Increased Fluorescence Intensity in $\text{CaTiO}_3\text{:Pr}^{3+}$ Phosphor Due to NH_3 Treatment and Nb Co-doping

K. S. Holliday^{1*}, T. A. Kohlgruber¹, I. C. Tran¹⁺, D. Åberg¹, Z. M. Seeley¹,
M. Bagge-Hansen¹, A. M. Srivastava², N. J. Cherepy¹, and S. A. Payne¹

¹Lawrence Livermore National Laboratory, 7000 East Ave., Livermore CA 94550 United States

²GE Global Research, One Research Circle, Niskayuna, NY 12309 United States

⁺Current Address: Irvine Materials Research Institute, UC Irvine, CA 92697

Keywords: Red phosphor; calcium titanate; praseodymium emission; lighting phosphor

Development of next generation red phosphors for commercial lighting requires understanding of how increased luminescence is achieved by various treatment strategies. In this work, we compare co-doping with Nb to NH_3 treatment of $\text{CaTiO}_3\text{:Pr}$ phosphors to reveal a general mechanism responsible for the increased luminescence. The phosphors were synthesized using standard solid-state synthesis techniques and the fluorescence was characterized for potential use in fluorescent lighting, with 254 nm excitation. The lifetime of the fluorescence was determined and used to identify a change in a trap state by the co-doping of Nb^{5+} in the phosphor. The oxidation state of the Pr was probed by NEXAFS and revealed that both Nb^{5+} co-doping and NH_3 treatment reduced the number of non-fluorescing Pr^{4+} centers. Calculations were performed to determine the energetically favorable defects. Vacuum annealing was also used to further probe the nature of the trap state. It was determined that NH_3 treatments reduce the number of Pr^{4+} non-fluorescing centers, while Nb^{5+} co-doping additionally reduces the number of excess oxygen trap states that quench the fluorescence.

1. Introduction

Despite intense research, alternative red phosphors for lighting applications remain a challenge. No alternative has been found to the original $\text{Y}_2\text{O}_3\text{:Eu}$ phosphor developed for the first tri-color fluorescent lamp more than 40 years ago [1], though our recent efforts did identify AlN:Mn as a possible option [2]. The red phosphor is particularly demanding, because it must emit within a very narrow energy range due to a sharp decrease in eye sensitivity at longer wavelengths and a poor red color rendering index at shorter wavelengths. Emission around 610 nm is an ideal compromise between these two competing factors [3]. For commercial applications, a phosphor emitting at 610 nm must also have high quantum efficiency so that the current demands for low energy consumption (lumens/watt) can be achieved.

Since the reporting of red luminescence in $\text{CaTiO}_3\text{:Pr}$ [4], it has been widely studied for lighting and display applications due to its ideal red emission at 610 nm [5]; however, the poor quantum efficiency limits its commercial application and has led to several further studies aimed

at increasing the photoluminescence brightness. Several methods to increase luminescence have been reported: codoping with Bi^{3+} in a B_2O_3 flux [6], the addition of SiO_2 [7], Zr^{4+} substitution [8], ammonia treatment [9], and codoping with Nb^{5+} [10]. While each of these reports an enhancement in brightness, none provide a clear mechanism for this improved light yield.

One possible path to enhanced luminescence is in eliminating any oxidized Pr^{4+} that may be quenching the fluorescence or reducing the number of fluorescent centers. For example, a reduction in oxidized Pr is proposed as the reason for enhanced fluorescence in $\text{CaTiO}_3\text{:Pr}$ when codoped with Al^{3+} ; however, this was not confirmed by a direct measure of the Pr oxidation state [11]. The oxidation of Pr from trivalent to tetravalent has been shown to occur with heat treatments in air as low as 1160 °C in other systems, so it must be considered [12].

Another possibility is that the codopant may enhance energy transfer to the fluorescence center directly, as was proposed with Bi^{3+} and B^{3+} codopants [6]. Additionally, several studies also show reduced strain and increased symmetry through a variety of treatments [7-9]. This occurs because the pristine, untreated CaTiO_3 has a non-centrosymmetric distortion in the Ti octahedron that increases lattice strain [13], which can be reduced by co-doping and ammonia annealing. This effect is thought to improve energy transfer to Pr^{3+} luminescent centers [7] or reduced trapping centers [8,9]. It should be noted that these studies did not measure Pr oxidation state and therefore did not eliminate the possibility that a reduction of oxidized Pr^{4+} is the mechanism for increased fluorescence.

