

Rare-earth doped transparent ceramics for spectral filtering and quantum information processing

Nathalie Kunkel,^{1,a} Alban Ferrier,^{1,2} Charles W. Thiel,³ Mariola O. Ramírez,⁴ Luisa E. Bausá,⁴ Rufus L. Cone,³ Akio Ikesue,⁵ and Philippe Goldner^{1,b}

¹PSL Research University, Chimie ParisTech–CNRS, Institut de Recherche de Chimie Paris, 11 rue Pierre et Marie Curie, 75005 Paris, France

²Sorbonnes Universités, UPMC Univ Paris 06, 75005 Paris, France

³Department of Physics, Montana State University, Bozeman, Montana 59717, USA

⁴Departamento Física de Materiales and Instituto Nicolás Cabrera, Universidad Autónoma de Madrid, 28049 Madrid, Spain

⁵World Laboratory, Mutsuno, Atsuta-ku, Nagoya 456-0023, Japan

(Received 20 July 2015; accepted 26 August 2015; published online 9 September 2015)

Homogeneous linewidths below 10 kHz are reported for the first time in high-quality Eu^{3+} doped Y_2O_3 transparent ceramics. This result is obtained on the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ transition in Eu^{3+} doped Y_2O_3 ceramics and corresponds to an improvement of nearly one order of magnitude compared to previously reported values in transparent ceramics. Furthermore, we observed spectral hole lifetimes of ~ 15 min that are long enough to enable efficient optical pumping of the nuclear hyperfine levels. Additionally, different Eu^{3+} concentrations (up to 1.0%) were studied, resulting in an increase of up to a factor of three in the peak absorption coefficient. These results suggest that transparent ceramics can be useful in applications where narrow and deep spectral holes can be burned into highly absorbing lines, such as quantum information processing and spectral filtering. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4930221>]

Trivalent rare-earth ions doped into single crystals have optical transitions that can exhibit very narrow homogeneous and inhomogeneous linewidths in which deep spectral holes can be burned at liquid helium temperatures.¹ Due to these properties, such materials are of great interest for application in quantum information processing (QIP)^{2–5} and spectral filtering. The latter includes radio frequency signal analysis,^{6,7} highly stable laser-locking,^{8,9} and ultrasound optical tomography (UOT).^{10,11} Recently, rare-earth doped transparent ceramics have been suggested as an alternative class of materials for these applications,¹² as for lasers¹³ and scintillators.¹⁴ Indeed, the ability of ceramics to be shaped into complex structures could be used to control the effects of perturbations on the optical transitions (e.g., frequency shifts) due to strain, vibrations, temperature, or pressure.^{8,15,16} This is particularly relevant when samples are cooled in closed-cycle cryostats that are inherently noisy. The isotropy of the ceramics due to their polycrystalline structure could also provide an averaging effect with respect to perturbations. Finally, transparent ceramics can be obtained in large dimensions useful when dealing with large étendues beams, as in UOT.¹⁰

Key spectroscopic parameters for the above applications are^{2,3,17,18} (i) the homogeneous linewidth Γ_h that determines spectral filtering resolution and quantum processing time, (ii) the absorption coefficient related to filtering and quantum memories' efficiencies, and (iii) the spectral hole lifetime that sets the residual ground state population after optical pumping in low-symmetry sites and filtering efficiency and quantum processing fidelity. As a single crystal, $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ is an attractive material showing among the lowest Γ_h and longest spectral hole lifetimes.^{5,19–22} However,

^aElectronic mail: nathalie.kunkel@chimie-paristech.fr

^bElectronic mail: philippe.goldner@chimie-paristech.fr

single crystals are very difficult to grow due to their high melting temperature (2400 °C) and phase transition below the melting point, resulting in uncontrolled variations in properties.¹⁹ Transparent Y_2O_3 ceramics could be an alternative to single crystals, and indeed, we measured $\Gamma_h = 59$ kHz in a 0.1% Eu: Y_2O_3 sample.¹² Although this value is still on the higher side of values measured on single crystals, it suggests that ceramics could be useful for applications in spectral filtering and QIP.

