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Neodymium zirconate ($Nd_2Zr_2O_7$) transparent ceramics as a solid state laser material

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Transparent neodymium zirconate ($Nd_2Zr_2O_7$) ceramics have been fabricated from nanoparticles prepared by combustion synthesis. Emission at 1054.5 nm has been demonstrated using a laser diode pump at 800 nm. A transmittance of 60% at wavelengths longer than ~900 nm was achieved. A consequence of the very high concentration of Nd ions (1.32×10^{28} ions/m^3) is that the absorption bands are wider than those of Nd doped $Y_3Al_5O_{12}$ (Nd:YAG) facilitating pumping over a broader range of wavelengths. The full width at half maximum of the emission peak is also larger than that of Nd:YAG, and the decay time is 460 μs making $Nd_2Zr_2O_7$ an excellent candidate for efficient high-power microchip lasers emitting at 1054 nm with diode pumping at ~800 or ~900 nm. © *2011 American Institute of Physics*. [doi:10.1063/1.3579526]

The development of ever more powerful, room-temperature semiconductor laser diodes continues to spur the search for solid state laser materials that can use these diodes for optical pumping. The search has principally been in the area of neodymium and ytterbium doped materials, such as Nd doped $Y_3Al_5O_{12}$ (Nd:YAG) and the sesqui-oxides, including both single crystals and polycrystalline ceramics. The latter class of material often enables higher concentrations of dopants to be incorporated than is possible in single crystals formed by solidification. In the majority of cases, though, the concentration of the active ion is still limited by concentration quenching of the emission and so the active ion is typically a dopant with low concentration rather than being a major constituent of the host crystal structure. In this contribution we demonstrate that $Nd_2Zr_2O_7$ (NZO), which has the cubic pyrochlore crystal structure, is a candidate solid state laser material for optical pumping of emission from the Nd ions. This suggests that other rare-earth oxides with the pyrochlore structure, such as $Eu_2Zr_2O_7$, might also be candidates for other diode pumped solid state lasers.

Key to the synthesis and densification of transparent material has been the use of combustion synthesis of $Nd_2Zr_2O_7$ powders prepared from nitrates of zirconium and neodymium using ethylene diamine tetra-acetic acid (EDTA) as the fuel. Neodymium nitrate was prepared by dissolving Nd_2O_3 in nitric acid and solutions of $ZrO(NO_3)_2$, were prepared by dissolving $ZrO(NO_3)_2$ in de-ionized water. Mixed solutions containing Nd^{3+} and Zr^{4+} ion were prepared from the as-prepared nitrate solutions to form a $Nd_2Zr_2O_7$ precursor solution with a molar ratio $Nd_2O_3:ZrO_2=1:2$. The solution was continuously stirred at 85–90 °C on a hot plate, and an appropriate amount of EDTA aqueous solution (EDTA to metal ion ratio of 1) was added to the metal ion solution while stirring. The solution slowly became more viscous, turning into a gel. The gel was then placed into a furnace preheated to 500 °C for the combustion, resulting in a tan-colored powder. This powder was then calcined for 2 h at 950 °C.

Although the powders are slightly agglomerated because of the formation of particle necks by sintering at the high calcining temperature, the average particle size is about 40 nm. An example is shown by the transmission electron microscopy (TEM) micrograph in the inset to Fig. 1. The particle morphology is near spherical, which also proves beneficial to fabrication of transparent ceramics. X-ray diffraction indicated that the powder was phase-pure $Nd_2Zr_2O_7$ and fully crystalline at this stage. In the next step in the fabrication, the powder was cold pressed into disks ≈20 mm in diameter at 70 MPa and then cold isostatically pressed at 200 MPa. Specimens were then pre-sintered at 1000 °C for 2 h in air to remove any residual organics. Finally, disk-shaped samples were sintered in dry hydrogen at 1800 °C for 6–12 h using a heating rate of 15 °C/min. After sintering, the samples were annealed at 1200 °C for 4 h in air for strain relief, then cooled down to room temperature in the furnace. X-ray diffraction of the sintered oxide indicates that the ma-

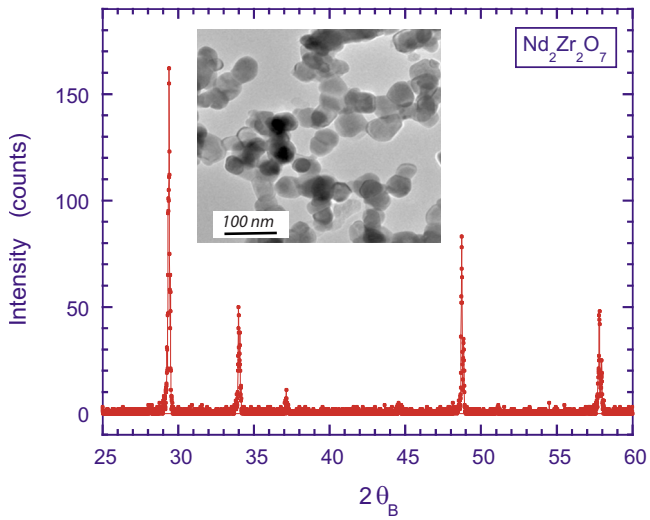

FIG. 1. (Color online) X-ray diffraction of a $Nd_2Zr_2O_7$ sample after sintering at 1800 °C for 6 h in hydrogen indicating that the material is single phase pyrochlore. The inset is a TEM micrograph of the powder after calcining at 950 °C but before sintering. The average particle size is ~50 nm.

