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LETTER TO THE EDITOR

Measurements of the lattice constant of ceria when doped with lanthana and praseodymia—the possibility of local defect ordering and the observation of extensive phase separation

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Abstract

Conventionally, the addition of sesquioxide cation dopants to ceria has been thought of as a class of almost model systems. The most important defect mechanism involves simple anion vacancy charge compensation with those vacancy defects associating themselves with the trivalent cation and being distributed randomly through the lattice. However, this simple model has been significantly challenged in recent years and it seems possible that these associated defects might cluster in ordered arrangements. Whilst evidence has been provided by theoretical work, only limited experimental data are available. This letter reports the first observation of local ordering in these systems as observed by careful powder x-ray diffraction studies. In detail, it is shown that measurements of the lattice parameter do not vary monotonically with dopant concentration. It is also shown that far from being ideal systems with very high dopant solubilities and true solid-state solutions, these systems have complex solubility.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Ceria (and doped ceria) has become one of the most important ceramic materials. It has a number of important and varied catalysis uses (most notably as an important component of the three-way automotive catalyst) [1]—as an ionic conductor [2], as a gas sensor [3] and

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as a component of fuel cells [4]. More recently, and of considerable interest in terms of data discussed in this letter, is the possible use of lanthanide-oxide-doped cerias as important optical materials. For example Bhattacharya *et al* [5] have detailed the optical properties of $\text{CeO}_2/\text{PrO}_x$ and other systems, pointing out that the variation of the refractive index with vacancy and dopant concentration may lead to uses as transparent ion intercalation films and optoionic smart windows. Özer [6] has suggested that ceria could be used in transmissive electrochromic devices.

The defect chemistry of ceria is relatively well established. It is generally thought that as a trivalent cation is added to the lattice, it is charge compensated for by the presence of anion vacancies. These are associated with the dopant cations and randomly distributed on anion sites within the fluorite lattice. In particular, whilst this may be the thermodynamically most important defect mechanism, other defect systems are possible as minority species [7] and experimental evidence for interstitial oxygen defects has been found for nanoparticles of ceria [8]. MAS NMR studies of lanthana-doped ceria also strongly suggest that local ordering of defects occurs [9] and there is some structural evidence via tunnelling microscopy for clustering of vacancies occurring at $\text{CeO}_2(111)$ surfaces [10].

Whilst these and other works indicate more complex defect chemistry than often thought, clear structural evidence is scant. In particular, the dependence of the lattice parameter on dopant concentration should provide some evidence for defect ordering. Several studies for various lanthanide–ceria combinations exist and in particular the lanthana–ceria system has been well documented [7, 11–13]. All of these indicate an (at least approximate) linear expansion of the lattice parameter as the dopant ion concentration is increased (towards maximum solubility). The slope of such graphs is dependent on the defect model as shown explicitly by Grimes *et al* [7]. It might also be expected that there could be sudden changes in the lattice parameter at specific dopant concentrations due to local defect ordering occurring within a certain concentration range. In our earlier MAS NMR work, it was reported that ‘clustering’ of vacancies occurred in certain concentration ranges [9]. The work reported herein is a very careful study of powder x-ray diffraction (PXRD) data from the $\text{CeO}_2/\text{La}_2\text{O}_3$ and $\text{CeO}_2/\text{PrO}_x$ systems which provides further evidence for complex defect arrangements in these materials.

2. Experimental details

Samples (at intervals of 1 or 2.5 mol%) were prepared by evaporation from the required mixtures of metal nitrate solutions. The concentrations quoted are in terms of cation content; i.e. 50 mol% La indicates that $\frac{1}{2}$ of the metal cations present are lanthanum. Samples were dried in an oven at 340 K. They were then calcined in air at 673 K for 8 h and subsequently further calcined in air at 1273 K for a period of one week. The samples were cooled rapidly, in air, from red heat (1273 K) to room temperature in 30 s. No attempt was made to allow thermodynamic equilibrium to be obtained during cooling. This treatment was adopted since nitrate solutions provide no contamination from precipitating agents. The unusually long heating time and the temperature were very carefully chosen to facilitate complete solution of the dopant lanthanide elements and provide ample time to ensure that local ordering could be achieved without nucleation of surface deposits of the dopant oxide. Some samples produced by slow cooling were also prepared for surface studies. Details are given below.

