Band Gap Engineering and Trap Depths of Intrinsic Point Defects in RAIO₃ (R = Y, La, Gd, Yb, Lu) Perovskites

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ABSTRACT: The possibility of band gap engineering (BGE) in RAIO₃ (R = Y, La, Gd, Yb, Lu) perovskites in the context of trap depths of intrinsic point defects was investigated comprehensively using experimental and theoretical approaches. The optical band gap of the materials, $E_g$, was determined via both the absorption measurements in the VUV spectral range and the spectra of recombination luminescence excitation by synchrotron radiation. The experimentally observed effect of $E_g$ reduction from $\sim$8.5 to $\sim$5.5 eV in RAIO₃ perovskites with increasing R³⁺ ionic radius was confirmed by the DFT electronic structure calculations performed for RMIIIO₃ crystals (R = Lu, Y, La; MIII = Al, Ga, In). The possibility of BGE was also proved by the analysis of thermally stimulated luminescence (TSL) measured above room temperature for the far-red emitting (Y/Gd/La)AlO₃:Mn⁴⁺ phosphors, which confirmed decreasing of the trap depths in the cation sequence Y → Gd → La. Calculations of the trap depths performed within the super cell approach for a number of intrinsic point defects and their complexes allowed recognizing specific trapping centers that can be responsible for the observed TSL. In particular, the electron traps of 1.33 and 1.43 eV (in YAlO₃) were considered to be formed by the energy level of oxygen vacancy (VO) with different arrangement of neighboring YAl and VY, while shallower electron traps of 0.9−1.0 eV were related to the energy level of YAl antisite complexes with neighboring VO or (VO + VY). The effect of the lowering of electron trap depths in RAIO₃ was demonstrated for the VO-related level of the (YAl + VO + VY) complex defect for the particular case of La substituting Y.

1. INTRODUCTION

Yttrium−aluminum perovskite (YAIO₃ or YAP) is a well-known host material for solid-state lasers, scintillators, and various kinds of converting and storage phosphors (see, e.g., refs 1−6 and references therein). YAIO₃ crystal possesses deformed perovskite GdFeO₃ type structure with orthorhombic symmetry (space group $D_{2h}^{15}$−Pbnm). The structure can be represented by a network of slightly distorted and turned AI₆ octahedra connected by apexes, where Y⁴⁺ ions are located inside, thus forming strongly distorted YO₁₂ cavities with the nearest 8 or 9 oxygen ions around Y⁴⁺ (see Figure 1). Other rare-earth-based aluminates and their solid solutions with the same type of structure, such as LuAlO₃, Y₁₋₅Lu₅AlO₃, GdAlO₃, YbAlO₃, etc., are also well-known.⁵−¹¹ A huge amount of important optical and luminescent properties of these materials is influenced by the energy levels formed inside the forbidden gap of the material by activator ions, native point defects, and uncontrolled impurities. The location of these energy levels relative to the edges of conduction or valence electronic bands is crucial for the radiation-induced and
thermally induced processes, like ionization, charge trapping and storage, recombination, energy transfer, etc.

Band gap engineering (BGE) in complex oxide crystals is a concept of elimination of shallow-trap defect states in the crystals by cation substitution. It was first proposed for R₃M₃⁺O₁₂ garnets by Fasoli et al. The concept is based on the assumption that substitution of M₃⁺ cations in such crystals can lead to the enveloping of some defect levels, initially located in their band gaps, by the band electronic states. Such deactivated defect states can improve the scintillation characteristics of the doped crystals (or mixed-cationic solid solutions) relative to initial undoped ones. For instance, if Al cations are substituted with Ga in R₃Al₅O₁₂ garnet crystal, some shallow defect levels in Al-garnet may be presumably enveloped by the conduction band states of Ga-garnet, because R₃Ga₅O₁₂ crystals have narrower band gaps than corresponding R₃Al₅O₁₂.

It is known that the conduction band (CB) of a YAlO₃ perovskite crystal is formed mainly by Y 4d states, whereas the valence band (VB) is formed by a superposition of O 2p and Al 3p states. Therefore, replacement of yttrium or aluminum in this kind of material by some other metal or rare-earth cation should affect the forbidden gap width. Applicability of the BGE approach in perovskites via variation of their composition has recently been confirmed experimentally. It has been shown that the variation of the Gd/La ratio in Gd₁₋ₓLaₓAlO₃ perovskites doped with Eu³⁺/Pr³⁺ or Eu³⁺/Tb³⁺ is an efficient tool for tuning of the defect- or dopant-related trap depths.

However, it is obvious that a key postulate has to be accepted to make the BGE concept valid: cation substitution should not only change the band gap but also decrease/increase the defect level position with respect to the band gap edges (which eventually results in enveloping the level by the band states). It is also obvious that the position of a shallow defect level in the band gap may be shifted as a result of cation substitution, thus keeping the energy depth of the corresponding charge carrier trap practically unchanged and thus eliminating the effect of BGE. The influence of cation substitution on a particular defect in a specific crystal is hardly predictable a priory.

Narrowing of the band gap width, E₀ by cation substitution has obtained computational evidence for several cases of garnet compounds, like Lu₃(Al₉Ga₁₋ₓ)O₁₂ and Y₃(Al₉Ga₁₋ₓ)O₁₂. However, to the best of our knowledge, there are no direct computational results demonstrating the changes of trap depths of specific defects in garnets or other oxide compounds.

There were also several computational efforts that considered the BGE problem in perovskites. Density functional theory (DFT)-based computational studies with use of defect-containing super cells were applied to LuAlO₃. It was shown that in such a crystal, substitution of M³⁺ cations from Al to Ga can lead to enveloping of the defect levels of some electron traps by the CB. In particular, the levels of LuₓLuₓGa₁₋ₓ and GaₓLuₓ defects fall into the conduction band of LuGaO₃. However, calculations of the defect levels were done by Liu et al. only for LuAlO₃ and LuGaO₃ crystal hosts. It is obvious that more reliable results on the defect level behavior with cationic substitution can be obtained with the use of super cells of the solid solutions, like LuₓAl₁₋ₓGaₓO₁₂.