There have been a few studies that have attempted to characterize the trapping centers in these materials. One study increased the Ca concentration, which led to an increase in trap states that were presumed to be oxygen vacancies [14]. The energies of these trap states were measured at different sintering temperatures and two traps were identified [15]. The first trap state was assigned to Pr^{4+} and the energy of this trap state remained approximately 0.53 eV regardless of sintering temperature. The other trap state was 0.70, 0.99, and 0.41 eV at 800, 1200, and 1400 °C, respectively and was presumed to be associated with oxygen vacancies [15]. A study of how Nb^{5+} doping effects these charge trapping states found that the energy of the trap state is reduced from 0.82 eV without Nb^{5+} to 0.62 eV with Nb^{5+} doping [16]. The possibility of this trapping center being a Ti^{4+} vacancy is mentioned, but not seriously considered. When we reconsider the temperature dependence of the charge trap state energy [15], it seems that the Nb^{5+} doping is reducing the energy of this same trap state, whatever it may be. This trapped state is still higher in energy than that measured and assigned to Pr^{4+} .

In this study we present $\text{CaTiO}_3\text{:Pr}$ phosphor heat treated with ammonia or co-doped with Nb^{5+} in an effort to understand the mechanism behind enhanced luminescence. The Pr oxidation state is measured directly by near-edge x-ray absorption fine structure (NEXAFS) in order to determine the quantity of Pr^{4+} in each sample. Samples were also heat treated under high vacuum to develop further insight into the nature of this trap state. Finally, calculations were performed to determine the most likely defects in these materials.

2. Experimental Section

2.1 Phosphor Synthesis

The starting precursor oxides ($\text{Ca}(\text{OH})_2$, TiO_2 , Pr_6O_{11} , and Nb_2O_5 , Alpha Aesar) were measured according to the desired stoichiometric ratios. A homogenous mixture of the precursor powders was made in a scintillation vial by mixing the oxides in a dilute solution of Darvan dispersing agent (ammonium polymethacrylate in water) with the aid of an agitation mixer (Thinky AR-250, USA) and an Ultra-sonicator (Cole Parmer Ultrasonicator Processor, USA). The suspension was then allowed to sit in an oven set at 50°C until dry. After the suspension dried, the powder mixture was finely ground with a mortar and pestle. This homogenous mixture was then heat treated to 1200°C for 15 hours in air with a ramp rate of $5^\circ\text{C}/\text{min}$ heating and cooling in order to obtain a sintered powder of CaTiO_3 in solid solution with the desired dopant (Pr or Pr and Nb). A subset of samples also underwent an ammonia treatment by heating to 450°C in flowing ammonia atmosphere for 4 hours. The amount of Pr dopant was held constant at 0.6 at. % and the Nb dopant was held constant at 5 at. % when present.

2.2 Vacuum Heating

Samples were heated stepwise to 550°C in high vacuum (10^{-8} Torr) in an effort to remove any volatile species present in the phosphor powder samples. Samples were loaded into a resistively heated ceramic crucible and installed within a stainless steel vacuum chamber and allowed to equilibrate overnight, thereby removing any surface adsorbed species. Then, samples were heated in three steps: first, to 150°C ; second, to 300°C ; and last, to 550°C . The gas evolved at each step was measured by line-of-sight quadrupole mass spectrometer (Stanford Research Systems RGA300). The system was allowed to return to the base pressure before proceeding to the next temperature step (~ 600 s). By maintaining the same experimental parameters and set up, as well as a consistent sample mass (NH_3 and Nb treatments did not affect surface area, see electron microscopy Section 3.1), the total pressure evolved from the sample over the course of heating is proportional to the amount of oxygen (in mass or moles) removed from the sample.

2.3 X-ray Diffraction

Powder x-ray diffraction (XRD) was performed with a Bruker D8 Advance diffractometer equipped with a Cu anode ($K\alpha_1 = 0.1540598$ nm). Samples were prepared by spreading the powder on a low-background sample holder (single crystal silicon wafer) with the aid of methanol. Patterns were taken using 40 mV and 40 mA from 10 to $90^\circ 2\theta$ with a step size of $0.025^\circ 2\theta$ and 1.5 s per step. Phases were identified using Bruker AXS EVA. Bruker AXS TOPAS was then used to fit the diffracted intensities and to perform least-square and Rietveld analysis. Structure input parameters were taken from the Inorganic Crystal Structure Database.

