

Holmium doped yttria transparent ceramics for 2- μ m solid state lasers

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Abstract

0.7 at.% Ho:Y₂O₃ transparent ceramics were fabricated by using vacuum sintering plus hot isostatic pressing (HIPing) process. Vacuum sintered at 1500 °C for 12 h followed by HIPing at 1450 °C for 4 h, the Ho:Y₂O₃ ceramics showed excellent in-line transmission and uniform grain size, with an average grain size of about 1 μ m. The Ho:Y₂O₃ ceramics showed good thermal conductivity thanks to the identical effective ionic radius between Ho³⁺ and Y³⁺. For the first time, room temperature laser oscillation from Ho:Y₂O₃ transparent ceramics was demonstrated. The uncoated 0.7

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at.% Ho:Y₂O₃ ceramic slabs were in-band pumped by a Tm: fiber laser at 1941 nm, and a maximum output power of 1.3 W at 2116.8 nm was achieved with a slope efficiency of 31.2%. It indicates that Ho:Y₂O₃ transparent ceramics could be excellent laser gain medias for 2 μm solid-state laser applications.

Keywords: holmium ions; yttria transparent ceramics; 2 μm; solid-state lasers;

1. Introduction

2 μm eye-safe lasers have many important applications, such as the remote sensing of atmospheric CO_2 and H_2O , medical treatment, LIDAR systems, and pump sources for mid-IR OPOs.^{1, 2} Trivalent holmium (Ho^{3+}), as a promising active ion for 2 μm lasers, has attracted great attention thanks to its 1.9-2.1 μm transition from the excited state ($^5\text{I}_7$) to the ground state ($^5\text{I}_8$).³ In recent years, Ho^{3+} doped single crystals, such as YVO_4 ^{4, 5}, KREW (RE=Lu, Gd, and Y)⁶, YAG⁷, and sesquioxides (Y_2O_3 , Lu_2O_3 , and Sc_2O_3),^{8, 9} have been fabricated and their laser oscillation at 2 μm has been demonstrated. However, considering the relatively high cost and difficulty of making large size single crystals, transparent ceramics are regarded as a highly attractive alternative host materials for high power solid-state lasers.^{10, 11} It is to note that by using Nd:YAG ceramics as the laser gain media, the 100 kW level solid-state lasers have been realized, confirming the great potential of transparent ceramics for high power laser applications.¹²

More recently, Y_2O_3 and other sesquioxide ceramics (e.g., Lu_2O_3 , Sc_2O_3) have attracted much attention for high power laser applications, due to their relatively high thermal conductivity and low phonon energy.^{3, 8} It is also worth mentioning that the effective ionic radius of Ho^{3+} (in six coordination) is 0.90 \AA , which perfectly matches with that of Y^{3+} (0.90 \AA , in six coordination).¹³ Therefore, it is believed that, after doping, Ho^{3+} ion would not cause much deterioration of the thermal conductivity of Y_2O_3 , because there is little disturbance to the lattice periodicity of Y_2O_3 .^{14, 15} In this respect, Y_2O_3 transparent ceramics are ideal hosts for the holmium active ion.

However, laser operation of the holmium doped yttria transparent ceramics has been less addressed. There has been no report on room temperature laser oscillation of Ho:Y₂O₃ ceramics at 2 μm. To the best of our knowledge, the only laser operation of Ho:Y₂O₃ transparent ceramics were carried out by Newburgh et al. in 2011², at liquid nitrogen temperature (77 K). In 2013, Kim et al.³ reported the first room temperature laser oscillation of Ho:Lu₂O₃ transparent ceramics, which were fabricated by using the combination of hot pressing and hot-isostatic pressing (HIP). The ceramics had average grain sizes of 40-50 μm. Nevertheless, due to the presence of small amount of scattering, lasing performance of the Ho:Lu₂O₃ ceramics was not promising.³ For example, a maximum output power of 182 mW and a slope efficiency of 1% were obtained by using the Ho:Lu₂O₃ ceramics.

In the present work, we report fabrication of laser grade Ho:Y₂O₃ transparent ceramics by using vacuum sintering plus HIP technique. The Ho:Y₂O₃ transparent ceramics exhibited excellent optical quality with sub-micro grain size, with which room temperature high efficiency laser oscillation was demonstrated for the first time.

