Optical and Magneto-Optical Properties of MgO Transparent Ceramics

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The transparent MgO sample was obtained by the arc plasma melting procedure using micro-sized powder. The structure of the sample was examined using X-ray diffraction. The transmittance of MgO was close to 75% in the wavelenght range from 430 to 1100 nm. The value of the optical angle of polarization rotation in transparent MgO has been measured at energy from 1.5 eV to 3.1 eV. The band gap energy determined from Tauc relation was estimated as 3.94 eV. The magnesium oxide transparent ceramics have a potential to be applied in high temperature furnaces.

topics: MgO, Verdet constant, arc plasma melting, transparent ceramics

1. Introduction

According to the Faraday effect, when linearly polarized light propagates along an external magnetic field through magneto-optical media, its plane of polarization is changed. The change of the angle of polarization is proportional to the optical length l in the material, the magnetic field strength H, and Verdet constant V. The magneto-optical rotation of the polarisation of light is due to Zeeman splitting of atomic energy levels.

Optical and magneto-optical materials like glass, crystals and ceramic are widely used in optical circulators, optical isolators, optical fiber sensors, etc. The transparent magneto-optical ceramic materials have been considered the most promising materials that can replace glass or single crystals due to their high mechanical properties, near-neat shaping, large size and easier production. Pure and rare earth-doped terbium aluminium garnets or terbium gallium garnets are typical commercial magneto-optic elements used as host material in optical isolators in high-power laser systems. There are two important ways which may affect the performance of magneto-optical devices by improving the Verdet constant: searching for new materials or maximizing Tb and Ho concentration. Garnets show high Faraday rotation (Terbium gallium garnet$>$ 130 rad/(T m)) and high optical quality (transmittance $>$ 75%). Transparent ceramics are predicted to have a better high heat-shock resistance than garnet structures due to their higher melting point and high thermal conductivity.

It should by highlighted that the Faraday effect in garnets depends on the crystallographic direction in contrast to sinters. High transparent magnesia ceramic has a lot of useful physicochemical properties like: low density (3.58 g/cm^3), a very high melting temperature (3123 K), good mechanical properties and face-centered cubic crystal structure at ambient pressure. MgO is an insulator because of the wide energy band gap (7.8 eV) [1–6]. The Mg ions occupy octahedral sites within the anion close packed structure [1–3].

Various techniques for the preparation of transparent sinters of magnesium oxides have been developed, including hot isostatic pressing, pressureless sintering vacuum, hot pressing, spark plasma sintering (SPS) and arc plasma melting [1–6]. Some sintering aids are used to decrease sintering temperature, but they involve negative effects on optical properties. Misawa reported that transparent MgO ceramics could be obtained by sintering it at 1600 °C for 2 h in a vacuum [1]. Kato fabricated a series of bulk samples using SPS and the transmittance of samples was around 20–50% in VIS region and the increase — in IR region [2]. Fang demonstrated that translucent MgO ceramics could by prepared by hot-pressing with LiF additive [3]. Jiang reported that translucent MgO ceramics could be obtained by SPS from powders with LiF additive after sintering at 900 °C for 5 min with a pressure of 30 MPa [4]. Transmittance was 85% in the wavelenght range of 3–5 μm, but in VIS region it reaches 40%. The main criterion when choosing a material suitable for magneto-optical application is a sufficiently high

Verdet constant and high transparency. Materials characterized by a low Verdet constant are also developed for special applications where a change of polarization is not desirable.

The main goal of this paper is to examine MgO after arc plasma melting as a potential matrix for a magneto-optical material. This paper describes the evolution of values of polarisation rotation angle in the wide energy range and spectroscopy studies of polycrystalline MgO. The results of physicochemical characterization show that the ceramics prepared are perspective for application as optical material.

