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Transparent yttrium oxide ceramics as potential optical isolator materials

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The objective of the presented study was to investigate the usefulness of transparent, sintered yttrium oxide for application as optical isolators, *i.e.*, materials with high Verdet constant. The study utilizes the magneto-optical Faraday effect. To obtain yttrium oxide sinters, a commercial Y_2O_3 powder was applied, with LiF added to facilitate sintering. As a result of hot-press sintering and heating, transparent, dense sinters were obtained. The structure and morphology of the powders and bulk samples and the optical properties of the latter were investigated by means of X-ray diffraction, scanning electron microscopy, visible and near-infrared reflectance spectroscopy, and a study of magneto-optical (Faraday) effects. Measurements of the Faraday effect in the wavelength range of 500–1000 nm indicate high Verdet constants for the above-described materials, which means that they can be effectively applied in laser optics.

Keywords: transparent ceramics, optical properties, yttrium oxide.

1. Introduction

One of the requirements for material applications in laser optics is to minimize the light absorption in the widest possible spectral range. Typical quartz glass does not exhibit physicochemical properties required by many industrial and technological applications. Alternative materials offering high refractive index and good optical polarization quality, while maintaining high transmittance and satisfactory chemical and mechanical stability, are attracting more and more attention. Yttrium oxide ceramics discussed in this paper is an example of such an alternative ceramic material. It crystallizes in the regular structure, has a high melting point of 2723 K, high chemical stability, rel-

atively good mechanical properties, and a low thermal expansion coefficient [1, 2]. Another important feature of this material is its transmittance, which can reach 80% [3–6]. Such high transmittance and low energy cut-off of phonons, as well as the feasibility to incorporate rare earth elements into the yttrium oxide lattice, make the transparent Y_2O_3 a good candidate for applications in Nd lasers [7].

Due to the extremely rapid development in the field of optoelectronics and laser techniques, efforts are being made to design new materials which can be used to produce optical isolators for application in optical devices that transmit light only in one direction. Studies on optical isolators utilize the Faraday effect, in which the plane of light polarization undergoes rotation when light travels through a medium placed in a magnetic field. When choosing a material suitable for this purpose, the main criterion is a sufficiently high Verdet constant [8, 9], *i.e.*, the optical constant of a material, named after the French physicist Èmile Verdet [10]. The Faraday effect can be observed in gaseous [11, 12], liquid, and solid samples, including ceramics [13, 14], amorphous substances [15, 16], and crystals, such as $Cd_{1-x-y}Mn_xFe_yTe$ [17]. The highest Verdet constants are observed for paramagnetic media, such as heavy flint glass doped with paramagnetic terbium ions or terbium gallium garnet – $Tb_3Ga_5O_{12}$ (TGG). At 632.8 nm, the Verdet constant for TGG is reported to be –134 rad/(T·m), whereas at 1064 nm it falls to –40 rad/(T·m). A TGG with an absorption coefficient of 0.0015 is resistant to damage caused by laser light [18]. Tb-doped glass with an absorption coefficient of 0.003, on the other hand, exhibits a Verdet constant equal to –70 rad/ (T·m) at 632.8 nm and –20 rad/ (T·m) at 1064 nm [19]. As previously reported [20], ceramics with the composition of $La_{0.1}Nd_{0.1}Y_{1.8}O_3$ is highly capable of rotating the light polarization, which reflects its potential to be used in optical isolators.

Yttrium is the initial material for the group of X-Y_2O_3 oxides doped with rare earth metals, *i.e.*, La, Eu, Th and Nd (all denoted by X in the formula). The determination of the properties of the initial material which exhibits magneto-rotation makes it possible to establish the influence of doping on the optical properties. A major issue concerning the wider application of transparent yttria-based ceramics, for example in the Y_2O_3-ThO_2 system, which exhibits a linear transmittance of over 70% [21], is the necessity of sintering the material at high temperature on the order of 2273–2473 K. The temperature and duration of sintering can be reduced via the application of hot isostatic pressing (HIP). When using this technique, it is possible to obtain Y_2O_3 materials with a density close to the theoretical one at lower temperatures, *i.e.*, in the range of 1973–2073 K, based on commercially available yttria powders [2, 22]. The rheological requirements set for powders sintered by means of HIP are therefore not as stringent as in the case of free sintering where the grain size and the degree of powder agglomeration are very significant [23]. To improve the transmittance of the Y_2O_3 ceramics for optical applications, some additions that facilitate sintering are also used. Based on the applied mechanism, these additions may be divided into two groups. The first group comprises compounds, which promote the formation of the liquid phase during sintering (*e.g.*, La_2O_3, Al_2O_3, MgO, LiF), while the second one includes compounds that change the sintering kinetics via the introduction of lattice defects (*e.g.*,

Eu_2O_3, ThO_2, HfO_2, ZrO_2, TiO_2, SrO) [22]. It should, however, be emphasized that the application of some additions helps to densify the material, but its final transmittance also strongly depends on the parameters of the applied powders and on the sintering procedure.