2.4 Electron Microscopy

Electron microscopy was performed on a FEI Inspect F scanning electron microscope. Micrographs were collected in both secondary electron and backscattered electron mode using an

accelerating voltage of 15 kV, working distance of 11.5 mm, and a spot size of 5.5. Samples were prepared by dispersing the powder onto conductive carbon tape.

2.5 Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS)

Phosphor powders were dispersed in ethanol and thin films of phosphor samples were made by drop-casting on to clean 10 x 10 mm Au/Si substrates. NEXAFS experiments on the phosphor samples were conducted at the beamline 8.2 of the Stanford Synchrotron Radiation Lightsource (SSRL, SPEARIII) at the Stanford Linear Accelerator Center (SLAC). The cross-section of the focused beam was approximately 1 mm in diameter at normal to the sample surface. NEXAFS spectra at Pr $M_{4,5}$ -edge were recorded in total electron yield (TEY). All TEY NEXAFS signals were normalized to I_0 current, which was recorded for the incident X-ray beam via a Au grid located upstream of the experimental sample.

2.6 Fluorescence Spectroscopy

To measure the absorption and emission spectra of the samples the phosphor powder was made into a solid film. Films were made by mixing 0.2 g of phosphor with an equivalent mass of fluoropolymer. Excitation and emission spectra were measured on a Thermo Scientific Lumina Fluorimeter. Emission spectra were obtained after exciting at 254 nm with 20 nm excitation slit, 0.5 nm emission slit, and 320 nm longpass filter. Excitation spectra were obtained at an emission wavelength of 610 nm with 0.5 nm excitation slit, 20 nm emission slit, and 530 nm longpass filter. The excitation spectra do not have any corrections for the declining intensity of the lamp at shorter wavelengths. Lifetime measurements were acquired using a flashlamp-pumped Nd:YAG laser at 266 nm with 20 ns pulses. Luminescence was collected with a monochromator, set to the emission wavelength, coupled to an R928 Hamamatsu PMT and read out by an oscilloscope. For each measurement, 25 traces were acquired and averaged to generate the decay curves, which were then fit in Igor Pro to obtain the decay components and their amplitudes.

2.7 Defect Modeling

Calculations were performed within density functional theory (DFT) using the projector augmented wave method [17] as implemented in the Vienna Ab initio Simulation Package [18,19]. Exchange-correlation (XC) effects were treated within the generalized gradient spin approximation (GGA) [20]. The plane wave energy cutoff was set to 520 eV and Gaussian smearing with a width of 0.1 eV was used to determine occupation numbers. CaTiO_3 belongs to space-group Pbnm. The employed lattice parameters as determined from GGA are $a=5.40$ Å, $b=5.51$ Å, and $c=7.69$ Å. Monoclinic $(2a, b, 0) \times (a, -2b, 0) \times (0, 0, 2c)$ supercells containing 200 atoms were used together with a Γ -point sampling of the Brillouin zone. Configurations were relaxed until ionic forces were less than 20 meV/Å. Point defect formation energies for charge state q were calculated as outlined in [21-23] according to

$$\Delta E_f = E_{def} - E_{id} + q(\varepsilon_{VBM} + \mu_e) - \sum_i \Delta n_i \mu_i,$$

where E_{def} is the total energy of the system containing the defect and E_{id} is the total energy of the ideal host. The second term describes the dependence on the electron chemical potential, μ_e , which is measured with respect to the valence band maximum (VBM), ε_{VBM} . The formation energy also depends on the chemical potentials of the constituents as given by the last term, where the difference between the number of atoms of type i in the ideal cell with respect to the defect cell is denoted by Δn_i . The spurious image charge interaction is taken into account via the standard Makov-Payne correction [24].

3. Results and Discussion

3.1 Physical Characterization of Phosphors

After synthesis, the phosphors were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), and photographed. It is evident from the physical appearance of the powders that $\text{CaTiO}_3\text{:Pr}$ appears as a brown-gray powder (Fig. 1). This is most likely due to a lattice defect acting as an absorption center. In order to show that the body color of the phosphor was not influenced by the small amount of Pr doping (0.6 at. %), a second batch of CaTiO_3 was made, without Pr doping, under the same conditions, resulting in the same color (Fig. 1). Upon heat treating with NH_3 or codoping with Nb, the phosphor body color changes to an off-white. This appears to be a greater and more lasting effect with Nb doping as compared to NH_3 treatment. The NH_3 treated sample darkened slightly over the course of several months. This change occurs regardless of the presence of Pr and therefore cannot be attributed to its oxidation state (Fig. 1).