In order to know the limits and possibilities of implementation of the BGE approach in the RAlO₃ perovskites, it is necessary to understand the effect of the R cation substitution on the electronic structure and, in particular, on the E₀ value. Only scarce information about this issue can be found in the literature. For example, from the luminescence studies under synchrotron radiation excitation, it is known that LuAlO₃ has a band gap width at least 0.6 eV larger than YAO₃, whereas GdAlO₃ probably has a narrower band gap than YAO₃. The replacement of Gd by La gradually decreases the E₀ of Gdₓ₋ₓLaₓAlO₃. Therefore, there is an obvious lack of a systematic study demonstrating the effect of various rare-earth (R) cations on the band gap width of RAlO₃ perovskites.

It is very important for controllable tuning of the defect- or dopant-related trap depths and for improvement thereby of the performance of scintillator materials, storage, or persistent luminescence phosphors. The present work is aimed to eliminate this shortage. Dependence of the E₀ of RAlO₃ perovskites on the type of the R cation (R = Y, La, Gd, Tb, Lu) is determined in systematic theoretical and experimental studies.

The DFT-based theoretical calculations with the use of the plane-wave pseudopotential method have been carried out in order to establish the effect of R cation substitution on the electronic band structure and E₀ value of RAlO₃ crystals. Results obtained from the calculations are compared with the experimental estimations of E₀ values for RAlO₃ perovskites. In particular, optical absorption of the single crystals in the UV–VUV range and luminescence measurements of the same crystals under synchrotron radiation excitation were performed. In addition, the thermally stimulated luminescence (TSL) measurements of the Mn⁴⁺-doped microcrystalline Y₁₋ₓGdₓAlO₃ and Gd₁₋ₓLaₓAlO₃ phosphors have been performed in the temperature range from 300 to 500 °C in order to determine the effect of Gd and La doping on the trap depths formed by native defects in these materials.

While the effect of R cation substitution on the E₀ of perovskites can be established in such systematic studies, the effect of such substitution on positions of the defect levels with respect to the band edges is a nontrivial problem and requires special studies for particular defects and hosts. In the present paper, we study this problem computationally by considering one meaningful example, namely, substitution of Y with La in YAO₃ crystal. The effect of La doping on the defect level positions in the band gap of YAO₃ was determined via calculations with the use of the DFT method within the super cell approach. A wide set of defects of different types has been considered in calculations in order to find such defect combinations that most probably determine the high-temperature TSL peaks of the synthesized perovskites crystals.
2. EXPERIMENTAL AND CALCULATION METHODS

2.1. Sample Preparation and Experimental Methods. Single-crystalline RAlO₃ perovskite crystals studied in this work were grown by the Czochralski method in inert gas atmosphere at the Institute of Physics PAS, Institute of Electronic Materials Technology or Norfolk State University (see Acknowledgments). For the absorption and luminescence measurements, the samples were prepared as plane-parallel double-side polished plates of 50–100 μm thickness.

Beside the single crystals, two series of Mn⁴⁺-doped ceramic samples were specially prepared for the purposes of this work. Namely, Y₁₋ₓGdₓAlO₃:Mn⁴⁺ (x = 0.2, 0.4, 0.6, 0.8, 1.0) and Gd₁₋ₓLaₓAlO₃:Mn⁴⁺ (y = 0, 0.2, 0.4) samples in the form of microcrystalline powders were synthesized by a conventional solid-state reaction in air atmosphere. For this purpose, starting materials of Y₂O₃, Gd₂O₃, La₂O₃, Al₂O₃, and MnO₂ in the form of high-purity (not worse than 99.99%) microcrystalline powders were used. To prompt higher TSL response of the Mn⁴⁺-doped ceramic samples, they were purposely synthesized from the R-rich composition corresponding to the nominal chemical formula of R₁₋ₓAlₓO₃ (R = Y, Gd, La). After thorough mixing, the mixture was pressed into pellets 1/2 in. in diameter and calcined at temperature up to 1600 °C in three stages (36 h overall) with an intermediate grinding and pressing in between. After synthesis, the solid ceramic samples were ground again to get the fine powder that has been studied.

The optical absorbance spectra were measured using a spectrophotometer JASCO V-660 with a double monochromator (1.5–6.5 eV) and laboratory setup based on a vacuum monochromator VMR-2 and a hydrogen discharge light source (5.5–11 eV). In the latter case, the constant number of exciting photons was achieved by varying the slit width of the monochromator and using the constant signal from sodium salicylate for normalization.

The luminescence properties of the perovskite single crystals in the VUV spectral range were examined using synchrotron radiation. The luminescence experiments were carried out on the photoluminescence end station FINESTLUMI²¹,²² of the FinEstBeAMS beamline,²³,²⁴ at the 1.5 GeV storage ring of MAX IV synchrotron facility (Lund, Sweden). The excitation spectra of luminescence were normalized utilizing the calibration curve obtained by the AXUV-100G diode. Luminescence detection in the UV–visible–IR spectral range (200–850 nm) was performed by the Andor Shamrock (SR-303i) 0.3 m spectrometer having two gratings (300 grooves/mm and blaze @300 nm (300/300) or blaze @500 nm (300/500)). The Andor Shamrock spectrometer was equipped with photomultiplier photon counting heads (H8259-01 Hamamatsu) covering the spectral range from 200 to 900 nm. The perovskite single crystals were mounted on the sample holder of the close-cycle cryostat inserted into the UHV (10⁻⁷ mbar) chamber, and experiments were carried out at 10 K.

