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Raman and x-ray studies of Ce$_{1-x}$RE$_x$O$_{2-y}$, where RE=La, Pr, Nd, Eu, Gd, and Tb


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Powdered samples of the type Ce$_{1-x}$RE$_x$O$_{2-y}$, where RE=La, Pr, Nd, Eu, Gd, and Tb, are synthesized over the range 0≤x≤0.5 starting from nitrate solutions of the rare earths. X-ray diffraction and Raman scattering are used to analyze the samples. These compounds, at least in the low doping regime and for strictly trivalent dopants, form solid solutions that maintain the fluorite structure of CeO$_2$ with a change in lattice constant that is approximately proportional to the dopant ionic radius. The single allowed Raman mode, which occurs at 465 cm$^{-1}$ in pure CeO$_2$, is observed to shift to lower frequency with increasing doping level for all the rare earths. However, after correcting for the Grüneisen shift from the lattice expansion, the frequency shift is actually positive for all the strictly trivalent ions. In addition, the Raman line broadens and becomes asymmetric with a low frequency tail, and a new broad feature appears in the spectrum at ~570 cm$^{-1}$. These changes in the Raman spectrum are attributed to O vacancies, which are introduced into the lattice whenever a trivalent RE is substituted for Ce$^{4+}$. This conclusion is supported by a simple model calculation of the effects of O vacancies on the Raman spectrum. The model uses a Green’s function technique with the vacancies treated as point defects with zero mass.

I. INTRODUCTION

Cerium dioxide is a common additive to catalysts used for removing hydrocarbons, CO, and nitrogen oxides from automobile exhausts$^1$ and for industrial processes such as cracking heavy oil in zeolites.$^2$ One of the reasons for adding ceria to automotive catalysts is to promote the storage and release of oxygen during transient excursions from rich to lean environments in the exhaust gas, thereby widening the air/fuel ratio window over which the catalyst can both oxidize CO and hydrocarbons and reduce NO$_x$. The ability to store oxygen is a result of cerium’s ability to change valence states and the presence of intrinsic O vacancies in the CeO$_2$ lattice. Recently Miki et al.$^3$ have shown that the addition of lanthanum oxide improves the oxygen storage capability of a typical precious metal/CeO$_2$ catalyst supported on alumina. The addition of La$^{3+}$ ions to CeO$_2$ results in solid solutions of the form Ce$_{1-x}$La$_x$O$_{2-y}$ that have the same fluorite structure as does CeO$_2$ up to atomic fractions of La as large as ~55%.$^4$ For every two La$^{3+}$ ions that replace Ce$^{4+}$ ions, one O vacancy is needed to balance the charge. These vacancies apparently increase the diffusion rate of O$_2$, thereby increasing the ease with which the material can absorb and give off O. If O vacancies are the key to improved O storage capability, then any trivalent cation that replaces the Ce$^{4+}$ in the CeO$_2$ lattice should produce similar benefits. In fact, Cho$^5$ found that Gd-submitted CeO$_2$ showed improvements in O storage that were similar to those seen by Miki et al.$^3$ for La substitution.

The purpose of this article is to investigate a number of systems of the form Ce$_{1-x}$RE$_x$O$_{2-y}$ in which RE=La, Pr, Nd, Eu, Gd, or Tb. Solid solutions containing a range of concentrations of each dopant are synthesized and studied by x-ray diffraction (XRD) and Raman scattering. We focus on the concentration ranges for which the solid solutions retain the fluorite structure of CeO$_2$. The lattice constants for the doped crystals are found to shift from that of CeO$_2$ by an amount that is approximately proportional to the dopant ionic size. These fluorite-structure crystals have only a single allowed Raman mode, and we find that all the dopants produce small systematic shifts in this mode. We also find a new, broad feature in the Raman spectrum peaked near 570 cm$^{-1}$. On the basis of a simple model calculation, we attribute these changes in the Raman spectrum to the presence of O vacancies.

Although many of the doped-CeO$_2$ systems investigated here have been studied previously by XRD,$^{4,6-8}$ we are not aware of any other Raman work. Actual catalysts are often difficult to analyze by XRD because of the high dispersion and low concentrations of some of the active constituents. Raman analyses are usually easier to perform than XRD, and they can often yield useful information. For example, Graham et al.$^9$ used Raman scattering to characterize CeO$_2$ particle size in field-aged automobile catalysts, and Otto et al.$^{10}$ used Raman scattering on model catalysts containing Pd to identify PdO and to follow the in situ reduction of PdO after exposure to hydrogen. The identification of a Raman signature for O vacancies has important implications for characterizing CeO$_2$-containing catalysts, since XRD is generally insensitive to the O vacancy concentration.

