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Abstract

Electron traps are known to a have great influence on the carriers transport process in Ce based scintillators. On the other hand, the role of hole traps in the scintillation process has been less considered. By means of electron spin resonance (ESR), we detected hole traps in highly Ce-doped LuAG:Ce,Mg ceramics in the form of σ-type O– centers. The g -tensor components turn out to be $g\perp = 2.0103$, and $g|| = 2.0023$, revealing the axial symmetry of these defects. Mg-perturbed variants of O– centers are proposed to exist in LuAG:Ce,Mg. Their occurrence is related to an elongated Mg–O bond as evidenced by DFT calculations. Finally, the multiple role of O– centers in the scintillation process is discussed.

1 Introduction

Divalent alkali earth ions (denoted as Me^{2+}) co-doping has been employed to improve the scintillation performance of several Ce^{3+} based scintillators, such as orthosilicate Lu_2SiO_5:Ce,Ca [1] , $(Lu,Y)_2SiO_5$:Ce,Ca , [2] $(Lu,Y)_2SiO_5$:Ce,Mg [2], Y_2SiO_5:Ce,Ca [3], and garnet $Lu_3Al_5O_{12}$:Ce,Mg [4,5] , $Gd_3Ga_3Al_2O_{12}$:Ce,Ca [6] compounds. Indeed, Me^{2+} co-doping has become a hot spot for the Ce-doped scintillators. The microscopic role of this co-doping has gradually been unveiled [2,5,6]. Interestingly, a positive role of Ce^{4+} in the scintillation response was verified. In a previous work, Blahuta et al. [2] illustrated that Ce^{4+} acts as a precursor of temporary $(Ce^{3+})^*$ excited centers, which are created following electron capture from the conduction band by Ce^{4+}, in accordance with previous results obtained on $Y_3Al_5O_{12}$ [7], and sol–gel silica glasses [8]. In the frame of this picture, the presence of a hole trap close to Ce^{4+} ions was predicted [2,5,6]. Therefore, the study of the nature of these hole traps is of great importance for both fundamental understanding of charge trapping phenomena and optimization of the performance of Me^{2+} co-doped scintillators. Recent progress in Mg^{2+} co-doping LuAG:Ce ceramics gave hints for this study [4].

Although $Lu_3Al_5O_{12}$:Ce (LuAG:Ce) scintillator was first reported in the nineties [9], its low light yield and slow components in the scintillation decay were considered serious drawbacks for a long time. Recently, we succeeded in fabricating an innovative LuAG:Ce ceramic using divalent co-doping and an appropriate annealing strategy [4]. By adding several hundreds of ppm of Mg, a light yield of 21900 ph/MeV (1 μs shaping time) was obtained, with a fast component intensity even higher than that of LuAG:Ce single crystal [4]. The optical absorption spectra of LuAG:Ce,Mg ceramics reveal the existence of stable Ce^{4+} ions [2,4]. O^- centers can be considered good candidates as hole traps [4,5].

In this Letter, we employed low temperature ESR experiments and DFT calculations to verify the existence and nature of the hole centers in Mg co-doped LuAG:Ce ceramics. The ESR signals prove the presence of the

O^- centers, suggested also by density functional theory (DFT) calculations. Based on the above results, the multiple role of O^- centers in the scintillation process is discussed.

2 Experimental conditions

2.1 Experiment

Ceramics of LuAG:Ce,Mg (with Ce concentration of 0.5 at% and 0.4 at% Mg) with 23 mm diameter and 5 mm thickness were prepared by solid-state reaction and vacuum sintering method. A post-growth air-annealing process was also performed (see [4] for details). Samples of 2 × 2 × 10 mm^3 were cut and polished for ESR study. ESR measurements were carried out from 70 K to 280 K using a Bruker EMX plus 10/12 X-band (~9.4 GHz) CW ESR spectrometer equipped with Oxford ESR910 cryostat. A mercury high-pressure arc lamp was used for in situ UV irradiation of the samples.

2.2 Calculation details

The DFT calculations on Mg-doped LuAG were performed by the Vienna Ab Initio Simulation Package (VASP) code [10,11], with the projector augmented-wave (PAW) method [12,13], on supercells containing 160 atoms. Perdew–Burke–Ernzerhof (PBE) [14] generalized gradient approximation (GGA) functionals are used with tested energy cutoff, and k -point sampling (using 2 × 2 × 2 k -point meshes of the Monkhorst–Pack type [15]). The supercells are fully relaxed until the residual force on each atom is less than 0.01 eV/Å.