PXRD data were collected on a Philips PW 3710 powder diffractometer ($\theta-2\theta$ mode) using $\text{Cu K}\alpha$ radiation from a ceramic anode at 30 kV and 40 mA. Prior to analysis, the position of the goniometer was calibrated to the $\text{Si}(111)$ and $\text{Si}(311)$ reflections from a powdered silicon wafer sample. The position was verified after analysis to ensure that no calibration change

Table 1. Comparison of target La/Ce ratios and measured XRF data.

Target La/Ce mole ratio	5.0	15.0	25.0	35.0	45.0	55.0	65.0
Calculated La/Ce mole ratio (K α derived)	4.85	15.05	24.37	34.94	45.72	54.27	66.1
Calculated La/Ce mole ratio (L α derived)	4.78	15.54	25.36	34.27	443.68	56.26	66.75

was required. All data were collected from the same sample holder. For each sample and the standard alignment of the sample, the height was verified by placing the sample at $\theta = 0^\circ$ and scanning the 2θ arm through the zero-angle position. Accuracy in the zero-angle position was found during Rietveld analysis of several pure MgO samples to be within $\pm 0.01^\circ$.

The relative amounts of metal ions were verified by x-ray fluorescence (XRF) spectroscopy. Standards were prepared by physically mixing amounts of lanthana and ceria. All samples for XRF spectroscopy were ball milled and 0.1 g of each sample collected. This was added to 0.9 g of alumina (this acted as a dilutant, preventing signal saturation and minimizing matrix absorption effects). 0.1 g of wax was added and the samples pressed at 4 ton pressure into 1 cm² discs. Data were collected on an Oxford Instruments ED2000 using Rh K α radiation, K α signals (Ce = 22.895°, La = 23.780°, Pr = 22.044°; 2-theta LiF(420) monochromating crystal) and L α signals (Ce = 79.0194°, La = 82.903°, Pr = 75.414°; 2-theta LiF (200) monochromating crystal).

X-ray photoelectron spectroscopy measurements were made on a Vacuum Generators MkIV system using Al K λ radiation and a pass energy of 50 eV, and using a three-component multi-channel detector. Samples were prepared like the XRF spectroscopy samples except that no alumina dilutant was added. Shirley-type backgrounds were used to find peak contributions and total (i.e. all spin-orbit and final state peaks) peak areas were used.

3. Results

The first point that has to be addressed is whether the samples show true solubility of the phases. In much of the work in the literature it is assumed that the absence of features in PXRD profiles indicative of lanthana phases mean that complete solubility has been achieved. In our opinion this is quite wrong. The PXRD is relatively insensitive to minority phases and material distributed in small particles. The concentration of dopant material was verified by XRF spectroscopy and found to be within 1% of the desired level. Similar concentrations were obtained from both low-energy (L α) and high-energy (K α) features in the XRF spectroscopy, suggesting that the near surface and bulk of the sample have very similar concentrations. Data are summarized in table 1.

However, these systems are very much more complex than usually thought. Solubility limits for the trivalent lanthanide oxides are often quoted between 40% and 70% [14]. We believe the true solubility limit (i.e. where a random solid solution is formed) to be much lower and that above about 20 mol% loadings, new locally ordered phases or compounds are being formed. There is still not enough long-range order for these phases to be observed by means of x-ray diffraction. At high calcination temperatures, lanthanum ions appear to segregate to the surface of the material as enriched phases or as lanthana. Example data are shown in figure 1 which plots the XPS-measured La:Ce 3d peak area ratio from a 15 mol% lanthanum-doped sample as a function of temperature. Note that compared to the samples studied by XRD and XRF spectroscopy, these samples were cooled very slowly at a cooling rate of 1 K min⁻¹ to allow thermodynamic equilibrium to be reached. We estimate the surface coverage of