2. Experimental Procedure

2.1 Ceramic Fabrication

HoCl₃ and YCl₃ solutions were mixed according to the formula (Ho_{0.007}Y_{0.993})₂O₃ (denoted as 0.7 at.% Ho:Y₂O₃ in short). A small amount of (NH₄)₂SO₄ was added as

the dispersant, with the $\text{SO}_4^{2-}/\text{Y}^{3+}$ molar ratio equaled 0.1. Then, the mixed solution of $\text{NH}_4\text{HCO}_3+\text{NH}_4\text{OH}$ was added dropwise into the mother solution at a constant rate of 6 mL/min, until the PH value achieved 8.5. After aging for 1 day, the precipitate was washed with deionized water for five times and ethanol for two times. After that, it was dried in an oven at 60 °C for 24 h and then calcined at 1200 °C for 5 h in a muffle furnace to obtain 0.7 at.% Ho:Y₂O₃ powder. The calcined powders were pressed by using a stainless steel die, and then cold isostatic pressed (CIP) under 200 MPa. The green compacts were vacuum sintered at 1500 °C for 12 h. After that, the compacts were HIPed at 1450 °C/4 h at 198 MPa in argon (Ar). Finally, the ceramics were air annealed at 1200 °C for 10 h in a muffle furnace to remove the color centers.

2.2 Characterization

Transmittance spectra of the samples were measured by using a UV-VIS-NIR spectrometer (Carry 5000, Agilent, Santa Clara, CA). Phase structure of the calcined powders was identified from X-ray diffraction (XRD) patterns (Cu Ka radiation, XRD-6000, Shimadzu Co. Ltd, Japan). Powder morphology was observed by using a field emission scanning electron microscope (SEM, Leo 1550, Cambridge, Cambridgeshire, UK). Surface morphologies of the samples were examined by using a scanning electron microscope (JSM-6360A, JEOL, Tokyo, Japan). A statistical method was utilized to measure the average grain size, with the Nano Measure software. At least 300 grains were counted for each ceramic. Thermal conductivity of

the samples was measured by using the laser flash method (Laser Flash:DLF 1200, TA Instruments, USA). Thermal expansion was recorded by using a thermo-mechanical analyzer (TMA:Q400, TA Instruments, USA).

3. Results and Discussion

Figure 1(a) shows the SEM image of the Ho:Y₂O₃ powders calcined at 1200 °C for 5 h. Primary particle size of the powders was about 100 nm. The powders showed good dispensability, without the detection of large aggregations. Figure 1(b) shows the XRD patterns of the Ho:Y₂O₃ powders calcined at 1200 °C for 5 h. It can be seen that the diffraction peaks are in good agreement with those of the cubic bixbyite-type crystal structure as identified by using the standard PDF card (Y₂O₃ JCPDS: 86-1326). Impurity phases were not detected in the XRD patterns.