Taking into account the possibility of reducing the sintering temperature of yttria via the addition of LiF as well as the advantages offered by HIP with regard to obtaining sinters with the appropriate microstructure, an attempt was made to synthesize transparent bulk yttria samples, and investigate their structure, microstructure, and the optical and magneto-optical (Faraday) properties.

2. Experiment

2.1. Sample preparation

The commercial yttria powder 39R-0803 of high purity (99.995%), purchased from Inframat Advanced Materials (USA), was used. As a sintering aid, 1 wt% of LiF powder was used (Aldrich, 99.995% purity). The Y_2O_3-LiF mixtures were prepared via 30 min of milling in an attritor mill with alumina balls and ethanol. The powder mixture was dried in air and crushed in an agate mortar. All sintering experiments were conducted using a hot-press (Astro Division, Thermal Technology, Inc.) with a graphitic interior and an argon (99.99% purity) atmosphere. The 25.4 mm diameter die was lined with graphite foil, and the foil disks were cut to fit on the ends of punches. Instead of fine powder, pressed pellets weighing *ca*. 12 g (120 MPa, isostatic pressing) were inserted into the graphite die. The sintering temperature was set to 1723 K and the dwelling time was 2 hours. A uniaxial load was applied during the hot-pressing process. A maximum pressure of 30 MPa was applied at 1573 K, and maintained for the whole dwelling time. The first series of bulk samples was prepared as described above, and the second series was additionally annealed for 1 hour in air at 1673 K.

2.2. Methodology

The particle (agglomerate) size of the yttria powders was determined by the laser light diffraction method (Mastersizer 2000S, Malvern Instruments).

The morphology of powders as well as the microstructure of ceramics were observed by a scanning electron microscope (SEM) (Carl Zeiss CrossBeam Workstation AURIGA).

X-ray diffraction measurements were performed by a Siemens D500 powder diffractometer, equipped with a high-resolution semiconductor Si:Li detector, using KαCu radiation $\lambda = 1.5418$ Å. The diffraction pattern was measured in the Bragg–Brentano mode, with a step of 0.05°, counting time of 4 s/step and 2θ range 10°–60°.

The relative density of the sintered samples was measured by means of the Archimedes floating method, using water as the immersion medium.

The absorption coefficient of yttria ceramics was measured over the wavelength region from 350 to 1100 nm using a visible and near-infrared (VIS/NIR) reflectance

spectrometer (AvaSpec-ULS3648). The applied light source was the SL1 12W halogen lamp, capable of emission in the range of 350–2200 nm, supplied by StellarNet, Inc. The sample thickness was 0.9 mm.

Measurements of the Faraday effect were carried out using the apparatus shown schematically in Fig. 1. The necessary value of the field induction B was adjustable by varying the distance between the magnets. For the described measurements, B was set to 0.2±0.001 T. To determine the spectral dispersion of the Verdet constant, rather than its single values, four different monochromatic light sources operating at different wavelengths were employed in the experiment: the second harmonic of the 532 nm Nd:YAG laser, a 633 nm He-Ne laser, and a diode laser with a wavelength of 780 nm.

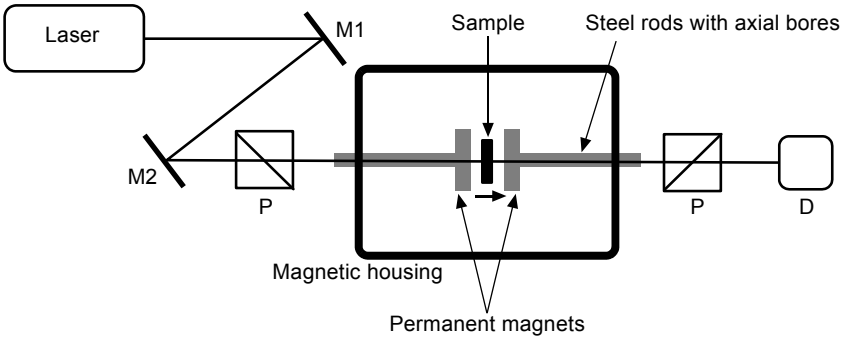

Fig. 1. Schematic diagram of the apparatus used for Faraday effect measurements (M1 and M2 – mirrors, P – crystal linear polarizers, D – photodetector).