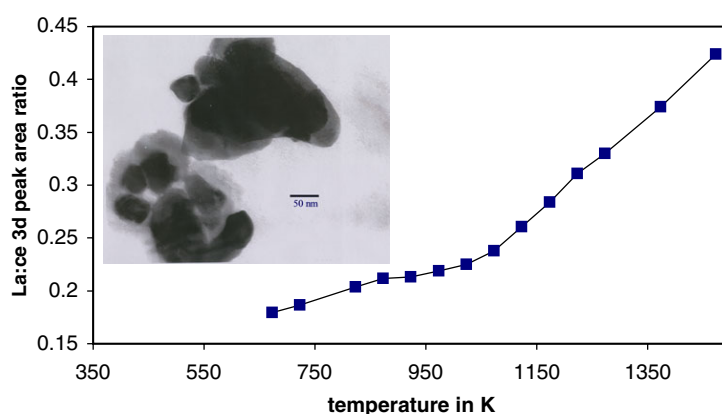


Figure 1. The La:Ce 3d peak area ratio for a 15 mol% La-doped ceria sample aged at various temperatures. The inset shows a 40 mol% sample calcined as described in the text. The dark particles are the dense ceria cores of particles and the halo of lighter material is due to a thick overlayer of segregated lanthana.

lanthana at 1273 K to be equivalent to around two monolayers (for the rapidly cooled samples described below, negligible segregation was observed). This evidence suggests that the true solubility limit is quite low and it is thermodynamically favourable for the materials to phase separate to some extent. The exact nature of this phase separation is discussed below. It is simplistic to relate this segregation process to temperature, however. Contrary to what might be expected, much greater phase separation can be obtained at even lower temperatures. The inset in figure 1 shows a TEM micrograph of a 40 mol% lanthanum-doped sample prepared by the normal process of calcination at 1273 K for one week followed by a calcination at 873 K for the same time. The lanthanum-enriched phase has formed a well-resolved surface covering about 30 nm thick. This and other data collected in these laboratories lead us to suggest that the irreproducibility in determination of solubility limits (noted by other authors [14]) is a result of complex balances between thermodynamic stability, entropy and initial preparation (which are usually controlled so as to produce atomic mixing of ingredients). On the basis of these and other results, it is unlikely that sample preparation by long-time ageing at 1273 K, when entropy might favour complete mixing, followed by quench cooling would result in an enriched surface distribution of dopant similar to that observed here.

Figure 2 shows a plot of the lattice parameter of ceria as a function of the lanthana concentration for samples prepared as detailed above but cooled rapidly. The lattice parameter was determined by Rietveld fitting (carried out to give the minimum R -value for fitting of a single stoichiometric fluorite phase of ceria by variation of the lattice parameter) of the collected PXRD profiles. At first glance this is an almost linear variation of the lattice parameter (a) with concentration. However, on careful inspection of the data, two areas of non-linearity can be determined, around 20 and 40 mol%. It was found that around these loadings, PXRD peak profiles showed strong asymmetries and even peak splitting into two distinct fluorite structures. No additional features were observed. Figure 3(a) shows a typical PXRD profile (35 mol% La). The data show clear peak asymmetry at low 2θ angles and peak splitting at higher angles. Figure 3(b) shows the variation in collected data between 35 and 39 mol% La. In this plot the scale used ensures that the splitting seen at 35% cannot be visually observed, but note particularly that at 37 and 38 mol% La, additional peak splitting can be readily observed especially for the higher-angle features where the resolution is higher. There is no evidence from either XPS Ce 3d line shapes or careful Rietveld fitting of the PXRD data to suggest that these

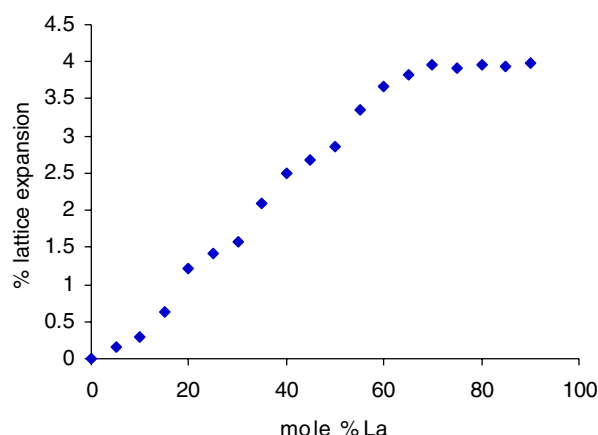


Figure 2. Lattice expansion versus metal-atom mol% of lanthanum added. The data were estimated by Rietveld fitting of a single fluorite phase of ceria to the PXRD profiles.

samples have significant anion non-stoichiometry beyond the concentration required to charge compensate for 3+ charges introduced into the lattice (i.e. are chemically reduced) and we propose that the system is separating into two phases with different lanthanum concentrations.

