:YAG/Lu:YAG composite transparent ceramics produced by a combination of powder pressing and material jetting: on the left side a schematic illustration of the inkjet printing routes used to fabricate the thin disk laser gain element, reprinted from* Ref. [33]*; the right side shows the top-view picture of the final sample, courtesy Thomas J. Rudzik.*

Table 2
Summary of AM techniques for the production of transparent ceramics.

AM technique	**Achievable resolution** [order of magnitude, μm]	**Size**	**Achievable transparency**	**Material costs**	**Machine costs**	**Potential applications**
DIW	10-100	moderate	**high [38]**	low-medium	low	photonics: lasers, scintillators, phosphors; protective windows; jewellery; multimaterials
SLA, DLP	10	moderate	**high [58], [61], [62]**	medium-high	medium	optics: lenses, optical elements; photonics: lasers, scintillators, phosphors; protective windows and domes; jewellery and watchmaking; transparent micoreactors; multimaterials
TPP	< 1	small	**high* [74]**	medium-high	high	very small optical and photonic components: microlenses, luminescent components, lasers;
DED	100	large	**moderate [77]**	medium	high	windows; jewellery; multimaterials
BJT	100	large	**moderate (better in IR) [78]**	low	medium	IR-transparent windows and domes
MJ	10	large	**high [33], [80]**	medium	low	use in hybrid approaches for multimaterial, optics and photonics, jewellery.

[a] The size of the parts complicates a thorough assessment of the optical quality.

industry. These patents highlight the focus on industrial applications, particularly in producing high-precision optical components.

3.1. Industrialization foresight

A significant portion of the patents in Table 3 refers to VPP (SLA/DLP) and DIW. These techniques can be currently considered closest to industrialization also based on the scientific results presented in Section 2. Both approaches lead to the production of green bodies with a high green density and a uniform microstructure without defects or large pores, that is a mandatory requirement for reaching transparency. The spatial resolution is higher in the case of vat photopolymerisation, illustrated by the microlenses shown in Fig. 3. DIW, on the other hand, offers a higher flexibility. To reach the market, a production process with a high repeatability has to be demonstrated.

The ongoing research and development efforts bring the AM of transparent ceramics towards industrialization, with successful precedents in other ceramic fields. Currently, there are numerous companies commercializing additive manufacturing of ceramic materials through various processes; for the techniques of interest, the technological leaders are Lithoz, 3DCeram Sinto and Admatec, all focusing on the vat photopolymerisation. These companies are technology providers for numerous producers of ceramics for applications in the dental sector, bioceramics, turbines, investment casting or electronics. The medium-to-high costs associated with SLA and DLP, also in terms of photopolymer resins, may pose challenges to large scale production, but components for optics and photonics are generally products with a medium-high added value.

To the best of the authors' knowledge, DIW is not being used for the industrial production of transparent ceramics, although the results presented by LLNL are promising [38–40], and with the patented know-how [50] it may be just a matter of time. The presented results focus on multi-component structures, which is one of the major advantages of transparent ceramics in photonics. This aspect has been covered also by another patent on DIW [49]. On the vat photopolymerisation side, different patents have been published as well with international jurisdiction, [63,70,88]. Generally, we can expect more, in particular from the hybrid approaches that combine different processes.

One limitation of both techniques is in the need for a relatively long and careful debinding process for the removal of organic components. In the case of aqueous systems this may be easier, but in any case, it is the presence of organic additives and their removal that limit the size of the components, viz. The wall thickness. The sintering of thick ceramic pieces to transparency is a very challenging process on its own, and the thickness of commercially available transparent ceramics is typically up to 10 mm after polishing. Otherwise thicker components are produced by bonding of polished parts. For vat photopolymerisation and DIW the sintered wall thickness limit may be similar or even lower.

3.2. Multimaterial components

Both SLA/DLP and DIW techniques are also suitable for the production of multimaterial components. The production of multimaterial parts represents one of the potential game changers, not being directly possible with single crystal technology, and only in a limited way by the standard ceramic production techniques. Multimaterial printing requires precise control of the internal structure. In particular for applications in photonics, which may include waveguides [35,80] or microchip laser gain media, as well as core-cladding structures, a high resolution is a fundamental requirement. From a technological viewpoint, DIW currently represents a simpler way to produce multimaterial parts, easily with more than two compositions with precise control over material deposition. The production of tailored multimaterial components has a breakthrough potential in the design of new photonic devices, paving way to more efficient laser devices, new geometries that are not limited by the current production techniques, while maintaining the properties of a crystalline material. And AM techniques provide the key to a production process with a high repeatability and precision that can hardly be achieved with other techniques.

Considering the possibilities of the traditional ceramic shaping technologies, the high-resolution automated multimaterial additive manufacturing and production of gradient-structured components is a game changer for components in photonics. Although the market may take some time to absorb the new possibilities, the chance to fine-tune a laser (or other) device through the internal structuring of the optical components may untie the hands of engineers and R&D teams. The DIW

Table 3

List of patents addressing the production of transparent ceramics via additive manufacturing.

