



CHORUS

This is the accepted manuscript made available via CHORUS. The article has been published as:

Band-gap engineering for removing shallow traps in rare-earth $\text{Lu}_{\{3\}}\text{Al}_{\{5\}}\text{O}_{\{12\}}$ garnet scintillators using $\text{Ga}^{\{3+\}}$ doping

M. Fasoli, A. Vedda, M. Nikl, C. Jiang, B. P. Uberuaga, D. A. Andersson, K. J. McClellan, and C. R. Stanek

Phys. Rev. B **84**, 081102 — Published 26 August 2011

DOI: [10.1103/PhysRevB.84.081102](https://doi.org/10.1103/PhysRevB.84.081102)

Band gap engineering for shallow trap removal in $\text{RE}_3\text{Al}_5\text{O}_{12}$ garnets

M. Fasoli,¹ A. Vedda,¹ M. Nikl,² C. Jiang,³ B.P. Uberuaga,³ D.A. Andersson,³ K.J. McClellan,³ and C.R. Stanek^{3,*}

¹*Dept. of Materials Science, University of Milano-Bicocca, Milan 20125 Italy*

²*Institute of Physics AS CR, Prague 162 53 Czech Republic*

³*MST-8 Structure and Property Relations, Los Alamos National Laboratory, Los Alamos, NM 87545 USA*

In this Letter, we employ a combination of first principles calculations and optical characterization experiments to explain the mechanism by which Ga^{3+} -doping prevents the trapping of free carriers due to shallow traps in $\text{RE}_3\text{Al}_5\text{O}_{12}$ garnet scintillators (where RE represents a 3+ rare earth cation). Specifically, we confirm that Ga^{3+} -doping does not reduce the defect concentration (defect engineering), but rather leads to shifts in the valence and conduction bands such that the energy level of shallow defects is no longer in the forbidden gap where electrons can be trapped (band gap engineering).

PACS numbers: 31.15.Qg, 61.72.Bb, 61.72.Ji

Improvements in the performance of scintillator materials can occur either via the discovery of new materials or the optimization of existing ones. Broad empirical searches have already significantly exploited wide compositional ranges, effectively limiting the domain for new materials discovery [1]. Typically in oxide scintillators, point defects are largely responsible for both significantly reduced and delayed light due to free carrier trapping. However, optimization of existing materials has historically been difficult due to several daunting challenges encountered when attempting to remove defects responsible for performance limitations, including: identification of the point defect composition, understanding the effect of those defects on performance, and finally, designing co-doping or synthesis approaches to reduce or remove the performance-limiting effect of the offending defect. Despite these challenges, there has been promising recent success in improving the performance of existing scintillator materials, chiefly through reducing the concentration of performance limiting point defects, either by doping with aliovalent species [2, 3] (defect engineering) or through synthesis methods with a lower process temperature than conventional single crystal growth [4].

In this Letter, we propose an alternative defect management approach, which relies on varying composition rather than synthesis route, and is particularly applicable to shallow traps. Specifically, rather than employing doping to reduce the concentration of deleterious defects (as is done in defect engineering), we propose to introduce dopants for the purpose of altering the electronic structure (band gap engineering). We demonstrate the efficacy of this approach by showing how the electron trapping effect of isovalent cation antisite defects in oxide scintillators $\text{Lu}_3\text{Al}_5\text{O}_{12}$ garnets (referred to as LuAG) can be removed by an admixture of Ga^{3+} .

The existence of cation antisite defects in garnets (e.g. Lu^{3+} on Al^{3+} sites in $\text{Lu}_3\text{Al}_5\text{O}_{12}$) is widely accepted (see [5] and references therein). Recently, thermally stim-

