Passive and Active Optical and Luminescent Ceramics in Research and Development

High-quality transparent ceramics combine the optical features of glasses and single crystals with typical ceramic properties, often they even exceed them. Thus, integration of active and passive transparent ceramics for instance in optical and lighting systems opens up the possibility for innovative applications, new products, superior performance and higher efficiency.

Introduction
High purity ceramics, mainly oxides with cubic crystal structure, can achieve transparencies comparable to that of optical glasses and single crystals. In some cases they exhibit even better performance. Additionally, in most cases the optical properties are accompanied by typical ceramic characteristics, such as high mechanical strength, surface hardness and wear resistance, thermal shock resistance and chemical stability. Furthermore, the characteristics of the ceramic fabrication route can provide certain advantages. Therefore, the number of examples for the successful implementation of transparent ceramic components in optical and lighting application has continuously increased over the last years and is expected to even expand further.

Motivation
Transparent and translucent ceramics have gained increasing interest during the past decades, beginning with the development and invention of translucent polycrystalline alumina (PCA) by Coble [1] at General Electric. Due to the optical anisotropy of the hexagonal crystal structure of alumina in combination with the relatively large mean grain size of these ceramics, initially however only translucency could be achieved. However, this translucency has proven sufficient for the use of PCA in arc tubes of high-pressure sodium lamps. Far more important is the fact that this was the starting point of the development of the high-quality transparent ceramics of today. High-purity ceramics, mainly oxides in a cubic crystal structure system with optical

Keywords
transparent ceramics, luminescent ceramics, optical ceramics, electrooptical ceramics

Fig. 1
Scanning electron microscopical image of a pore and secondary phase-free microstructure of a YAG ceramic

Fig. 2
Highly transparent $Y_3Al_5O_{12}$ yttrium aluminum garnet (YAG) ceramic sample

Jan Werner, Nadja Kratz
Research Institute for Inorganic Materials – Glass/Ceramics – GmbH
56203 Höhr-Grenzhausen, Germany
E-mail: jan.werner@fgk-keramik.de
isotropy nowadays can attain transparencies comparable to that of optical glasses and single crystals, when, under the prerequisite of a highly polished surface, all kind of impurities and scattering centres like secondary phases, defects, inclusions, pores, etc. in the microstructure have been avoided. This can be demonstrated by a highly transparent ceramic made of yttrium aluminium garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$), produced at FGK (Fig. 1–2).

As mentioned before, in some cases transparent ceramics exhibit even better performance than glasses with respect e.g. to their refractive properties, making them especially attractive for instance for small lens systems. In comparison with single crystals, ceramics offer a higher variability in chemical composition and more complex shaping possibilities. In this regard, ceramic fabrication can provide definite advantages especially when compared with the manufacturing of single crystal or glass based products. Additionally, in most cases exceptional optical properties are accompanied by typical ceramic characteristics, such as extraordinary mechanical strength, surface hardness and wear resistance, thermal shock resistance and last but not least outstanding chemical stability. This combination of optical and non-optical properties then allows the utilization of transparent ceramics under various harsh environmental and operating conditions.

Transparent or translucent ceramics can also have active optical properties. For instance in so called phosphor-converted light emitting diodes (pcLeDs) luminescent ceramics (often referred to as ceramic phosphors) are effectively used for the light conversion of ultra violet or blue excitation radiation into radiation with less energy and emission of light in the visible spectral range [2]. By smart combination of excitation source and ceramic light converter materials, overall light emission with customized colour temperature and high luminous efficiency can be achieved. Because the high power input also leads to heat generation, ceramics show clear benefits compared with luminescent powders embedded in polymeric matrices. Advantages lie in higher efficiency, durability and higher thermal stability.

Other examples for optical active performance of transparent ceramics are the excitation of transition metal ions like chromium ($\text{Cr}^{3+}$) or rare earth metal ions like neodymium or ytterbium ($\text{Nd}^{3+}$, $\text{Yb}^{3+}$) and light amplification by stimulated emission of radiation in ceramic laser host materials [3, 4]. Also complementary to single crystals electrooptical ceramics are of great interest [5]. These topics will be illustrated in more detail below.

**Examples for recent activities from the research laboratory**

Since years nearly no general conference on ceramics takes place without a separate session on optical or transparent ceramics. Continuously expanding activities on transparent ceramics can be noticed worldwide, as well from academia as from industry. This impetus for development has also been taken up by the working group for optical ceramics at the Research Institute for Inorganic Materials, Glass/Ceramics (Forschungsinstitut für Anorganische Werkstoffe – Glas/Keramik – GmbH, FGK). Some of the current topics addressed here will be given in this publication in the following chapters.