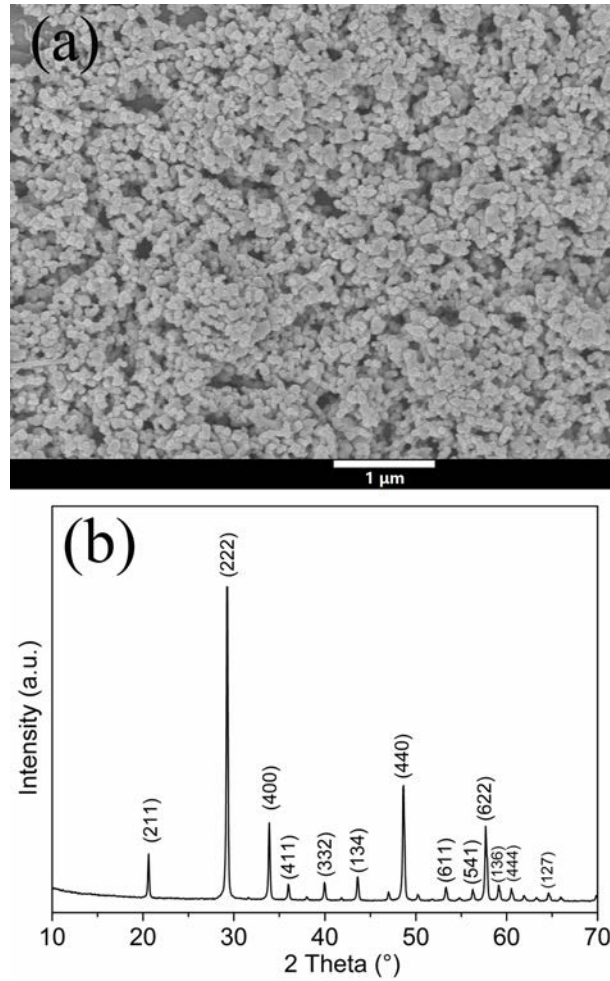


Fig. 1. (a) SEM image and (b) XRD patterns of the Ho:Y₂O₃ powders calcined at 1200 °C for 5 h.

Figure 2(a) shows SEM image of the Ho:Y₂O₃ ceramics after vacuum sintered at 1500 °C for 12h. It can be seen that open porosity has been eliminated almost completely. Relative density of the ceramics reached about 97.1%, leaving very small amount of isolated grain boundary pores (marked red). Meanwhile, average grain size of the ceramics was as small as 0.8 μm, without the detection of any intragranular pores, implying the ceramic has been ready for the subsequent full densification using HIP. After HIPing at 1450 °C for 4 h, the ceramic exhibited homogeneous and dense microstructure, with little further grain growth (Fig. 2(b)).

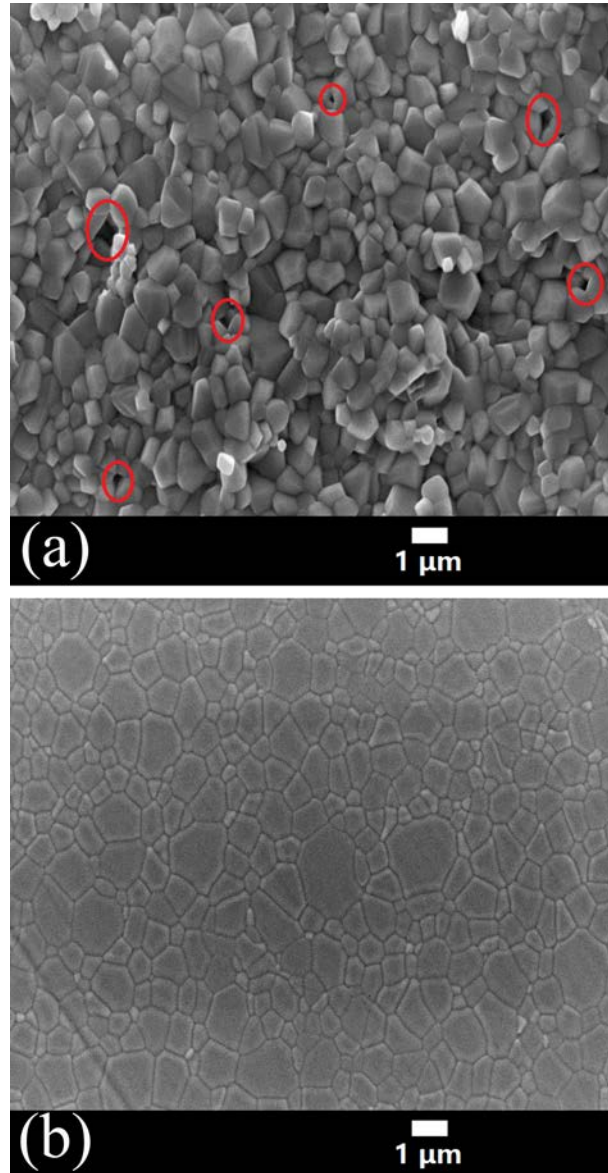


Fig. 2. SEM images of the Ho:Y₂O₃ ceramics after (a) 1500 °C/12 h vacuum sintering and (b) vacuum sintering followed by 1450 °C/4 h hot isostatic pressing.