The method of measurement and the procedure used for data analysis are described elsewhere [24]. The measurement procedure involved recording the intensity of light transmitted by the sample placed between two crossed crystal linear polarizers (P) in a given magnetic field. The light intensity was measured with a photodiode D (ThorLabs, S120C), and calibrated with a power meter (ThorLabs, PM100D). The measured values of the Verdet constant were determined on the basis of the relationship

$$V = \frac{\theta}{Bs}$$

where θ is the measured Faraday rotation angle, B is the magnetic field strength, and s is the sample length.

3. Results

3.1. Powder characteristics

XRD analysis of the as-received yttria powder (Inframat 39R 0803) indicated a single-phase structure consisting of Y_2O_3 (JCPDS card no. 83 0927).

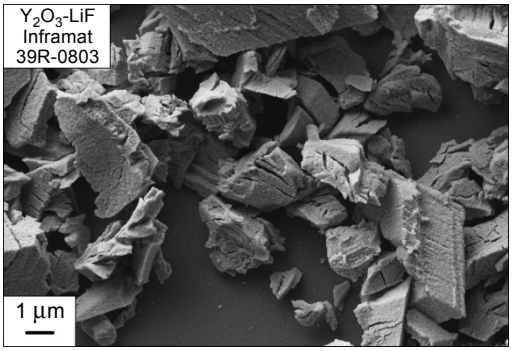

Fig. 2. SEM microphotograph of the Y_2O_3-LiF powder obtained after milling and drying.

To obtain information about the shape and size of the powder particles, their morphology was studied by means of the SEM technique. An SEM microphotograph of Y_2O_3-LiF mixtures obtained after milling followed by drying in air is presented in Fig. 2. As can be seen, this material is characterized by the presence of large, irregular agglomerates with dimensions ranging from about 0.2 to 12 µm. The grain-size distribution of the Y_2O_3-LiF powder presented in Fig. 3 suggests that this material exhibits a single-modal agglomerate distribution.

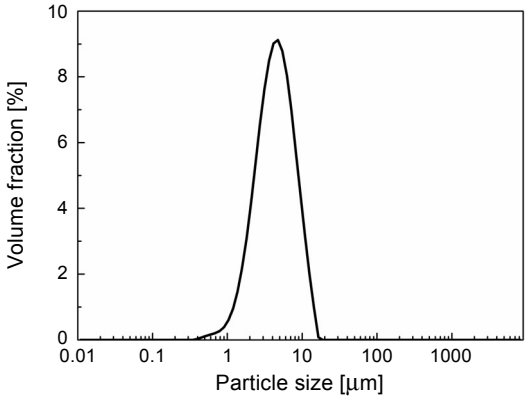

Fig. 3. Mass particle size distribution of the Y_2O_3-LiF powder obtained after milling and drying.

The size of the mode inferred from this distribution, *i.e.*, the diameter of the most significant grains in the distribution, is $D_{mod} = 4$ µm.

3.2. Bulk sample characteristics

Figure 4 presents the X-ray diffraction patterns of the two types of yttria sinters obtained after 2 hours of hot-press sintering in argon at 1723 K. The XRD studies of sinters without any additional thermal treatment (Fig. 4**a**) and after 1 hour of annealing

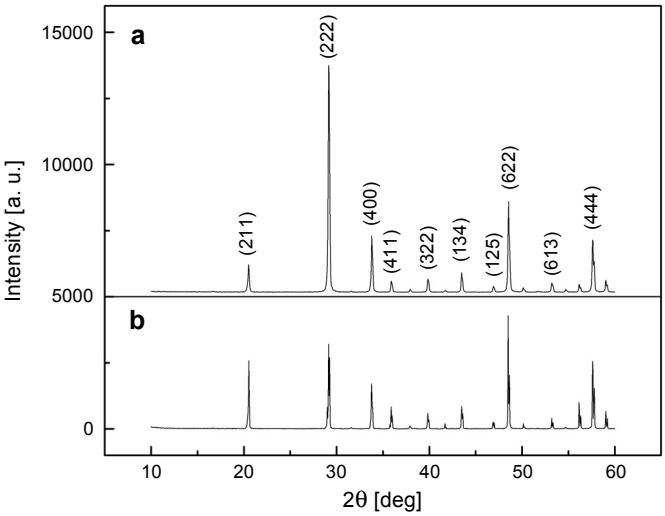

Fig. 4. XRD patterns of yttria samples obtained after 2 hours of hot-press sintering in argon at 1723 K without annealing (**a**) and after 1 hour of annealing in air at 1673 K (**b**).

in air at 1673 K (Fig. 4**b**) confirmed their single-phase composition featuring Y_2O_3 with a cubic structure.