Here, we provide further evidence for the potential of these materials. In transparent 0.5 and 1 at. % Eu^{3+} -doped yttria ceramics, we demonstrate an order of magnitude decrease in homogeneous linewidth and a factor of three increase in peak absorption compared to our previous results. Moreover, we measure for the first time the spectral hole lifetime in a ceramic and find that it can exceed 15 min at 6 K, which enables the efficient optical pumping necessary for spectral filtering and QIP applications.

The transparent ceramics were prepared according to the procedure described in Ref. 12 with 99.999% pure Y_2O_3 and 99.99% pure Eu_2O_3 powders. 0.5 at. % ZrO_2 was added to some samples in order to reach higher transparency, as in ceramics used as laser gain media.²³ Grain sizes were determined by optical microscopy. An average grain size of about 2 μm was observed at the center of all ceramics where the optical measurements were carried out. X-ray diffraction data were collected on a *Bruker D8 Advance* with focusing Bragg-Brentano geometry. Y_2O_3 crystallizes in the rare-earth sesquioxide C-type structure, space group $Ia\bar{3}$. Eu^{3+} can occupy two sites of C_2 and S_6 symmetries and all optical experiments were performed on the former, for which electric dipole transitions are stronger. Crystal structure refinement was carried out via Rietveld analysis using TOPAS 4.2²⁴ together with the fundamental parameter approach.²⁵ The samples were single phase and showed very sharp reflections, which were narrower than those of the reference standard LaB_6 , and strain was negligible within the resolution of the instrument. Crystallite sizes were found to be larger than 1 μm , in agreement with optical microscopy results. Refined lattice constants are given in Table I. An increase of a with increasing Eu^{3+} concentration is observed as expected from the slightly larger effective ionic radius of Eu^{3+} compared to Y^{3+} (IR (Eu^{3+} , VI): 0.950 Å, IR (Y^{3+} , VI): 0.892 Å²⁶). This finding, together with the observation of very narrow reflections, suggests that Eu^{3+} is well incorporated into the crystallites. Substitution of Y^{3+} by Zr^{4+} (IR 0.72 Å, VI) leads to a small decrease in a .

Measurements of the inhomogeneous and homogeneous linewidths as well as the hole lifetime were carried out. Inhomogeneous linewidths of the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transition were recorded in transmission using a cw dye laser with a 1-MHz linewidth centered at 580.87(5) nm (vacuum). They were recorded at 15 K and at low laser intensity (~ 2 mW/cm²) to avoid hole burning and transition saturation effects. Homogeneous linewidths were determined by two pulse photon echo experiments at the center of the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transition, while the laser was scanning 1 GHz in ~ 3 s to minimize hole burning. The length of the exciting and rephasing pulses was 3.1 and 4 μs , respectively. A single exponential decay of the photon echo intensity as a function of pulse separation was observed. In order to measure the lifetime of spectral holes, first, a spectral hole was burned into the absorption line and afterwards scanned every 60 s with a weak intensity and 1 ms long laser pulse.

Values for the transmission at 580 nm are given in Table I. Reflection losses of about 10% are expected at each surface due to the yttria refractive index at 580 nm $n = 1.9318$. The transmission

TABLE I. Refined lattice constants of $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ transparent polycrystalline ceramics (space group $Ia\bar{3}$), room temperature transmission extrapolated at 580 nm without taking Eu^{3+} absorption into account (sample thickness: 6.1 mm), absorption coefficients for the center of the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ line at 15 K, inhomogeneous linewidths at 15 K, $^5\text{D}_0$ excited state lifetimes T_1 , and coherence lifetimes T_2 .

[Eu ³⁺] (%)	Additive	Refined a (Å)	Transmission (%)	α (cm ⁻¹)	Γ_{inh} (GHz)	T_1 (μs)	T_2 (μs)
0.5	None	10.606 17(2)	48	1.0	19.5	941	42
0.5	ZrO ₂	10.604 57(1)	64	<0.1	>100	943	35
1.0	None	10.607 55(1)	42	1.6	24.2	986	42
1.0	ZrO ₂	10.606 0(2)	73	0.3	70	947	...
0.1 ¹²	None	0.5	8.7	~ 1000	5.4