ulated luminescence (TSL) experiments confirmed the presence of defect-induced shallow traps in LuAG:Ce [6], which are responsible for degraded scintillation performance [7]. Furthermore, antisites were determined to be the lowest energy defect present in a range of aluminate garnets via atomistic simulation [8–11], providing additional support for the presence of this type of defect. Recognizing cation antisites as the defect responsible for degraded scintillator performance, the next step is to remove these defects, or at least reduce the degree of electron trapping (and corresponding delayed scintillation) associated with them. Typically, via so-called “defect engineering”, these materials would be either co-doped or synthesized in a manner other than single crystal growth in order to reduce the concentration of defects, as has been done for oxygen vacancies in YAlO_3 (YAP) [2]. However, reducing the concentration of cation antisites in garnets is not trivial via defect engineering since (1) the formation energy for antisites is low [8–11] and (2) in these compounds cation antisites are charge neutral and therefore can not be removed via aliovalent doping techniques that lead to defect recombination. While thin films synthesized by liquid phase epitaxy or optical ceramics have shown that specific TSL peaks associated with antisites (120-200 K in LuAG:Ce and 90-120 K in YAG:Ce) are significantly reduced [6, 12], synthesis of bulk quantities of antisite-free garnet single crystals has been challenging.

Interestingly, recent experiments have shown that the same TSL peaks attributed to cation antisites are removed when LuAG is admixed with Ga^{3+} and the response time is consequently decreased [13]. Although it is clear that Ga^{3+} additions certainly improve the scintillator performance, there is no clear explanation of how Ga^{3+} -doping influences antisite defect behavior. It has been observed that the concentration of antisites in yttrium gallium garnet (YGG) is greater than YAG [14], which is expected since Ga^{3+} is closer in size to Y^{3+} (or any other RE^{3+}) than Al^{3+} [15]. Further, using atomistic simulations based on a Born-like, ionic description of the lattice and the Buckingham potential to describe the short range interactions between ions (previously em-

*Electronic address: stanek@lanl.gov

ployed by these authors to calculate a variety of defect properties in garnets [11, 16]), we find that the defect formation energy of antisites in YAG and LuAG decreases with increasing Ga concentration, by ~ 0.4 eV for full Al replacement by Ga (i.e. the antisite concentration increases with Ga doping). Based upon these findings, a reduction in antisite concentration is an unlikely explanation for the observed TSL peak disappearance.

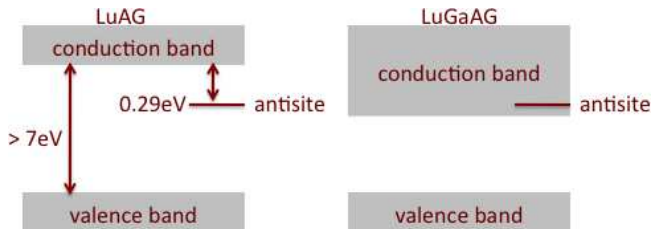


FIG. 1: Schematic of the band structure of undoped LuAG (left), with a band gap of > 7 eV and an antisite trap depth of 0.29 eV, compared to the proposed band shift due to Ga-doping (right), where the antisite defect is no longer in the forbidden gap, but rather is enveloped by the CB.

An alternative explanation involves the effect of Ga doping on the band structure of garnet. Zorenko has proposed that the YAG band gap decreases with increasing Ga^{3+} concentration [17] and Nikl *et al.* further postulated Ga^{3+} doping might remove defect states due to antisites by lowering the conduction band (CB) below the defect states, effectively eliminating them from the band gap [18]. Figure 1 schematically describes how the trap state in the forbidden gap of LuAG (and similarly YAG) associated with antisites might be enveloped by the CB via Ga-doping. That is, since the trap depth in LuAG is only 0.29 eV, the CB need only shift by that much with Ga-doping to remove the trapping nature of the antisite defect (assuming that the trap remains fixed independent of the CB shift).

