Oxygen Vacancy-Related Cathodoluminescence Quenching and Polaronic Effects in CeO$_2$

Thanveer Thajudheen, Alex G. Dixon, Sandra Gardonio, Iztok Arčon, and Matjaz Valant$^*$

ABSTRACT: We used cathodoluminescence (CL) spectroscopy to characterize the oxygen vacancies (V$_O$) in ceria (CeO$_2$). The effects of the processing atmosphere and thermal quenching temperature on the nature and distribution of the intrinsic defects and on the spectroscopic behavior were investigated. The presence of polarons and associates of the polarons with the oxygen vacancies such as (V$_O$$^ullet$$-$Ce$^ullet$)$^\circ$ is demonstrated. CL intensity quenching above a critical concentration of V$_O$ has been shown. Even though the emission centers in all samples are the same, their concentration changes with the oxygen partial pressure of the processing atmosphere. Deconvolution of the observed CL spectra shows that the emissions originating from the F$^0$ centers prevail over those of F$^+$ centers of V$_O$ when the defect concentration is high.

INTRODUCTION
Because of its fundamental ability to accommodate a large number of defects without destabilizing the crystal structure, cerium oxide (ceria, CeO$_2$) has become a technologically important material that finds its use in many areas. Perhaps, the most widespread of which is its application in automobile exhausts as a catalyst$^1$ because of its ability to absorb and release oxygen under oxidizing and reducing conditions. From a crystallographic point of view, this means that the ceria crystal structure can tolerate a high density of oxygen vacancies and reduced cerium ions, Ce$^{3+}$. The density of these defects is associated with the external oxygen partial pressure.

Other important properties of CeO$_2$, such as a high dielectric constant and good epitaxy on the Si substrate, make it a potential material for future microelectronic applications. In particular, epitaxial CeO$_2$ films are considered to be very promising candidates for high quality and highly stable insulating thin films.$^7$ There have been extensive studies on defects in ceria, which focused on their formation by doping, treatment in reductive or oxidative atmosphere,$^{3,4}$ and the dependence on a crystal size$^{5,6}$ and atomic surface structures.$^7$ Despite its ability to unravel the defect structures of crystals, cathodoluminescence (CL) spectroscopy has found little use in the study of CeO$_2$ emissions related to oxygen vacancies. CL spectroscopy is highly sensitive to relatively low defect concentrations and can be used to determine carrier recombination pathways that involve these defects. This makes it a technique of choice for studies of the defect structures in bulk and nanostructures.$^9$ Previously, it has been shown that CL can be used as a direct tool for studying the oxygen vacancy concentration in the vicinity of oxide surfaces.$^{10}$ CL is also able to provide information on mechanical stresses originating from oxygen vacancies.$^{11}$

The emissions associated with oxygen vacancies in ZrO$_2$-related materials, as well as Al$_2$O$_3$ and TiO$_2$, have been studied by spectrally and spatially resolved CL spectroscopy.$^{12,13}$ It has been reported that the CL intensity for Y-doped ZrO$_2$ decreases with an increase in the concentration of oxygen vacancies. In this study, Boffelli et al.$^{11}$ proposed two hypotheses to explain the observed intensity quenching. The first hypothesis, called the “strained lattice hypothesis”, states that because the efficiency of the CL intensity is directly related to Zr$^{4+}$ bonding and the increased concentration of oxygen vacancies redistributes the highly localized lattice strain, the CL emission intensity lowers with the higher vacancy concentration. The second, the “charge trap hypothesis”, states that the decrease in the CL intensity under the electron excitation occurs because of the fact that the oxygen vacancies act as charge traps and thereby decrease the

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The presence of charged vacancies is put forth to explain many of the experimental observations. The possibility of the formation of oxygen vacancy complexes has been proposed and experimentally observed. In the case of doped ceria, a conductivity maximum has been observed as a function of dopant concentration. Initially, it was explained by the presence of a minimum in the activation enthalpy as the dopant concentration increases. Later, this was rejected by Faber et al. who argued that the lattice relaxations around the dopant ions will screen any columbic effects arising from the dopant. They ascribe the presence of the minimum to changes in the energy of the oxygen sites in the vicinity of the dopant. Altogether, it is proposed that the presence of this minimum in the concentration dependence of the activation enthalpy can be taken as an indicator of defect association, which limits the conductivity of doped ceria.