Patent name	AM technology	Patent number; ref.	Jurisdiction and status[a]	Inventorship (academia/ industry)	Priority (year)
Method for preparing special-shaped YAG transparent ceramic through laser additive manufacturing technology	Selective laser sintering (SLS)	CN116675535 [85],	CN (P)	industry	2023
Preparation method of transparent ceramic based on laser sintering 3D printing $MgAl_2O_4$ powder	SLS	CN117486597 [86],	CN (P)	industry	2023
Transparent ceramics fabricated by material jet printing	MJ	US20230110835 [81],	US (P)	academia	2022
Support-free 3D printing method for transparent ceramic with complex shape	SLA/DLP	CN115010481 [68],	CN (G)	academia	2022
Rare earth gradual change doped transparent ceramic and preparation method thereof	DIW	CN116178004 [87],	CN (P)	academia	2022
Method for preparing transparent ceramic through one-time forming based on photocuring 3D printing technology	SLA/DLP	CN114800767 [71],	CN (P)	industry	2022
Method for preparing YAG (yttrium aluminum garnet)-based transparent ceramic by direct writing forming	DIW	CN114853462 [48],	CN (P)	academia	2022
Material and process for fabricating and shaping of transparent ceramics	SLA	EP4063337 [88], WO/2022/200629, AU2022242046, CA3212753, CN117120395, KR1020230160886, EP4313908, JP2024514442, US20240140877	EP (P), WO (P), AU (P), CA (P), CN (P), KR (P), EP (P), JP (P), US (P)	industry	2021
Preparation method of transparent ceramic slurry for direct writing	DIW	CN115432998 [53],	CN (G)	academia	2021
Methods of stereolithography 3D printing of transparent YAG ceramics	SLA	WO2023003511 [70],	SG (P); WO (P)	academia	2021
Water-based aluminum oxynitride transparent ceramic slurry for 3D printing and preparation method of water-based aluminum oxynitride transparent ceramic slurry	DIW	CN114014668 [54],	CN (G)	academia	2021
YAG transparent ceramic optical fiber preparation method based on 3D gel printing technology	DIW (3D gel printing)	CN112390641 [55],	CN (G)	academia	2021
Manufacturing method of transparent ceramic spectacle lens	DIW	CN113716960 [51],	CN (P)	academia	2021
Lithography-based process for the production of transparent ceramic bodies with at least two zones of different composition and transparent ceramic bodies thus obtained	DLP	WO2021186076 [63], IT202000005998, CN115335221, EP4121288, US20230138537, JP2023517746	IT (G), CN (G), EP (P), US (P), JP (P)	academia	2020
Process for preparing transparent ceramic through 3D printing	DLP	CN110951000 [67],	CN (P)	industry	2019
Method for preparing rod-shaped composite transparent ceramic on basis of direct writing shaping 3D printing technology	DIW	CN109761608 [49],	CN (P)	academia	2019
Laser gain media fabricated via direct ink writing (DIW) and ceramic processing	DIW	WO2017218895 [50], US20190348809; US20210098957; US20240250491	US (G, P), WO (P),	academia	2016

[a] Status is based on WIPO database; Abbreviations: P – Pending, G - Granted.

results presented by the group from LLNL are very promising in this sense. However, some issues still remain, as presented by Osborne et al. [40], who showed a difference in the final structure depending on the printing orientation. The difference is in the “striping” caused by interpenetration of differently doped ink layers during printing. Such pattern may limit or compromise the advantages deriving from the structure and the performance of the laser. In order to avoid the deviation from the original model, printing only in a specific direction may be required. The authors propose several optimisation approaches that can mitigate the issue, viz. Variation of extrusion rate, rheology of the inks or different programming of the nozzle tip spacing between the two inks, and it is likely that it will be resolved. In the case of vat photopolymerisation, the process has not yet been substantially implemented in the industrial production, but first scientific publications are available [63,89]. Nohut and Schwentenwein [90] also identified the major challenges and technical issues, in particular the requirement of as similar behaviour of the slurries and of the printed parts during heat treatments, or the prevention of cross-contamination for multi-vat systems.

Among those listed in Table 3, there are patents that cover the production of multimaterial components using both DIW [49,50,87] and DLP [63]. In all four the inventorship is from academia. This suggests that while these inventions are based on cutting-edge research, they may still require further development and optimisation before being fully implemented in industrial settings. Two of the patent applications on DIW are currently filed nationally in China [49,87], the other two have international jurisdictions, one referring to DIW [50] and one to DLP [63].

An interesting alternative is material jetting, for which a patent application has also been filed [81]. Its use in hybrid approaches, such as combining material jetting for the deposition of certain parts of the component with faster conventional shaping techniques, may offer higher flexibility in the production of various photonic components. Examples may include microchip discs with a controlled dopant gradient, or a variety of waveguides structures illustrated in Ref. [35]. For interested readers, a recently published comprehensive review addresses well the different ceramic AM approaches for multimaterials [82].