To understand precisely how Ga-doping modifies the electronic structure of aluminate garnets, we have performed density functional theory (DFT) calculations. We used the VASP code [19–22] with the projector augmented wave method [23, 24] on supercells containing 160 atoms. We used the PBE generalized gradient approximation functionals and tested convergence of our results versus energy cutoff, k-point sampling (using $2 \times 2 \times 2$ k-point meshes of the Monkhorst-Pack type [25]), and spin polarization. Related calculations have been performed in other aluminate garnets in the past. Xu *et al.* explored a range of Ga^{3+} and Sc^{3+} -doped $\text{Gd}_3\text{Al}_5\text{O}_{12}$ garnets [26], though they did not focus on the relationship between doping and band gap. Garcia and Seijo examined the effect of Ga on the electronic structure of YAG, but looked at single Ga ions as opposed to higher doping concentrations [27]. Here, we are interested in the modification of the band structure as a function of Ga concentration and thus consider garnets with Ga contents from 0 to 100% Ga replacement of Al. The garnet structure

has two crystallographically unique Al sites, where 40% are octahedrally coordinated and 60% are tetrahedrally coordinated. Since the calculated energy difference between placing Ga on either of the two sites is low, we assume that Ga is randomly distributed amongst all of the sites, using the special quasirandom structures (SQS, [28]) approach to generate representative structures. Although our calculated band gap results for perfect LuAG and YAG agree well with previous DFT calculations (e.g. [29]), the experimental band gaps has been measured to be considerably larger [30, 31]. Despite this typical underestimation of band gap by DFT, in this study, we are more interested in the changes in band gap, where we expect these errors to be less pronounced, and indeed, we show that the agreement in the change in bandgap between theory and experiment is quite good. Specifically, in order to determine how Ga-doping modifies the CB independent of the valence band (VB), we have thus shifted all of our calculated density of states (DOS) such that deep levels below -20 eV are aligned, as has been described in the past by Wei and Zunger [32].

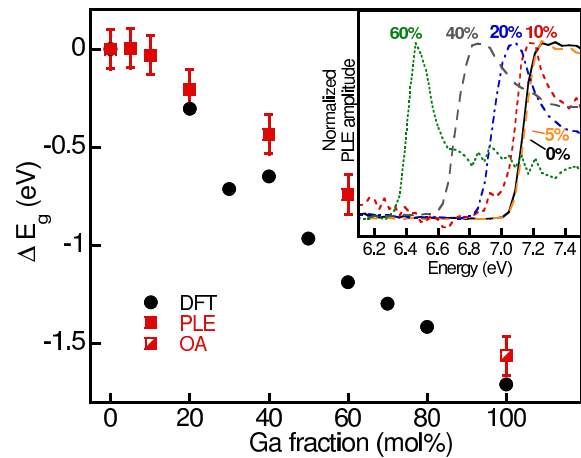


FIG. 2: Comparison between DFT calculations and experimental (PLE and OA) results of the LuAG band gap variation as a function of Ga concentration. The inset shows the low energy shift of the PLE data that corresponds to band gap reduction.

Our DFT results are compared to photoluminescence excitation (PLE), optical absorption (OA), and TSL experiments. Ce and Eu-doped $\text{Lu}_3(\text{Ga}_x\text{Al}_{1-x})_5\text{O}_{12}$ (LuGAG) single crystals were grown by the micro-pulling down technique ([13, 33, 34]). PLE spectra were measured in the VUV-UV region at the Superlumi station, HASYLAB, DESY synchrotron [35] and in the UV range with a spectrofluorometer [36]. All the spectra are corrected for experimental distortions. OA measurements were performed at room temperature (RT) and TSL measurements were performed by heating the samples after RT x-ray irradiation up to 500 $^\circ\text{C}$ with a constant heating rate of 1 $^\circ\text{C}/\text{s}$. Two different detection systems were employed: a photomultiplier tube and a wavelength resolved apparatus [36, 37], which allow for consideration

of emission from only Ce^{3+} and Eu^{3+} respectively.

First, we compare DFT results of band gap variation in LuGAG as a function of Ga concentration to OA and VUV-UV PLE data. The shift of the absorption edge from OA measurements could be evaluated only for LuGAG crystals doped with 60% and 100% Ga, the absorption edge lies in the VUV region for lower concentrations of Ga. For this reason, we evaluated the band gap shift for low Ga concentration by monitoring the excitation spectrum of an intrinsic excitonic emission at 4.0-4.1 eV, which can be used reliably for host absorption band monitoring [38]. Theory and experiment are compared in Figure 2, which clearly demonstrates that the band gap of LuGaG decreases with increasing Ga content. Furthermore, the agreement between DFT results and experimental data is remarkable, with both methodologies showing a band gap reduction of ~ 1.6 eV upon complete replacement of Al with Ga.