3 Results and discussion

3.1 Spectroscopic data

Figure 1 shows ESR spectra for LuAG:Ce,Mg ceramic after UV irradiation at 70 K. Three resonances are clearly revealed, whose g -factors are $g_{\mathrm{I}} = 2.0103$, $g_{\mathrm{II}} = 2.0023$, and $g_{\mathrm{III}} = 1.9891$. Previous studies [16] showed that in most cases (both σ- and π-type ground state) there is a characteristic g -factor of around $g_s = 2.0023$ (free-electron value) for the O^- centers in oxides, which is indeed found (g_{II}) in our sample. Besides, the g -factor for O^- centers in LuAG:Sc is 2.010 [17], which is also one of the g -factor tensor components (g_{I}) in our ESR spectra. Hence, we assume that our ESR spectra include ESR signals (g_{I} and g_{II}) of the O^- centers.

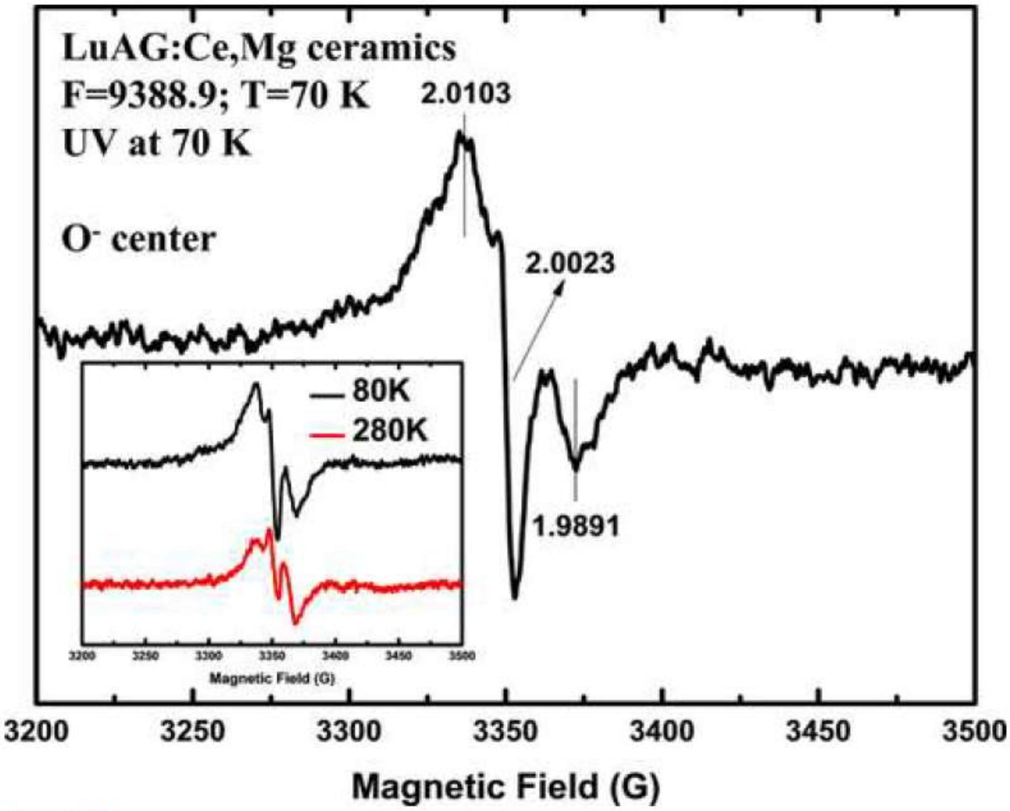

Figure 1

ESR spectra of LuAG:Ce,Mg ceramics after UV irradiation at 70 K for 15 min. The inset shows the ESR spectra meas-ured at 70 K after annealing at indicated temperatures.