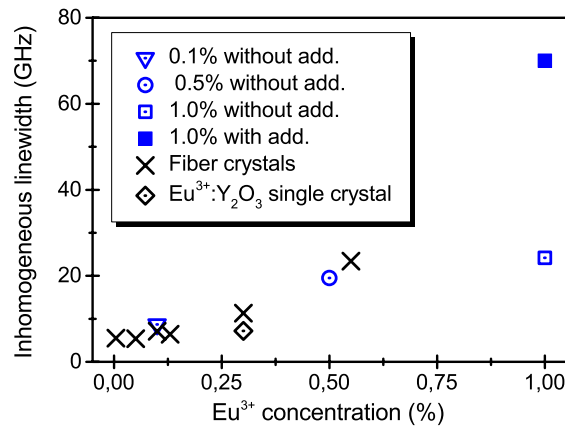


FIG. 1. Γ_{inh} of $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ transparent ceramics and crystals. Values of the 0.1% $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ ceramic and the single crystal fibers are taken from Refs. 12 and 19.

of approximately 70% found in the samples with additives is therefore not far from the theoretical limit of 81%, whereas ceramics without additives show a transmission of only 40%-50%. Thus, as expected, the use of additives leads to a significant reduction in scattering losses. In Fig. 1, the inhomogeneous linewidths Γ_{inh} obtained for the ceramics are compared to those found in the single crystal fibers studied in Ref. 19. For comparison, we also measured the laser absorption spectrum of a bulk 0.3% $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ single crystal sample where we observed an inhomogeneous linewidth of 7.2 GHz.

The observed inhomogeneous linewidths Γ_{inh} for samples without additives are within the range of those observed for single crystals (Table I). Interestingly, for the 1% doped ceramic, $\Gamma_{inh} = 24.2$ GHz is close to the value of 19.5 GHz found in the 0.5% one. This suggests that the linewidth is only partly due to the mismatch between Eu^{3+} and Y^{3+} effective ionic radii (Ref. 26). Because of the weak dependence of Γ_{inh} on Eu^{3+} concentration, peak absorption coefficients of 1.6 cm^{-1} were observed in the 1% doped ceramic, about three times higher than that found in a 0.1% doped sample.¹² The product $\Gamma_{inh} \times \alpha$ scales linearly with Eu^{3+} concentration, indicating that the transition oscillator strength does not vary significantly with doping concentration. Table I also shows that the addition of 0.5% ZrO_2 during the synthesis leads to a very large broadening of the absorption line and a corresponding decrease in the peak absorption coefficient. This is explained by both the charge and ionic radii mismatches between Zr^{4+} and Y^{3+} ions (see discussion above and Ref. 16). Thus, while addition of 0.5% ZrO_2 decreases scattering losses, it also leads to a factor of three increase in linewidth and a strong reduction of the peak absorption coefficient. Such a low absorption would make spectral filtering or quantum storage rather inefficient. A lower level or different additives²³ could lead to a better compromise between transparency and absorption.

The dependence of the homogeneous linewidths Γ_h of the 0.5% sample without ZrO_2 on the laser power is shown in Fig. 2. A linear increase in linewidth with increasing excitation power is observed and related to an instantaneous spectral broadening due to ion-ion interactions.²⁷⁻²⁹ The extrapolated zero power homogeneous linewidths are $\Gamma_h = 7.5 \pm 0.2$ kHz (corresponding to a coherence lifetime $T_2 = 1/(\pi\Gamma_h)$ of 42 μs) at 3.5 K. The same value was found for the 1.0% sample without additives, while the 0.5% sample with additives showed a slightly larger homogeneous linewidth of 9.2 ± 0.6 kHz ($T_2 = 35 \mu\text{s}$). Even though those homogeneous linewidths are still about one order of magnitude larger than that observed in the very best crystal known ($\Gamma_h = 760$ Hz),²⁰ they are in the lower range of values observed for $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ crystals ($\Gamma_h = 2.4 - 42$ kHz¹⁹) and considerably narrower than that previously reported in transparent ceramics $\Gamma_h = 59$ kHz.¹² The contribution to the homogeneous linewidth Γ_h from the excited state population is given by $\Gamma_{pop} = 1/(2\pi T_1)$. The excited-state lifetimes measured in the ceramic samples (Table I) are similar to those reported for single crystals.¹⁹ Thus, Γ_{pop} is less than 200 Hz and therefore much smaller than the observed Γ_h .