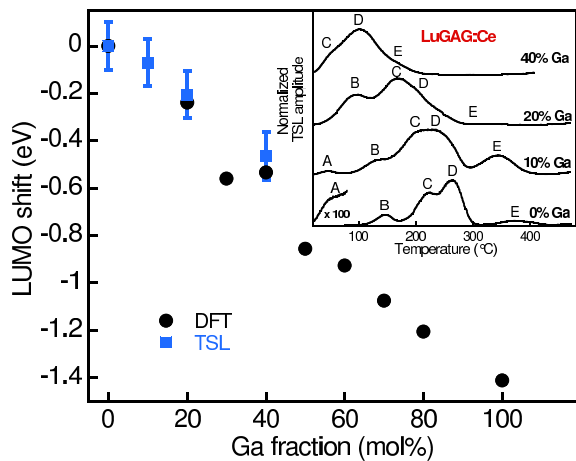


FIG. 3: Comparison between DFT and TSL of the LUMO shift in LuAG as a function of Ga concentration and experimental (TSL) results. The inset shows the shift of TSL peaks to lower temperatures with Ga doping.

From PLE and OA experiments, it is not possible to identify the individual contributions of CB and VB shifts to the overall band gap reduction, and subsequently how the defect trap states are affected by those shifts. Therefore, we employed TSL and expanded preliminary results [33] to evaluate the energy difference between an electron trap and the CB edge (and a hole trap and the VB edge) to determine the effect of Ga-doping on band edge shifts. Specifically, we investigated TSL glow curves following x-ray irradiation of LuGAG crystals doped with 0.7 mol% Ce and 0.1 mol% Eu, and with Ga concentrations up to 40% for Ce-doped samples and from 0 mol% to 100% for Eu-doped samples. Due to their different electronic configurations in the $3+$ valence state, Ce^{3+} is likely to trap holes while Eu^{3+} is likely to trap electrons. Thus, Ce and Eu ions serve as recombination centers for the carriers freed from electron traps located close to the CB and for hole traps located close to the VB, respectively. If the localized trap levels are not significantly affected by Ga-

doping, then the quantitative CB and VB shifts can be obtained from TSL measurements on Ce- and Eu-doped LuGAG samples.

For Ce-doping, as many as five electron traps are observed (see the inset of Fig. 3), which is typical in complex oxide hosts [36, 37]. Although precise determination of the nature of these peaks requires further study, in this work we are interested in the peak shifts. The thermal trap depths (relative to the CB) were evaluated by the initial rise method employed after partial cleaning of the glow curves [39]. With increasing Ga concentration, the entire glow curve shifts to lower temperatures, and for 40 mol% Ga the thermal depths of all traps are approximately 0.5 eV lower, indicating a corresponding lowering of the CB edge. In Fig. 3, we compare DFT results related to the lowest unoccupied molecular orbital (LUMO) to the TSL data for the CB-shifts. As for the band gap reduction, the agreement between TSL and DFT is very good. DFT data are extended up to complete Ga substitution, predicting a CB shift of 1.4 eV.

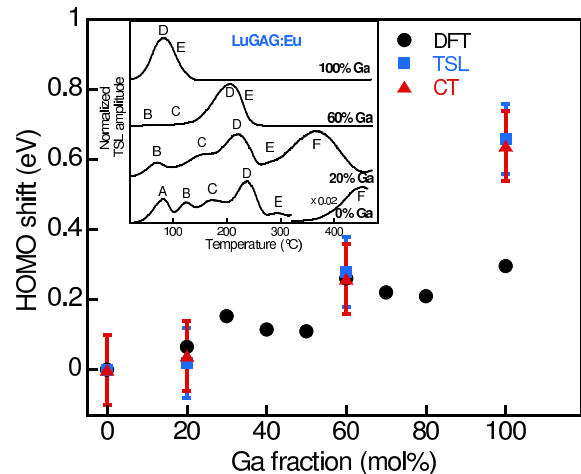


FIG. 4: Comparison between DFT, TSL and CT results of the HOMO shift in LuAG as a function of Ga concentration. The inset shows the shift of TSL peaks to lower temperatures with Ga doping.