II. EXPERIMENTAL DETAILS

A. Sample preparation

The samples were prepared as powders starting from SPECPURE ICP standard nitrate solutions obtained from Johnson Matthey. The starting solutions contained 10 mg/ml of the RE in 5% HNO$_3$ and were combined to produce 20 ml mixtures containing 2%, 5%, 10%, 35%, and 50% (additionally 0.5% and 1% for Pr) by volume of each of the rare earth solutions in the cerium nitrate solution. The mixtures were put in ceramic crucibles (Coors) and heated slowly to a few
hundred °C to decompose the nitrides. The dried residue was then ground, fired in a furnace overnight at 1000 °C, quench cooled, and reground. After obtaining XRD and Raman data on each sample, we refired them overnight in Pt crucibles at 1200 °C. The XRD and Raman analyses were then repeated.

B. XRD measurements

The samples were prepared for analysis by dusting the powders onto a greased low-background plate, and were x-rayed with a Siemens θ-2θ diffractometer using Cu Kα radiation. Diffracted intensity data were recorded at 0.025° intervals over the range 20°-148°. The high angular range was chosen to obtain accurate lattice constant values. The eight diffraction peaks found in this range were indexed to the fluorite structure and fit with Lorentzian lineshapes. The resulting line centers and widths were used to determine lattice constants and estimate particle sizes. The uncertainty in the lattice constant determinations was typically ±0.0005 Å.

C. Raman measurements

The Raman spectra were obtained using a SPEX Triplemate spectrometer, an intensified diode array detector system, and an Ar⁺-ion laser. For calibration purposes, we chose to excite the Raman signal with the 457.9 nm line, and at the same time introduce a second, highly attenuated beam at 476.5 nm from another laser into the beam path. The Rayleigh scattering from the second beam thus produced a calibration line in the spectrum at an effective Raman shift of 850.1 cm⁻¹. The spectrometer was adjusted so that the peak intensity from this line always fell on the same pixel of the array. The resolution, as determined from the full width at half-maximum of the calibration line, was ~4 cm⁻¹. Peak frequencies from the single Raman line were determined by fitting the data to a Lorentzian lineshape with a sloping background using a 5-parameter least squares fit. The accuracy of the frequency determined in this manner was a few tenths cm⁻¹ for the more heavily doped samples in which the line becomes broader and asymmetric. We verified that there were no interferences with fluorescence lines by also recording the spectra with other laser wavelengths. The samples lightly doped with Eu were the only ones that showed a fluorescence line near the 457.9 nm laser excitation. This line was at 466.4 nm, an effective Raman shift of 395 cm⁻¹, and had no influence on the fit to the Raman feature.

The laser power was kept low, normally ~2 mW, in an effort to avoid sample heating, since small changes in temperature can easily produce small changes in the frequency and width of the Raman line. At this power, laser heating was not a problem for pure CeO₂ or the samples doped with La, Pr, Gd, or Nd, since these samples were all light beige in color. (It is interesting to note that when viewed under fluorescent light the Nd samples appear as successively darker shades of mint green with increasing x.) However, laser heating was of concern for the samples doped with Eu, which progressed in color from rust to black, and Tb, which progressed in color from light brown to brown with increasing x. For these samples we recorded spectra at 0.5, 2, and 5 mW laser power, and then extrapolated the results to zero laser power. This correction had the effect for the darkest samples of shifting the frequency of the G₂₇ mode measured at 2 mW up by ~2 cm⁻¹.

III. RESULTS

A. XRD results

The XRD results are summarized in Fig. 1, where we plot the change in lattice constant compared with pure CeO₂ (a₀=5.411 Å) for the full range of samples studied. These data are for the powders sintered at 1200 °C. The lattice constants determined following sintering at 1000 °C were similar; however, the particle sizes were much smaller, e.g., due to a few hundred Å, compared with a few thousand Å for the powders after sintering at higher temperature. Consequently, the x-ray lines from the 1200 °C samples were narrower, and we were able to obtain more accurate lattice constant values and could more easily identify multiple phases when they occurred. For both temperatures, there was a trend of diminishing particle size with increasing doping level.