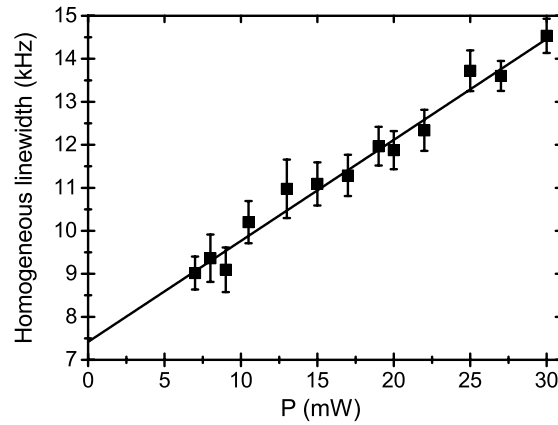


FIG. 2. Power dependence of Γ_h in the 0.5% $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ ceramic without additives at 3.5 K.

Other possible contributions to Γ_h are dynamic structural fluctuations due to tunneling between configurations with nearly equal energy referred to as two-level systems (TLSs). However, a considerable influence of this process, usually found in disordered environments like amorphous solids, can be excluded on the basis of the temperature dependence of the homogeneous linewidth (Fig. 3). Indeed, in case of pronounced TLS influence, a “quasi-linear” temperature dependence of Γ_h in the low temperature regime is expected.¹⁹ Here, a behavior similar to that of single crystals is observed (Fig. 3) with a nearly flat region up to 9 K followed by a steep increase due to phonon scattering typical of single crystals.¹⁹ The same result was also previously obtained in the 0.1% Eu^{3+} doped transparent ceramics.¹²

The remaining contribution to Γ_h at low temperature should come from electronic and nuclear spin fluctuations.¹ As the magnetic moments of Y^{3+} and O^{2-} are both small, the influence of spin fluctuations $\Gamma_{ion-spin}$ in pure Y_2O_3 is predicted to be small, as evidenced by the observation of very long T_2 in one single crystal.²⁰ Given the low Eu^{3+} magnetic moment, Eu-Eu spin interactions are also unlikely to be a limitation even at a concentration of 1%, as observed in $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$.¹⁶ The additional dephasing in the ceramics is therefore attributed to magnetic impurities, e.g., very small amounts of transition metal ions or defects.^{12,19,30,31} This is in very good agreement with the presence of electron spin impurities (probably transition metal ions) detected by electron paramagnetic resonance for previous samples^{12,32} with larger Γ_h . For the samples studied here, these impurities could not be detected, presumably because of the higher purity of the Y_2O_3 starting material (99.999% vs. 99.99%). This is likely to be the reason for their narrower Γ_h , although other defects (produced, e.g., during thermal treatments) could also play a role. The fact that T_2 does not

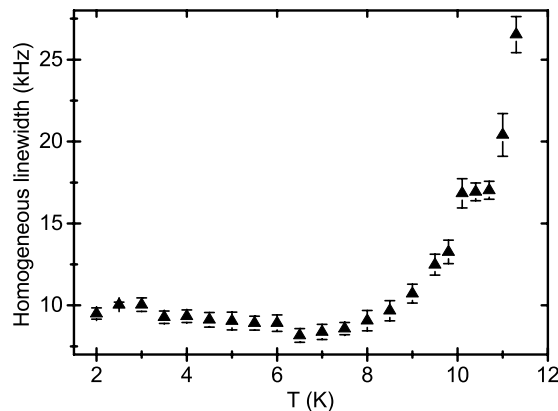


FIG. 3. Temperature dependence of Γ_h in 0.5% $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ without additives (16 mW laser power).

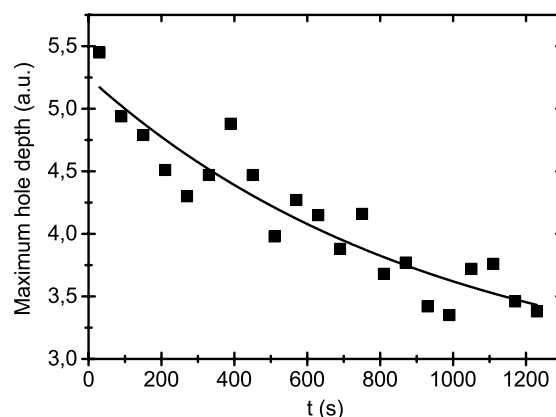


FIG. 4. Decay of the spectral hole in the 0.5% $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ ceramic without additives at 6 K.

significantly vary for samples with additive also suggests that T_2 is still limited by paramagnetic impurities or defects in the samples studied here. Indeed, additional dephasing due to $^{91}\text{Zr}^{4+}$ nuclear spins ($I = 5/2$, abundance 11.2%) is not observed.