The focus is here put on powder synthesis, special processing, shaping techniques and particular application driven aspects. The materials dealt with range from simple oxides to complex quaternary systems and even multiple component composite ceramics.

**Medium-pressure injection moulding of transparent cubic zirconium oxide ceramics $c$-$\text{ZrO}_2$ for the fabrication of high-refractive lenses and prisms**

In a high-purity ceramic with a chemical purity in the range of 99.99 mass-% and mineral phase purity at least below the detectability limits of state-of-the-art X-ray analysis, the main objective in the fabrication of transparent ceramics is to achieve highest possible density by avoiding any residual porosity in the final ceramic body. Therefore, it is of utmost importance to generate a green body with an optimal particle packing and green density. Krell, et al. [6] and other researchers showed that the chosen processing route has a substantial impact on the required sintering temperature and the necessary dwell time, correlated to the homogeneity and packing density of fine-grained ceramic powders. As a consequence, wet shaping techniques like gel-casting (GC), pressure casting (PC) and also electrophoretetical densification (EPD) are advantageous compared to axial pressing (AP) or cold isostatic pressing (CIP). For small, complex-shaped parts that are being produced in large or medium-sized quantities, powder injection moulding (PIM) (high-pressure injection moulding – HPIM) as well as medium- and low-pressure injection moulding – MPIM an LPIM) are attractive
particularly with regard of fabrication costs. For example, highly refractive materials with high transmission and low scattering losses are required, like fully stabilized cubic zirconia with near to zero porosity [7]. They allow ceramic fabrication of high-quality passive optical compounds like prisms and lenses. Using near-net shape forming techniques, materials consumption of such valuable powders can be minimized as well as expenses for further mechanical processing steps and surface finishing.

Therefore, at FGK a processing route for highly refractive \( N_g = 2.158 \) at a wavelength of 589.3 nm sodium light) transparent cubic zirconium oxide ceramics \( (c-ZrO_2) \) has been developed. This work will enable the cost-effective fabrication of ceramic lenses and prisms with high index of refractivity. On account of the optically isotropic character of cubic \( ZrO_2 \), no losses in transparency are expected in this respect. A mouldable feedstock based on low melting thermoplastic polymers has been developed with a commercially available 8 mol.-% fully stabilized cubic zirconium oxide \( (8\text{-YSZ}) \) (patent application in preparation). By low- and medium pressure injection moulding (LPIM, MPIM) and a debinding and sintering process that was specially adapted to the composition, nearly defect free green ceramics could be achieved. The moulded parts can subsequently be processed in the green state, resulting in visually transparent ceramics of high optical quality after sintering, subsequent hot isostatic pressing, annealing and final polishing. The different processing steps and the progressively increasing transparency are demonstrated in Fig. 3–4.

**Lead free ceramics for electrooptical applications**

Electrooptical ceramics belong to the class of active optical and functional ceramics. Electric and magnetic fields induce changes in materials optical and dielectric coefficients and refractive indices. Thus, their refractive indices can be controlled by applying an external electrical field. Electrooptical materials are suitable for converting electrical to optical information, and vice versa. Frequently, those materials are applied in form of single crystals (e.g. \( \text{LiNbO}_3 \), \( \text{LiTaO}_3 \)) or liquid crystals. Ceramic materials are also suitable for applications like electrically controlled panels, colour filters or light modulators. The core properties of these ceramics are optical transparence, a high electrooptimally coefficient, rapid response time and low energy consumption. The predominant feature is light modulation. When using an electrooptic device in prism or lens shape a beam can be deflected or focused by varying the refractive index.