Phase and structural characterization of the materials prepared was performed by the X-ray powder diffraction (XRPD) technique. Experimental diffraction patterns were collected on the modernized X-ray powder diffractometer DRON-3 M in Cu Kα radiation (λ = 1.54185 Å) in the 2θ range of 15–120° and 2θ step of 0.02°. Structural parameters of the studied Y₁₋ₓGdₓAlO₃:Mn⁴⁺ and Gd₁₋ₓLaₓAlO₃:Mn⁴⁺ samples were derived from the experimental XRPD data by full profile Rietveld refinement using the WinCSD software package.²⁵ In the refinement procedure, lattice parameters, coordinates, and displacement parameters of atoms of the main perovskite phase were refined together with profile parameters and corrections for absorption and instrumental sample shift. Simultaneous multi-phase Rietveld refinement was also used for a quantitative phase analysis of the materials synthesized.

TSL measurements of the Mn⁴⁺-doped microcrystalline phosphors were done above room temperature using a laboratory TL-reader with a Hamamatsu R928 photomultiplier. A red long-pass filter (cutting off <650 nm) was used in the TSL measurements. To estimate an activation energy from the thermal glow (TSL) curves, the initial rise method and the partial cleaning procedure were used.

2.2. Theoretical Calculations. The geometry-optimized electronic structure calculations were carried out in spin-polarized mode using the DFT-based plane-wave pseudopotential method implemented in CASTEP²⁶ package of commercial program pack.²⁷ The ion–electron interactions were modeled by Vanderbilt-type nonlocal ultrasoft pseudopotentials.²⁸ The following orbital electrons were regarded as valence electrons: Y 4f⁰5s²5p², Hf 5d²6s², and O 2s²2p⁴. The partial densities of states (PDOS) were calculated using the following correlation functionals and related approximations:²⁷ GGA-PBE, PBE0, HSE03, B3LYP, and several others for perfect RAlO₃ Approach. The super cells were constructed as 2×2×2 unit cell and comprised 160 atoms of the crystal. The symmetries of super cells were set to primitive group P1. Calculations for the defect-containing super cells were done.
for the $\Gamma$ point of the Brillouin zone with use of GGA-PBE approximation of exchange–correlation potential. Other approximations and parameters of computational procedure were the same as in the case of perfect RAlO$_3$ crystals (see above).

Several kinds of point defects and defect combinations were modeled in the super cells of YAlO$_3$: natural vacancies ($V_{O\uparrow}, V_{Y\uparrow}, V_{A\uparrow}$) and vacancy complexes ($V_{O\downarrow} + V_{Y\downarrow}$) and ($V_{O\downarrow} + V_{A\downarrow}$), interstitial oxygen defects $O_i$, and combinations of such interstitials with natural vacancies ($V_{O\uparrow} + O_i$) and ($V_{Y\uparrow} + O_i$), cationic antisites ($Y_{A\uparrow}, Al_{Y\uparrow}$), iso- ($La_{A\uparrow}, La_{A\uparrow}$) and aliovalent cationic substitutions ($Hf_{A\uparrow}, Si_{A\uparrow}$), as well as several other combinations of such defects ($Y_{A\uparrow} + V_{O\downarrow}$), ($Y_{A\uparrow} + V_{Y\downarrow}$), ($Y_{A\uparrow} + V_{A\downarrow}$), ($Y_{A\uparrow} + O_i$), ($Y_{Al\uparrow} + Al_{Y\uparrow}$), ($2Y_{A\uparrow} + V_{O\downarrow}$), ($Y_{A\uparrow} + V_{O\downarrow} + O_i$), ($Y_{A\uparrow} + V_{O\downarrow} + V_{Y\downarrow}$), ($V_{O\uparrow} + V_{Y\uparrow} + 2Y_{A\uparrow}$), including ($Y_{A\uparrow} + V_{O\downarrow}$) defect in Y$_{0.75}$La$_{0.25}$AlO$_3$ mixed-cationic solid solution. In the super cell of the latter defect, eight nearest-neighboring to $Y_{A\uparrow}$ octahedral cationic positions of YAlO$_3$ lattice were filled by lanthanum atoms ($La_{A\uparrow}$, substitutions), while the remaining 24 octahedral positions were occupied by $Y_{A\uparrow}$, thus providing the Y$_{0.75}$La$_{0.25}$AlO$_3$ chemical formula for the crystal. Corresponding structural *cif files of geometry optimized for perfect and defect super cells of the YAlO$_3$ crystal are provided in the Supporting Information as an archive file (cifs.zip). The defects were modeled by removing (adding) the neutral atoms from the super cells without imposing any additional charge to the system. The choice of the above-described set of defects is substantiated in 3.4 Theoretical Calculations.

It should be noted that at the used super cell size (10.4 × 10.7 × 14.7 Å$^3$), the distance between defects in the nearest super cells is not larger than ~7 Å, whereas the longest interatomic distance in the most spatially extensive complex defect modeled here equals 3.3 Å, which is approximately twice smaller. Therefore, there is a good reason to assume in calculations that the mutual influence of defects from the neighboring super cells is negligible in calculations.

Positions of the defect levels with respect to the band edges of YAlO$_3$ crystal were derived from a thorough comparison between PDOS distributions of the perfect and defect-containing super cells calculated with smearing width 0.01 eV.

3. RESULTS AND DISCUSSION

3.1. VUV Absorption Measurements. A commonly used technique for determination of the optical band gaps of crystals (in some approximations, the optical band gap characterizes the $E_g$ value of a crystal, but usually underestimates it) is a construction of the Tauc plots using the experimentally measured optical absorbance spectra (see, e.g. Zatovsky et al.$^{39}$ and references therein). In this technique, the optical absorption spectra $\alpha(\hbar\nu)$ are used for the construction of $\alpha(\hbar\nu)^{1/n}$ dependencies on $\hbar\nu$. The crossing points are then taken as the optical band gap values. The choice of $n$ parameter depends on the origin of electronic transitions. For crystals, it should be taken as $n = 1/2$, if the band-to-band transitions are direct, or as $n = 2$ if the interband transitions are indirect. Then the linear regions in these dependencies are extrapolated until crossing the abscissa.