The objective of this work is to demonstrate the CL behavior of CeO₂ and its dependence on oxygen vacancy concentration. We report that the intrinsic oxygen vacancies in CeO₂ cause CL intensity quenching when only above a critical concentration. It is shown that a careful understanding of CL emissions of CeO₂ could help to comprehend the interaction between vacancy centers. We examine the possibility of oxygen vacancy association with electron polaron and their consequence on the occurrence of differing charge states of the intrinsic point defects in CeO₂. The ability of the CL technique to explore different charge states of intrinsic point defects is demonstrated.

**METHODS**

High-purity CeO₂ nanopowders (Sigma-Aldrich, 99.95% pure, size <50 nm) were sintered at 1450 °C for 8 h in air (C-A), oxygen (C-O), and nitrogen (C-N). In the second step, all the three samples were subjected to quenching after 10 h of annealing at different temperatures to achieve a frozen state with differing defect concentrations. The systematic change in defect concentration was verified by electrical impedance analysis.

A Rigaku MiniFlex diffractometer was used for the XRD measurements. Ni-filtered Cu Kα radiation, steps of 0.05° with a collection time of 1 s per step, was used to acquire the data. XRD was analyzed using X’Pert HighScore software.

Microstructural images and CL spectra were taken using a field-emission gun scanning electron microscope [SEM JEUJSJ 7100 TTLS (FEG)]. For the CL measurements, the same experimental conditions were applied for all samples to avoid introducing additional variables. The acceleration voltage and the beam current were set for all experiments at 25 keV and 2 nA, respectively. The CL spectra were acquired in the wavelength region 300–800 nm. The reported CL spectra have been corrected by grating response and detector response in the wavelength region 350–750 nm. The microscope was equipped with a CL device (GATAN MonoCL4) consisting of a parabolic mirror and a bundle of optical fibers used to collect and to focus the electron-stimulated luminescence emitted by the sample into a monochromator with 2 nm spectral resolution.

The dielectric properties of the samples (pellets) were studied using a frequency response analyzer (Agilent LCR E4980A). The impedance curves were obtained over a frequency range from 100 Hz to 2 MHz, using a two-probe measurement with copper tape electrodes in a capacitor geometry.

X-ray absorption spectra in the energy range of Ce L₃ edge (5724 eV) of the high-purity CeO₂ nanopowder samples, before sintering and sintered at 1450 °C for 8 h in air (C-A), oxygen (C-O), and nitrogen (C-N), and crystalline CeVO₄ as a reference for Ce⁴⁺ were measured in the transmission detection mode at the XAFS beamline of the ELETTRA synchrotron radiation facility in Trieste, Italy. A Si(111) double-crystal monochromator was used with an energy resolution of about 0.6 eV at 6 keV. Higher harmonics were eliminated by detuning of the second monochromator crystal to 60% of the maximum in the rocking curve. The intensity of the monochromatic X-ray beam was measured using three 30 cm-long consecutive ionization detectors filled with optimal gas mixtures for a given energy range: 350 mbar N₂ and 1650 mbar He (first); 1900 mbar N₂ and 100 mbar He (second); and 230 mbar Ar, 1000 mbar N₂, and 670 mbar He (third).