3.3. Industrial potential of other candidate techniques

While VPP, DIW and possibly MJ are considered the most promising

AM methods for industrial production of transparent ceramics in the near future, other approaches should not be overlooked. Among these, DED is an interesting candidate for the production of large components. It is currently not viable for industrial-scale production due to challenges like stress-induced cracking, low production speed, and poor resolution of details. The high-temperature gradients inherent to DED often induce cracks, which are a major limitation for producing transparent ceramics. While mitigation through additional heating of the platform or material is possible, it may increase lead times, making the process less efficient.

However, the industrial potential of DED for transparent ceramics may not lie in the typically highlighted advantage of additive manufacturing—namely, the high flexibility in shapes—but rather in its ability to eliminate the sintering step, which is particularly advantageous for large components such as windows or domes. The costs associated with acquiring and maintaining presses capable of handling components with diameters of 20–30 cm or more are extremely high. In contrast, DED is not constrained by component size, making it a more cost-effective solution for large-scale production, assuming the process can be sufficiently scaled and accelerated. Further insights can be found in the review by Pfeiffer et al. [91] on laser-based DED, Laser additive manufacturing.

Another promising technique is Selective Laser Sintering (SLS), offering high flexibility in shape including overhangs and the possibility to produce large components. SLS has been patented for use in the production of transparent YAG [85] and $MgAl_2O_4$ spinel [86], indicating its potential for transparent ceramics. However, to the authors' best knowledge, no scientific publications or other tangible results have been published that would allow for a comprehensive assessment of the feasibility of production. The patents dedicate a significant amount of space for the description of the pre-treatment and granulation of powders, to avoid the presence of defects in the microstructure.

Binder jetting also presents an advantage in producing large components; however, this technology is currently limited to IR-transparent parts due to the presence of pores that induce scattering of light and attenuation of transparency in particular in the visible range. As in the case of SLS, careful treatment of the feedstock powders could significantly improve the outcomes of BJ for transparent ceramics.

3.4. Challenges

Numerous challenges remain on the path to full implementation of AM in serial production of transparent ceramics. However, recent developments have brought a lot of interesting result with a significant application potential. It is possible that in the longer run, other technologies will also emerge as viable options. An example of such technologies might be those requiring a specific, not readily available, feedstock (e.g., fused deposition modelling).

One critical aspect to consider is the need for surface finishing. For some applications, e.g. laser components, a high-quality polishing will most likely remain a must, regardless of the production process. For many others, however, the requirements on the surface quality are less stringent. In an industrial production setting, it would be a major advantage if the surface of the as-produced part was already considered final. Some AM processes can provide a high resolution, which may suffice for certain applications. Alternatively, a coating step could be considered during the production process, to reduce surface roughness of the sintered part.

4. Conclusions

In the presented review, our objective was to offer a comprehensive overview of the state of the art of the production of transparent ceramics by additive manufacturing. Transparent ceramics are a group of materials with applications in hi-tech fields like photonics, aerospace or defence, and the implementation of additive manufacturing technology in their production presents both a noteworthy opportunity and a challenge.

Of particular interest is the high flexibility in shape and a small form factor, ideal for applications like lighting components. Additionally, the use of multimaterial additive manufacturing for producing components for photonics, e.g., laser gain media, has a breakthrough potential, particularly in the field of compact laser solutions or in high-power lasers.

Encouraging results have been presented using both direct ink writing and vat photopolymerisation techniques like stereolithography and digital light polymerisation. In both cases the achieved optical quality of presented experimental results is relatively high, and both approaches provide the route to print multimaterial components. However, navigating the path towards industrialization stands as a major challenge. The AM-derived layering of the microstructure may still be a limitation and has to be addressed carefully.

In the case of components for optics and lasers, the requirements for optical quality are high, and both very low optical losses due to scattering (i.e., the presence of porosity or secondary phases) and optical homogeneity are requested. Generally, the most challenging is the complete elimination of porosity. This can be achieved through a careful optimisation of the process, starting from the selection and possible treatments of raw materials and the use of sintering aids, and ending with the suitable sintering processes. The additive manufacturing is the shaping step, which is not final in the production process. However, it is the step that makes a difference.

Other applications may have less stringent requirements for the optical quality of the material (e.g. scintillators, phosphors or protective windows) and represent thus less challenging scenarios. Considering the recent fast uptake of the technology, we expect to see a variety of additively manufactured ceramic components transparent in the visible or infrared region penetrate different markets in the upcoming years.

CRediT authorship contribution statement

Andrea Volfi: Writing – review & editing, Writing – original draft, Data curation, Conceptualization. **Laura Esposito:** Writing – review & editing, Writing – original draft, Conceptualization. **Valentina Biasini:** Writing – review & editing, Writing – original draft, Conceptualization. **Andreana Piancastelli:** Writing – review & editing, Writing – original draft, Conceptualization. **Jan Hostaša:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

The authors are affiliated as employee or shareholders to Zenit Smart Polycrystals, a start-up company that produces transparent ceramic components by additive manufacturing. The connection is also explicitly stated in the author affiliations, and we do believe it does not pose a problem for the presented work.

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