As our calculations of $E_g(k)$ curves show (band dispersion curves calculated for two spin directions $\alpha$ or $\beta$ and partial densities of states are presented in the Supporting Information, in Figures S1 and S2, respectively, and corresponding band gap parameters are listed in Table S2), some of the studied RM$^{3+}$O$_3$ crystals are indirect-band gap materials (YAlO$_3$, LaAlO$_3$, and YInO$_3$), whereas all others have direct band gaps. For this reason, we estimate the optical band gaps of YAlO$_3$, LaAlO$_3$, and YInO$_3$ from Tauc plots constructed with $n = 2$ and use $n = 1/2$ for all other crystals.

The optical absorption spectra of single-crystalline RAlO$_3$ compounds are presented in Figure 2, whereas corresponding Tauc plots and extrapolations constructed with $n = 2$ and $n = 1/2$ are given in Figure S3. The band gap values estimated from the Tauc plots are shown in Figure 3 as a function of the mean ionic radius of the R cation and also given as numerical data in Table S3. The band gap values estimated for YbAlO$_3$ are shown in Figure S3 as a function of the mean ionic radius of the R cation and also given as numerical data in Table S3. The band gap values estimated from the Tauc plots were chosen from the Tauc plots with $n = 1/2$ or 2, dependent on the type of the band gap (direct or indirect) of RAlO$_3$ crystals determined in calculations.

As Figure 2 shows, among the studied crystals, the nearest absorption edge at about 5.0 eV can be identified for YbAlO$_3$. However, the optical absorption measurements of the YAlO$_3$:Yb(4%) crystal reveal a strong band at 5.7 eV obviously caused by Yb$^{3+}$ ions. The spectral position of this band is typical
Figure 4. Excitation (left) and emission (right) spectra of RAlO₃ crystals measured at 10 K. The corresponding wavelength (energies) of the emitting and exciting photons are indicated.
for absorption bands formed by the \( O^2− → Yb^{3+} \) charge transfer (CT) transitions in oxide hosts.\(^{40−44}\) Therefore, we suppose that the edge-like absorption observed for the \( YbAlO_3 \) crystal (see corresponding curve in Figure 2) is formed by an intense absorption band caused by CT transitions from 2p states of \( O^2− \) to 4f states of \( Yb^{3+} \) ions. Such interpretation of the absorption edge of \( YbAlO_3 \) is further confirmed by the luminescence excitation spectra (corresponding data will be analyzed in 3.2 Luminescence Excitation by Synchrotron Radiation).

After exclusion of the \( O^2− → Yb^{3+} \) CT band in \( YbAlO_3\), the smallest \( E_g \) value of 5.5−5.7 eV identified by absorption is that for the \( LaAlO_3 \) crystal. It should be mentioned here that pure \( LaAlO_3 \), at room temperature, represents the rhombohedral (\( Rh \)) structure type, while \( Gd_{0.68}La_{0.32}AlO_3 \) and others from Table S3 are orthorhombic (\( O \)). In such a way, the band gap data for \( Gd_{0.68}La_{0.32}AlO_3 \) are well in line with a general tendency of \( E_g \) lowering with \( R^{3+} \) cation radius in the frames of orthorhombic structure shown in Figure 3.

\( LuAlO_3 \) undoubtedly has the largest among the studied crystals value of \( E_g \geq 8.0 \) eV; however, its precise value was impossible to estimate from our absorption measurements because the optical density range limit of about 3.0 was already reached at 7.8 eV.

### 3.2. Luminescence Excitation by Synchrotron Radiation

The band gap values of \( RAlO_3 \) compounds can be determined from the excitation spectra of their intrinsic luminescence of recombination type. It is well-known that the luminescence excitation spectra, the same relative changes on the intrinsic (native) point defects and Mn\(^{4+} \) ions, can be used for an approximate estimation method, either from the absorption spectra or \( E_g \) values of oxide crystals (see Table S3). The results obtained are in good agreement with numerous literature data for the \( YAlO_3 \) and \( GdAlO_3 \) compounds\(^7\), as well as for the mixed \( Y_0.5Gd_{0.5}AlO_3 \) orthoaluminate\(^{45} \), thus proving the formation of a continuous solid solution with orthorhombic perovskite structure in the \( Y_{1−x}Gd_xAlO_3 \) system. In contrast, the \( GdAlO_3−LaAlO_3 \) system, two types of solid solutions with orthorhombic and rhombohedral perovskite structures can be formed\(^{42} \). All three \( Gd_{1−y}La_yAlO_3:Mn^{4+} \) materials used in the present work fall in the orthorhombic perovskite region, and their structural parameters (Table S4) are in good agreement with earlier published data for the corresponding \( Gd_{1−y}La_yAlO_3 \) compositions\(^7\).

An analysis of the structural parameters shown in Table S4 indicates that unit cell volume of the \( Y_{1−x}Gd_xAlO_3:Mn^{4+} \) series synthesized (Table S4) agree well with the literature data for the nominally pure \( YAlO_3 \) and \( GdAlO_3 \) compounds\(^7\), as well as for the mixed \( Y_0.5Gd_{0.5}AlO_3 \) orthoaluminate\(^{45} \), thus proving the formation of a continuous solid solution with orthorhombic perovskite structure in the \( Y_{1−x}Gd_xAlO_3 \) system. In contrast, the \( GdAlO_3−LaAlO_3 \) system, two types of solid solutions with orthorhombic and rhombohedral perovskite structures can be formed\(^{42} \). All three \( Gd_{1−y}La_yAlO_3:Mn^{4+} \) materials used in the present work fall in the orthorhombic perovskite region, and their structural parameters (Table S4) are in good agreement with earlier published data for the corresponding \( Gd_{1−y}La_yAlO_3 \) compositions\(^7\).