The La-, Pr-, and Nd-doped samples appeared to be single phase for the full doping range. The remaining dopants all showed evidence of small amounts of an additional phase for some x values. In a few cases, where the extra phase appeared to be pure CeO₂, it was possible to use the XRD peak intensities to estimate the x value for the rare-earth doped fluorite phase. However, in many cases the samples appeared to contain some of the C-type cubic phase characteristic of the sesquioxides, and it was impossible to determine the x value of the rare-earth doped fluorite phase. These multi-phase samples are indicated by the large error bars in Fig. 1.
bars in the figure; the uncertainties for the other points are too small to be displayed. Note that it is not a simple matter to detect the presence of small amounts of the cubic C-type phase, such as Gd2O3, in the presence of the fluorite phase.6 The C-type phase has the metal atoms in the same positions as in the fluorite structure, the lattice constant is twice as big, and there is an ordered array of O vacancies. The strong x-ray lines from the two structures thus overlap.

The lattice constant shifts shown in Fig. 1 are directly correlated with the ionic size of the dopants; the larger or smaller dopants will dilate or contract the lattice, respectively, with the amount of change in lattice constant being approximately proportional to the ionic size. This trend is demonstrated in Fig. 2, where we plot the initial slopes of the lattice constant versus x curves in Fig. 1 as a function of the RE3+ ionic radius, as given by Shannon.7 These slopes are determined by fitting the data in Fig. 1 to a quadratic function of x and extracting the linear term. For comparison we have included data from several other authors on other rare earths. The lanthanides expected to be in the 3+ valence state show a common trend as indicated by the dashed line. This line was determined from a least-squares linear fit to all the data, excepting Tb and Pr. Clearly Tb and Pr points do not follow this trend, which indicates that these dopants are probably in mixed valence states. If the Tb and Pr points were plotted at their 4+ ionic radii, 0.88 and 0.96 Å, respectively, then the points would fall well to the left of the dashed line.

The trend shown in Fig. 2 is not determined solely by the ionic radius, however, since the dashed line crosses zero at ~1.025 Å, well above the ionic radius corresponding to Ce4+ (0.97 Å) and well below that for Ce3+ (1.143 Å). Thus Coulomb effects, O vacancies, and changes in the force constants introduced by RE3+ doping may also play important roles in determining the resulting lattice constants.

B. Raman results

Fluorite structure metal dioxides have only a single allowed Raman mode, which has F2g symmetry and can be viewed as a symmetric breathing mode of the O atoms around each cation. Since only the O atoms move, the mode frequency should be nearly independent of the cation mass. In CeO2 this frequency is 465 cm⁻¹, whereas in ThO2 where the cation mass is 65% larger the frequency is only about 1 cm⁻¹ higher.8 We see small systematic shifts of the F2g mode to lower frequency in all of our doped samples. Examples of the data are shown in Figs. 3 and 4 for La and Pr doping, respectively. These data and all subsequent data in this section are from the samples sintered at 1200 °C. For these samples the particle size (10³ Å range) is large enough that it should have no influence on the Raman spectra.9

In addition to the negative frequency shift, the F2g mode for the La-doped samples in Fig. 3 becomes asymmetric with a long low-frequency tail as x increases. The line develops more of a Fano-type lineshape than a Lorentzian. There is also in the La-doped samples a weak shoulder on the high frequency side of the line that evolves into a broad peak at ~570 cm⁻¹ for larger x values. These features are common to the La-, Nd-, Eu-, and Gd-doped samples. In the Pr-doped samples the F2g line shows a similar negative frequency shift, but the line retains a symmetric Lorentzian shape as is shown in Fig. 4. There is also a broad peak near 570 cm⁻¹ that is distinct from the F2g mode even at the lowest doping level. This peak is relatively larger and narrower than the corresponding feature in the La-doped samples. Results for the Tb-doped samples are very similar to those for Pr doping.
There are thus quantitative differences between the results for Pr and Tb and those for the other lanthanides, even though the qualitative trends are the same for all dopants.

The spectra in Figs. 3 and 4 are plotted on the same relative intensity scale. However, differences between peak heights for different x values are indicative of changes in Raman strength only for the uncolored compounds. For La, Eu, and Gd, the integrated $F_{2g}$ mode intensity remains fairly constant for all x. We can thus conclude, for example, that the intensity of the 570 cm$^{-1}$ feature from the La-doped samples in Fig. 3 increases uniformly with x. However, for those compounds that become more colored with increasing x (Nd, Tb, Pr), increased optical absorption will tend to make the volume sampled smaller as x increases, which would have the effect of reducing the observed intensity of all the Raman peaks. Hence the 570 cm$^{-1}$ feature for the Pr-doped samples in Fig. 4 also increases uniformly with x, but only after the spectra are normalized with respect to the integrated $F_{2g}$ mode strength.

