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Subsolidus Phase Relations in the Systems CeO_2–RE_2O_3 (RE_2O_3 = C-type Rare Earth Sesquioxide)

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The systems CeO_2–RE_2O_3 (RE_2O_3 = C-type rare earth sesquioxide) were studied to: (1) investigate the claims of several workers for the existence of a complete solid-solution series between CeO_2 and RE_2O_3 and (2) to characterize the weak C-type X-ray diffraction peaks reported by others from samples in the single-phase fluorite solid solution region. It is shown that a complete solid solution series does not exist, and an explanation for the observations of others reporting such is tendered. It is also shown that the observation of C-type reflections in the supposed single-phase fluorite field can be attributed to the partial reduction of Ce^{4+} to Ce^{3+} at the firing temperature, resulting in the movement of the bulk composition into a two-phase field of the CeO_2–RE_2O_3–Ce_2O_3 phase diagram, rather than the formation of a domain structure due to ordering.

Introduction

The rare earth (RE) sesquioxides crystallize in the A (hexagonal), B (monoclinic), C (cubic), H (hexagonal), and X (unknown symmetry) structures (*1*). The rare earth dioxides crystallize in the cubic fluorite (CaF_2) structure. Only the C-type and fluorite modifications will be of concern here. Ions forming C-type oxides at temperatures greater than about 1000°C include the rare earths Gd^{3+} to Lu^{3+} and Y^{3+}, In^{3+}, and Sc^{3+}. Ions forming fluorite-structured dioxides include the rare earths Ce^{4+}, Pr^{4+}, and Tb^{4+} as well as the actinides Th^{4+} and U^{4+}.

The fluorite and C-type structures are closely related (*2*). The C-type unit cell can be viewed as being derived from the fluorite-type unit cell by substituting a M^{3+} (M = metal atom) for each M^{4+} with charge compensation provided by the creation of one oxygen vacancy for every two M^{4+} replaced by M^{3+}. The key difference between the C-type structure and that of oxygen-deficient fluorite-structured oxides is that the oxygen vacancies in the C-type unit cell are ordered. The result is a change of space group from the fluorite structure ($Fm3m$, No. 225) to the C-type structure ($Ia3$, No. 206) with a need to double the

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fluorite unit cell edge to account for all Bragg reflections.

The X-ray powder diffraction patterns of each structure are quite similar with respect to their intense reflections. Figure 1 compares the powder diffractograms of CeO_2 and Gd_2O_3. The most intense reflections in body-centered cubic (bcc) Gd_2O_3 and face-centered cubic (fcc) CeO_2 are due to contributions from the metal sublattice. Their 2θ positions are nearly identical because the unit cell edge of Gd_2O_3 (10.813 Å (*3*)) is almost exactly twice that of CeO_2 (5.4110 Å (*4*)). The superlattice bcc-type reflections must be observed in order to distinguish Gd_2O_3.

The similarity of the diffractograms appears to have caused problems in the determination of CeO_2-RE_2O_3 subsolidus phase relations. In early studies of these systems by Brauer and Gradinger (*5*) and McCullough and Britton (*6*) a complete solid solution and a continuous structural transition between CeO_2 and RE_2O_3 was proposed on the basis of X-ray diffraction (XRD) data. While complete solid solution is possible in principle, it may not necessarily be the case. A two-phase region normally separates (but is not required by Gibbs' phase rule) phases based on distinct structure types. The two-phase region may be as broad so as to include almost the entire system or it may be less than 1 mole% or merely a line on the phase diagram. Later work on these systems and the related systems UO_2-RE_2O_3 and ThO_2-RE_2O_3 (*7–17*) has shown that a region of $(F_{ss} + C_{ss})^1$ does indeed exist. Yet as recently as 1970, Benz *et al.* (*18*) in a study of the U–UO_2–UN_2 system concluded that a complete solid solution series exists between UO_2 (5.4701 Å (*19*)) and α-U_2N_3 (C-type structure, 10.682 Å (*20*)) at temperatures above 1350°C. Here again, a complete solid solution may exist, or the two-phase region may be unobservable due to an inability to distinguish F_{ss} from C_{ss} in X-ray diffractograms because of a possible 1 to 2 relationship of the cell constants (assuming that the cell constants tend to converge due to solid solution).