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FIG. 2. (Color online) Transparent $Nd_2Zr_2O_7$ pellets sintered under hydrogen atmosphere at 1800 °C for 6 h (polished, thickness=1 mm).

terial is a single phase pyrochlore as shown in Fig. 1.

The samples obtained were transparent but had a grayish hue as shown in Fig. 2. Moreover, objects 1 or 2 m away could be resolved through polished 1 mm thick disks when held to the eye. Optical transmission spectra were obtained on a UV 2501 PC spectrophotometer (Shimadzu, Japan) from 200 to 1100 nm. The spectral transmittance of a 1.5 mm thick sintered $Nd_2Zr_2O_7$ disk is compared to that of a Nd:YAG (Nd doped $Y_3Al_5O_{12}$) ceramic disk of the same thickness in Fig. 3. As expected, both compounds exhibit the same absorption bands. Notably, though, all the absorption bands, particularly those of interest for optical pumping 900, 800, 750, 590 nm, are all significantly broader as evident from the spectra. In part this is attributed to the higher concentration of Nd ions in $Nd_2Zr_2O_7$. It is also because of the different crystal field splitting associated with the crystallographic site symmetry of the Nd^{3+} ions in $Nd_2Zr_2O_7$; Nd^{3+} ions in $Nd_2Zr_2O_7$ have a D_{3d} symmetry whereas the site symmetry of Nd^{3+}, which substitutes for the Y^{3+} ions in YAG, is D_2.[1] As shown in Fig. 3, the transmittance of $Nd_2Zr_2O_7$ is lower than that of Nd:YAG, which is consistent with the differences in their refractive indices (Table I). Based on their refractive indices, the ideal transmittance in the absence of scattering or absorbance would be 71.8% for $Nd_2Zr_2O_7$ and 84% for YAG.

The emission spectra and fluorescence lifetime were obtained by exciting the sample at room temperature with a 800 nm GaAlAs diode laser (pulse width: <5 μs; pulse frequency: 20 Hz; output power: 100 mW), through an infrared optical fiber with a numerical aperture of 100 μm. A Fluorolog-3 spectrofluorimeter (Jobin Yvon) and R5509-72 detector (Hamamatsu, Japan) were also used for the measurements. An example of the emission spectrum of NZO excited by 800 nm LD laser is presented in Fig. 4. The emission peak is at 1054.5 nm, which is somewhat shorter than that of Nd:YAG (1064 nm). The fluorescence lifetime of NZO transparent ceramics was found to be approximately 460 μs, which is almost twice the 240 μs reported for 1% Nd:YAG,[2] but similar to that of 1%Nd:$YLiF_4$ (Table I).

Comparison of the crystal structures and average Nd–Nd ion distances in $Nd_2Zr_2O_7$ and in other Nd laser materials provides an explanation for the potential of $Nd_2Zr_2O_7$ as a laser host material. Table I compares the Nd concentration and the refractive index of Nd_2O_3, Nd:YAG, $KNd(PO_3)_4$, $NdAl_3(BO_3)_4$ with that of $Nd_2Zr_2O_7$. As the lattice parameter of $Nd_2Zr_2O_7$ is 1.0648 nm,[3] and the number of formula units in the unit cell, Z=8, the Nd concentration of $Nd_2Zr_2O_7$ is near 1.32×10^{28} ions/m^3. This is higher than either $KNd(PO_3)_4$ phosphate and $NdAl_3(BO_3)_4$ borate, which have concentrations of $\sim5\times10^{27}$ ions/cm^3)[4] but notably less than in Nd_2O_3. As the average Nd–Nd distance between ions varies with the inverse cube of the concentration, the average Nd–Nd distance in $Nd_2Zr_2O_7$ falls between that of Nd_2O_3 and Nd:YAG. Another significant difference is that in there is considerable statistical variation in the distance between Nd ions in Nd:YAG, which is determined by substitutional disorder, whereas in $Nd_2Zr_2O_7$ the spacing between Nd ions is fixed by their positions in the unit cell. This is possibly responsible for the significantly longer room temperature lifetime exhibited by the $Nd_2Zr_2O_7$ ceramic.