Figure 5 shows the $F_{2g}$ mode frequency shifts measured for all the dopants. These data are restricted to the low-doping range, $x \leq 0.2$, since the line becomes asymmetric at higher dopings and we are using a symmetric Lorentzian lineshape to determine the peak position. Also we have omitted the $x = 0.2$ data for Eu, Gd, and Tb, since XRD analyses of these showed two distinct phases for $x \geq 0.2$, and there was no way to sort out which phase was giving the Raman results. The remaining data all correspond to single-phase fluorite-structure materials. A conservative estimate of the uncertainty of these frequency shifts is $\pm 1$ cm$^{-1}$, thus the trends observed are well outside of any experimental errors.

There are at least two mechanisms contributing to the frequency shifts seen in Fig. 5. The first is increased O vacancies, which will be discussed in the following section; the second is dilation or contraction of the lattice. The frequency shift $\Delta \omega$ of the Raman mode produced by a change $\Delta a$ in lattice constant can be written in terms of the Grüneisen parameter:

$$\Delta \omega = -3 \gamma \omega_0 \Delta a/a_0,$$

where $\omega_0$ is the Raman frequency in pure CeO$_2$, $a_0$ is the CeO$_2$ lattice constant, and $\gamma = B/\omega d\omega/dP$ is the Grüneisen constant with $B$ the bulk modulus and $d\omega/dP$ the linear shift of the Raman frequency with hydrostatic pressure. Kouroykis et al. have measured $d\omega/dP = 3.29$ cm$^{-1}$/GPa for CeO$_2$ using a diamond anvil cell. They then used the bulk modulus for ThO$_2$ ($B = 204$ GPa) to obtain a Grüneisen parameter of 1.44 for CeO$_2$. Satoh and Tateyama refer to an unpublished measurement of the bulk modulus for CeO$_2$ and give elastic constants for CeO$_2$ that produce a value $B = 176$ GPa, which would lead to $\gamma = 1.24$. It is not clear which of these values is most reliable, but to be consistent with our own previous analysis of CeO$_2$ lattice dynamics, we will use the latter value.

Figure 6 shows the data from Fig. 5 after subtracting the Grüneisen shifts. These shifts are calculated from Eq. (1) using the lattice constant changes measured by XRD, as discussed in the previous section, and taking $\gamma = 1.24$. Now most of the dopants show a small positive frequency shift with increased doping. The two exceptions are Pr and Tb, which we will discuss here. The remaining lanthanides crystallize in oxides of the form RE$_2$O$_3$, indicating they are in the 3+ valence state. For every two trivalent ions that are substituted for Ce in CeO$_2$, there should be one oxygen vacancy introduced to balance the charge. In fact, the counting is not quite that simple, since there are intrinsic O vacancies in

FIG. 4. Raman spectra of Pr-doped cerium oxide as in Fig. 3.

FIG. 5. Measured shift of the Raman mode in RE-doped CeO$_2$ with doping fraction.
undoped CeO₂ and their concentration may change somewhat with doping. Nevertheless, we would expect the O vacancy concentration to increase as the RE³⁺ concentration increases. We are led to conclude from Fig. 6 that the small positive frequency shifts of the Raman line are caused by these vacancies.

The frequency shifts observed for Pr and Tb remain a puzzle. These rare-earths, along with Ce, are known to form a series of well-defined but nonstoichiometric oxides of the type ReO₃, where 1.5 < x < 2.¹⁷-¹⁹ The stable phases contain varying ratios of RE³⁺/RE⁴⁺ together with appropriate numbers of O vacancies to balance the charge. Under normal conditions, CeO₂ is stable and forms readily in air, but neither Pr nor Tb tend to crystallize in the dioxide or sesquioxide phases; rather they form compounds with nominal compositions Pr₆O₁₁ and Tb₄O₇. Thus we should expect that doping CeO₂ with either Pr or Tb should increase the O vacancy concentration. Consistent with this conclusion is the fact that the Raman peak near 570 cm⁻¹ that we have identified as arising from O vacancies is quite prominent in the Pr- and Tb-doped samples. We do not understand, however, why the shift in the Raman line for these ions is in the opposite direction.

