Rare Earth Distribution in Na*R*F_4: Effect on Up-Conversion Intensity

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The $NaYF_4$:Yb^{3+},Tb^{3+} (x_{Yb}: 0.20, x_{Tb}: 0.04) materials were prepared by the co-precipitation method. The as-prepared material was washed with and without water and thereafter annealed at 500 °C. This resulted in materials with moderate (with water) and very high (without water) up-conversion luminescence intensity. The structural details causing the differences in luminescence intensity were investigated at room temperature with X-ray powder diffraction and Rietveld analyses. All materials crystallized in the hexagonal form ($P6_3/m$, No. 176, Z: 1.5) with a composition very close to stoichimetric. The local structural details revealed microstrains in the rare earth sublattice that were relaxed for the material with very high up-conversion luminescence intensity thus decreasing energy losses and enhancing up-conversion.

Key Words: X-ray powder diffraction, up-conversion, ytterbium, terbium, $NaYF_4$

https://doi.org/10.1017/S0885715613001164 Published online by Cambridge University Press

I. INTRODUCTION

Up-conversion (*UPC*) luminescence materials convert lower energy radiation to higher energy one by piling up photons *via* long-lived excited states (see Auzel, 2004, for a review). Currently, the most efficient and intense up-conversion luminescence from NIR to visible is obtained by using the combination of an Yb^{3+} sensitizer (absorber) and an Er^{3+} activator (emitter). These materials show the green and/or red emission of Er^{3+} with the intensity ratio depending on the efficiency of quenching processes. Other established combinations already used in commercial *UPC* materials are Yb^{3+}+Ho^{3+} (green emission) and Yb^{3+}+Tm^{3+} (blue). The up-conversion phenomenon has applications in *e.g.* anti-counterfeit security marking, lighting and display technology as well as in IR quantum counters (Auzel, 2004). Nanomaterials with efficient *UPC* luminescence are also very attractive reporters in quantitative homogeneous whole blood immunoassays (Kuningas *et al.*, 2005). The *UPC* materials have been shown to enhance the harvesting of solar energy both in photosynthesis (Antal *et al.*, 2012) and solar cells (Shalav *et al.*, 2005).

The Na*R*F_4 (*R*: rare earth) materials are known to exist in three different structures – all stable at room temperature (Harju *et al.*, 2011). As a result of annealing below 400 °C or above 700 °C, the Na*R*F_4 material crystallizes in a cubic fluorite (CaF_2) type structure ($Fm\bar{3}m$, No. 225, *Z*: 2). The high-temperature cubic form has the Na and *R* atoms randomly occupying the single cation site, whereas the low-temperature form shows partial cation ordering. Following annealing at intermediate temperatures, the structure of Na*R*F_4 becomes hexagonal ($P6_3/m$, No. 176, *Z*: 1.5).

$NaYF_4$ is considered as one of the best host matrices for *UPC* luminescence materials, but only if the structure is hexagonal (Hyppänen *et al.*, 2010). The hexagonal $NaYF_4$:Yb^{3+},Er^{3+} form was found to be close to stoichiometric, whereas the low- and high-temperature cubic ones are clearly enriched in rare earths, which requires additional fluoride for charge compensation. The hexagonal form thus contains less defects to quench luminescence resulting in superior *UPC* efficiency in comparison with the cubic ones. The more compact hexagonal structure with shorter *R*-*R* distances may favor the $Yb^{3+}\rightarrow Er^{3+}$ energy transfer (Harju *et al.*, 2011), as well.

Hexagonal $NaYF_4$:Yb^{3+},Tb^{3+} has been reported to show *UPC* luminescence influenced by an Er^{3+} impurity (Brito *et al.*, 2012). The up-conversion intensity from Tb^{3+} can be enhanced by 1 to 2 orders of magnitude by not using washing with water before annealing (Hölsä *et al.*, 2012). In

https://doi.org/10.1017/S0885715613001164 Published online by Cambridge University Press

this work, the structural details causing this enhancement were studied by X-ray powder diffraction data.