However, not all these three *g* -factors could be ascribed to the O^- centers, as it was evidenced also by ESR measurements after annealing. The inset in Fig. 1 shows the ESR spectra of the LuAG:Ce,Mg ceramics measured after few minutes annealing at a specific temperature and re-cooling back to 70 K. The annealing temperatures of 80 K (black line) and 280 K (red line) were chosen as examples. By comparing the two ESR spectra, we observed that the intensities of both g_{I} and g_{II} display a simultaneous 35% decrease, while the intensity of g_{III} was almost unaffected. This is in accordance with our assumption that only two *g* -factors: $g_{\mathrm{I}} = 2.0103$, $g_{\mathrm{II}} = 2.0023$ are related to the O^- centers. The ESR signal with *g* -factor of 1.9891 (below the free-electron value) is possibly due to the F_A^+ center, in accordance with its *g* -factor in YAG [18,19], ; the formation of a F_A^+ defect complex stabilized by Mg can be suggested. This is supported by the fact that Mg favors the formation of O vacancies in YAG [20]. The spectra of O^- centers can be explained by former theoretical calculation results on the axial symmetry of polycrystalline materials [21], i.e. in those cases when the centrosymmetric resonance is perpendicular to the magnetic field. Therefore, the *g* -factors can be denoted as $g_{\perp} = 2.0103$, $g_{\parallel} = 2.0023$, which means a smaller Δg (the difference between g_s) is measured along the orientation of the magnetic field. Thus, the O^- centers display the σ-type O-2p ground state [16], i.e. the ground state 2p lobe is parallel to the axis of the perturbing defect (or the symmetry axis). For this kind of O^- center, the perturbing defect must be a charged defect (such as Mg'_{Lu}), with an elongated bond between charged defect and the O^- centers.

3.2 Local structure and creation mechanism

Previous work in $YAlO_3$ (YAP) single crystals showed that O^- centers can be created either by self-trapping or holes trapped at an oxygen ion bound to perturbing defects [22]. At least 6 kinds of O^- centers were found in YAP. The thermal activation energies vary from 0.024 eV to 0.49 eV, while two very deep O^- centers are even stable for several days at room temperature [22]. Actually, these results can be applied to the garnets. In our sample, the O^- centers would not vanish up to 280 K. Similarly to the O^- centers stable at room temperature in YAP single crystals, the O^- centers found in our samples should be ascribed to Mg-stabilized O^- centers [22]. Regular O site in LuAG single crystal locates in a slightly distorted tetrahedral symmetry structure (Fig. 2(a)) [23]. As discussed above, the O^- centers are most probably Mg-related. From the viewpoint of ionic radii, Mg^{2+} (0.89 Å, dodecahedron) is more likely to substitute Lu^{3+} (0.98 Å, dodecahedron) sites, for only a 8% distortion compared with 36% and 49% for Mg'_{Altet}, and Mg'_{Altet} respectively [24]. When Mg^{2+} substitutes for Lu^{3+}, the charged defect Mg'_{Lu}would stabilize a hole into any of 8 oxygen sites around. Therefore, the most possible structure for O^- centers is the one reported in Fig. 2(b).

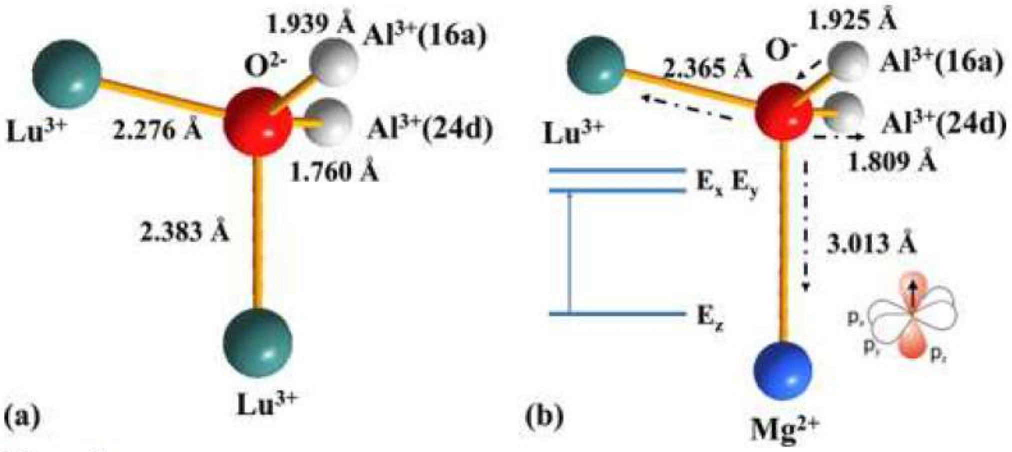

Figure 2

(a) Idealized fragment of LuAG crystal structure by experiment, (b) calculated model of O^- centers in LuAG:Ce,Mg ceramics.

3.3 O– center structure simulation

We performed first-principles calculations for a better understanding of the local structure of O^- centers in LuAG:Ce,Mg ceramics. The atomic structure of LuAG:Mg is simulated by replacing one of the Lu^{3+} sites by Mg^{2+} and allowing full ionic relaxation. In order to describe the localized O-2p hole states, we used the DFT + *U* approach [25], which has been successfully employed to describe defective oxide systems with O^- centers in Li-doped MgO [26], and Al-doped SiO_2 [27]. By adding an orbital dependent term, the DFT + *U* approach can account for the on-site electron–electron interaction and correctly localize the electron. An optimized parameter *U* on the O-2p orbit was chosen based on previous Refs. [26,27].