Similar TSL measurements were done on Eu-doped LuGAG to investigate the VB shift (the inset of Fig. 4 shows the glow curves). Similar to Ce-doped LuGAG, multiple peaks are observed. However, only the most intense peak labeled “D” could be quantitatively monitored for all Ga concentrations. Figure 4 shows a comparison of the DFT-derived highest occupied molecular orbital (HOMO) shift and TSL thermal trap depth (relative to VB) for Eu-activated LuGaG. Except for the case of full replacement of Al with Ga, for which an explanation is not available at the moment, the agreement between the calculations and experiments is very good. The shift in the VB is less pronounced as a function of Ga concentration than that observed for the CB. Additionally, the VB shift was also evaluated through the shift of the broad absorption/excitation band due to the charge transfer (CT)

transition from oxygen ($2p$) levels forming the VB top to the Eu^{2+} ($4f$) ground state level ($\text{O}^{2-} \Rightarrow \text{Eu}^{2+}$) [40]. Excitation spectra of the intense ${}^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition at 591 nm were measured. For 0% Ga this CT band is centered at about 5.8 eV, and a low energy shift is observed with increasing Ga content; see Fig. 4. The agreement between DFT and CT is again very good.

Further analysis of the calculated density of states reveals additional detail concerning the mechanism by which the band edges overlap the trap states. For example, we observe that the conduction band edge of the Ga-free system is due to Lu d states. However, when Ga is added, new states appear that derive from Ga 4s, which now represent the band edge. For the valence band edge, the observed shifts upon Ga-doping are due to a corresponding shift or widening of the O 2-p states induced by the presence of Ga.

Our theoretical and experimental results show that not only does the band gap of LuGAG decrease with increasing Ga content, but that the CB and VB shift independently (with a greater shift in the CB). With this improved understanding of the relationship between composition and electronic structure, it is possible to prescribe compositions for which band edges overlap with the shallow trap states, consequently preventing them from de-

grading scintillator performance, even though the absolute number of these defects likely increases. Furthermore, although demonstrated here for Ga-admixtures in LuAG, this approach should generally apply to other dopants and compounds. For example, we predict with DFT that band gap shifts in LuAG will be more pronounced per atom for In admixtures than for Ga, which has been similarly observed in semiconductors [41]. In conclusion, via a combination of theoretical calculations and experimental techniques, we have been able to identify the mechanism by which isovalent doping of garnets improves scintillation performance and, by so doing, predicted other doping strategies that may provide even better performance, allowing for bandgap engineering and predictive design of scintillator compositions.

A. Yoshikawa and H. Ogino at Tohoku University are acknowledged for providing samples. Financial support of Czech GACR project 202/08/0893 and CARIPLO Foundation Project "Energy transfer and trapping phenomena in nanostructured scintillator materials" (2008-2011) is gratefully acknowledged. Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396.