II. EXPERIMENTAL

The $Na(Y_{0.76}Yb_{0.20}Tb_{0.04})F_4$ materials were prepared by co-precipitation from a mixture of aqueous solutions of NaF and RCl_3 using a high Na/*R* ratio (12.5) to force the formation of the $NaRF_4$ phase instead of RF_3. This procedure has been described in detail earlier (Hyppänen *et al.*, 2010). Part of the as-prepared low-temperature cubic form was washed with water and ethanol and the other only with ethanol. Both were thereafter annealed at 500 °C for 5 h in static N_2 + 10 % H_2 to produce the hexagonal form.

The NIR-vis up-conversion luminescence spectra were measured at room temperature with an Ocean Optics PC2000-CCD spectrometer using a 200 μm optical fiber. The NIR excitation (λ_{exc}: 976 nm) source was a Hamamatsu L9418-04 NIR laser diode. The sample was inside a capillary tube and the emission was collected at a 90^o angle to the excitation.

The room temperature XPD data were collected with a Huber G670 image plate Guinier camera (2θ range: 4-100°, data interval: 0.005°). The dataset was summed from twelve half an hour measurements. Preferred orientation was minimized by oscillating the sample horizontally. Monochromatic copper $K_{\alpha 1}$ radiation (λ: 1.5406 Å) was used. The Rietveld analyses (Rietveld, 1969) were carried out with the FullProf2k program (Rodriguez-Carvajal, 2007).

The microstrains and crystallite sizes were calculated from the reflection widths of the whole diffraction pattern by Williamson-Hall plots [Eq.] (Williamson and Hall, 1953; Ungár, 2000). The relative reflection broadening (ΔK) is defined as:

$$\Delta K = (1/D) + 2\varepsilon d^*$$

where $\Delta K = 2\cos\theta(\Delta\theta)/\lambda$ with Δθ equal to a half of FWHM (in radians), D the crystallite size, ε the strain and d^* the reciprocal d spacing (= $2\sin\theta/\lambda$). The crystallite size and the r.m.s. strain were obtained from the intercept and the slope of the ΔK vs. d^* plot, respectively. Silicon powder (NIST standard 640b) was used as the reference for reflection widths.

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III. RESULTS AND DISCUSSION

A. General characterization

All materials studied were found to crystallize in the hexagonal $NaYF_4$ structure. No impurities were detected, but the material washed with both water and ethanol contained a trace amount of NaF. The up-conversion luminescence measurements confirmed the clear difference in emission intensity in favor of the material washed only with ethanol (Figure 1). Hereafter, these materials are referred to as those with moderate and very high *UPC* intensity.