The SEM data was analyzed to determine phosphor morphology and particle size (Fig. 2). The morphology consists of primary particles that are 0.5-1 micron diameter and are irregularly shaped, exhibiting angular surfaces. These primary particles have the tendency to agglomerate into spherical clusters in the tens of microns in diameter. The ammonia treatment or Nb^{5+} doping do not seem to affect the morphology or agglomeration of these particles.

Crystallographic phases were identified and quantified by XRD (SI Fig. 1). It was found that Pr and Nb were soluble in CaTiO_3 at the levels of doping used in this study (0.6 and 5.0 at. % for Pr and Nb, respectively). A small amount of TiO_2 in the form of rutile was also identified. It was possible to reduce the amount of titanium starting material and form a single phase material, but this consistently resulted in degradation of the fluorescence. This is likely due to the fact that the perovskite structure cannot accommodate excess oxygen, and instead creates cation vacancies [25]. These cation vacancies result in excess Ti in the form of TiO_2 . The excess TiO_2 was quantified to be between 2-4 wt. % in all samples and seemed to have no effect on the fluorescence properties. The crystallite size by XRD was calculated to be between 500 and 550

nm for CaTiO₃:Pr and NH₃ treated CaTiO₃:Pr, while the Nb doped CaTiO₃:Pr had a crystallite size of 130 nm.

3.2 Fluorescence Properties

The fluorescence and excitation spectra were measured as described above. It was found that the maximum excitation is achieved at 330 nm to produce the 610 emission (Fig. 3). The emission spectra were, however, excited at 254 nm in an effort to explore the applicability of these phosphors to traditional tri-color fluorescent lamps. The fluorescence spectra collected at 330 nm do not show any appreciable difference aside from their absolute intensity (not shown). The ammonia treatment and the Nb⁵⁺ codoping do not significantly alter the shape or position of the excitation spectra, nor the fluorescence emission. The ammonia treatment shows a slight (10%) increase in the excitation spectrum, while the fluorescence emission is double that of the CaTiO₃:Pr without ammonia treatment. (Fig. 3) The Nb⁵⁺ treatment has a significant increase in the intensity of the excitation spectrum of around 5x and a corresponding increase in the fluorescence emission at 610 nm that is proportional (5x). (Fig. 3)

The lifetime of the fluorescence decay was also measured and found to be bi-exponential in all cases. A summary of the fit data can be found in Table 1. Interestingly, there is no significant difference in the as-synthesized CaTiO₃:Pr and the NH₃-treated CaTiO₃:Pr with regard to fluorescence decay (SI Fig. 2a and 2b). The sample that was co-doped with Nb, however, shows a reduction in the contribution of the fast component from 0.9 to 0.76 in A₁. Additionally, the time-scale of the fast lifetime has doubled from 14 μsec to 28 μsec (SI Fig. 2c). This suggests that the nature of one of the trap states or quenching mechanisms has changed due to Nb⁵⁺ doping, but not due to the ammonia treatment. The change in lifetime for the Nb⁵⁺ doped sample also suggests that this improved fluorescence is not due to reduced concentration quenching, which would result in a lower contribution but the same lifetime.

3.3 Near Edge X-ray Absorption Fine Structure (NEXAFS)

The oxidation state of Pr was probed by NEXAFS (SI Fig. 3). The NEXAFS spectrum of Pr₆O₁₁ is shown for comparison, which clearly indicates the contribution of both Pr³⁺ and Pr⁴⁺ in the starting materials for the synthesis of CaTiO₃ powders. Fitting the M5 feature of NEXAFS spectra allows for a quantitative determination of the contribution of Pr³⁺ and Pr⁴⁺ in the samples. The starting Pr₆O₁₁ contains ~36.5% of Pr³⁺, which is close to the stoichiometric amount of 33.3%. The synthesis process is expected to reduce Pr⁴⁺ to Pr³⁺, which results in the fluorescence emission of the CaTiO₃:Pr powders. In as synthesized CaTiO₃:Pr it was found that the amount of Pr³⁺ increases to 56.5%. However, as much as 43.5% of the Pr was still present in the (IV) oxidation state and therefore not participating in the fluorescence emission (Fig. 4). After treating the sample at 450°C in NH₃ atmosphere, it was found that the amount of Pr⁴⁺ was reduced to less than 13%. This explains the approximately 2-fold increase in fluorescence emission due to the increase in fluorescent centers that can participate in the emission. The sample that is co-doped with Nb⁵⁺ also has less than 13% Pr⁴⁺. This Nb⁵⁺ doped sample may

have slightly less Pr^{4+} than the ammonia treated sample (Fig. 4), but it is unlikely that this small difference is the cause of the change in fluorescence lifetime and dramatic increase in fluorescent emission intensity beyond that of the improvement from NH_3 .