3.3. Applying the BGE to Far-Red Emitting (\( Y,Gd,La\)-\( AlO_3:Mn^{4+} \) Phosphors.

3.3.1. XRD Characterization. According to XRD examination, as-prepared \( Y_{1−x}Gd_xAlO_3:Mn^{4+} \) (\( x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 \)) and \( Gd_{1−y}La_yAlO_3:Mn^{4+} \) (\( y = 0.2, 0.3, 0.4 \)) materials adopt orthorhombic \( Pbmm \) perovskite structure isotypic with \( GdFeO_3 \). Apart of the main perovskite phase, the materials synthesized contain a minor amount of the monoclinic \( R_2Al_2O_5 \) phase and traces of \( R_3Al_5O_12 \) garnet phase (see Figures S5 and S6 for an example). A minor amount of the monoclinic phase in the studied samples even without the garnet phase is definitely due to the R-rich composition used for their synthesis (see 2.1 Sample Preparation and Experimental Methods for details). Exemplary graphical results of simultaneous two- and three-phase Rietveld refinement for some \( Y_{1−x}Gd_xAlO_3:Mn^{4+} \) and \( Gd_{1−y}La_yAlO_3:Mn^{4+} \) samples are shown in Figures S5 and S6.

Obtained structural parameters of the \( Y_{1−y}Gd_yAlO_3:Mn^{4+} \) series synthesized (Table S4) agree well with the literature data for the nominally pure \( YAlO_3 \) and \( GdAlO_3 \) compounds\(^7\), as well as for the mixed \( Y_0.5Gd_{0.5}AlO_3 \) orthoaluminate\(^{45} \), thus proving the formation of a continuous solid solution with orthorhombic perovskite structure in the \( Y_{1−x}Gd_xAlO_3 \) system. In contrast, the \( GdAlO_3−LaAlO_3 \) system, two types of solid solutions with orthorhombic and rhombohedral perovskite structures can be formed\(^{42} \). All three \( Gd_{1−y}La_yAlO_3:Mn^{4+} \) materials used in the present work fall in the orthorhombic perovskite region, and their structural parameters (Table S4) are in good agreement with earlier published data for the corresponding \( Gd_{1−y}La_yAlO_3 \) compositions\(^7\).

### 3.3.2. TSL Studies above Room Temperature.

When the \( RAlO_3 \) perovskite is doped with manganese in relatively small concentration, the \( Mn^{4+} \) ions occupying the aluminum octahedra are usually observed without any codoping.\(^{44−49} \) As has been shown previously, \( Mn^{4+} \) in the perovskite host lattice, like \( YAlO_3 \), can be easily photoionized already by visible blue-green light (via the \( Mn^{3+} → Mn^{4+} + e^- \) process) that proceeds simultaneously with the accumulation of the released electrons on the intrinsic (native) point defects and \( Mn^{4+} \) ions (\( Mn^{3+} + e^- → Mn^{4+} \)) acting as deeper electron traps.\(^{50−52} \) It is considered that the intrinsic traps acting in this case have an electron- rather than a hole-related origin.\(^{50−52} \) Under subsequent
has been a subject of discussion for a long time (see, e.g., refs 61–66). Supposing that all the RAlO3 perovskites have the same type of intrinsic electron traps, probably connected with RAl antisite defects,64–67 one can expect that their energetic depths should be strongly dependent on the crystal composition. Our TSL results shown in Figure 6 confirm such an assumption: when the R cation is gradually replaced from Y to Gd and next to La, a similar structure of TSL curves is maintained; however, a systematic shift of the peak maxima toward lower temperature is clearly observed. Such a shift evidently correlates with the above-presented decreasing of the RAlO3 band gap in the R sequence Y → Gd → La (taking into account the TSL results for the (Y–Lu)AlO3:Mn2+ crystals presented by Zhydachevskyy et al.68 one can also expand this sequence of the E2 decreasing to Lu → Y → Gd → La). The data presented in Figure 6 definitely indicate a systematic lowering of the depths of the traps related to the TSL peaks in the Lu → Y → Gd → La sequence of cations.

To analyze such a tendency quantitatively, we have estimated the depths of acting traps from the TSL data presented in Figure 6. The trap depths were estimated by the initial rise method as shown in Figure S7. Results of the estimations are collected in Figure 7, where the data for YAlO3:Ce and LuAlO3:Ce from Wojtowicz et al.52 are also given. As is shown in Figure 7, the depth of the shallower trap (marked by us as trap I) decreases from 1.46 to 1.03 eV, and that for the deeper trap (trap II) decreases from 1.74 to 1.14 eV, when content of the R cations changes from Lu to Gd0.6La0.4.

Note that the above-mentioned results demonstrate how the BGE approach can be applied on purpose to move from the long-time storage phosphor, like YAlO3:Mn,55 to the efficient persistent luminescence phosphor, like (La–Gd)-AlO3:Mn (known from Du et al.)55 At the same time, it is obvious that the following questions should be answered in order to clarify the origin of the tendency observed in TSL. First, is the observed decrease of the trap depth related only to the lowering of the crystal band gaps in the mentioned sequence of R cations? Second, does the depth (i.e., the energy distance from the defect level in the band gap to the CB minima) of the trap depth significantly indicate a far-red or near-IR light have recently become of high interest as converting phosphors in solid-state lighting for indoor plant growth; night-vision surveillance; environment inspection; and, in particular, for in vivo biomedical applications.53–60

The origin of the traps responsible for the radiation-induced coloration as well as the high-temperature TSL of YAlO3 and related perovskite crystals is not postulated unambiguously and has been a subject of discussion for a long time (see, e.g., refs 61–66). Supposing that all the RAlO3 perovskites have the same type of intrinsic electron traps, probably connected with RAl antisite defects,64–67 one can expect that their energetic depths should be strongly dependent on the crystal composition. Our TSL results shown in Figure 6 confirm such an assumption: when the R cation is gradually replaced from Y to Gd and next to La, a similar structure of TSL curves is maintained; however, a systematic shift of the peak maxima toward lower temperature is clearly observed. Such a shift evidently correlates with the above-presented decreasing of the RAlO3 band gap in the R sequence Y → Gd → La (taking into account the TSL results for the (Y–Lu)AlO3:Mn2+ crystals presented by Zhydachevskyy et al.68 one can also expand this sequence of the E2 decreasing to Lu → Y → Gd → La). The data presented in Figure 6 definitely indicate a systematic lowering of the depths of the traps related to the TSL peaks in the Lu → Y → Gd → La sequence of cations.