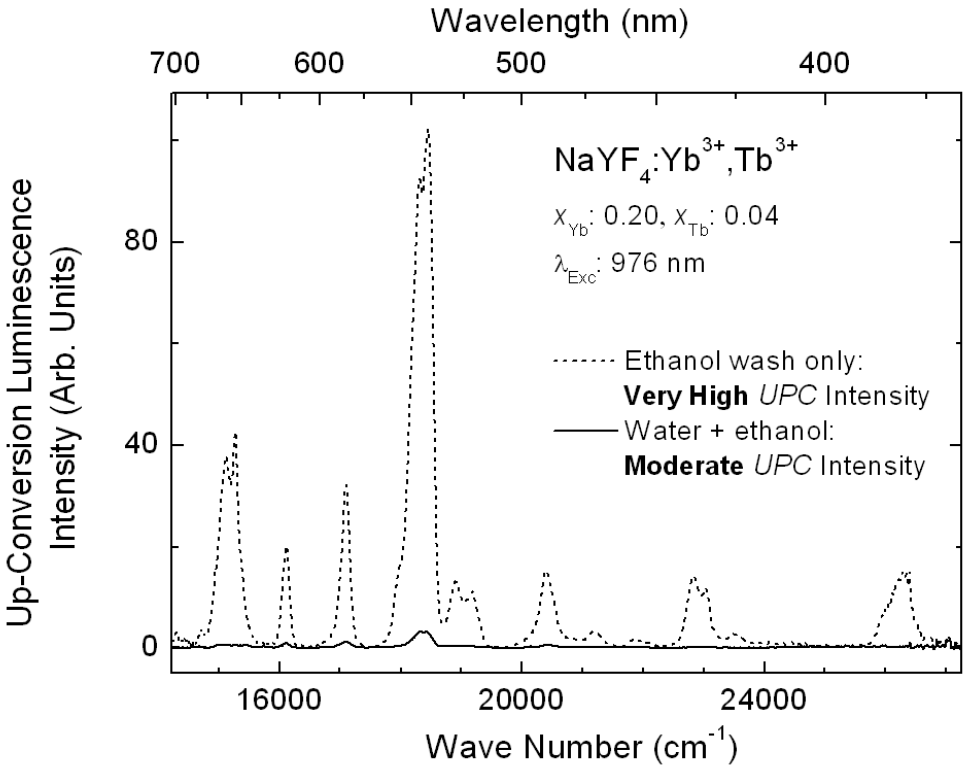


Figure 1. Effect of pre-annealing washing schemes on the up-conversion luminescence of the $Na(Y_{0.76}Yb_{0.20}Tb_{0.04})F_4$ materials.

The Williamson-Hall analyses (Figure 2) suggested that the materials with different washing schemes possess rather similar crystallite sizes: 94 (water + ethanol) and 110 nm (ethanol only). Although the increasing crystallite size strongly enhances the luminescence intensity, one can conclude that in the present case the size effect is not the dominant one and other reasons should be sought for the drastic intensity enhancement. Structural strains are expected to deteriorate luminescence intensity. This is because strains resulting from structural defects create additional energy levels which may trap energy as well as facilitate non-radiative relaxation. The creation

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of such trapping levels due to strains has been acknowledged *e.g.* for minerals (Bergues and Chayé d'Albissin, 1990). For the materials studied here, the microstrains are clearly more important for the material with moderate *UPC* intensity as shown by the ε value five times that for the material with very high *UPC* intensity (0.04 and 0.008 %). This is due to the fact that without washing with water, the cubic to hexagonal phase transition takes place at a temperature 100 ^{o}C lower than with water washing (Hölsä *et al.*, 2012). Therefore, in the former case, more time is available during the annealing to relax the structural strains resulting from the phase transition. According to the Williamson-Hall data, no anisotropy was found for the strains in either material.

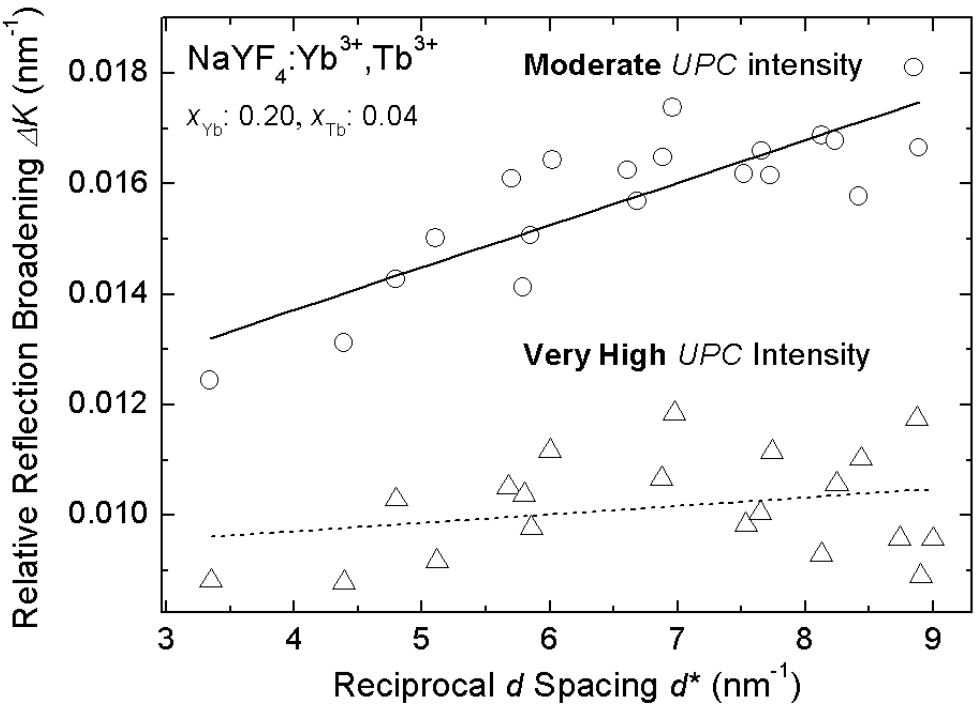


Figure 2. Williamson-Hall plots of the $Na(Y_{0.76}Yb_{0.20}Tb_{0.04})F_4$ materials with different *UPC* luminescence intensities. The linear fits to the data are shown, as well.