In order to explain the further improvement in fluorescence due to Nb^{5+} co-doping, the other elements were also probed by NEXAFS to determine any other structural changes. It was found that there was little difference in the NEXAFS spectra of Ca and Ti (not shown). The oxygen spectra; however, was markedly different in the sample that was co-doped with Nb (Fig. 5). This suggests that Nb^{5+} changes something in the oxygen lattice. It is likely due to the Nb^{5+} inducing a change in the oxygen atoms that were previously interacting with a cation vacancy within the lattice.

3.4 Defect Modeling

To determine point defect formation energies, we need to specify the relevant chemical potentials μ_i , which we typically rewrite as $\mu_i = \mu_i^{\text{bulk}} + \Delta\mu_i$. Here, μ_i^{bulk} denotes the chemical potential of constituent i in its standard reference state. The chemical potentials are only allowed to vary within a limited range, determined by the formation enthalpies of CaTiO_3 and competing phases [26]. As a result, the chemical potentials are restricted to the dark green area in Fig. 6. In particular, we will in this manuscript restrict our attention to the oxygen rich conditions, marked with a circle in Fig. 6. This was chosen because of x-ray diffraction results which indicate a small amount of TiO_2 within the sample. Defect formation energies are displayed in Fig. 7, where we note that the dominant donor and acceptor defects under oxygen-rich conditions are the titanium-on-calcium antisite at low chemical potential, and cation vacancies (calcium or titanium) at high chemical potential. Although oxygen vacancies have been speculated to be the trap state in other studies [14,15], this result indicates that oxygen vacancies are an unlikely defect and cannot be the trap state for these samples. The trap state in this system is more likely due to cation vacancies and their interaction with surrounding oxygen atoms.

3.5 Vacuum Heating

To identify the nature of the change in oxygen environment found by NEXAFS of the Nb^{5+} doped CaTiO_3 , a simple test was designed to heat the phosphor in ultra-high vacuum (10^{-8} torr) and monitor the gases that are evolved. It was found that the first two temperature steps of 150°C and 300°C evolved water, while the last step of 550°C evolved both carbon dioxide and water. Oxygen evolving from the sample reacts to form water and carbon dioxide in route to the gas analyzer, because of the availability of hydrogen and carbon and the subsequent stability of water and carbon dioxide. Higher volumes of water and carbon dioxide evolved from the sample indicate higher amounts of removable oxygen within the sample. The total gas evolved for each sample was integrated over the course of the experiment and is presented in Table 2. Because the experimental parameters and setup were held constant, as well as the amount of phosphor that was heated, the integrated pressure is proportional to the amount of oxygen removed from the sample and can be directly compared. The as-synthesized $\text{CaTiO}_3\text{:Pr}$ outgassed the most at $1.6 \times$

10^{-7} torr, while the NH_3 treated $\text{CaTiO}_3\text{:Pr}$ outgassed only slightly less at 1.4×10^{-7} torr. The best performing phosphor, Nb^{5+} doped $\text{CaTiO}_3\text{:Pr}$, outgassed nearly an order of magnitude less at 2.7×10^{-8} torr. Because this sample has the smallest crystallite size by XRD and the same particle size by SEM, it is unlikely that this is oxygen at the surface or trapped in grain boundaries. This suggests that Nb^{5+} doping eliminates, or concentrates and immobilizes, oxygen that is interacting with a cation vacancy. We hypothesize that this reduces the quenching effect on the luminescence by eliminating this trap state, which is identified as an oxygen-cation vacancy pair, not an oxygen vacancy as previously hypothesized [14,15]. The NH_3 treatment seems to have less of an effect, or perhaps only affects the surface, in healing this trap state. The body color of the phosphor further supports this assertion. The Nb-doped $\text{CaTiO}_3\text{:Pr}$ has a noticeably whiter body color than either the as synthesized or NH_3 treated $\text{CaTiO}_3\text{:Pr}$ (Fig. 1). After vacuum annealing, the as synthesized and NH_3 -treated $\text{CaTiO}_3\text{:Pr}$ also appear white as seen in Fig. 8. The Nb-doped $\text{CaTiO}_3\text{:Pr}$ developed a slightly darker body color and appears off-white after vacuum annealing (Fig. 8). It is important to note that the defect modeling found that oxygen interstitials have a higher formation energy and are unlikely to form, supporting the assertion that perovskites cannot accommodate excess oxygen and the outgassing is therefore not due to interstitial oxygen. Instead we propose that oxygen interacts with a cation vacancy to create a trap state, and the Nb^{5+} doping eliminates, or concentrates and immobilizes, these defects so that they have less of a quenching effect on the luminescence.