2. Methodology

X-Ray diffraction (XRD) data was obtained by the X'Pert PANalytical XRD using CuK_α radiation. Highscore Plus software (Panalytical) and the standard data set of PCPDFWIN v.2.3. were used for data analysis. The crystallite size was calculated based on the XRD data, using the Scherrer equation [7]:

$$D_{\mathrm{XRD}} = \frac{K\lambda}{\beta\cos(\theta)}, \tag{1}$$

where K — the shape coefficient for the reciprocal lattice point ($K = 0.89$), λ — the wavelength of X-rays ($\mathrm{CuK}_\alpha = 0.15406$ nm), β — the line broadening at half the maximum intensity (FWHM).

Lattice parameter a for the sample was calculated using:

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2}, \tag{2}$$

where d_{hkl} is the distance between adjacent planes, and h, k and l denote the Miller indices.

The minimum dislocation density ρ was estimated using the relation:

$$\rho \approx \frac{1}{\langle D_{\mathrm{XRD}}\rangle^2}. \tag{3}$$

The absorption coefficient was evaluated using a Specord 210 V Plus Analytik Jena spectrometer in the spectral range from 200 to 1090 nm with a 0.3 nm step.

The density of the melted sample was measured using helium gas pycnometer (Accupyc 1340). The apparent density of the ceramic pellets was measured at room temperature with the use of the Archimedes method using alcohol as the immersion medium, and theoretical density was calculated based on crystallographic data.

We developed the measurement system that can continuously measure the value of the polarisation rotation angle in the range from 1.5 eV to 3.1 eV. The description of measuring the system was included in an earlier paper [8]. The entire experiment was performed at room temperature. Fourier transform infrared (Jasco 570 FTIR) spectrum was recorded in KBr pellets in the range 400–4000 cm^{-1}. The Raman measurement of MgO have been performed on a Raman system from Horiba Jobin-Yuon (LABRAM HR-800) spectrometer equipped with a confocal aperture.

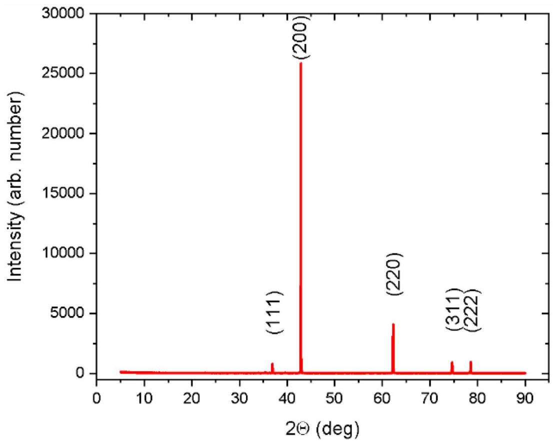

Fig. 1. XRD pattern of the MgO sample after arc plasma melting.

TABLE I

The value of lattice parameter a, unit cell volume V, lattice spacing $\mathrm{d_{hkl}}$, crystallite size D_{XRD} and dislocation density ρ of MgO.

A [nm]	V [nm^3]	d_{hkl} (200) [nm]	D_{XRD} [nm]	ρ [10^{14} m^{-2}]
4.23	75.69	24.36	15.3	0.424

3. Synthesis

The MgO powder (Sigma Aldrich, 99.9% purity) was used as the starting material. The powder was formed into green body via biaxial pressing under the pressure of 80 MPa. The pellet was melted under argon (99.99% purity) flow, using a lab-scale benchtop arc melted furnace. The sample was cooled down to room temperature at cooling rate of 20 K/s in the first seconds. After melting the sample displayed double-side polishing. The pellet thickness was 1.5 mm.

4. Experimental

Figure 1 shows the XRD pattern of the MgO bulk sample obtained after arc plasma melting. The diffraction peaks of the ceramic can be indexed as a cubic phase (JCPDS card, No. 45-0946) with the $Fm-3m$ space group. No other phases were detected. The calculated value of lattice spacing d_{hkl}, lattice parameter a and unit cell volume V, with a calculated crystallite size D_{XRD} and dislocation density ρ of MgO are presented in Table I. The main XRD peak (200) was used to estimate the parameters. The density, apparent density and theoretical density of the MgO sample were 99.7%, 99.6% and 99.5%, respectively. The obtained results are consistent with the data reported in [9].