In comparison to single crystals, ceramics can be produced very cost-efficiently, especially large scale devices. Well-known examples of transparent oxide electrooptic ceramic materials are \( \text{Pb}_{1-x} \text{La}_x \text{Zr}_2 \text{Ti}_3 \text{O}_{12} \) (PLZT), \( \text{Pb} (\text{Mg}_{1/3} \text{Nb}_{2/3})_2 \text{O}_7 \cdot \text{PbTiO}_3 \) (PMN-PT), and \( \text{Pb}(\text{Zn}_{1/3} \text{Nb}_{2/3})_2 \text{O}_7 \cdot \text{PbTiO}_3 \) (PZN-PT). All of these materials have high-quality electrooptical effects but they are containing lead. Typical lead free materials like \( \text{LiNbO}_3 \) or \( \text{RbTiOPO}_4 \) require relatively high operating voltages of several thousands of volts for electrooptical modulators. High operating voltages complicate electrical controlling and miniaturisation [5]. Alternative materials with a high electrooptical effect can be potassium tantalate niobate \( (\text{KTa}_{0.9} \text{Nb}_{0.1})_2 \text{O}_7 \) (KTN) or barium strontium titanate \( (\text{Ba}_{0.5} \text{Sr}_{0.5})_2 \text{Ti}_4 \text{O}_{12} \) (BST). For electrooptical applications KTN material has been realized by single crystal growth only in a few cases (Fig. 5). During single crystal growth from a melt small temperature fluctuations occur, leading to concentration fluctuations in atomic dimensions which in turn may influence the Curie temperature [9]. Such concentration fluctuations can be avoided during ceramic processing. To date, only a few studies deal with the development of transparent KTN based ceramics [9–11]. The working group for optical ceramics at the FGK research institute now focuses on the development of these transparent lead free ceramic materials. The research encompasses powder production, shaping, sintering and hot isostatic pressing when necessary. In an ongoing project, further developments are carried out in cooperation with a working group at the research institute FEE – Forschungsinstitut für mineralische und metallische Werkstoffe-Edelsteine/Edelmetalle-GmbH.

Within this effort already after relatively short time good progress can be shown regarding the powder synthesis and processing route of KTN, allowing the fabrication of first demonstrators with high optical transculency (Fig. 6).

Based on this, future activities at the FGK will focus on the optimization of the thermal processing and microstructure design, which is challenging with respect to the melting and solubility behaviour of the single components \( \text{K}_2\text{Nb}_2\text{O}_7 \) and \( \text{K}_2\text{Ta}_2\text{O}_7 \) in the phase system of \( \text{K} (\text{Nb}, \text{Ta})_2\text{O}_7 \).

**Luminescent ceramics for high-performance LEDs**

As already mentioned, luminescent ceramics play an important role in so called phosphor-converted light emitting diodes (pcLEDs) as they can effectively be used for the light conversion of ultra violet or blue excitation radiation into radiation in the visible spectral range of 400 – 700 nm. Compared with luminescent powders embedded in polymeric matrices, over all light emission with customized colour temperature and high power output can be achieved by combination of a suitable excitation source with appropriate ceramic light converter materials. On the one
fore, ceramic based pc LEDs, e.g. based on Ce:YAG enable the generation of high performance white light (Fig. 7–8 emitting LEDs [2]). If combined with other luminescent ceramic materials, high-quality white emitting LEDs with high color rendering indices, tailored colour temperature and high efficiency can be obtained.

Fig. 9–10 present some current results of R & D-projects from FGK with different luminescent ceramics based on rare earth (RE) ion doped orthovanadates of the tetragonal zircon-type RE:YVO₄ and based on rare earth ion doped cubic yttrium and lutetium aluminum oxide garnets RE:(Y/Lu)AG. Depending on the particular RE-doping element blue, green and red emitting ceramics can be produced and combined with each other.

Ceramics for laser application

The excitation of transition metal ions (e.g. Cr³⁺) or RE metal ions (e.g. Nd³⁺, Yb³⁺) in solids allows light amplification by stimulated emission of radiation (laser). Therefore, besides glass and single crystals, nowadays also solid state lasers based on transparent ceramics provide new possibilities. Since the pioneering works on Nd:YAG ceramic laser host materials with laser output in the mW-range by Ikeshue and co-workers [3], impressive technical progress has been achieved, resulting in ceramic laser sys-
tems which nowadays can gain more than 100 kW output power [4]. Such high power lasers are of interest for various present and future high-performance applications. The R & D activities in the field of transparent ceramics at FGK started with a cooperation with FEE – Forschungsinstitut für mineralische und metallische Werkstoffe-Edelsteine/Edelmetalle-GmbH. At first, commercial raw materials were employed. With respect to enormous costs and batch-dependent varying qualities of some of these powders FGK strived for an independent powder source, leading to the investigation and establishment of an innovative powder synthesis route based on a wet chemical co-precipitation in a so called micro-jet reactor (MJR).