4. Conclusions

The as-synthesized $\text{CaTiO}_3\text{:Pr}$ suffers from two problems that limit its fluorescence efficiency. First, as much as 43.5% of the Pr in the sample is present as Pr^{4+} and therefore does not contribute to the fluorescence yield. Secondly, cation vacancies interacting with oxygen atoms form traps that quench the fluorescence and result in a darker body color. We have shown that both NH_3 treatment and Nb^{5+} doping reduce the amount of Pr^{4+} in the phosphor to less than 13%, increasing the fluorescence centers. The Nb^{5+} doping; however, results in a superior light output compared to the NH_3 -treated sample because it effectively removes, or concentrates and immobilizes, these trap states. This increases the fluorescence lifetime and light yield. It is possible that NH_3 treatment also eliminates these trap states as suggested by Yoon et al. [9], but that this effect may be limited to the surface, while Nb^{5+} doping eliminates traps throughout the bulk sample. An energy level diagram outlines these processes in Fig. 9. This new understanding of how the fluorescence may be improved in $\text{CaTiO}_3\text{:Pr}$ can help guide further improvement of this phosphor.

Acknowledgements

The authors thank Alex Drobshoff for his assistance with fluorescence lifetime measurements. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under contract DE-AC02-76SF00515. Funding was provided by the DOE EERE

Critical Materials Institute, and work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344.

References

- [1] J. M. P. J. Verstegen, D. Radielovic, and L. E. Vrenken, A new generation of “deluxe” fluorescent lamps, combining an efficacy of 80 lumens/W or more with a color rendering index of approximately 85, *J. Electrochem. Soc.* 121 (1974) 1627-1631.
- [2] N. J. Cherepy, S. A. Payne, N. M. Harvey, D. Åberg, Z. M. Seeley, K. S. Holliday, I. C. Tran, F. Zhou, H. P. Martinez, J. M. Demeyer, A. D. Drobshoff, A. M. Srivastava, S. J. Camardello, H. A. Comanzo, D. L. Schlagel, T. A. Lograsso, Red-emitting manganese-doped aluminum nitride phosphor, *Opt. Mat.* 54 (2016) 14-21.
- [3] Th. Jüstel, H. Nikol, C. Ronda, New developments in the field of luminescent materials for lighting and displays, *Angew. Chem. Int. Ed.* 37 (1998) 3084-3103.
- [4] A. Vecht, D. W. Smith, S. S. Chadha, C. S. Gibbons, J. Koh, and D. Morton, New electron excited light-emitting materials, *J. Vac. Sci. Technol. B* 12(2) (1994) 781-784.
- [5] D. Haranath, A. F. Khan, and H. Chander, Bright red luminescence and energy transfer of Pr^{3+} -doped $(\text{Ca,Zn})\text{TiO}_3$ phosphor for long decay applications, *J. Phys. D Appl. Phys.* 39(23) (2006) 4956-4960.
- [6] W. Tang and D. Chen, Enhanced red emission in $\text{CaTiO}_3:\text{Pr}^{3+}$, Bi^{3+} , B^{3+} phosphors, *Phys. Status Solidi A* 206(2) (2009) 229-232.
- [7] R. Chen and D. Chen, Enhanced luminescence properties of $\text{CaTiO}_3:\text{Pr}^{3+}$ phosphor with addition of SiO_2 by solid-state reaction, *Spectrochim. Acta A* 127 (2014) 256-260.
- [8] J.-C. Zhang, X. Wang, and X. Yao, Enhancement of luminescence and afterglow in $\text{CaTiO}_3:\text{Pr}^{3+}$ by Zr substitution for Ti, *J. Alloys Compd.* 498 (2010) 152-156.
- [9] S. Yoon, E. H. Otal, A. E. Maegli, L. Karvonen, S. K. Matam, S. Riegg, S. G. Ebbinghaus, J. C. Fallas, H. Hagemann, B. Walfort, S. Pokrant, and A. Weidenkaff, Improved photoluminescence and afterglow of $\text{CaTiO}_3:\text{Pr}^{3+}$ by ammonia treatment, *Opt. Matter. Express* 3(2) (2013) 248-259.
- [10] F. Erazo and A. Stashans, Quantum chemical studies of Nb-doped CaTiO_3 , *Phil. Mag. B* 80(8) (2000) 1499-1506.
- [11] W. Jia, D. Jia, T. Rodriguez, D. R. Evans, R. S. Meltzer, and W. M. Yen, UV excitation and trapping centers in $\text{CaTiO}_3:\text{Pr}^{3+}$, *J. Lumin.* 119-120 (2006) 13-18.
- [12] J. Herrero-Martín, J. L. García-Muñoz, S. Valencia, C. Frontera, J. Blasco, A. J. Barón-González, G. Subías, R. Abrudan, F. Radu, E. Dudzik, and R. Feyerherm, Valence change of praseodymium in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$ investigated by x-ray absorption spectroscopy, *Phys. Rev. B* 84 (2011) 115131.
- [13] P. Boutinaud, L. Sarakha, E. Cavalli, M. Bettinelli, P. Dorenbos, and R. Mahiou, About red afterglow in Pr^{3+} doped titanate perovskites, *J. Phys. D: Appl. Phys.* 42 (2009) 045106.
- [14] E. H. Otal, A. E. Maegli, N. Vogel-Schäuble, B. Walfort, H. Hagemann, S. Yoon, A. Zeller, and A. Weidenkaff, The influence of defects formed by Ca excess and thermal post-treatments on the persistent luminescence of $\text{CaTiO}_3:\text{Pr}$, *Opt. Matter. Express* 2(4) (2012) 405-412.
- [15] X. Zhang, C. Cao, C. Zhang, S. Xie, G. Xu, J. Zhang, and X. Wang, Photoluminescence and energy storage traps in $\text{CaTiO}_3:\text{Pr}^{3+}$, *J. Mater. Res. Bull.* 45 (2010) 1832-1836.