IV. RAMAN SIGNATURE FOR O VACANCIES

To assist with the interpretation of the Raman spectra of doped CeO₂, we present in this section a simple model for the effects of oxygen vacancies. Although it is very crude, we will see that this model explains the appearance of a new peak near 570 cm⁻¹ and is consistent with the observed shifts and broadening of the main Raman peak for the 3+ dopants. The simplicity of the present approach is justified by the lack of a fully satisfactory dynamical model for pure CeO₂. In an earlier paper we argued that the available experimental information for this compound is too limited at present to constrain a shell model of the phonon spectrum, while a rigid-ion model (RIM) significantly underestimates the frequencies of the uppermost optical phonon branch. By rigidly shifting the top portion of a RIM phonon density of states (DOS), we were able in that work to account for all of the prominent features in the second-order Raman spectrum of pure CeO₂. The resulting DOS is shown as the solid curve in Fig. 7. The dashed curve is the projection of this DOS on O sites, also obtained by shifting the RIM result. Since the phonons in the shifted portion are almost exclusively O vibrations, the resulting O projection is likely to be a good approximation to that of pure CeO₂. We will see below that this projection is the key input in our treatment of vacancy effects.

We model an O vacancy as a substitutional impurity with a mass \( M_{\text{vac}} = 0 \). We ignore all changes in charge, force constants, and Raman polarizabilities, as the incorporation of any one of these effects would require us to know the full dynamical matrix for the pure compound.²⁰-²² We also do not consider the direct effects of alloying on the Ce sublattice.²³ By subtracting the O-projection from the total DOS in Fig. 7, one can see that these effects would be most significant for the acoustic modes below 270 cm⁻¹. Even there the effects would be quite small since the maximum relative mass difference for a RE dopant in the present study is only 12% (for Tb). At the higher frequencies of greatest concern for Raman scattering, the direct effects of Ce substitutions are safely neglected.

The problem of substitutional mass disorder is conveniently treated by Green’s function techniques.²⁰-²⁶ Using a self-energy ansatz, we write the average Green’s function for CeO₂₋γ as

\[
\tilde{G} = \tilde{P} + \Sigma \tilde{G},
\]

where \( \tilde{P} \) is the Green’s function for the crystal without vacancies and \( \Sigma \) is a translationally invariant, complex self-energy that varies with frequency \( \omega \). The perfect crystal
Green's function is diagonal in a representation of phonon eigenstates \( |j,k\rangle \), where \( k \) is the wave vector and \( j \) is the branch index:

\[
P(\omega^2+i\Omega^+) = \sum_{j,k} \frac{|j,k\rangle\langle j,k|}{\omega^2 - \omega_j^2(k) + i\Omega^+}.
\]  

(3)

The self-energy has nonzero matrix elements only between states associated with \( O \). In a real-space representation, this quantity is diagonal within the \( O \) subblock with all diagonal matrix elements the same by symmetry. The diagonal component may be written as \( M_O^2 \sigma(\omega) \), where \( M_O \) is the \( O \) mass. We assume that the \( y \) vacancies, with mass defects \( \epsilon = (M_O - M_{\text{atom}})/M_O \), are randomly distributed over the two \( O \) sublattices in the fluorite structure. For small \( y \), it is straightforward to show that

\[
\sigma(\omega) = \frac{y/2}{1 - M_O^2 P_O(\omega^2 + i\Omega^+)}.
\]  

(4)

\( P_O(\omega^2+i\Omega^+) \) is any \( O \)-site-diagonal real-space matrix element of the perfect crystal Green's function (all equal by symmetry). This quantity is related to \( g_O(\omega) \), the normalized \( O \)-projected DOS of pure \( \text{CeO}_2 \) (which we obtain from Fig. 7) as

\[
P_O(\omega^2+i\Omega^+) = \frac{1}{M_O} \left( \int \frac{d\eta \; g_O(\eta)}{\eta^2 - \omega^2 - i\pi \frac{g_O(\omega^2)}{2\omega}} \right),
\]  

(5)

where the \( P \) on the right denotes the principal part of the integral.