If the PXRD profiles are now re-analysed by Rietveld fitting with two individual fluorite phases, much better data analysis is achieved and this allows the lattice parameters of the two phases to be determined. Figure 4 shows the trend in the lattice parameter as a function of content. At low concentrations only a single phase is observed (although this may be a result of sensitivity and similar experimental limitations). There is a relatively small lattice expansion (compared to the total amount observed at high concentrations) suggesting that the dopant ions and resultant anion vacancies are isolated species and the larger La^{3+} ions are accommodated by local strain of the lattice rather than uniform lattice expansion. This explains why the peak width of the PXRD features is observed to increase by a factor of around 1.5 with dopant concentration between 0 and 10% dopant levels. The presence of a single phase is maintained until the dopant concentration reaches a limiting value of about 25 mol% when a second fluorite phase appears (it is convenient to label these phases P1_{high} and P2_{low} where ‘high’ and ‘low’ refer to the lanthanum concentration). It is suggested that at this limiting concentration of between 20 and 25 mol% La, the mixed lanthanum–cerium oxide fluorite phase is particularly thermodynamically stable. This must be due to the fact that the dopant ions and vacancies have attained some local ordering so as to minimize/maximize the repulsive/attractive interactions of the defects. There is clearly very little long-range ordering, as no additional reflections (or changes in peak intensity ratio) can be observed. This observation is consistent with the additional stability of defect arrangements predicted theoretically [7, 9, 13] and observed for undoped ceria in surface studies [10].

Above this limiting concentration, some of the doped ceria of optimum stability has to accommodate additional lanthanum ions added to the lattice so as to maintain the maximum concentration of the high-stability phase. In this way, maximum thermodynamic stability is maintained by producing two phases: one lanthanum rich (P1_{high}) and one lanthanum deficient (P1_{low}). Thus, the lattice parameter of the $\text{P1}_{\text{low phase}}$ remains almost constant. There is no driving force for complete phase separation (into ceria and lanthana), as it is generally thought that even up to relatively high concentrations the doped systems have additional thermodynamic stability compared to undoped systems [7, 13]. The ceria with high lanthanum concentrations continues to undergo lattice expansion as the dopant concentration is increased.

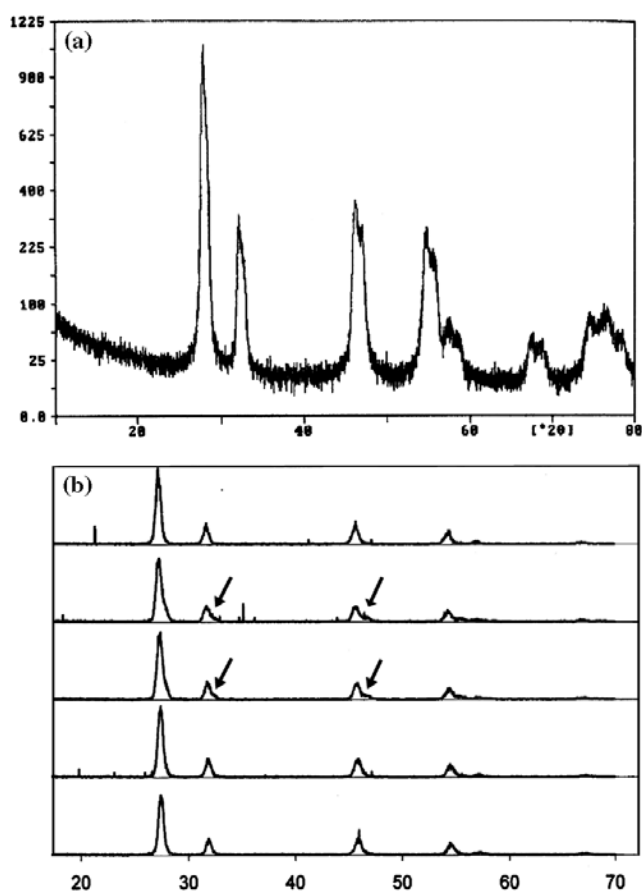


Figure 3. Illustrative PXRD patterns for ceria-lanthana mixtures. (a) Data from a 35 mol% sample. (b) A collection of PXRD profiles between 35 and 39 mol% La (from top to bottom respectively). Arrows indicate the dramatic peak splittings at 37 and 38 mol% La dopings.