- [16] J. Zi-Qiang, W. Yu-Hua, and G. Yu, Doping effects of Nb^{5+} on red long afterglow phosphor $\text{CaTiO}_3:\text{Pr}^{3+}$, *Chin. Phys. B* 19(2) (2010) 027801.
- [17] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B*, 50 (1994) 17953.
- [18] G. Kresse, J. Hafner, *Ab initio* molecular dynamics for liquid metals, *Phys. Rev. B* 47 (1993) 558.
- [19] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* 6 (1996) 15.
- [20] J. P. Perdew, K. Burke, M. Ernzerhof, Ceramic expansion by water layers on magnesium oxide: *Ab Initio* study, *Phys. Rev. Lett.* 77 (1996) 3865.
- [21] S. B. Zhang, J. E. Northrup, Chemical potential dependence of defect formation energies in GaAs: Application to Ga self-diffusion, *Phys. Rev. Lett.* 67 (1991) 2339.
- [22] C. Persson, Y.-J. Zhao, S. Lany, A. Zunger, n-type doping of CuInSe_2 and CuGaSe_2 , *Phys. Rev. B* 72 (2005) 035211.
- [23] D. Åberg, P. Erhart, A. J. Williamson, V. Lordi, Intrinsic point defects in aluminum antimonide, *Phys. Rev. B* 77 (2008) 165206.
- [24] G. Makov, M. C. Payne, Periodic boundary conditions in *ab initio* calculations, *Phys. Rev. B* 51 (1995) 4014.
- [25] R. I. Dass, J.-Q. Yan, J. B. Goodenough, Oxygen stoichiometry, ferromagnetism, and transport properties of $\text{La}_{2-x}\text{NiMnO}_{6+\delta}$, *Phys. Rev. B* 68 (2003) 064415.
- [26] P. Erhart, K. Albe, Thermodynamics of mono- and di-vacancies in barium titanate, *J. Appl. Phys.* 102 (2007) 084111.

Tables

Table 1: Bi-exponential fitting parameters of $\text{CaTiO}_3:\text{Pr}$, $\text{CaTiO}_3:\text{Pr}$ treated with NH_3 , and $\text{CaTiO}_3:\text{Pr}$, Nb according to the general equation: $\text{Intensity} = A_1\exp(-\tau_1 t) + A_2\exp(-\tau_2 t)$.