Finally, we studied the persistent spectral hole lifetime in a 0.5% $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ sample without additives. The decay of the spectral hole depth at 6 K is shown in Fig. 4. An exponential fit to the data gives $T_{\text{hole}} = 15 \pm 5$ min. As the holes were several MHz wide due to laser jitter, T_{hole} is unlikely to include a contribution from spectral diffusion. The ratio $T_{\text{hole}}/T_1 = 9 \times 10^5$ is high enough to lead to negligible residual ground state population after optical pumping.^{17,21} This conclusion would hold even better at lower temperatures, as at 3.5 K the hole depth showed no decay within 30 min. We note that the hole lifetime at 6 K is shorter than that of the single crystal studied in Ref. 21 (≈ 54 h at 6 K), which could be due to interactions with small amounts of flipping magnetic impurities or defects.

In conclusion, we have observed homogeneous linewidths below 10 kHz in Y_2O_3 transparent ceramics doped with 0.5 and 1% Eu^{3+} . This is about one order of magnitude lower than values previously reported in ceramics. The higher Eu^{3+} concentration also increases the peak absorption coefficient to a value of 1.6 cm^{-1} at 580.87 nm with an inhomogeneous broadening of 24.2 GHz for the 1% Eu-doped samples. Hole lifetimes of 15 ± 5 min have been obtained, allowing for efficient optical pumping and spectral tailoring. Together, these results suggest that high quality transparent ceramics can meet the requirements of spectral filtering and quantum information processing applications, while providing advantageous structural properties (e.g., complex shaping) compared to single crystals.

This work was supported by the ANR projects RAMACO (No. 12-BS08-0015-01) and DIS-CRYS (No. 14-CE26-0037-01), Idex No. ANR-10-IDEX-0001-02 PSL★, and Nano’K project RECTUS. C.W.T. and R.L.C. acknowledge support from National Science Foundation (NSF) Award Nos. CHE-1416454 and PHY-1415628 and M.O.R. and L.E.B. from Project No. MAT2013-43301-R of the Spanish Ministry of Economy and Competitiveness (MINECO) and Comunidad Autónoma de Madrid under Grant No. S2013/MIT-2740. We would like to thank L. Binet for help with the EPR measurements, R. M. Macfarlane for providing the $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ single crystal, R. Haberkorn for help with the XRD analysis, and J. Bartholomew for useful comments.

¹ R. M. Macfarlane, *J. Lumin.* **100**, 1 (2002).

² W. Tittel, M. Afzelius, T. Chanelière, R. L. Cone, S. Kröll, S. A. Moiseev, and M. J. Sellars, *Laser Photonics Rev.* **4**, 244 (2010).

³ Ph. Goldner, A. Ferrier, and O. Guillot-Noël, *Handbook on the Physics and Chemistry of Rare Earths* (North Holland, Amsterdam, 2015), Vol. 46, p. 1.

⁴ F. Bussi eres, C. Clausen, A. Tiranov, B. Korzh, V. B. Verma, S. W. Nam, F. Marsili, A. Ferrier, Ph. Goldner, H. Herrmann, C. Silberhorn, W. Sohler, M. Afzelius, and N. Gisin, *Nat. Photonics* **8**, 775 (2014).

⁵ C. W. Thiel, T. B ottger, and R. L. Cone, *J. Lumin.* **131**, 353 (2011).

⁶ J.-L. Le Gou  t, F. Bretenaker, and I. Lorger  , in *Advances in Atomic, Molecular, and Optical Physics*, edited by P. R. Berman, C. C. Lin, and E. Arimondo (Elsevier, 2006), Vol. 54, p. 549.