To analyze such a tendency quantitatively, we have estimated the depths of acting traps from the TSL data presented in Figure 6. The trap depths were estimated by the initial rise method as shown in Figure S7. Results of the estimations are collected in Figure 7, where the data for YAlO3:Ce and LuAlO3:Ce from Wojtowicz et al.52 are also given. As is shown in Figure 7, the depth of the shallower trap (marked by us as trap I) decreases from 1.46 to 1.03 eV, and that for the deeper trap (trap II) decreases from 1.74 to 1.14 eV, when content of the R cations changes from Lu to Gd0.6La0.4.

Note that the above-mentioned results demonstrate how the BGE approach can be applied on purpose to move from the long-time storage phosphor, like YAlO3:Mn,55 to the efficient persistent luminescence phosphor, like (La–Gd)-AlO3:Mn (known from Du et al.)55 At the same time, it is obvious that the following questions should be answered in order to clarify the origin of the tendency observed in TSL. First, is the observed decrease of the trap depth related only to the lowering of the crystal band gaps in the mentioned sequence of R cations? Second, does the depth (i.e., the energy distance from the defect level in the band gap to the CB minima) of the electron trap (typical for RAlO3 crystal) change (lower) in this sequence of R cations? These questions will be analyzed in detail.
in the electronic structure computational studies presented in the following section.

3.4. Theoretical Calculations. 3.4.1. Band Gap Values. The band gap values \( E_g^{\text{calc}} \) of RAlO\(_3\) perovskites calculated with various exchange–correlation functionals are presented in Figure 8 (corresponding numerical data are given in Table S4), where also a wider set of functionals is presented in the case of YAlO\(_3\). These calculations were done only for the \( M^{\text{III}} = \text{Al} \) and \( M^{\text{III}} = \text{Y} \) cations. Figure 8 also clearly indicates that for such cations, the use of various functionals can only increase the \( E_g^{\text{calc}} \) values for these two cations are not in line, most probably because of the use of the LSDA+U approximation. Further adjustment of the band gaps for GdAlO\(_3\) and YbAlO\(_3\) to experimental values requires additional calculations. For this reason, we model the BGE effect in computational studies considering only perovskites with \( R = \text{Y} \) and \( \text{La} \). However, it would not be hard to extend our approach and inferences to perovskites with other R cations.

It is well-known that fitting of the calculated \( E_g \) to experimental values by means of searching through appropriate exchange–correlation functionals is a procedure well-justified only for the band-periodic electron states of crystals or solid solutions, and such procedure is barely applicable for the states of defects in the crystal band gap. Therefore, in our computational studies presented in the next subsection, we analyze the results for the defect level positions in the crystal band gaps obtained with the GGA-PBE exchange–correlation functional and without further fitting of \( E_g^{\text{calc}} \) to experimental values. Such an approach has been generally used in computational studies of defects in RAlO\(_3\). The adequacy has never been in question.

3.4.2. Intrinsic Point Defects and Their Trap Depths. Despite the main experimental tendencies of the crystal band gaps and trap depths obtained for the Mn\(^{4+}\)-doped samples (see previous sections), we do not consider in calculations presented here any Mn-related defects in perovskites. We believe that the TSL properties (namely, traps I and II) analyzed in the previous section are formed by native (intrinsic) defects of the crystal hosts and are not related to Mn impurity ions (for more details, see Przybylińska et al. and references therein). Due to the experimental results reported in refs 64–67, these are electron traps related, most probably, to Y\(_\text{Al}\) antisites stabilized by other intrinsic point defects. For this reason, along with considering in calculations the most commonly encountered single native and substitution defects, we focus our attention on Y\(_\text{Al}\)-containing complex defects in YAO\(_3\).

The calculated trap depths of all studied defects in YAO\(_3\) are presented in Table S5. The depths were obtained as the energy difference between the defect level position and the VB maximum, \( E_D - E_v \) for hole traps, and correspondingly, as \( E_v - E_E \) for the electron traps (assuming that if the defect level \( E_D \) lies closer to the CB minimum, it can act as an electron trap, and if the level is closer to VB maximum, this defect can form a hole trap). As our calculations show (see Table S5), the calculated trap depths of some defects in YAO\(_3\) substantially depend on type of spin polarization (different spin polarizations are denoted in Table S5 as \( \alpha \) and \( \beta \)). However, for defects which are the focus of analysis of this paper (presented in Figure 9), such difference is negligible (less than \( 10^{-3} \) eV). For this reason, in order to avoid additional complication of analysis, herein we consider trap depths calculated only for one (\( \alpha \)) spin polarization.

It should be noted that the determination of energy position of defect levels in the crystal band gap by the DFT method as...
well as the use of finite-size super cells may lead to some inaccuracy in the obtained trap depths. However, the super cell size, computational parameters, and approximations of the method applied here are typical for the present-day computational modeling of the electronic structure of YAO3 crystals with defects (see, e.g., ref 77). Taking into account the possible inaccuracy of the obtained calculation results, we can make only assumptions regarding the role of specific defects in the formation of the TSL properties of RAO3 crystals. The assumptions can be formulated as the following.

As follows from the analysis of the TSL data presented above or available literature data,50,52,78,79 the defects, which form the main high-temperature TSL peaks in YAO3 and YAO3:Mn4+, usually have depths from 1.20 to 1.43 eV. It is commonly assumed that these defects are electron traps.50,64,65 According to Table S5, none of the single point defects like YAl, VO, or VY have energy levels of appropriate depth with respect to the CB to be responsible for the high-temperature TSL or the radiation-induced coloration of YAO3 crystals stable at room temperature. However, as our calculation results show, the trap depths of single defects can be considerably changed if the defects are complexed with each other. For example, the deep energy level of VO (electron trap of 2.38 eV depth) becomes much shallower (0.93 or 0.47 eV) when the VO is complexed with cation vacancy (VAl or VY, respectively). At the same time our calculations of the (VO + VY + 2YAl) complex reveal also some down-shift of the YAl-related level (see Figure 9), so it can tentatively also correspond to some type of YAl trapping centers observed by the EPR technique by Laguta et al.65

Our calculations also indicate that doping of YAO3 with La can make the electron traps shallower. As Figure 9 shows, the VO-related level of the (YAl + VO + VY) complex defect (associated with the electron trap II, see above) in Y0.75La0.25AlO3 has the depth of 1.24 eV, which is 0.17 eV smaller than the depth of the corresponding level in YAO3 (1.41 eV). Such a 0.2 eV shift of trap depth is consistent with the experimental results on the cation-related TSL activation energy shifts. For example, trap II in Gd0.9La0.1O3 is by 0.2 eV shallower than that in YAO3 (see Figure 7).