Figure 5 shows the surface morphology of a fractured yttria bulk sample obtained after 2 hours of hot-press sintering in argon at 1723 K followed by 1 hour of annealing in air at 1673 K.

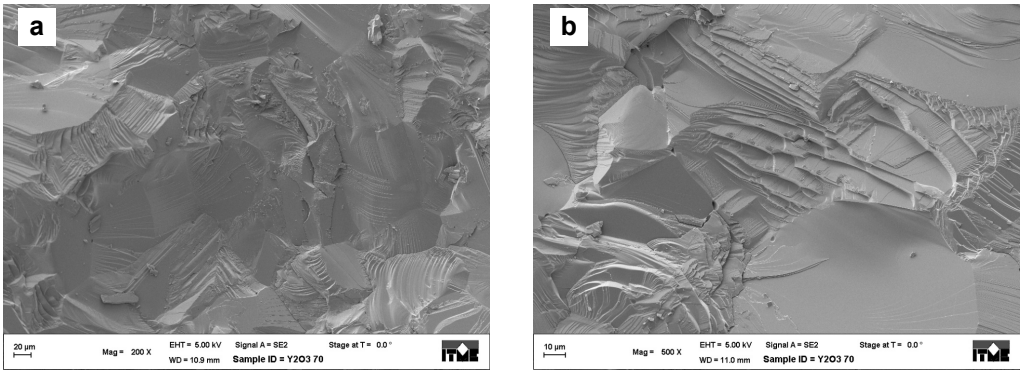

Fig. 5. SEM microphotographs of the surface of a fractured yttria bulk sample obtained after 2 hours of hot-press sintering in argon at 1723 K followed by 1 hour of annealing in air at 1673 K. Magnification: 200× (**a**) and 500× (**b**).

The examination of the morphology of the surface of this sinter revealed a coarse--crystalline, compact grain structure with well-developed, irregular grains. The size of these grains ranged from *ca*. 5 to *ca*. 75 µm. Small amounts of isolated pores with

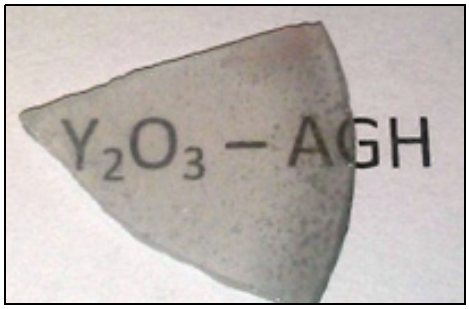

Fig. 6. A photograph of a 0.9 mm thick yttria bulk sample obtained after 2 hours of hot-press sintering in argon at 1723 K followed by 1 hour of annealing in air at 1673 K.

a diameter that did not exceed 0.5 μm were observed in the sinter; these pores were surrounded by large grains. The relative density of the ceramics was approximately 99.2 ± 0.5%.

A fragment of sintered Y_2O_3 prepared for optical studies is shown in Fig. 6. The sinter has high transmittance in the range of visible light. The very low porosity of the yttria samples translates to their high transmittance due to the lack of diffraction of incident light.

Light transmittance is the main optical property considered when evaluating transparent ceramics. The maximum transmittance of a 0.9 mm thick yttria bulk sample obtained after 2 hours of hot-press sintering in argon at 1723 K was 33%, up to 1000 nm; for the same sample this value increased to 48% after additional annealing.

Figure 7 shows the absorption spectrum of the two studied types of samples in the wavelength range of 350–1100 nm.