Figure 3 shows the in-line transmission of the HIPed Ho:Y₂O₃ ceramic with a thickness of 3.0 mm. The main absorption peaks are attributed to the trivalent holmium absorption transitions of $^5I_8 \rightarrow ^5I_7$ (1760-2000 nm), $^5I_8 \rightarrow ^5I_6$ (1070-1240 nm), $^5I_8 \rightarrow ^5F_5$ (610-690 nm), and $^5I_8 \rightarrow ^5F_4 + ^5S_2$ (515-580 nm), respectively.¹⁶ The ceramic after HIPing exhibited excellent in-line optical transmittance through the entire wavelength range. For example, the in-line transmittance was 80.0% at the

wavelength of 600 nm, very close to that of Y_2O_3 single crystals. The transmittance of Y_2O_3 single crystals was calculated to be 80.9% (at 600 nm) based on the formula of $T = 100[1 - ((n-1)/(n+1))^2]^2$ (n is the refractive index of Y_2O_3 single crystal)¹⁷.

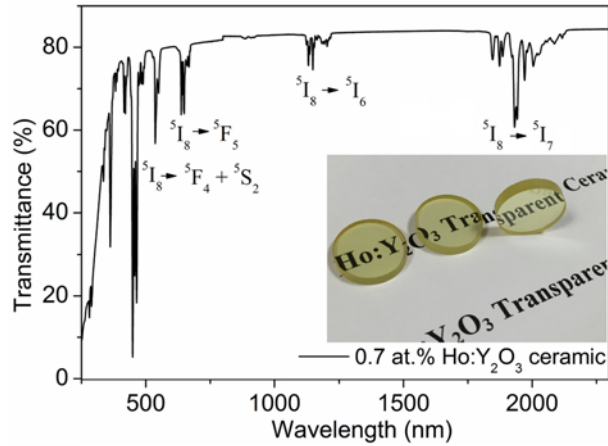


Fig. 3. In-line transmission of the Ho:Y₂O₃ ceramics after HIPing at 1450 °C/4 h, with the inset showing the corresponding photograph.

Thermal properties of the ceramics are important because they determine the cooling properties during lasing. Figure 4(a) shows the thermal conductivity (TC) of the Ho:Y₂O₃ ceramics versus temperature. The room temperature thermal conductivity of the Ho:Y₂O₃ ceramic is 11.1 W·m⁻¹·K⁻¹, which is superior to that of pure YAG (10.8 W·m⁻¹·K⁻¹)¹². This value is slightly lower than that of pure Y₂O₃ ceramics (13.6 W·m⁻¹·K⁻¹), due to the doping of holmium ions. Figure 4(b) shows the thermal expansion (TE) and thermal expansion coefficient (TEC) of the Ho:Y₂O₃ ceramics versus temperature. Both the thermal expansion and thermal expansion coefficient are increased almost linearly with increasing temperature up to 900 °C. At 900 °C, the values of TE and TEC are 0.0071 and 8.3·10⁻⁶K⁻¹, respectively, which are close to the values reported by Harris et al.¹⁸

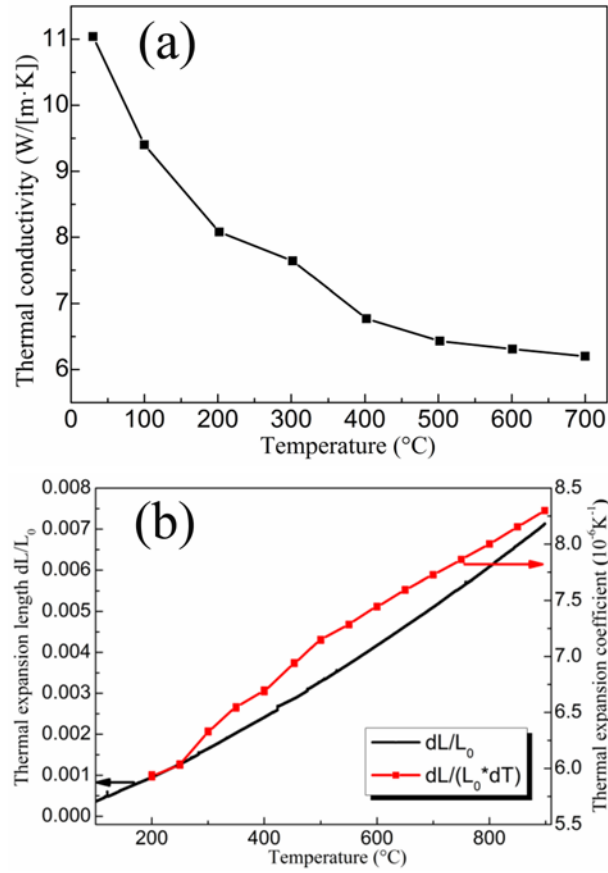


Fig. 4. (a) Thermal conductivity and (b) Thermal expansion and thermal expansion coefficient of the Ho:Y₂O₃ ceramics versus temperature.