As our calculations show, among all the defect complexes considered in the present work, only the (YAl + VO + VY) complexes have an electron trap depth (1.41 eV) close to the experimental values for trap II (see 3.3.2 TSL Studies above Room Temperature). For this reason we consider the levels of such complex defects in more detail in Figure 9 (corresponding schemes for other defects are given in Figure S8).

As Figure 9 shows, the (YAl + VO + VY) defect has several levels in the crystal band gap. Two of them are related to VY vacancies and can form shallow traps for the holes. It is clearly seen that the level of the (YAl + VO + VY) defect of 1.41 eV depth originates from the oxygen vacancy VO. However, a single VO forms a much deeper electron trap of 2.38 eV (a similar result is typically obtained in the DFT-based calculations).73,74 In such a way, one can assume that the electron trap of 1.43 eV acting in TSL of YAO3 (trap II) can be attributed to the VO-related level of the (YAl + VO + VY) complex defect in yttrium aluminum perovskite. However, we must be aware that it is just a tentative assignment based on the presented results because not all possible combinations of the single defects have been considered.

Two more shallow electron traps (with 0.606 and 0.146 eV depths) of the (YAl + VO + VY) defect are related to the electronic states of YAl antisite substitution (as Figure 9 shows, a single YAl has no levels in the crystal band gap). These electron traps are too shallow to correspond to the (YAl + VO) complexes observed previously by the EPR technique by Laguta et al.65 (owing to the thermal stability of the centers reported by Laguta et al.65 their depth should be about 0.9–1.1 eV). However, the YAl-related levels of the (2YAl + VO) complex of the 0.91 eV depth for electrons (see Table S5) can exactly be the YAl-related electron traps known from Laguta et al.65

The electron trap I of 1.33 eV depth found in experiments for YAO3 can be presumably formed by a complex like (YAl + VO + VY) with an up-shifted VO-related level (experimental upshift from trap II level to trap I is 0.1 eV). Such a shift can arise, for example, in the same complex, but with slightly different spatial configuration of VAl and VY. However, the trap depth of this level (see Table S5) is 1.015 eV and does not fit well the experimentally determined depth of trap I. At the same time our calculations of the (VO + VY + 2YAl) complex reveal also some down-shift of the YAl-related level (see Figure 9), so it can tentatively also correspond to some type of YAl trapping centers observed by the EPR technique by Laguta et al.65

As our calculations show, among all the defect complexes considered in the present work, only the (YAl + VO + VY) complexes have an electron trap depth (1.41 eV) close to the experimental values for trap II (see 3.3.2 TSL Studies above Room Temperature). For this reason we consider the levels of such complex defects in more detail in Figure 9 (corresponding schemes for other defects are given in Figure S8).

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Our calculations also indicate that doping of YAO3 with La can make the electron traps shallower. As Figure 9 shows, the VO-related level of the (YAl + VO + VY) complex defect (associated with the electron trap II, see above) in Y0.75La0.25AlO3 has the depth of 1.24 eV, which is 0.17 eV smaller than the depth of the corresponding level in YAO3 (1.41 eV). Such a 0.2 eV shift of trap depth is consistent with the experimental results on the cation-related TSL activation energy shifts. For example, trap II in Gd0.9La0.1O3 is by 0.2 eV shallower than that in YAO3 (see Figure 7).

According to Figure 9, the 0.17 eV decrease in trap depth of the VO-related level of the (YAl + VO + VY) defect in Y0.75La0.25AlO3 is related to the decrease (by 0.07 eV) of the level position with respect to the CB minimum of the mixed crystal, as well as to the lowering (by 0.1 eV) of the CB minimum (Ecb) of Y0.75La0.25AlO3 relative to YAO3 case. The mechanism of such Ecb lowering may be explained as follows. A single La defect in YAO3 creates defect levels of La d character just below the CB
of the crystal (see Figure S8). If the concentration of $La_Y$ defects is low, their mutual influence is negligible and they can form only defect levels in the crystal band gap. If concentration of $La_Y$ defects is sufficiently high, as for example in $Y_{0.75}La_{0.25}AlO_3$ solid solution, the defect levels can already form periodic bands in the reciprocal space lying below $E_g$ of YAlO$_3$ crystal. In real space, the electronic states which correspond to these bands may form quasi-infinite regions for spatial movement of free electrons. For this reason, the appearance of $La_Y$-related bands below $E_g$ of YAlO$_3$ may be regarded as lowering of the CB minimum of the crystal.

Therefore, it could be argued that our calculations provide direct computational evidence for the possibility of BGE in RAlO$_3$ perovskites using $R = Y$ and La as an example. Extending the analysis to RMII$_3$O$_9$ perovskites with other $R$ and M$^{III}$ cations, as well as consideration of a wider set of defects, should be a subject of further computational studies.

4. CONCLUSIONS

The following observations and conclusions result from the complex experimental and theoretical studies presented above:

(1) Depending on the $R$ and M$^{III}$ cations, the RMII$_3$O$_9$ perovskite crystals may be direct- ($LuAlO_3$-$GaDAlO_3$, LaAlO$_3$-$YbAlO_3$, and YGaO$_3$) or indirect-band gap materials (YAlO$_3$, LaAlO$_3$, and YInO$_3$).