CaTiO_3 doped with:	A_1	$t_1(\mu\text{sec})$	A_2	$t_2(\mu\text{sec})$
0.6%Pr	0.9	14	0.1	170
0.6%Pr, NH_3 treated	0.9	15	0.1	125
0.6%Pr, 5%Nb	0.76	28	0.24	175

Table 2: Total amount of gas evolved from each phosphor due to stepwise annealing in ultra-high vacuum to a temperature of 550°C .

CaTiO_3 doped with:	Pressure rise due to evolved gas ($\text{torr} \times 10^{-8}$)
0.6% Pr	15.87
0.6% Pr, NH_3 treated	14.39
0.6% Pr, 5% Nb	2.65

Figures

1)

2)

3)

4)

5)

6)

7)

8)

9)

Figure Captions

Fig. 1: Photograph of CaTiO_3 as prepared, after subsequent NH_3 treatment at 450°C , and CaTiO_3 codoped with Nb^{5+} . Top row does not contain Pr^{3+} , while the bottom row is doped with 0.6 at. % Pr^{3+} .

Fig. 2: SEM secondary electron micrographs of a) $\text{CaTiO}_3\text{:Pr}$, b) $\text{CaTiO}_3\text{:Pr}$ after subsequent NH_3 treatment at 450°C , and c) $\text{CaTiO}_3\text{:Pr}$ codoped with Nb^{5+} .

Fig. 3: Excitation spectra monitoring 610 nm emission from 200 – 450 nm and emission spectra excited at 254 nm from 450 – 900 nm in $\text{CaTiO}_3\text{:Pr}$, $\text{CaTiO}_3\text{:Pr}$ treated with NH_3 , and $\text{CaTiO}_3\text{:Pr, Nb}$.

Fig. 4: Fitting total electron yield Pr M_5 NEXAFS with the contribution of Pr^{3+} and Pr^{4+} in $\text{CaTiO}_3\text{:Pr}$, $\text{CaTiO}_3\text{:Pr}$ treated with NH_3 , and $\text{CaTiO}_3\text{:Pr, Nb}$.

Fig. 5: Total electron yield NEXAFS of O K edge in $\text{Ca}(\text{OH})_2$, TiO_2 , $\text{CaTiO}_3\text{:Pr}$, $\text{CaTiO}_3\text{:Pr}$ treated with NH_3 , and $\text{CaTiO}_3\text{:Pr, Nb}$.

Fig. 6: Stability diagram of CaTiO_3 , which is stable within the dark green area. The point marked with a circle corresponds to the maximally oxygen-rich conditions and is associated with an oxygen chemical potential of $\Delta\mu_{\text{O}} = 0$.

Fig. 7: Formation energies of the relevant intrinsic defects (vacancies v_{X} , antisites X_{Y} , and oxygen interstitials O_{i}) in CaTiO_3 as a function of the electron chemical potential (Fermi level) under the oxygen-rich conditions indicated in Fig. 6. The slope of a line corresponds to the defect charge, and the symbols indicate the points at which the charge states changes (thermodynamic transition levels). The dominant donor and acceptor defects under these conditions are the titanium-on-calcium antisite, calcium vacancy, and titanium vacancy, respectively.

Fig. 8: Photograph of $\text{CaTiO}_3\text{:Pr}$ as prepared, after subsequent NH_3 treatment at 450°C , and $\text{CaTiO}_3\text{:Pr}$ codoped with Nb^{5+} before and after vacuum annealing.

Fig. 9: Energy level diagram for functionality of $\text{CaTiO}_3\text{:Pr}$.

Supplemental Information

SI 1)

SI 2)

SI 3)

SI Figure Captions

SI Fig. 1: X-ray diffraction of $\text{CaTiO}_3\text{:Pr}$, $\text{CaTiO}_3\text{:Pr}$ treated with NH_3 , and $\text{CaTiO}_3\text{:Pr, Nb}$.
SI Fig. 2: Fluorescence decay at 610 nm, fit with the general bi-exponential decay equation $\text{Intensity} = A_1\exp(-\tau_1 t) + A_2\exp(-\tau_2 t)$ for a) $\text{CaTiO}_3\text{:Pr}$, b) $\text{CaTiO}_3\text{:Pr}$ treated with NH_3 , and c) $\text{CaTiO}_3\text{:Pr, Nb}$.
SI Fig. 3: NEXAFS of Pr $M_{4,5}$ edge in Pr_6O_{11} , $\text{CaTiO}_3\text{:Pr}$, $\text{CaTiO}_3\text{:Pr}$ treated with NH_3 , and $\text{CaTiO}_3\text{:Pr, Nb}$ by total electron yield.