To evaluate the laser performance of the Ho:Y₂O₃ transparent ceramics, a two-mirror cavity (18 mm in length) was employed in the laser experiment. A home-made Tm: fiber laser at 1941 nm with 0.1 nm bandwidth was utilized as the pumping source. The fiber laser was collimated and focused onto the Ho:Y₂O₃ ceramics with a beam radius of $\sim 167 \mu\text{m}$. The dimension of the polished but uncoated ceramic slab was 2 mm \times 3 mm \times 12 mm. The input plano-plano mirror M1 was dichroic coated with high transmittance at 1850-1960 nm and high reflection at 2050-2250 nm. An output coupler (O.C.) with transmission of 20% was utilized in the experiment. The slab was wrapped with indium foil and mounted in a copper block, whose temperature was controlled by water-cooling at 15 °C. The laser output power was measured with a

laser power/energy meter (NOVA II , OPHIR).

Room temperature laser performance of the 0.7 at.% Ho:Y₂O₃ ceramics was evaluated. Figure 5 shows the CW laser output power as a function of the absorbed pump power. The laser threshold was about 2.7 W. The output power increased linearly with the increase of absorbed pump power, and no power saturation was observed. A maximum output power of 1.3 W was achieved at 6.7 W absorbed pump power, corresponding to a slope efficiency of 31.2%. The relative large laser threshold and low conversion efficiency can be attributed to the large cavity losses of the current laser system. As the ceramic was uncoated, the surface Fresnel reflection introduces big cavity losses and degrades the laser performance. Figure 4 (b) shows the typical optical spectrum under the maximum output power of 1.3 W. It can be seen that the center wavelength of the laser was about 2116.8 nm measured with a high resolution optical spectrum analyzer (AQ6375, Yokogawa Electric, Tokyo).

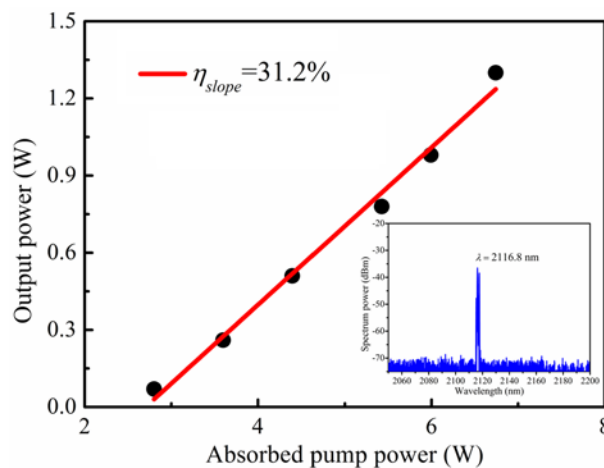


Fig. 5. CW laser output power as a function of the absorbed pump power. Inset, output spectrum of the Ho:Y₂O₃ ceramic laser at 2116.8 nm.

4. Conclusions

Highly transparent 0.7 at.% Ho:Y₂O₃ ceramics were fabricated by using vacuum sintering plus HIPing. The ceramics after vacuum sintering at 1500 °C/12 h achieved a relative density of 97.1%, with a sub-micron grain size of 0.8 μm. After HIPing at 1450 °C for 4 h, the Ho:Y₂O₃ ceramics had an in-line transmission of 80.0% at 600 nm. For the first time, room temperature laser oscillation of the Ho:Y₂O₃ transparent ceramics was demonstrated. A maximum output power of about 1.3 W with slope efficiency of 31.2% was achieved at the 2116.8 nm.