(2) The gradual decrease of band gap value ($E_g$) of RAlO$_3$ perovskites from $\sim$8.5 to $\sim$5.5 eV with increase of cationic radius, i.e., in sequence of R cations Lu $\rightarrow$ Yb $\rightarrow$ Y $\rightarrow$ Gd $\rightarrow$ La, has been shown experimentally using both the optical absorption measurements in VUV spectral range and the spectra of luminescence excitation by synchrotron radiation. Such a wide ($\sim$3 eV) variation of band gap values obviously provides a strong potential for the band gap engineering of RAlO$_3$ perovskite compounds.

(3) The DFT electronic structure calculations confirm perspectives of the BGE approach in perovskites: the band gaps of RMII$_3$O$_9$ crystals gradually decrease in the Lu--Y--La sequence of R cations and Al--Ga--In sequence of M$^{III}$ cations.

(4) When the R cation of RAlO$_3$ is gradually replaced from Y to Gd and next to La, a similar structure of thermally stimulated luminescence curves (two main peaks associated with the traps denoted as I and II) is systematically shifted toward lower temperature. Such a shift indicates a lowering of the energy depth of acting traps in the Y $\rightarrow$ Gd $\rightarrow$ La sequence of cations. When the content of the R cations changes from Lu to Gd$_{0.2}$La$_{0.8}$, the depth of the shallower trap I decreases from 1.46 to 1.03 eV and the depth of the deeper trap decreases from 1.74 to 1.14 eV.

(5) Calculations indicate that trap depths of single-point defects $Y_{Al}$, $V_{O}$, or $V_{Y}$ in YAlO$_3$ can be considerably changed when these defects are complexed with each other. In particular, the energy level of the $Y_{Al}$ antisite (which has no energy levels in the band gap when alone) can be as deep as 0.89 eV with respect to the CB when $Y_{Al}$ is complexed with a neighboring $V_{O}$ and even of 1.0 eV when two $Y_{Al}$ antisites are complexed with neighboring $V_{O}$ and $V_{Y}$, which is consistent with the experimental results reported by Laguta et al.$^{65}$ The deep energy level of $V_{O}$ ($2.38$ eV for electrons) became much shallower (0.93 or 0.47 eV) when the oxygen vacancy was complexed with cation vacancy ($V_{Al}$ or $V_{Y}$ respectively). At the same time, the energy level of the O$_{interstitial}$ (which does not have deep levels in the band gap when alone) can serve as an electron trap of 0.65 eV depth when complexed with the $Y_{Al}$ antisite.

(6) The performed calculations allow the tentative assumption that the experimentally observed trap II (1.43 eV depth in YAlO$_3$) can be formed by the $V_{O}$-related energy level of the ($Y_{Al}$ + $V_{O}$ + $V_{Y}$) complex defect which captures an electron. The shallower electron trap I (1.33 eV in YAlO$_3$) presumably can be formed also by the energy level of oxygen vacancy in the same complex defect, but with somewhat different arrangement of neighboring $Y_{Al}$ and $V_{Y}$.

(7) Calculations provide direct computational evidence for the possibility of BGE in RAlO$_3$ perovskites using $R = Y$ and La as an example. In particular, the predictions calculate shallowing of the $V_{O}$-related level of the ($Y_{Al}$ + $V_{O}$ + $V_{Y}$) complex defect in La-containing YAlO$_3$ crystal by 0.17 eV, which is consistent with the experimental results regarding the cation-related shifts of TSL activation energies. The 0.17 eV decrease of the trap depth is related to the decrease (by 0.07 eV) of the level position with respect to the CB minimum and to the lowering (by 0.1 eV) of the band gap ($E_g$) of $Y_{0.75}La_{0.25}AlO_3$ relative to YAlO$_3$.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c06573.

Additional data including calculated electronic band structures, partial densities of states, and band gap values of RMII$_3$O$_9$ perovskites ($R = Y, La, Lu, Gd, Yb$; M$^{III} = Al, Ga, In$); calculated energy levels and trap depths of several defects within the band gap of YAIo$_3$; Tauc plots from the room-temperature optical absorption spectra of the RAlO$_3$ single crystals; excitation and emission spectra of Mn-doped ($Y, Gd, La, Lu$)AlO$_3$ solid solutions obtained under excitation by synchrotron radiation at 10 K; band gap values of RAlO$_3$ crystals estimated experimentally from the VUV absorption and excitation spectra by synchrotron radiation; trap depth estimation procedure from TSL; crystal structure parameters of the $Y_{1−x}Gd_{x}AlO_3: Mn^{2+}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) and $Gd_{1−x}La_{x}AlO_3: Mn^{2+}$ ($y = 0.2, 0.3, 0.4$) phosphors (PDF).

Structural ( cif) files of geometry optimized for perfect and defect super cells of YAIo$_3$ crystal (zip)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The work was supported by the Polish National Science Centre (Project No. 2018/31/B/ST8/00774), by the NATO SPS Project G5647, and by the Ministry of Education and Science of Ukraine (Project DB/Kinetyka no. 0119U002249). L.V. acknowledges support of the National Research Foundation of Ukraine under Grant No. 2020.02/0373 “Crystalline phosphors’ engineering for biomedical applications, energy saving lighting and contactless thermometry”. Researchers from Tartu were supported by the ERDF fundings in Estonia granted to the Centre of Excellence TK141 “Advanced materials and high-technology devices for sustainable energetics, sensors and nanoelectronics (HiTechDevices)” (Grant No. 2014-2020.4.01.015-0011) and Estonian Research Council Grant PRG-629. The Institute of Solid State Physics, University of Latvia as the Center of Excellence acknowledges funding from the H2020-WIDESPREAD-01-2016-2017-Teaming Phase2 under Grant Agreement No. 739508, Project CAMART2. N.K. was supported by the National long-term project No. WQ20142200205 (Recruitment Program of Global Experts, PRC). Authors are thankful to George Loutts from Norfolk State University, United States, and Dorota Pawlak from Institute of Electronic Materials Technology, Poland for providing some single crystals studied in the work, as well as to Kirill Chernenko from FinEstBeAMS of MAX IV for his assistance with synchrotron experiments.

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