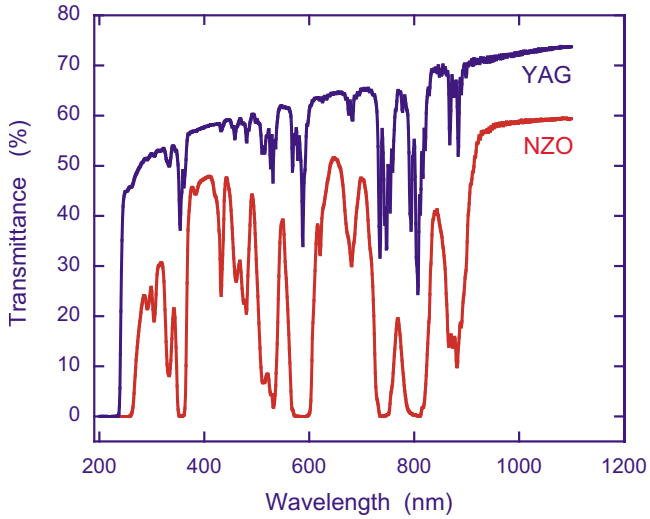

FIG. 3. (Color online) Comparison of the spectral transmittance of 1 mm thick disks of $Nd_2Zr_2O_7$ and YAG transparent ceramics.

The combination of broad full width at half maximum (FWHM) absorption bands, larger FWHM emission and the longer lifetime makes $Nd_2Zr_2O_7$ an attractive material for high-power applications. The broader absorption bands, especially at ~800 and ~900 nm, reduce the requirements for temperature stability of the pump laser. The ability to pump at ~900 rather than ~800 nm, reduces the heat generated during pumping. In addition, the broader emission at 1054.5 nm implies that a shorter laser pulse can be created than using Nd:YAG as a laser material. Studies of the dependence of pump power on output power are underway and will be reported later.

TABLE I. Characteristic features of Nd laser host materials.

Compound	Nd concentration (ions/m^3)	Average Nd–Nd distance (nm)	Refractive index	Lifetime (μs)	Emission FWHM (nm)
Nd_2O_3	1.29×10^{30}	0.376	n_x=2.11, n_z=2.1 (Ref. 6)	···	None concentration quenching
Nd (1 at %):YAG	1.38×10^{26}	1.935	1.82	240	5 @ 1064 nm
$KNdP_4O_{12}$	4.08×10^{27}(Ref. 4)	0.698	n_x=1.592, n_y=1.600 n_z=1.608 @632 nm (Ref. 7)	90 (Ref. 7)	5 @ 1051 nm (Ref. 4)
$NdAl_3(BO_3)_4$	5.43×10^{27} (Ref. 7)	0.560	n=1.75 @ 1.06 μm (Ref. 8)	16 (Ref. 9)	2.5–3 @1065 nm (Ref. 4)
$Nd_2Zr_2O_7$	1.32×10^{28}	0.463	2.11 (Ref. 10)	460	20 @ 1054.5 nm
Nd (1a/o): $YLiF_4$	1.39×10^{26}	1.928	n_o=1.45 n_e=1.47 (Ref. 11)	460 (Ref. 2)	20 @ 1054.7 nm (Ref. 12)

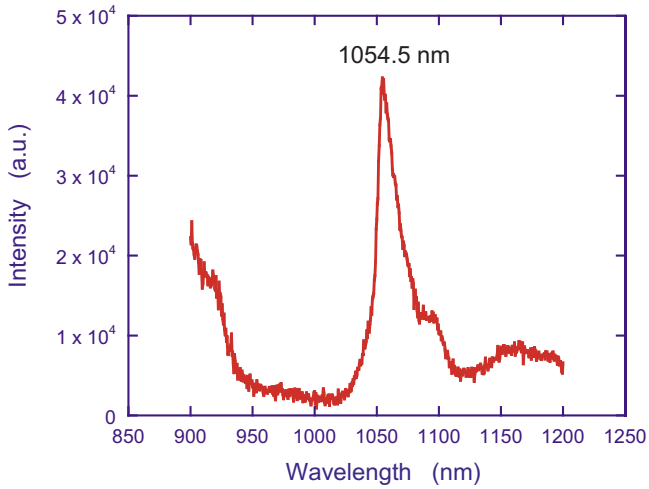

FIG. 4. (Color online) Emission at 1054.5 nm from a 1 mm thick $Nd_2Zr_2O_7$ transparent disk pumped with a 800 nm GaAlAs diode laser.

In summary, we have fabricated transparent $Nd_2Zr_2O_7$ ceramics from nanocrystalline powders prepared by a combustion method and shown that they emit at 1054.5 nm when pumped with a semiconductor 800 nm laser diode. The results also suggest that other rare-earth pyrochlores and the related delta-phase crystal structures may also promising laser materials. For instance, strong emission and long lifetimes (1 ms) at room temperature have previously been reported from $Eu_2Zr_2O_7$.[5]

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