-
- [1] M.J. Weber, Nucl. Inst. Meth. A **527**, 9 (2004).
 [2] M. Nikl, et al., Nucl. Inst. Meth. A **486**, 250 (2002).
 [3] M. Nikl, phys. stat. sol. (a) **178**, 595 (2000).
 [4] Yu. Zorenko, et al., J. Lumin. **114**, 85 (2005).
 [5] V. Lupei, A. Lupei, C. Tiseanu, S. Georgescu, C. Stoicescu, and P. Nanau, Phys. Rev. B **51**, 8 (1995).
 [6] M. Nikl, E. Mihokova, J. Pejchal, A. Vedda, Yu. Zorenko, and K. Nejezchleb, phys. stat. sol. b **242**, R119 (2005).
 [7] M. Nikl, phys. stat. sol. (a) **202**, 201 (2005).
 [8] H. Donnerberg and C.R.A. Catlow, J. Phys.: Condens. Matt. **5**, 2947 (1993).
 [9] M.M. Kukulja, J. Phys.: Condens. Matt. **12**, 2953 (2000).
 [10] C. Milanese, V. Buscaglia, F. Maglia, and U. Anselmi-Tamburini, Chem. Mater. **16**, 1232 (2004).
 [11] C.R. Stanek, K.J. McClellan, M.R. Levy, C. Milanese, and R.W. Grimes, Nucl. Instrum. Methods A **579**, 27 (2007).
 [12] E. Mihokova, et al., J. Lumin. **126**, 77 (2007).
 [13] M. Nikl, et al., Appl. Phys. Lett. **88**, 141916 (2006).
 [14] G. Shirinyan, et al., Nucl. Inst. Meth. A **537**, 134 (2005).
 [15] R.D. Shannon, Acta Cryst. A **32**, 751 (1976).
 [16] C.R. Stanek, K.J. McClellan, M.R. Levy, and R.W. Grimes, phys. stat. sol. (b) **243**, R75 (2006).
 [17] Yu. Zorenko, Optics and Spectroscopy **88**, 551 (2000).
 [18] M. Nikl, A. Vedda, and V.V. Laguta, Radiat. Meas. **42**, 509 (2007).
 [19] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
 [20] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).
 [21] G. Kresse and J. Furthmüller, Comp. Mater. Sci. **6**, 15 (1996).
 [22] G. Kresse and J. Furthmüller, Phys. Rev. B **55**, 11169 (1996).
 [23] P. Blöchl, Phys. Rev. B **50**, 17953 (1994).
 [24] G. Kresse and J. Joubert, Phys. Rev. B **59**, 1758 (1999).
 [25] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).
 [26] Y.N. Xu, W.Y. Ching, and B.K. Briceen, Phys. Rev. B **61**, 1817 (2000).
 [27] A.B. Munoz-Garcia and L. Seijo, Phys. Rev. B **82**, 184118 (2010).
 [28] A. Zunger, S.H. Wei, L.G. Ferreira, and J.E. Bernard, Phys. Rev. Lett. **65**, 353 (1990).
 [29] Y.N. Xu and W.Y. Ching, Phys. Rev. B **59**, 10530 (1999).
 [30] Y. Zhan and P.D. Coleman, Appl. Opt. **23**, 548 (1984).
 [31] T. Tomiki, et al., J. Phys. Soc. Jpn. **62**, 1388 (1993).
 [32] S.H. Wei and A. Zunger, J. Appl. Phys. **78**, 3846 (1995).
 [33] E. Mihokova, et al., Optical Materials **32**, 1298 (2010).
 [34] H. Ogino, A. Yoshikawa, M. Nikl, J. Mares, J. Shimoyama, and K. Kishio, J. Cryst. Growth **311**, 908 (2009).
 [35] G. Zimmerer, Radiat. Meas. **42**, 859 (2007).
 [36] A. Vedda, M. Martini, F. Meinardi, J. Chval, M. Dusek, J.A. Mares, E. Mihokova, and M. Nikl, Phys. Rev. B **61**, 8081 (2000).
 [37] A. Vedda, M. Nikl, M. Fasoli, E. Mihokova, J. Pejchal, M. Dusek, G. Ren, C.R. Stanek, K.J. McClellan, and D.D. Byler, Phys. Rev. B **78**, 195123 (2008).
 [38] M. Nikl, J. Pejchal, A. Vedda, M. Fasoli, I. Fontana, V.V. Laguta, V. Babin, K. Nejezchleb, A. Yoshikawa, H. Ogino, et al., IEEE Trans. Nucl. Sci. **55**, 1035 (2008).
 [39] S.W.S. McKeever, *Thermoluminescence of Solids* (Cambridge University Press, 1985).

[40] P. Dorenbos, J. Phys.: Cond. Matter **15** (2003).

[41] S.H. Wei and A. Zunger, Appl. Phys. Lett. **72**, 3199

(1995).