B. Structural details

The Rietveld refinements of the XPD patterns of all materials studied (Figure 3) resulted in good agreement with the hexagonal $P6_3/m$ space group as indicated by the values of the agreement indices R_B and χ^2 (Table I). In this structure, the sodium atoms (Na1) partially (ideally 25%) occupy the 4*e* (0, 0, *z*), sodium (Na2) and rare earth the 2*c* (1/3, 2/3, 1/4) (ideally with a 25/75 Na/*R* ratio) and fluorine the 6h (*x*, *y*, 1/4) site. The structure is composed of distorted $(Na1)F_6$

https://doi.org/10.1017/S0885715613001164 Published online by Cambridge University Press

octahedra and $(Na_2/R)F_9$ polyhedra. The unit cell volumes are very similar for the two materials, but the material with very high *UPC* intensity is slightly (0.2 %) denser along the unit cell a axis while the one with moderate *UPC* intensity is denser (0.4 %) along the c axis (Table I). The composition of both materials is very similar and practically stoichiometric, as well. The material with very high *UPC* intensity has a minute deficit of R^{3+} (Na:R ratio: 101 %), which is also witnessed by the minutely smaller (0.1 %) unit cell volume resulting from the absence of fluoride ions required for charge compensation.

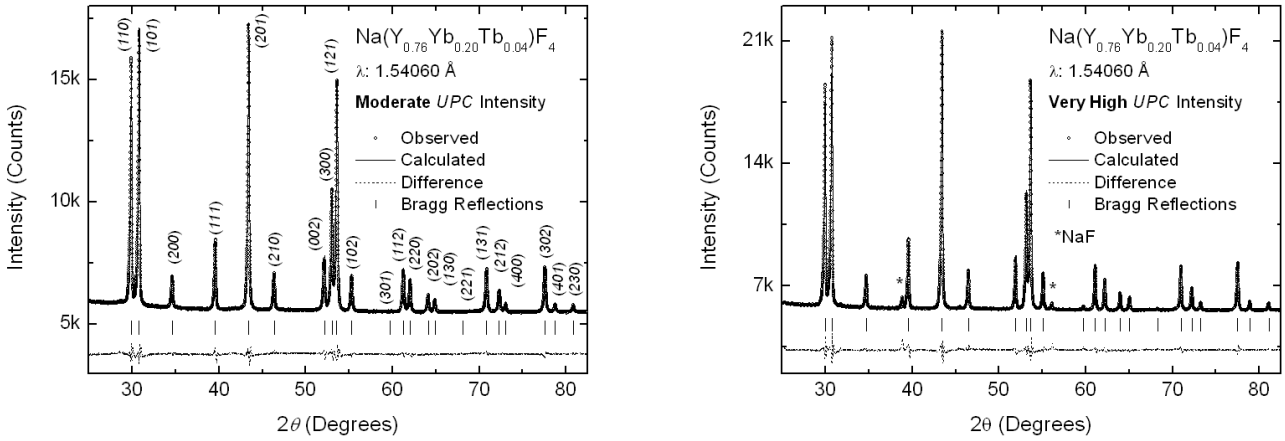


Figure 3. Rietveld plots of the $Na(Y_{0.76}Yb_{0.20}Tb_{0.04})F_4$ materials with moderate (left) and very high (right) *UPC* intensity.

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Table I. Structural data and agreement factors for the hexagonal $Na(Y_{0.76}Yb_{0.20}Tb_{0.04})F_4$ materials.