The CeO₂ samples were prepared in the form of homogeneous pellets, pressed from micronized powder mixed with micronized boron nitride (BN), with a total absorption thickness of about 1 above the Ce L₃ edge, and placed in the monochromatic beam between the first two ionization detectors. The absorption spectra were measured in the energy region from −150 to +400 eV relative to the Ce L₃ edge. Scans were stopped at the Ce L₂ edge (6165 eV). Equidistant energy steps of 0.3 eV were used in the X-ray absorption near-edge spectroscopy (XANES) region, while for the extended X-ray absorption fine structure region, equidistant k steps of 0.03 Å⁻¹ were adopted, with an integration time of 2 s/step. The exact energy calibration was established with simultaneous absorption measurement on the nanopowder CeO₂ reference sample placed between the second and the third ionization chambers. Absolute energy reproducibility of the measured spectra was ±0.03 eV. The quantitative analysis of XANES spectra was performed with the Demeter (IFEFFIT) program package.

**RESULTS AND DISCUSSION**

Samples C-O, C-A, and C-N have been sintered in oxygen, air, and nitrogen atmospheres, respectively, with the scope of obtaining CeO₂ samples having an increasing concentration of oxygen vacancies because of processing in higher to lower oxygen partial pressure atmospheres.

Scanning electron microscopy showed no detectable difference in the microstructures of the investigated samples. The level of porosity and grain size are the same for all the samples. XRD analysis showed the presence of the pure CeO₂ phase with no traces of Ce₂O₃. A typical microstructure and XRD are shown in Figure 1.

The relative amounts of Ce⁴⁺ and Ce⁵⁺ species in the catalyst after sintering in different atmospheres were determined from the Ce L₃-edge XANES spectra. Different local environments of the Ce cation result in different L₃-edge profiles in the XANES spectra, and the energy position of the absorption edge is correlated with the valence state of the absorbing atom in the sample. With increasing oxidation state, the absorption edge is shifted to higher energies. In the case of Ce⁴⁺ cations, a characteristic peak is present at 5726 eV, while Ce⁴⁺ cations can be identified by two characteristic peaks, at 5730 and 5736 eV. A detailed comparison of the three XANES spectra show that the spectra of C-O and C-A samples are identical within the noise level, while the spectrum of the C-N sample
sintered in nitrogen exhibits some differences in the pre-edge region at 5726 eV, which can be ascribed to the presence of a small amount of Ce\(^{3+}\) in the crystal structure of CeO\(_2\). Relative amounts of Ce\(^{3+}\) species are quantitatively determined by a linear combination fit analysis.\(^{17,20}\) The XANES spectrum of the CeO\(_2\) sintered in nitrogen (C-N) can be completely described by a linear combination of three reference XANES profiles (Figure 2): the spectrum of CeO\(_2\) nanopowder sintered in nitrogen (C-N) as references for Ce\(^{4+}\), 11.9% crystalline unsintered CeO\(_2\) nanopowder as a reference for Ce\(^{4+}\), and 1.8% crystalline CeVO\(_4\) as a reference for Ce\(^{3+}\).

The narrow peaks in the spectra were recognized as emissions from impurities. It is known from photoluminescence (PL) studies that Sm\(^{3+}\) gives emissions corresponding to the transitions \(^4G_{5/2} \rightarrow ^4H_{11/2}\) and \(^4G_{5/2} \rightarrow ^4H_{15/2}\) within the range 550 nm (2.25 eV) to 800 nm (1.54 eV).\(^{21}\) The presence of 0.4 mg/kg Sm impurity has been confirmed in our starting CeO\(_2\) powder by inductively coupled plasma mass spectrometry. Correspondingly, the narrow emission lines are assigned to the Sm impurity similarly to in Balestrieri et al.\(^{21}\) The Sm\(^{3+}\) concentration is constant throughout all the samples because all samples used the same starting CeO\(_2\) powder.

Calculations\(^{22}\) predict that for CeO\(_2\) with a neutral oxygen vacancy (V\(_O^0\) according to Kroger–Vink notation), the electronic density of states has two gap states between the O 2p and the Ce 4f bands, lying well inside the band gap. Because the two band gaps of CeO\(_2\) are beyond the observed emission lines, it is reasonable to conclude that the emission centered at 550 nm originates from the defect energy levels within the band gap which can act like electron traps.