For pure LuAG, the difference in bond length between calculation and experiment [24] (by refined XRD results) is within 2%. Although the calculated band gap is underestimated (5.0 eV) when compared with experiment results (8.2 eV) [28], it fits well with previous DFT calculation on YAG (4.7 eV) [29]. Hence, the calculation is sufficiently reliable. After ionic relaxation of the LuAG:Mg supercell, the calculated bond lengths in LuAG:Mg are shown in Table 1. After ionic relaxation, we found the oxygen sites stay almost the same, except for one oxygen ion that is bonded to the dopant. The bond length of this site and Mg^{2+} site is elongated by 24.25%. Interestingly, it can be ascribed to the O^- center in LuAG:Mg. Figure 3 displays the DOS (density of states) and PDOS (partial density of states) of LuAG:Mg, O^- centers and normal O sites, respectively. From Fig. 3(b), a localized hole trap is evidenced in O^- center. The coupling of charge localisation (the O^- centers) and bond distortion is a polaron, which was evidenced by Schirmer [16] as well as in Ref. [26,27].

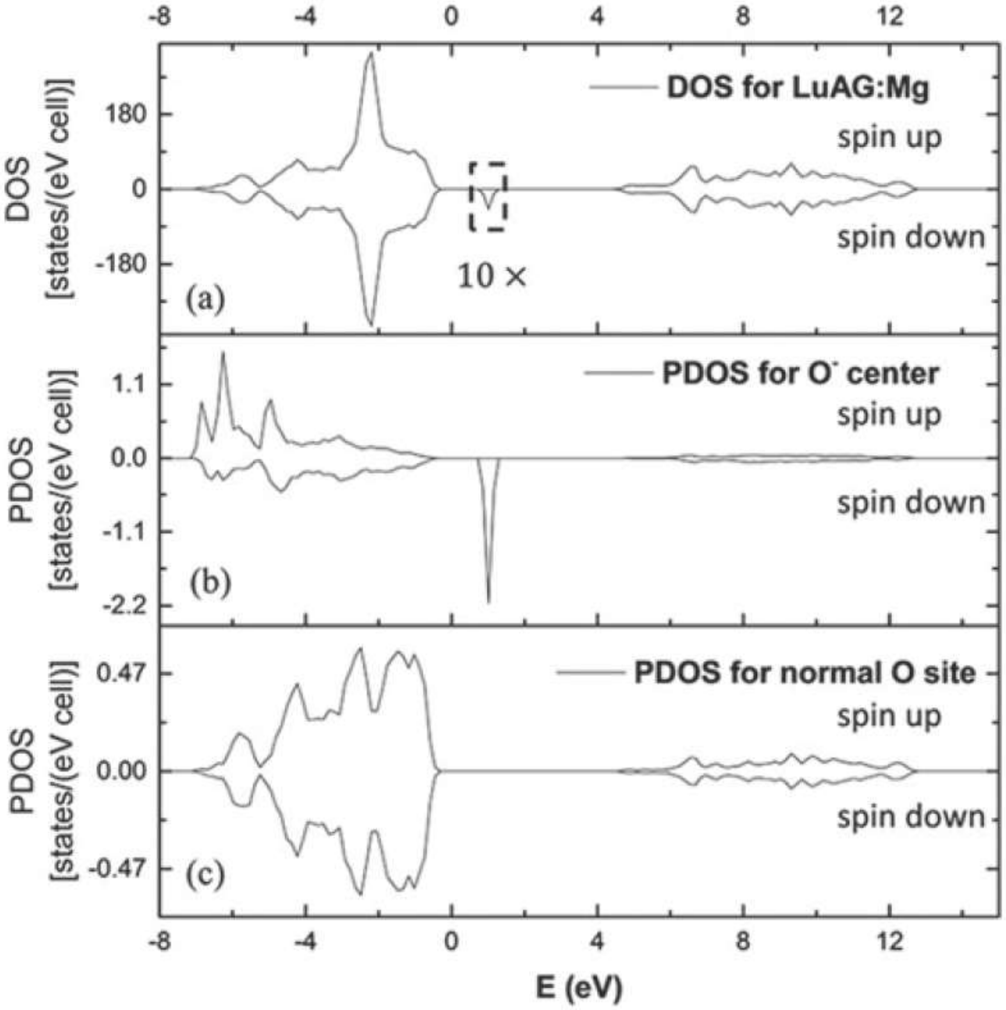

Figure 3

(a) Total DOS of LuAG:Mg, (b) PDOS for O^- center in LuAG:Mg, (c) PDOS for normal oxygen site.