With the Raman polarizabilities assumed to be the same as in pure \( \text{CeO}_2 \), the Raman intensity \( I_R(\omega) \) is related to the \( O \)-projected DOS of pure \( \text{CeO}_2 \) (which we obtain from Fig. 7) as

\[
I_R(\omega) = -\text{Im} \left\{ \left( \frac{\epsilon}{\eta} \frac{\omega^2}{2\pi} - \frac{\eta}{\omega^2} \right) \right\}
\]  

which reduces to

\[
I_R(\omega) = -\frac{1}{\omega_R^2} \left( 1 - \frac{\epsilon}{2\pi} \right) \left( 1 - \frac{\omega_R^2}{\omega^2} \right),
\]  

(7)

where \( \omega_R \) is the Raman frequency. The evaluation of the self-energy matrix element in Eq. (6) is particularly simple because the Raman mode is a pure \( O \) vibration. Equation (7), together with Eqs. (4) and (5), relate the effects of \( O \) vacancies to the perfect crystal \( g_O(\omega) \). While the methodology exists for treating vacancies in a more sophisticated manner than considered here, \( \sigma(\omega) \) involves additional matrix elements that are currently undetermined. It is for a similar reason that we consider only a dilute concentration of vacancies; the generalization of Eq. (4) to arbitrary \( y \) within the coherent potential approximation involves the \( O \)-site-diagonal matrix element of \( \tilde{G} \) instead of \( P \), which again requires that we have a more complete description of the perfect crystal.

Figure 8 shows results obtained from Eq. (7) for three different vacancy concentrations. Since the mass disorder is the only source of broadening we include, the dotted curve for \( y = 0 \) exhibits a very sharp peak at \( \omega_R = 465 \text{ cm}^{-1} \). As \( y \) increases, this main Raman peak broadens and shifts up in frequency by 1–2 cm\(^{-1}\). At the same time, a new feature appears with a maximum near 570 cm\(^{-1}\). This feature results from a disorder-induced mixing of the Raman mode with the uppermost optical phonon states in Fig. 7. We emphasize that the location of these states was not adjusted in the present work, but was chosen in Ref. 16 to fit the second-order Raman spectrum of pure \( \text{CeO}_2 \). The broadening of the main Raman peak in Fig. 8 also reflects a mixing of the Raman mode with nearby states. The small upward shift of this peak is the net perturbation due to the mixing with states at many different frequencies. Mathematically, this shift is determined by \( \text{Re} \sigma(\omega) \). Since vacancies tend to narrow bands by reducing the average coordination, \( \text{Re} \sigma(\omega) \) is negative near the top of each nonzero region of \( g_O(\omega) \) and positive near the bottom. \( \text{Re} \sigma(\omega) \) turns out to be positive, but its magnitude is small because \( \omega_R \) is close to where \( \text{Re} \sigma(\omega) \) changes sign.

The above results are qualitatively consistent with the changes observed in the Raman spectra of doped \( \text{CeO}_2 \), shown for example in Figs. 3 and 4. There is a new Raman feature near 570 cm\(^{-1}\); the main Raman line broadens, developing a low frequency tail, and after correcting for the Grüneisen shift from the change in lattice constant, there is a small positive frequency shift of the Raman line center. The main deficiency of the vacancy model presented here is that the intensity of the disorder-induced feature near 570 cm\(^{-1}\) is two orders of magnitude too small. The magnitude of the predicted shift of the main Raman line is also considerably smaller than in Fig. 6. The intensity problem is most likely due to our neglect of polarizability changes in the vicinity of a vacancy; such changes would introduce additional incoherent scattering terms that generally enhance the defect-induced structures. We suspect that the present underestimate of the shift of the main Raman line is due to our neglect of force constant changes. Since this shift is a subtle consequence of phonon scattering at many different frequencies, it is conceivable that a more complete model of RE doping might even be able to explain the apparent negative shifts observed in Pr- and Tb-doped \( \text{CeO}_2 \).

**V. CONCLUSIONS**

In summary, we have shown that doping \( \text{CeO}_2 \) with any of the lanthanides La, Pr, Nd, Eu, Gd, or Tb leads to fluorite-
structure mixed crystals with increased O vacancies. For the strictly trivalent ions, the rate of change in lattice constant with the doping concentration is proportional to the ionic radius of the dopant. Small systematic changes in the $F_2g$ Raman line are induced by all the dopants, but the most significant change in the spectrum is a new, broad feature near $570$ cm$^{-1}$ that we attribute to O vacancies. The strength of this line increases with doping level, and its position agrees well with that predicted from a Green's function model calculation of the effects of O vacancies on the Raman spectrum.

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