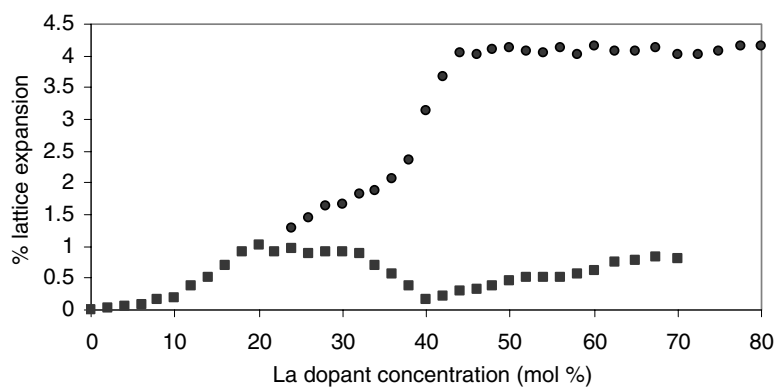


Figure 4. Lattice expansion versus metal-atom mol% of lanthanum added. The data were estimated by Rietveld fitting of two fluorite phases to the PXRD profiles (additional data are included compared to figure 2). The ● represent the P1_{high} phase and the ■ the P2_{low} phase respectively.

At a total concentration of around 38 mol% La there is another dramatic event, as seen in figure 3(b), and more dramatically manifested by the sudden lattice parameter expansion of the $P1_{\text{high}}$ phase. There is also a corresponding decrease in the lattice parameter of the $P2_{\text{low}}$ phase suggesting transport of material between the two phases. This is reflected in the very sudden changes in the PXRD profiles (figure 3(b)) associated with a dramatic well-defined splitting of the profile into two easily observed different fluorite phases. It is suggested here that there is a very strong local ordering of the lanthanum ions and oxygen vacancies and mass transport of species to form a well-ordered local structural phase. Note that this stabilized phase is of a concentration somewhat greater than 38 mol% La (indeed the lattice parameter moves very close to the upper limit of about 0.562 nm observed at 50 mol% La). Above this composition of 38 mol%, additional lanthana is accommodated into the low-concentration phase, and this feature moves to lower angles and phase merging is observed, so eventually all the material present has the 'favoured' lanthana concentration of around 50%. No further expansion of the lattice beyond actual loadings of 50% is observed, suggesting that the solubility limit has been reached. At this point the concentration of the $P2_{\text{low}}$ phase is negligible.

Results of the very careful measurement of the ceria lattice expansion during praseodymia doping show even more unusual detail but again provide evidence for local ordering of the doped systems. These results are described in detail elsewhere and only relatively low loadings are discussed here [15]. Up to 50 mol% Pr loadings there is no indication of the same sort of peak asymmetry or splitting as is typical of the lanthana work described above (although above this dopant level phase separation begins and the phase diagram of the system becomes very complex [15]). Although dramatic changes in the PXRD profiles can be observed in terms of position changes, it is unlikely that effects such as peak splitting deriving from phase separation and differing cation concentrations could be observed, as the ionic radii of Ce^{4+} and Pr^{4+} are almost identical (within 1%) and this would not be resolved in this experimental arrangement. Thus, the PXRD patterns observed are those expected from a single fluorite lattice (although phase separation may have occurred). Typical data are shown in figure 5 for samples between 12 and 16 mol% Pr, prepared as detailed for the La-doped PXRD samples.