Based on spectrophotometric measurements carried out in the visible spectrum, it was found that the additional annealing caused a reduction of absorption, especially for

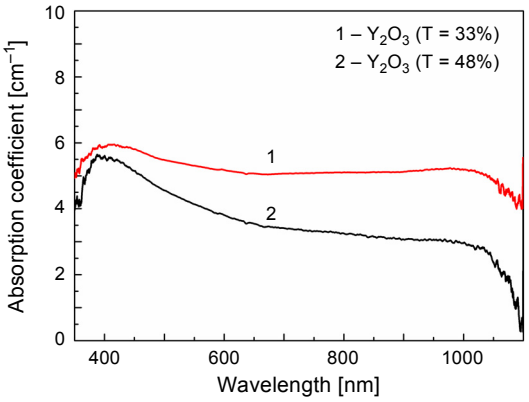

Fig. 7. Optical absorption coefficient of the two types of sintered Y_2O_3: the sample without annealing (spectrum 1) and the sample after 1 hour of additional annealing in air at 1673 K (spectrum 2).

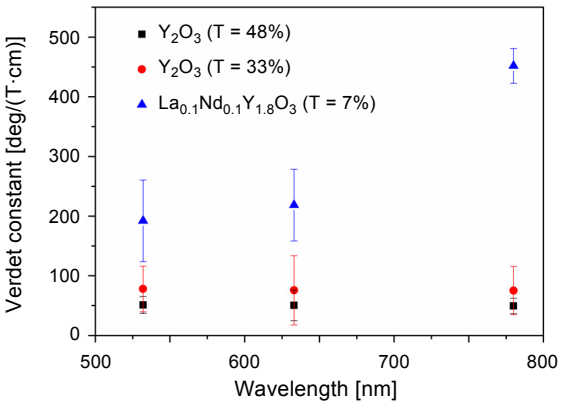

Fig. 8. Verdet constants of the two types of sintered Y_2O_3: the sample without annealing (●) and the sample after 1 hour of additional annealing in air at 1673 K (■). The results obtained for the $La_{0.1}Nd_{0.1}Y_{1.8}O_3$ ceramics are included for reference (▲) [20].

the longer wavelengths. The increase in the transmission of visible light after the annealing of the samples in air is most likely due to the reduction in the number of point defects (oxygen vacancies) in the crystal lattice [25]. When sintering polycrystalline yttria under pressure in graphite moulds, annealing in air or oxygen is indispensable for the restoration of the material's stoichiometry; this is due to the partial reduction of yttria. A more extensive explanation of this phenomenon requires further research.

Figure 8 shows the results of Verdet constant measurements for the two different types of yttria bulk samples, performed at three different wavelengths: 532, 633 and 780 nm. As can be seen, varying transmittance has a very little effect on the Verdet constant. Its values are similar for both types of samples, *i.e.*, over 50 deg/(T·cm), regardless of the wavelength. For the comparison, the plot also shows the results of the Verdet constant measurements for the $La_{0.1}Nd_{0.1}Y_{1.8}O_3$ material sintered for 2 hours in argon at 1973 K by means of hot isostatic pressing (HIP) [20]. Doping Y_2O_3 increased the value of the Verdet constant about two times, but resulted in decreased transmittance (7% at 1000 nm) [20].

In general, the relation between the absorption coefficient and the refractive index of a given material is the Kramers–Kronig relation, which predicts strong spectral variations of the refractive index around the absorption resonance of the sample under consideration [26]. The Verdet constant, however, is the quantity which reflects not just the sample's refraction, but rather its magnetic/polarization anisotropy (birefringence). Its spectral dependence is not directly related to its absorption.

Based on the spectrophotometric measurements of absorption and the Verdet constant, performed in the wavelength range of 500–1000 nm, the possibility of applying sintered Y_2O_3 as an optical isolator was demonstrated. Doping with lanthanum and neodymium is recommended in order to increase the value of the Verdet constant.

4. Conclusions

The as-received material was the commercially available Y_2O_3 powder supplied by Inframat Advanced Materials (USA). After milling, the powder consisted of fine grains in the form of plates with the ability to agglomerate. The efficacy of the LiF powder as a lubricant facilitating the sintering process without the need to modify the crystal lattice of Y_2O_3 was confirmed. The study of the morphology of the sintered Y_2O_3-LiF powder obtained by means of hot-pressing revealed the presence of grains with a regular shape and a very low number of visible pores. Annealing the studied sinters for 1 hour in air improves their transmittance to 48% compared to the 33% obtained for the samples without any additional annealing. The Verdet constants for the two types of samples were measured at three wavelengths: 532, 633 and 780 nm. The influence of the transmittance of the sintered Y_2O_3 samples on their Verdet constants was found to be insignificant. The obtained values of the Verdet constants (>50 deg/(T·cm)) were indicative of the high potential of the material for use as a good optical isolator.

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