Figure 1.

**Figure 1.** SEM micrograph and XRD (inset) acquired from the C-N sample. All sample preparations showed a similar structure with no variation in porosity or grain size.

Figure 2.

**Figure 2.** Ce L3-edge XANES spectrum of the CeO\(_2\) nanopowder sintered in nitrogen (C-N). Dots are experimental data; the dashed magenta line is the best fit from a linear combination of reference Ce L3-edge XANES profiles [86.3% CeO\(_2\) nanopowder sintered in oxygen (C-O) as a reference for Ce\(^{4+}\) (blue), 11.9% crystalline unsintered CeO\(_2\) nanopowder as a reference for Ce\(^{4+}\) (dark blue), and 1.8% crystalline CeVO\(_4\) as a reference for Ce\(^{3+}\) (red)].

Figure 3a shows the representative CL spectra acquired under identical conditions on CeO\(_2\) samples, sintered in different atmospheres. CL spectra of the different samples showed a pronounced variation in their intensities. The three spectra are composed of a broad band, centered at approximately 550 nm (2.25 eV), along with two additional narrow peaks at 575 nm (2.15 eV) and 617 nm (2.00 eV).

A discernible variation in the CL intensity (see Figure 3a) revealed the influence of defect concentration on the emissions of CeO\(_2\). Conventional wisdom suggests that we should observe a linear relationship between the CL intensity and concentration of defects, that is, the emission intensity should increase with the defect concentration.\(^{11,25–27}\) Surprisingly, the intensity of the C-O sample lies in between the C-N and C-A samples. Accordingly, we deduce that as the concentration of VO increases, the CL intensity increases up to some critical concentration.\(^{22}\)

Figure 4.

**Figure 4.** Room temperature frequency dependence of the dielectric constant (\(\varepsilon'\)) and dielectric loss (\(\varepsilon''\)) measured from 100 Hz to 2 MHz. The values of \(\varepsilon'\) and \(\varepsilon''\) are extracted from impedance analysis. The existence of a polaron state can be seen mainly from the dielectric loss (\(\varepsilon''\)) at high frequencies because of hopping conduction with a classical power-law dependence versus frequency. The dielectric constant increases significantly with increasing oxygen vacancies from C-O to C-N.

\(\varepsilon' = \varepsilon'' = \varepsilon''''\)
Figure 3. (a) CL spectra collected for CeO$_2$ samples sintered in air (C-A), oxygen (C-O), and nitrogen (C-N) atmospheres. CL spectra for samples thermally quenched from different temperatures in (b) air, (c) oxygen, and (d) nitrogen atmospheres. Q6, Q8, Q10, and Q12 stand for thermal quenching at 600 °C, 800 °C, 1000 °C, and 1200 °C, respectively. The C-A samples show a higher overall CL intensity and higher temperature dependence in vacancy formation.

Figure 4. Room temperature frequency dependence of the (a) real part of the dielectric constant $\varepsilon'$ and (b) imaginary part of the dielectric constant $\varepsilon''$ for CeO$_2$ samples sintered in air, oxygen, and nitrogen atmospheres, showing an increase in dielectric constant with decreasing oxygen partial pressure of the processing atmosphere.
The greater polarizability of a crystal with structural point defects as compared to an ideal defect-free crystal can be explained mainly by the high polarizability of the two electrons trapped in the vacant sites and the reduction in bond stiffness. According to the literature, $V_O$ reduces the bond stiffness of some bonds which increases bond deformation. Because the bonds with reduced stiffness in the defective oxides deform more readily under an electric field, this also means that they are more readily polarized. This substantiates that the $V_O$ concentration increases in the order C-O < C-A < C-N. Moreover, from the XANES analysis, we have seen that for the C-O and C-A samples, the presence of Ce$^{3+}$ cations was below the detection limit for the method, whereas in the C-N sample, the amount of Ce$^{3+}$ ions was estimated at 1.8%.