Figure 5 also plots the d -spacing changes derived from measurements of the peak positions of the (111) and (311) reflections over the composition range 0 to 45 mol% Pr. The (111) plane appears to be almost constant (as might be expected for Pr^{4+} doping) except for a localized dramatic expansion of the lattice at 15 mol% Pr. The (311) d -spacing shows a similar expansion and another dramatic event around 30 mol% Pr. Since the changes in lattice parameter differ in form from plane to plane, it is clear that some of the changes are anisotropic through the lattice. The data can be rationalized in that at certain very well-defined concentrations, the praseodymium is added as the larger 3+ ions. That it occurs at prescribed coverages suggests that local structural defect arrangements are formed and that these involve complex arrangements in preferred crystallographic directions. These observations agree with previous work where it was observed that the rate of oxidation increased dramatically at certain compositions and it was argued that vacancy arrangements must be being formed to provide 'tunnel' or low-energy routes for oxygen mass transport through the system [16].

4. Discussion and conclusions

It is necessary to review these results to obtain an overall description of these systems. This is necessary because the overwhelming conclusion is that contrary to the generally accepted view these systems are really quite complicated, having obviously complex phase diagrams. The data presented here are a 'snapshot' of the phase diagram. Unlike the case for metal alloy systems, the very high melting points of the materials and limited mass transport at reasonable

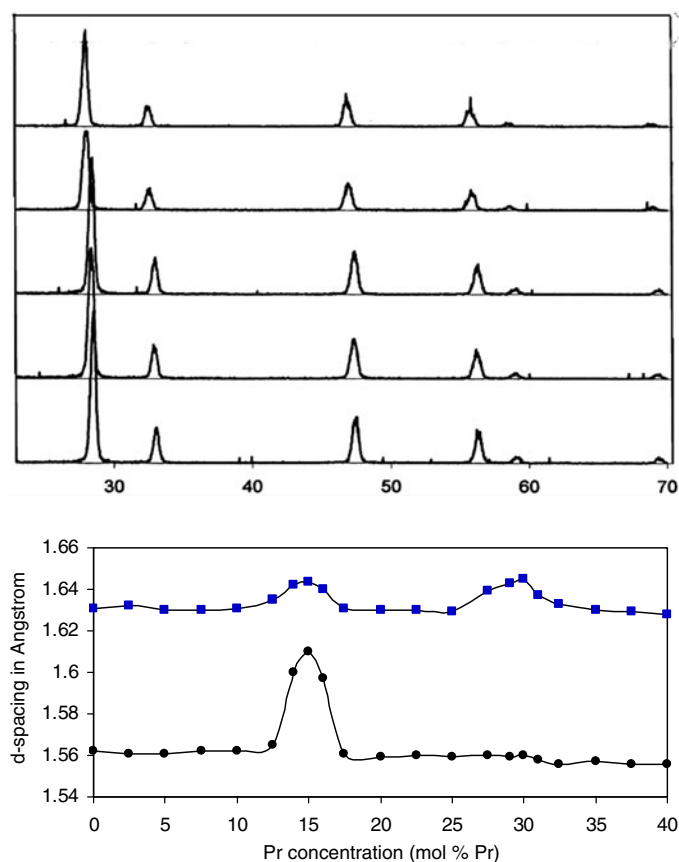


Figure 5. The upper plot shows a series of PXRD profiles collected at 12, 13, 14, 15 and 16 mol% La (from bottom to top respectively). The dramatic expansion at around 15 mol% can be seen in the upper traces. The lower plot shows d -spacing versus metal-atom mol% of praseodymium added. The ● show the d -spacing of the (111) plane divided by 2. The ■ show the (311) d -spacing.

temperatures (because of ionic bonding) make the collection of enough quality data to allow equilibrium phase diagrams to be drawn up an almost impossible task.

This is the first important point. A great many authors have measured lattice expansion as a function of doping in these systems and for a relatively simple experiment there is significant disagreement. A comprehensive review of the experimental data is given by Balducci [17] and this is also discussed by Grimes *et al* [7]. Where thermodynamic equilibrium is so difficult to achieve, where several very closely related phases exist which are also only partially ordered and where very exact preparation and measurement is required, it is unlikely that any authors have worked on exactly the same samples! In this work, preparation times of one week may be considered extreme.