Table 1. Experimental and DFT calculation bond lengths in LuAG, LuAG:Mg, and the change before and after Mg doping (in Å)

	exp. LuAG[a]	**calc. LuAG**	**calc. O^- in LuAG:Mg**	**–change –in length**
Lu–O/Mg–O	2.383	2.425	3.013	–24.25%
Lu–O	2.276	2.304	2.365	–2.65%
Al(16a)–O	1.939	1.936	1.925	–6.56%

Al(24d)–O	1.760	1.778	1.809	−1.74%

[a] Ref. [24]

Compared with normal oxygen sites in LuAG:Mg, the O^- center is highly paramagnetic, which indicates that the O^- center could be detected by ESR. Besides, a hole trap in the band gap is also found in the DOS of LuAG:Mg. 44.9% of this hole center, is in the form of the above mentioned O^- center. Therefore, we conclude that by Mg co-doping a hole is trapped mainly at the O^- center site. This result strongly supports the model of Mg-perturbed O^- centers in LuAG:Ce,Mg ceramics. Besides, in our calculation, the position of the O^- hole state relative to the VB edge, i.e. the trap depth, is 1.0 eV. Such a deep trap would surely be stable at room temperature.

3.4 The role of O– centers in scintillation process

The above discussion has shown that hole traps are stabilized in the form of O^- centers and their role in scintillation process needs discussion. As depicted in the abstract figure, the O^- centers play the role of hole traps in the lattice. As discussed above, the O^- centers in LuAG:Ce,Mg are rather stable even up to 280 K. They act as non-radiative centers in the lattice which would cause a light loss (reduce the RL intensity). Moreover, in LuAG:Ce,Mg ceramics, part of Ce^{3+} centers are oxidized to Ce^{4+} centers [4,5]. As illustrated in the abstract figure, after capturing a free electron from the conduction band, Ce^{4+} is transformed into an excited Ce^{3+} center. After the luminescence photon is emitted, the center still needs to capture non-radiatively a hole for restoring its initial Ce^{4+} state. The O^- centers, which stay nearby the Ce^{4+} centers, are thus an important "hole source" for restoring of Ce^{4+}. This makes the Ce^{4+} scintillation cycle possible, and there is no contribution to afterglow as such a hole transfer is non-radiative. Therefore, in Mg co-doped samples, Ce^{4+} would act as precursor of a temporary Ce^{3+} emission center, free from delayed emission. This mechanism has already been proved not only in Mg co-doped LuAG:Ce [5], but also in Ca co-doped LSO:Ce [1], YSO:Ce [3], GGAG:Ce [6], and Mg or Ca co-doped LYSO:Ce [2].

4 Conclusion

Me^{2+} co-doping appears as an efficient tool to improve the scintillation of Ce-doped oxide scintillators [1-5]. However, the microscopic mechanism of such an improvement was not clear. For a long time, only the Ce^{3+} emission centers and electron traps were regarded as the key elements in the scintillation process. Consequently, the research efforts concentrated on minimizing the amount of Ce^{4+} to optimize scintillation properties [30]. This Letter reveals the paramagnetic O^- centers and their cooperative role with stable Ce^{4+} centers in the scintillation mechanism of LuAG:Ce,Mg which paves the way for a complete understanding of the scintillation cycle. Relying on the ESR experiments, completed further with DFT calculations, the nature of hole traps in the form of σ-type O^- centers is evidenced in LuAG:Ce,Mg ceramics. The O^- centers are rather stable even up to 280 K. The local structure around O^- centers is simulated by first-principles calculations. A double role of O^- centers in LuAG:Ce,Mg ceramics is proposed: (i) acting as non-radiative centers, reducing the radioluminescence intensity; (ii) stabilizing and dynamically restoring the Ce^{4+} centers which provide an additional fast recombination pathway in the scintillation mechanism, without any afterglow effects. This work consequently provides a guidance for further optimization of scintillation properties of these oxide scintillators. The key factor is the ratio between the O^- centers and Ce^{4+} centers. When the concentration of O^- centers noticeably exceeds that of Ce^{4+} centers, the non-radiative effect of O^- centers dominates, decreasing radioluminescence and light yield. The O^-/Ce^{4+} ratio can be controlled by Mg and Ce concentrations, preparation atmosphere and annealing process.

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