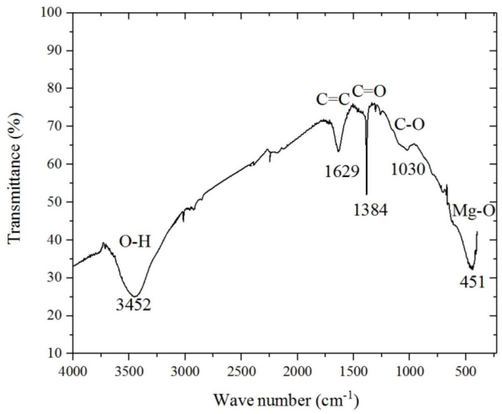

Fig. 2. FT-IR spectrum of MgO after arc plasma melting.

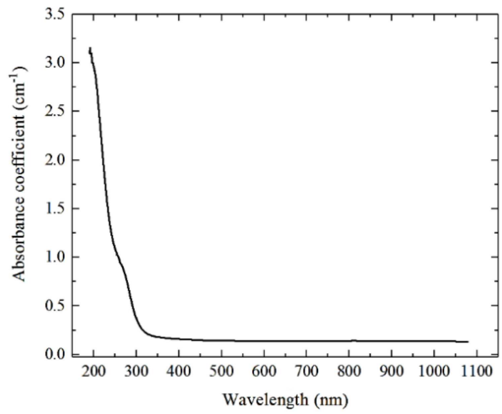

Fig. 4. UV-VIS-IR absorption coefficient of MgO after arc plasma melting.

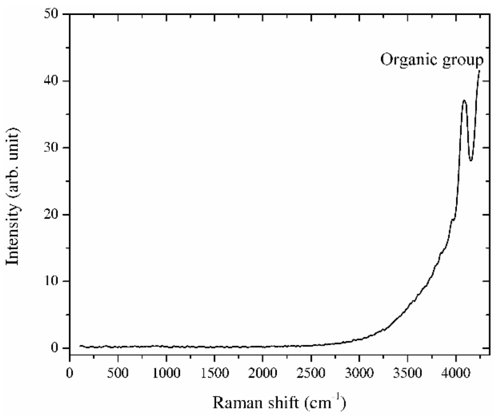

Fig. 3. Raman spectrum of MgO after arc plasma melting.

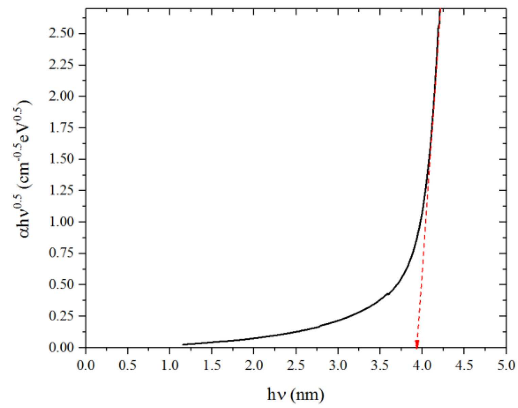

Fig. 5. Tauc plot of MgO after arc plasma melting.

Figure 2 shows the FT-IR signal of MgO powder obtained after crushing the bulk sample. Figure 2 reveals the characteristic absorption peaks for the organic group at 3452, 1629, 1384, and 1030, which can be attributed to O-H-O stretching, C=C in-plane stretching vibration, alkoxy C–O stretching, and epoxy C–O stretching vibration, respectively. Bands over 450 cm^{-1} are assigned to the organic group from KBr powder. A band with the minimum at 451 cm^{-1} is assigned to the Mg–O vibration. The Raman Spectra of MgO bulk sample in the range 100–4000 cm^{-1} is shown in Fig. 3. In the present Raman spectrum, a band of around 3500–4100 cm^{-1} is observed which can be attributed to organic groups. Any additional bands are not detected.