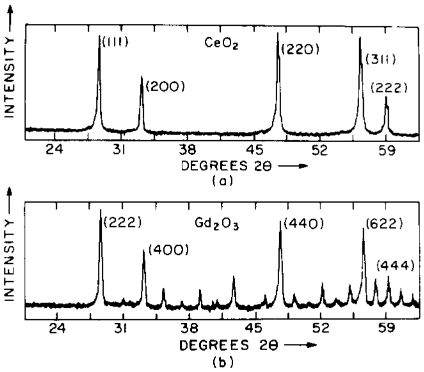

FIG. 1. Powder diffractograms of CeO_2 (a) and Gd_2O_3 (b). Peaks are indexed on the basis of the appropriate unit cell; the indices of the low-intensity peaks of Gd_2O_3 are omitted for clarity. Log intensity scale; Cu$K\alpha$ radiation.

The defect structures of the solid solutions formed at either end of the CeO_2–RE_2O_3 systems show that a two-phase region must exist. In the CeO_2-rich regions (fluorite fcc structure) anion vacancies form on the addition of RE_2O_3 (*21–24*) according to the defect reaction (in the Kroger–Vink notation (*25, 26*)):

$$RE_2O_3 \xrightarrow{CeO_2} 2RE'_{Ce} + 3O_0 + 1V_0^{\cdot\cdot} \quad (1)$$

At high RE_2O_3 concentrations (C-type bcc structure), additional anions form as CeO_2 is added (*11, 13, 24*):

$$2CeO_2 \xrightarrow{RE_2O_3} 2Ce_{RE} + 3O_0 + 1O''_i \quad (2)$$

On adding Ce^{4+} to the C-type RE_2O_3, a continuous solid solution series could, in principle, form by the filling of the "oxygen vacancies" in the C-type structure by the compensating oxygen ions (Eq. (2)). Cell constants would be expected to be an ap-

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[1] The abbreviations "F_{ss}" and "C_{ss}" will be used to refer to solid solutions of the fluorite and C-type structures, respectively.

proximately linear function of composition. This appears, however, to not be the case. Work on the system CeO_2–Gd_2O_3 (*5, 17, 27*) has shown that the cell constants of solid solutions within the system are greater than those of either end member. It would seem that the extra oxygen ions formed by adding CeO_2 to RE_2O_3 are not filling the "oxygen vacancies" but are entering the structure at other interstitial sites, resulting in a net expansion of the cell. Thus the character of the defects formed at either end of these systems is such that a continuous structural transition and a complete solid solution series is impossible.

We present here a method of confirming the existence of a two-phase region in the CeO_2–RE_2O_3 systems based on XRD data. We employ extrapolations from CeO_2–RE_2O_3 systems where the F_{ss} and C_{ss} can be adequately resolved.

A second issue in the subsolidus CeO_2–RE_2O_3 phase relations is also examined. Bevan *et al.* (*17*) have observed a fluorite-structured solid solution at high CeO_2 concentration giving way to a C-type solid solution at high RE_2O_3 concentration. They also observe the intervening region of (F_{ss} + C_{ss}). They report, however, observing one set of fcc diffraction maxima plus "diffuse" and weak lines characteristic of the bcc C-type structure in samples supposedly within the F_{ss} region. The bcc lines were of lower intensity relative to the fcc reflections than would be expected from a C-type oxide and there was no splitting of the fcc lines. They attribute the presence of these bcc lines to long-range structural ordering of oxygen vacancies to produce "domains" of C-type material in the F_{ss} matrix. Hyde and Eyring (*28*) attempted to explain these results by arguing that oxygen vacancies order to produce "strings" of defects that resemble the C-type structure.

The distinction between a "domain structure" and a true second phase is that the "domain structure," being coherent with the parent phase, has essentially the same cell constants as the parent phase. This is not true for the case of a second phase. Differentiation of these cases is difficult, however, in systems such as CeO_2–Cd_2O_3, where the cell constants of the phases in the (F_{ss} + C_{ss}) region are almost equal. Domain structures, however, produce diffraction maxima that are more or less diffuse. In their paper, Bevan *et al.* describe a set of peaks for which the α_1–α_2 doublet is well resolved as being diffuse (their Fig. 4). This description cannot be correct. If the peaks characteristic of C-type "domains" in the single-phase F_{ss} region are as "diffuse" as those illustrated, it is likely that these reflections (which are quite sharp) are due to a second phase.

We contend that an alternative explanation is the partial reduction of Ce^{4+} at the firing temperature that moves the bulk composition of the F_{ss} into a two-phase region of the CeO_2–RE_2O_3–Ce_2O_3 system. We support this contention by modeling this reaction with the CeO_2–Y_2O_3–Nd_2O_3 system.