To further investigate the dependence of the defect concentration on the CL intensity, we performed a series of experiments where we thermally quenched the samples at different temperatures and in different atmospheres, the results of which are depicted in Figure 3b–d. For the C-A sample, it was found that the CL intensity decreases with the increase in quenching temperature (Figure 3b), while for C-O (Figure 3c) and C-N (Figure 3d), the intensity stays nearly constant. The observed variations in the CL intensity can be explained by the fact that processing CeO$_2$ in different atmospheres sets different initial oxygen vacancy concentrations, which are later varied as a function of quenching temperature. In the C-O samples, the oxidation potential of the oxygen atmosphere limits the creation of oxygen vacancies, and this effect strongly dominates over any thermal variation; thus, quenching temperature has little effect on the vacancy concentration. However, in the C-A samples, the oxygen partial pressure is significantly lower and the thermal quenching temperature can lead to a considerable variation of the defect concentration and thus the CL intensity. In contrast, the quenched C-N samples all show very similar emission intensities because of similar vacancy concentrations. This can be explained with the fact that for high vacancy concentration, the formation energy of new vacancies within the bulk progressively increases.$^{29,30}$ Therefore, there are no significantly more vacancies created at the higher temperatures and no significant variation in the CL intensity is seen.

A detailed understanding of the relative concentration of the different charge states of F centers associated to oxygen vacancies for the different CeO$_2$ samples has been obtained by curve fitting analysis of CL spectra, as reported in Figure 3a. For the deconvolution of the spectral lines, a set of eight...
Gaussian bands were used, and the results are reported in Figure 5. Note that the wavelength dispersion is presented in the energy scale (eV) so that a meaningful comparison of the spectral weights of the components becomes possible.

Five sharp peaks are found at 2.00, 2.10, 2.16, 2.20, and 2.35 eV, while three much broader peaks are located at 1.87, 2.11, and 2.70 eV referred to as P1, P2, and P3, respectively. The sharp peaks are the clear signature of the Sm trace impurity in and above the valence band.31,32 According to the calculations,22 a function of oxygen partial pressure indicates that this is expected at 3 eV. 23 Additionally, some studies33,34 have dismissed this P1 peak as being a product of the Ce3+ around the oxygen vacancies is observed clustering of Ce3+ around the oxygen vacancies. Castleton et al.40 showed that the energy level of (V O−CeCe)− is present at ~1.7–2.0 eV. Because there is no distinction between (V O−CeCe)− and V O except for the electronic structure of the two defect species, we ascribe emission P1 to Ce3+ in configuration of F+ in Figure 6a.

Based on the calculations by Zacherle et al.35 mentioned above, we attribute the CL band (P2) observed in the region 2.11 eV to F0 center transition. At low oxygen partial pressures, the Ce3+ concentration increases and the cluster of a doubly charged oxygen vacancy with two polarons (CeCe−V O−CeCe)− becomes the energetically most favorable species; hence, P2 emission originates from the configuration equivalent to F0.

From a crystallographic point of view, the reduction of CeO2 introduces strain in the crystal lattice because of the formation of oxygen vacancies and Ce3+, which has a larger ionic radius (1.01 Å and 0.87 Å for Ce3+ and Ce4+, respectively).41 The observed clustering of Ce3+ around the oxygen vacancies is driven by a reduction of the lattice strain and consequent reduction of free energy. With an increase in overall defect concentration, the strain increases, and the structure compensates by bringing yet another Ce3+ ion into the first coordination sphere around the vacancies. This explains why the increase in P2 emissions coincides with the decrease in P1 emissions.

The emission P3 in all the samples studied stays almost constant irrespective of processing atmosphere or temperature, with a slight increase as the oxygen partial pressure decreases. We ascribe this emission to F++ configuration which is consistent with Costantini et al.34 According to them, the CL emission at P3 in CeO2 originates from Ce3+ ions which are not spatially adjacent to oxygen vacancies. As the F++ configuration describes oxygen vacancies surrounded by Ce4+ ions, their presence would imply the vacancy electron localized on a Ce3+ ion at an undistorted site further from the vacancy.