The absorbance coefficient of MgO was measured in a wide range of the spectral band from 200 to 1100 nm, with 0.5 nm resolution (Fig. 4). In UVA region magnesia is not transparent. The absorption coefficient visibly decreases from 215 nm to 370 nm. As revealed by the in-line transmission spectra of the transparent MgO, the sample (1.5 cm) exhibited very high optical transmittance (76.5% at over 600 nm). The result is consistent with Mie and Rayleigh's theory. No absorption peaks were detected in the spectrum.

The optical band gap value was calculated using the Tauc plot [10], according to

$$\alpha h\nu = A\left(h\nu - E_g\right)^n, \tag{4}$$

where α is the absorption coefficient, $h\nu$ means the photon energy (eV), E_g is the band-gap energy, and A is a constant. Here, n is indicative of the nature of transition and for MgO it is equal 1/2. The optical band gap of the sample was determined using a linear extrapolation to the Tauc plot as shown in Fig. 5. The optical band gap is equal to 3.94 eV.

The angle of polarization rotation of MgO transparent ceramics was measured from 3.2 to 1.5 eV (5 nm resolution), and the result is presented in Fig. 6. The values of angle of polarization fall with decreasing energy from 3.2 eV to 2.6 eV. Next, the angle of rotation increases with energy above 2.5 eV, probably due to the dispersion. The relationship between Verdet constant V and dispersion of the material $\mathrm{d}n/\mathrm{d}\lambda$ is the following:

$$V = -\frac{e\lambda}{2mc^2}\frac{\mathrm{d}n}{\mathrm{d}\lambda}, \tag{5}$$

where e is charge of electrons, m is a mass of electron, and c is the light velocity.

The obtained values of the angle of polarization rotation of pure MgO are relatively small as compared with garnet crystals. The Verdet constant of the MgO sample (max. 3.5 rad/(T m))

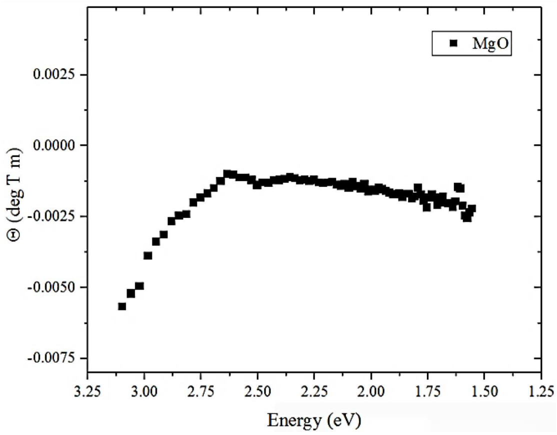

Fig. 6. The angle of polarization rotation of MgO after arc plasma melting.

indicates a lower value (∼ 50 times) than TSAG (156 rad/(deg m)) and TGG (more than 130 rad/(T m)) crystal, or pure yttria ceramics (20 rad/(deg m)) [11–13]. Pure MgO is not a typical magneto-optical material, however it can be used as an appropriate matrix material due to a high transmittance and easy incorporation of paramagnetic ions.

6. Conclusion

Highly transparent and dense sample was manufactured using state-of-the-art arc plasma melting process. The XRD studies confirmed a single-phase composition of MgO. Absorption bands were not detected. The calculated optical band gap is estimated at 3.94 eV. However, MgO could be applied in furnace sight, IR windows or devices working in extremely high temperatures. The value of Verdet constant can be increased after by doping with paramagnetic ions, e.g. Tb or Pr. Spectroscopic studies confirmed that the pure transparent MgO ceramics were prepared, however some change in crystal parameters in comparison to sintering materials were observed. MgO is a promising optical material due to its high transparency in VIS spectrum and physicochemical properties. To improve the magneto-optical properties of MgO it is necessary to incorporate paramagnetic ions.

Acknowledgments

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