Parameter	Moderate *UPC* Intensity	Very High *UPC* Intensity
a (Å)	5.97840(1)	5.96351(1)
c (Å)	3.50517(1)	3.51898(1)
V:*Z* (Å^3)	72.33	72.25
z_{Na}	0.10575(6)	0.09907(11)
x_F	0.39445(1)	0.39323(2)
y_F	0.31111(1)	0.31193(1)
B_{Na1} (Å^2)	0.245(14)	0.844(22)
$B_{Na2/R}$ (Å^2)	0.186(1)	0.138(1)
B_F (Å^2)	0.716(3)	1.180(5)
Occ.Na_{Na1} (%)	19	17
Occ.$Na_{Na2/R}$ (%)	31	34
Occ.$R_{Na2/R}$ (%)	69	66
Composition	$Na_{1.00}R_{1.00}F_{4.00}$	$Na_{1.00}R_{0.99}F_{4.00}$
Na:*R* ratio (%)	100	101
Na1-F (Å)	2.211(1) x3	2.209(1) x3
	2.488(1) x3	2.471(1) x3
<Na1-F> (Å)	2.350	2.340
(Na2/*R*)-F (Å)	2.330(1) x3	2.315(1) x3
	2.350(1) x6	2.359(1) x6
<(Na2/*R*)-F> (Å)	2.343	2.344
Na1-Na2/*R* (Å)	3.488(1) x3	3.484(1) x3
	3.670(1) x3	3.656(1) x3
	4.125(1) x3	4.135(1) x3
	4.573(1) x3	4.559(1) x3
Na1-Na1 (Å)	3.505(1) x2	3.519(1) x2
Na2/*R*-Na2/*R* (Å)	3.505(1) x2	3.519(0) x2
	3.871(1) x6	3.867(1) x6
R_B (%)	3.5	3.6
χ^2	0.3	0.8

There is a clear difference in how the Na atoms are distributed over the Na1 and Na2/*R* sites: the ratio is 55:45 and 50:50 for the materials with moderate and very high *UPC* intensity, respectively. This difference – manifesting the dilution of the rare earths in the Na2/*R* site – is observed also in the intensity ratio of the (*110*) and (*101*) reflections at *ca.* 30 degrees (in 2θ) (Figure 3). This intensity ratio is highly dependent on the electron density ratio of the cation sites: a higher intensity ratio of the (*110*) and (*101*) reflection intensities indicates a higher Na1:Na2/*R* electron density ratio, and vice versa. Thus, a decrease in the *R* content of the Na2/*R* site is witnessed as a decrease of the (*110*) reflection intensity.

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For the material with very high *UPC* intensity, the Na-F distances around the Na1 site are shorter (0.4% on average) and less spread. On the other hand, the Na2/*R*-F distances are spread wider for this material with the average value of 2.34 Å not changing between the two materials. Considering the ionic radii (Shannon, 1976) of Na^{+} (1.02 and 1.24 Å for *CN*: 6 and 9, respectively), Y^{3+} (0.900 and 1.075), Yb^{3+} (0.868 and 1.042) and Tb^{3+} (0.923 and 1.095) as well as F^{-} (1.31 Å for *CN*: 4), it is possible to calculate the expected distances for Na-F (2.32 and 2.55 Å for *CN*: 6 and 9 respectively), Y-F (2.21 and 2.39), Yb-F (2.18 and 2.35) as well as Tb-F (2.23 and 2.41). This suggests that the average size of the Na1 site fits well to the size of the Na^{+} ion and the Na2/*R* site with the R^{3+} ions. However, the shorter Na-F distances of the Na1 site resemble the expected *R*-F distances for coordination number 6. The possibility of the rare earths occupying also the Na1 site was thus tested. Unfortunately, the results of this modeling proved to be inconclusive, since it was not possible to have a significant amount of rare earths in the Na1 site without destroying the intensity ratio of the (*110*) and (*101*) reflections and the refined chemical composition.

In luminescent materials, the distance between the optically active ions plays an important role *e.g.* in energy transfer and the resulting enhancement or quenching of emission intensity. In the present work, there seem to be no significant differences in cation-cation distances (Table I) between the two materials. However, the wider spread of the (Na2/*R*)-F distances for the material with very high *UPC* intensity may be an indication of ordering (clustering) of the Na and *R* cations. This would enhance the $Yb^{3+} \rightarrow Tb^{3+}$ energy transfer and intensify the up-conversion.

IV. CONCLUSIONS

The structural details affecting the *UPC* luminescence intensity in the $Na(Y_{0.76}Yb_{0.20}Tb_{0.04})F_4$ materials were determined by combining the Rietveld and Williamson-Hall analyses of X-ray powder diffraction data. The overall structures of the materials with drastically different *UPC* luminescence intensity are very similar, but the material with much higher intensity is somewhat diluted of R^{3+} in the Na2/*R* site. This may increase the *UPC* luminescence by limiting excess energy migration in the Yb sublattice. The local structural details revealed microstrains in the *R* sublattice that are relaxed for the material with very high *UPC* intensity thus decreasing energy losses. The Rietveld results also suggest cation ordering for the material with very high *UPC*

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intensity. In the future, the local structure around the rare earth ions will be studied in more detail with EXAFS measurements and subsequent calculations to verify this possibility. The Y/Yb/Tb(/Er) composition of the materials will be optimised further in order to increase the *UPC* intensity.