In the MJR the reaction of an acidic metal ion containing solution (e.g. nitric solution of aluminum and neodymium) and a basic precipitation solution (e.g. ammonium bicarbonate) takes place by mixing the two reactant solutions under high pressure. Inside the resulting small droplets, very small particles <100 nm of hardly soluble precipitates can be formed (Fig. 11). Further preparation steps typically include subsequent washing, separation and calcination of the precipitated precursor powders, thus, completing the synthesis. During sintering the precursor powders could completely be converted into the target phase, resulting in highly dense sintered transparent ceramics of pure Nd:YAG (Fig. 12).

Recently the successfully transfer of this MJR powder synthesis to the wet chemical precipitation of nano-scaled rare-earth doped yttrium orthovanadates \( \text{RE:YVO}_4 \) by MJR technology was achieved. In deviation to the fabrication of Nd:YAG the target composition and phase of \( \text{YVO}_4 \), is already formed directly during precipitation from aqueous solutions of ammonium vanadate \((\text{NH}_4)_3\text{VO}_4\) and yttrium acetate \((\text{Y(CH}_3\text{COO})_3\)). Differently to \( \text{YAG}, \text{YVO}_4 \) crystalizes in a Zircon type non-cubic structure with anisotropic optical refraction.

Preliminary results of an ongoing research project demonstrate that MJR-synthesis provides an excellent starting position for the fabrication of chemically and crystallographically pure and nano-scaled \( \text{YVO}_4 \) powders, necessary to achieve the desired polycrystalline microstructure for the envisaged use of \( \text{YVO}_4 \)-ceramics, not only for luminescent ceramics for lighting applications, but potentially also for high-power laser-applications.

**Summary and outlook**

Translucent and transparent ceramics have gained considerable interest during the last decades. Beyond translucent alumina tubes for high-pressure sodium lamps and transparent ceramics as ballistic armour protection, light transmitting ceramics have increasingly been exploited successfully for high-tech applications in artificial lighting and optical technologies. They can be utilized as highly refractive lenses, electro-optical lenses or beam deflectors, high-power solid-state laser media, inorganic scintillators in radiation detectors for e.g. medical diagnostics and luminescent compounds in light emitting diodes, to mention just a few prominent examples. During the last years, FGK has continually been setting up the complete production line for transparent ceramics and offers its technical systems and the gained know-how to industrial and institutional partners within the scope of co-operative, bilateral development projects, as well as within the scope of national and international research projects with major project consortiums. Throughout the whole ceramic process chain, the FGK contributes know-how and system technology for the production of transparent ceramic elements, from powders and a broad range of available forming techniques through to sintering, especially in vacuum-firing technology and hot isostatic pressing (HIP) post-treatment.

Practically oriented and with the goal of enabling highly efficient future optical and lighting technologies and reducing costs for optical ceramic compounds, the working group for optical ceramics at the FGK research institute pursues four future main strategic development targets:

- innovative powder synthesis pathways and strategies,
- exploitation of inorganic compounds that are novel in ceramics,
- elaboration of sophisticated powder processing and shaping techniques and
- adaption of thermal processing related to the aforementioned topics.

The activities in the field of optical ceramics are characterised by intensive research and progressive technological development. Hence, the number of examples for the successful implementation of transparent ceramic components in optical and lighting application is increasing continuously. With an increasing number of potential users from different industries that are being introduced to the opportunities that transparent ceramics can give, it

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**Fig. 11** Scanning electron micrograph of a Nd:YAG-powder with primary particle size <100 nm, calcined at 900 °C

**Fig. 12** Nd:YAG ceramic under ultraviolet irradiation (405 nm)
is expected that in the future further interesting applications will be facilitated by research and development.

Acknowledgements

The authors would like to thank Dr. Daniel Rytz and his coworkers from FEE, Forschungsinstitut für mineralische und metallische Werkstoffe-Edelsteine/Edelmetalle-GmbH, for their cooperation during the research and for their helpful advice regarding single crystal growth and electrooptics. The authors thankfully acknowledge financial funding of their work on electrooptical ceramics by the foundation Rheinland-Pfalz für Innovation, grant 961-386261/1159K and of their work on ceramics for laser and ceramic phosphor converted LED applications, grants 0810-68503 and 965-52207-6/40.

References


ACPM EXPO 2017

International Exhibition for Advanced Ceramics and Powder Metallurgy Technology, Equipment & Products

DATE 1st- 4th June, 2017
VENUE Canton Fair Complex, Guangzhou

ORGANIZERS China Ceramic Industrial Association UNIFAIR EXHIBITION SERVICE

CONTACT Tel: + 86-20- 8327 6369 / 6389 Email: acpmexpo@unifair.com Web: www.acpmexpo.com