However, it is clear from the work reported herein that for lanthana doping, two compositions are associated with additional thermodynamic stability. These have been reasonably ascribed to the presence of local ordered arrangements of defects. Anion vacancies in these systems are reasonably mobile [9]; however, there are high energies of association of the vacancies with the trivalent dopant ions (but not 4+ cations) [7, 11, 13, 17] which would prevent long-range ordering of the vacancies without ordering of the dopant cations. It is

the energy limitations of cation transport which probably prevent long-range ordering of the system. It is also important to consider how much long-range ordering is required to produce changes in the PXRD pattern associated with new ordered phase formation. The patterns are quite insensitive to the anion/vacancy content and are dominated by the cations. However, the cations have very similar x-ray scattering coefficients. In this way, observation of an ordered phase (especially if present in small particles) might be extremely difficult and the systems described here may have quite well-ordered arrangements.

Some cation mass transport is clearly possible in the $\text{La}_2\text{O}_3\text{-CeO}_2$ system; otherwise the observation of fluorite-like phases of obviously differing lanthana contents could not be observed. This observation is not due to preparation effects such as coring where the preparation method ensures a concentration gradient across a single particle which is slowly removed by heating. The opposite effect is observed: samples which are well mixed on heating show phase separation into dopant-rich and dopant-deficient phases. The TEM image in figure 1 was formed from initially homogeneous particles of well-defined morphology, and heating produced the phase separation observed. The image suggests that cation movement can be 'rapid' (the sample was heated for a week) at temperatures as low as 873 K. However, this is extreme. In the normal preparation, the product is determined by the degree of atomic mixing at the highest temperature and phase separation that can occur as the sample is cooled. The first effect is governed by entropy, the second by thermodynamic equilibrium. Both are dependent on the kinetic limitation of mass transport. Clearly, on cooling, some phase separation occurs. The TEM images and suchlike suggest that the separation occurs within a crystalline particle rather than separate particles. A suitable model might be similar to that for metal alloys when strata or lamellar phases are formed (within a grain), the size of which is dependent on the cooling rate etc. This is very much dependent on the assumption that a mechanism of spinodal decomposition is operative. There is a clear tendency for phase separation to the surface, but that might simply be related to enhanced mass transport at the surface rather than being driven by very different surface energies for each phase. Surface segregation in ceramics is not unknown but studies are somewhat rare because of the limitations of mass transport in these systems. The segregation is dependent on the presence of pores and other macroscopic defects which provide low-energy mass transport to the surface and result from the relative thermodynamic stability of the segregating phase compared to the host lattice [18]. We very tentatively suggest here that the enhanced surface concentrations observed result from the same spinodal decomposition as seen in the bulk, but because of enhanced mobility at the surface and in the near-surface region, reasonably high concentrations of the high-dopant-concentration phase result. These high surface concentrations may result in eventual nucleation and growth of lanthana at the surface and this is currently being investigated [15].

The ceria-praseodymia system provides further evidence for local ordering of defects. However, there is a distinct difference between the two systems. For the ceria-lanthana system, movement of a vacancy from the dopant cation is unfavourable as the result is a vacancy in the host lattice (and since Ce^{3+} is thermodynamically stable, this is probably not a limiting effect) and a La^{3+} ion surrounded by a full CeO_2 -like complement of oxygen anions, and so represents the formation of a highly unfavourable localized permanent dipole. For the ceria-praseodymia system this limitation does not exist, as both elements have 3+ and 4+ cations that are readily formed and anions should be very much more mobile in this system. The possibility of forming ordered structures of anion vacancies clearly drives the system towards solution of praseodymium atoms as 3+ cations at compositions where such defect ordering is favourable.

Finally, both systems seem to show solubility limits of 50 mol% dopant. It is tempting to ascribe this to the additional stability of the pyrochlore phase ($\text{A}_2\text{B}_2\text{O}_7$) discussed by

Grimes *et al* [7]. No evidence is provided here. Indeed, local arrangements of structure into perovskite arrangements (ABO_3) may be just as likely. The importance of the 50 mol% dopant concentration can be seen from simple calculation. As indicated in figure 3, at about 35 mol% La there are about equal concentrations of $P1_{high}$ and $P2_{low}$. If $P1_{low}$ contains 24 mol% (i.e. indicative of the limiting value), then $P1_{high}$ has a concentration of 46 mol%. As the concentration of lanthana in the system is increased further, the $P1_{high}$ concentration approaches 50% and structural rearrangement occurs at the 37–38 mol% dopant concentration. Further experimental work is required to study these structural changes further, in order to understand both the process and the ordering of the system.

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