References:

- [1] H. Yang, J. Zhang, X. Qin, D. Luo, J. Ma, D. Tang, H. Chen, D. Shen, Q. Zhang, Polycrystalline Ho:YAG transparent ceramics for eye-safe solid state laser applications, *J. Am. Ceram. Soc.* 95 (1) (2012) 52-55.
- [2] G.A. Newburgh, A. Word-Daniels, A. Michael, L.D. Merkle, A. Ikesue, M. Dubinskii, Resonantly diode-pumped Ho³⁺:Y₂O₃ ceramic 2.1 μm laser, *Opt. Express* 19 (4) (2011) 3604-3611.
- [3] W. Kim, C. Baker, S. Bowman, C. Florea, G. Villalobos, B. Shaw, B. Sadowski, M. Hunt, et al., Laser oscillation from Ho³⁺ doped Lu₂O₃ ceramics, *Opt. Mater. Express* 3 (7) (2013) 913-919.
- [4] G.A. Newburgh, M. Dubinskii, Resonantly diode pumped Ho³⁺:YVO₄ 2.05-μm laser, *Laser Technol. Def. Secur.* VII 8039 (2011) 803905-1-803905-6.
- [5] Z.D. Fleischman, L.D. Merkle, G.A. Newburgh, M. Dubinskii, Spectroscopic analysis of efficient laser material Ho³⁺:YVO₄, *Opt. Mater. Express* 3 (8) (2013) 1176-1186.
- [6] V. Jambunathan, X. Mateos, M.C. Pujol, J.J. Carvajal, M. Aguiló, F. Díaz, U. Griebner, V. Petrov, Diode-pumped Ho-doped KLu(WO₄)₂ laser at 2.08 μm, *Appl. Phys. Express* 4 (7) (2011) 72601-1-72601-3.
- [7] D.Y. Shen, A. Abdolvand, L.J. Cooper, W.A. Clarkson, Efficient Ho:YAG laser pumped by a cladding-pumped tunable Tm: silica-fibre laser, *Appl. Phys. B* 79 (5) (2004) 559-561.

- [8] P. Koopmann, S. Lamrini, K. Scholle, M. Schafer, P. Fuhrberg, G. Huber, Multi-watt laser operation and laser parameters of Ho-doped Lu₂O₃ at 2.12 μm, *Opt. Mater. Express* 1 (8) (2011) 1447-1456.
- [9] P. Koopmann, S. Lamrini, K. Scholle, M. Schäfer, P. Fuhrberg, G. Huber, Holmium-doped Lu₂O₃, Y₂O₃, and Sc₂O₃ for lasers above 2.1 μm, *Opt. Express* 21 (3) (2013) 3926–3931.
- [10] A. Ikesue, Y. Aung, Ceramic laser materials, *Nat. Photonics* 2 (2008) 721–727.
- [11] J. Wang, J. Zhang, K. Ning, J. Ma, D. Luo, D. Yin, H. Yang, D. Tang, L.B. Kong, Densification of zirconia doped yttria transparent ceramics using co-precipitated powders, *Ceram. Int.* 42 (9) (2016) 10770-10778.
- [12] J. Sanghera, W. Kim, G. Villalobos, B. Shaw, C. Baker, J. Frantz, B. Sadowski, I. Aggarwal, Ceramic laser materials, *Materials (Basel)* 5 (12) (2012) 258-277.
- [13] R. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Cryst. A* 32 (1976) 751-767.
- [14] R. Gaumé, B. Viana, D. Vivien, J.-P. Roger, D. Fournier, A simple model for the prediction of thermal conductivity in pure and doped insulating crystals, *Appl. Phys. Lett.* 83 (7) (2003) 1355-1357.
- [15] A. Ikesue, Y.L. Aung, V. Lupei, *Ceramic Lasers*, Cambridge University Press (2013).
- [16] V. Singh, V.K. Rai, B. Voss, M. Haase, R.P.S. Chakradhar, D.T. Naidu, S.H. Kim, Photoluminescence study of nanocrystalline Y₂O₃:Ho³⁺ phosphor, *Spectrochim. Acta Part A* 109 (2013) 206-212.

[17] Y. Nigara, Measurement of the optical constants of yttrium oxide, *Jpn. J. Appl. Phys.* 7 (4) (1968) 404-408.

[18] D.C. Harris, L.R. Cambrea, L.F. Johnson, R.T. Seaver, M. Baronowski, R. Gentilman, C.S. Nordahl, T. Gattuso, et al., Properties of an infrared-transparent MgO:Y₂O₃ nanocomposite, *J. Am. Ceram. Soc.* 96 (12) (2013) 3828-3835.