ACKNOWLEDGMENTS

Financial support from the Palomaa-Erikoski foundation, Academy of Finland and CNPq Brazil, Finnish Funding Agency for Technology and Innovation (TEKES), the Graduate School of Materials Research (Turku, Finland), Nordic Energy Research as well as the European Union is gratefully acknowledged.

Antal, T., Harju, E., Pihlgren, L., Lastusaari, M., Tyystjärvi, T., Hölsä, J. and Tyystjärvi, E. (**2012**). "Use of near-infrared radiation for oxygenic photosynthesis via photon up-conversion," Int. J. Hydrogen Energy **37**, 8859-8863.

Auzel, F. (**2004**). "Upconversion and anti-Stokes process with f and d ions in solids," Chem. Rev. **104**, 139-173.

Bergues, J. and Chayé d'Albissin, M. (**1990**). "Thermoluminescence as a scalar measure of plastic strain in experimentally and naturally deformed crystalline limestones," Tectonophysics **172**, 223-234.

Brito, H.F., Hölsä, J., Laamanen, T., Laihinen, T., Lastusaari, M., Nunes, L.A.O. and Pihlgren, L. (**2012**). "Role of Er^{3+} impurity in the Yb^{3+}-Tb^{3+} up-conversion luminescence in $NaYF_4$," Proc. 8th Int. Conf. f-Elements (ICfE 2012), Udine, Italy, August 26-31, 2012, SST 11P.

Harju, E., Hyppänen, I., Hölsä, J., Kankare, J., Lahtinen, M., Lastusaari, M., Pihlgren, L. and Soukka, T. (**2011**). "Polymorphism of $NaYF_4$:Yb^{3+},Er^{3+} up-conversion luminescence materials," Z. Kristallogr. Proc. **1**, 381-387.

Hyppänen, I., Hölsä, J., Kankare, J., Lastusaari, M., Pihlgren, L. and Soukka, T. (**2010**). "Preparation and up-conversion luminescence properties of $NaYF_4$:Yb^{3+},Er^{3+} nanomaterials," Terrae Rarae **2009**, 16-1-6.

Hölsä, J., Laihinen, T., Laamanen, T., Lastusaari, M., Nunes, L.A.O., Pihlgren, L. and Soukka, T. (**2012**). "Serendipitous enhancement of up-conversion luminescence from $NaYF_4$:Yb^{3+},Tb^{3+}," Proc. 3rd Int. Conf. Phys. Opt. Mater. Devices (ICOM 2012), Belgrade, Serbia, September 3-6, 2012, P2.1-23.

Kuningas, K., Rantanen, T., Ukonaho, T., Lövgren, T. and Soukka T. (**2005**). "Homogeneous assay technology based on upconverting phosphors," Anal. Chem. **77**, 7348-7355.

https://doi.org/10.1017/S0885715613001164 Published online by Cambridge University Press

Rietveld, H.M. (**1969**). ”A profile refinement method for nuclear and magnetic structures,” J. Appl. Crystallogr. **2**, 65-71.

Rodriguez-Carvajal, J. (**2007**). FullProf.2k, Version 4.00 May 2007 (Computer Software), Laboratoire Leon Brillouin (CEA-CNRS), Gif-sur-Yvette, France, unpublished.

Shalav, A., Richards, B.S., Trupke, T., Krämer, K.W., and Güdel, H.U. (**2005**). “Application of $NaYF_4:Er^{3+}$ up-converting phosphors for enhanced near-infrared silicon solar cell response,” Appl. Phys. Lett. **86**, 013505.

Shannon, R.D. (**1976**). “Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides,” Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. **32**, 751-767.

Ungár, T. (**2000**). “Warren-Averbach applications,” in *Industrial applications of X-ray diffraction*, edited by F. H. Chung and D. K. Smith (Marcel Dekker, New York NY, USA), pp. 847-852.

Williamson, G. K. and Hall, W. H. (**1953**). “X-ray line broadening from filed aluminium and wolfram,” Acta Metall. **1**, 22-31.

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