According to Zacherle et al.,35 at high oxygen partial pressures, doubly charged oxygen vacancies V O− are the dominant vacancy species. Considering the energy of the formation of various charged defects, the next possible candidate is (V O−CeCe)− which resembles single-charged oxygen vacancy. Castleton et al.36 showed that the energy level for (V O−CeCe)− is present at ~1.7–2.0 eV. Because there is no distinction between (V O−CeCe)− and V O except for the electronic structure of the two defect species, we ascribe emission P1 to Ce3+ in configuration of F+ in Figure 6a.

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\[
\begin{align*}
V_O^{--} + Ce_{Ce}^{+} & \rightarrow (V_O^{--} - Ce_{Ce})^{+} \\
V_O^{--} + 2Ce_{Ce}^{+} & \rightarrow (Ce_{Ce}^{+} - V_O^{--} - Ce_{Ce}^{+})^{x}
\end{align*}
\]
Therefore, we conclude that the observed trend in variation of bands can be explained as follows: at high oxygen partial pressure, Ce$^{3+}$ ions are readily found in F' centers, and the band P1 is the dominant emission in the C-O sample. As reduction induces more vacancies and thus more Ce$^{3+}$ ions into the crystal structure, the configuration F' is favored; hence, P2 becomes dominant in the C-N samples. An illustration of the radiative electronic transitions on CeO$_2$ samples is reported in Figure 6b.

The increase in oxygen vacancy concentration will lead to a change in the crystal field around the vacancy centers, in turn, resulting in the energy levels that favor emission in the infrared region of the spectrum (beyond our experimental capability). Effectively, it could be manifested as CL intensity quenching. Moreover, it is possible that the increase in V$_{O}$ concentration can facilitate energy transfer between the centers of luminescence as the separation between the centers decreases. When the sample is irradiated with an electron beam, the energy is transferred between the donors before it is absorbed by one center which acts as a nonradiative sink.42 Because the polaron−vacancy association is plausible, it is likely to open up nonradiative decay paths through energy transfer between F centers. As the concentration increases beyond a critical value, energy transfer becomes efficient and leads to intensity quenching.

■ CONCLUSIONS

The oxygen vacancy-related CL emission from pure CeO$_2$ heat-treated in different atmospheres was presented here. The relative concentration of different charge states of F centers depends on the oxygen partial pressure during sintering. We found that for low oxygen pressure, F$^0$ centers prevail over F$^+$ centers in CeO$_2$, while for high oxygen pressure, F$^+$ centers are more dominant than F$^0$ centers. The dielectric polarizability of the CeO$_2$ crystal increases with decreasing oxygen partial pressure in the atmosphere of heat treatment, which confirms the continuous increase in defect concentration with decreasing oxygen partial pressure. However, the CL emission intensity does not follow this trend. Instead of a continuous increase, the CL emission reaches a maximum and starts decreasing with the increase in vacancy concentration. The polarons and associates of polarons with oxygen vacancies, such as ($V_{O}^{**}$−Ce$^{3+}$)$^*$, are demonstrated as the cause of the observed CL intensity quenching at higher oxygen vacancy concentrations. The demonstrated ability of CL spectroscopy to distinguish between various charge states of oxygen vacancies is useful for defect-engineered property enhancements of CeO$_2$-related solid solutions.

■ AUTHOR INFORMATION

Corresponding Author
Matjaz Valant — Materials Research Laboratory, University of Nova Gorica, 5270 Ajdovščina, Slovenia; Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, 610054 Chengdu, China; orcid.org/0000-0003-4842-5676; Phone: +386 53653502; Email: matjaz.valant@ung.si

Notes
The authors declare no competing financial interest.

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