- ⁷ H. Linget, T. Chanelière, J.-L. Le Gouët, P. Berger, L. Morvan, and A. Louchet-Chauvet, *Phys. Rev. A* **91**, 023804 (2015).
- ⁸ M. J. Thorpe, L. Rippe, T. Fortier, M. S. Kirchner, and T. Rosenband, *Nat. Photonics* **5**, 688 (2011).
- ⁹ P. B. Sellin, N. M. Strickland, J. L. Carlsten, and R. L. Cone, *Opt. Lett.* **24**, 1038 (1999).
- ¹⁰ Y. Li, H. Zhang, C. Kim, K. Wagener, P. Hemmer, and L. V. Wang, *Appl. Phys. Lett.* **93**, 011111 (2008).
- ¹¹ H. Zhang, M. Sabooni, L. Rippe, C. Kim, S. Kröll, L. V. Wang, and P. R. Hemmer, *Appl. Phys. Lett.* **100**, 131102 (2012).
- ¹² A. Ferrier, C. W. Thiel, B. Tumino, M. O. Ramirez, L. E. Bausá, R. L. Cone, A. Ikesue, and Ph. Goldner, *Phys. Rev. B* **87**, 041102 (2013).
- ¹³ A. Ikesue and Y. L. Aung, *Nat. Photonics* **2**, 721 (2008).
- ¹⁴ S. R. Podowitz, R. Gaumé, and R. S. Feigelson, *J. Am. Ceram. Soc.* **93**, 82 (2010).
- ¹⁵ M. J. Thorpe, D. R. Leibrandt, and T. Rosenband, *New J. Phys.* **15**, 033006 (2013).
- ¹⁶ F. Könz, Y. Sun, C. W. Thiel, R. L. Cone, R. Equall, R. Hutcheson, and R. M. Macfarlane, *Phys. Rev. B* **68**, 085109 (2003).
- ¹⁷ S. Hastings-Simon, B. Lauritzen, M. U. Staudt, J. L. M. van Mechelen, C. Simon, H. de Riedmatten, M. Afzelius, and N. Gisin, *Phys. Rev. B* **78**, 085410 (2008).
- ¹⁸ B. Lauritzen, N. Timoney, N. Gisin, M. Afzelius, H. de Riedmatten, Y. Sun, R. M. Macfarlane, and R. L. Cone, *Phys. Rev. B* **85**, 115111 (2012).
- ¹⁹ G. P. Flinn, K. W. Jang, J. Ganem, M. L. Jones, R. Meltzer, and R. M. Macfarlane, *Phys. Rev. B* **49**, 5821 (1994).
- ²⁰ R. M. Macfarlane and R. M. Shelby, *Opt. Commun.* **39**, 169 (1981).
- ²¹ W. R. Babbitt, A. Lezama, and T. W. Mossberg, *Phys. Rev. B* **39**, 1987 (1989).
- ²² M. J. Sellars, R. S. Meltzer, P. T. H. Fisk, and N. B. Manson, *J. Opt. Soc. Am. B* **11**, 1468 (1994).
- ²³ L. Zhang, Z. Huang, and W. Pan, *J. Am. Ceram. Soc.* **98**, 824 (2015).
- ²⁴ Bruker, TOPAS V4.2, General profile and structure analysis software for powder diffraction data, AXS, Karlsruhe, Germany, 2008.
- ²⁵ A. A. Coelho, *J. Appl. Crystallogr.* **36**, 86 (2003).
- ²⁶ R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.* **25**, 925 (1969).
- ²⁷ R. L. Cone and G. K. Liu, *Bull. Am. Phys. Soc.* **33**, 676 (1988).
- ²⁸ J. Huang, J. M. Zhang, A. Lezama, and T. W. Mossberg, *Phys. Rev. Lett.* **63**, 78 (1989).
- ²⁹ C. W. Thiel, R. M. Macfarlane, Y. Sun, T. Böttger, N. Sinclair, W. Tittel, and R. L. Cone, *Laser Phys.* **24**, 106002 (2014).
- ³⁰ R. M. Macfarlane, Y. Sun, R. L. Cone, C. W. Thiel, and R. W. Equall, *J. Lumin.* **107**, 310 (2004).
- ³¹ A. Perrot, Ph. Goldner, D. Giaume, M. Lovrić, C. Adriamiamanana, R. R. Goncalves, and A. Ferrier, *Phys. Rev. Lett.* **111**, 203601 (2013).
- ³² N. Kunkel *et al.*, “Influence of preparation method and defects on the coherence properties of rare earth doped ceramics” (unpublished).