Experimental

All samples used in this study were prepared by mixing calculated volumes of standardized aqueous solutions of the metal nitrates. The mixtures were dried and then calcined at 500°C to drive off the nitrogen oxides. The residue was an X-ray amorphous mixture of the oxides which was then ground in a mortar, pressed into pellets, and fired at 1200°C in air in a SiC resistance-type furnace on platinum trays supported by firebrick. After a soak of 1 week, the pellets were cooled to room temperature, ground thoroughly, pressed into pellets again, and refired for another week. Cooling to room temperature was accomplished by removing the pellets from the furnace and pulling the platinum trays on to a cooled copper plate. The pellets were observed to cool to a temperature less than red hot (about 600°C) in less than 5 sec.

After both firing cycles all samples were characterized by X-ray powder diffraction. Standard diffractometers using Cu$K\alpha$ radiation were used. The diffractometers were set at highest sensitivity in order to detect the weak bcc lines characteristic of the C-type structure. A detection limit of 2.5 mole% RE_2O_3 in CeO_2 was obtainable using this technique. No changes in the X-ray diffractograms were observed between samples from the first and second firings, indicating steady-state conditions had been achieved after the first firing. Descriptions of the samples prepared and further characterization techniques are discussed in the next section.

Results and Discussion

Our approach to the question of the two-phase region in the CeO_2–RE_2O_3 systems was prompted by results from the analogous ThO_2–RE_2O_3 systems. Both Keller *et al.* (*7, 11*) and Sibieude and Foex (*12*), in work on the systems ThO_2–RE_2O_3, have shown that at a given subsolidus temperature the phase boundaries and the breadths of the (F_{ss} + C_{ss}) phase regions display a systematic dependence on the ionic radius of the rare earth end-member. The (F_{ss} + C_{ss}) region has a maximum breadth in the ThO_2–Sc_2O_3 system, where there is a maximum difference in the ionic radius of Th^{4+} and Sc^{3+} which decreases with increasing RE^{3+} radius. It was thought, therefore, that a study of the phase boundaries in the systems CeO_2–RE_2O_3 should show analogous behavior and permit approximation, by extrapolation, of the position and breadth of the (F_{ss} + C_{ss}) phase field, even in systems where its detection by XRD is difficult.

Samples were prepared at 5-mole% intervals throughout the systems CeO_2–RE_2O_3 (*RE* = In, Yb, Tm, Er, Ho, Dy, and Gd) using the techniques described above. Phase relations at 1200°C were established by XRD analysis on the basis of phase assemblage data in those systems where the F_{ss} and C_{ss} lines could be adequately resolved. Phase boundaries were estimated to within ±3 mole% CeO_2 and were plotted as a function of the effective ionic radius of the RE^{3+} in eightfold coordination using the values calculated by Shannon (*29*). The plot (Fig. 2) shows that the breadth of the two-phase region decreases with increasing RE^{3+} radius in agreement with the results of Keller *et al.* and Sibieude and Foex. By extrapolation, it can also be seen that the (F_{ss} + C_{ss}) region has a finite width for all the CeO_2–RE_2O_3 systems investigated. The extrapolation indicates that the two-phase region in the system CeO_2–Gd_2O_3 could be as wide as 20 mole%.

The F_{ss} and C_{ss} cell constants were measured in the (F_{ss} + C_{ss}) region of the above systems and also in the systems CeO_2–Sc_2O_3 and CeO_2–Lu_2O_3. The data are plotted in Fig. 3 as a function of RE^{3+} radius. Figure 3 shows that the difference in the F_{ss} unit cell and that of the C_{ss} decreases with

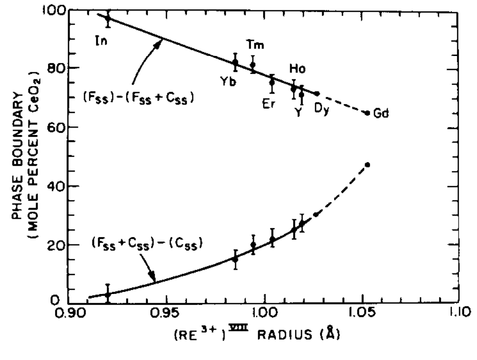

FIG. 2. Plot of the (F_{ss}) − (F_{ss} + C_{ss}) and (F_{ss} + C_{ss}) − (C_{ss}) phase boundaries (in mole% CeO_2) as a function of RE^{3+} radius in the systems CeO_2–RE_2O_3 at 1200°C in air. Data points for each system are labeled with the *RE* endmember. The dashed lines are extensions to the RE^{3+} radii of those systems whose phase boundaries could not be placed by conventional XRD techniques.

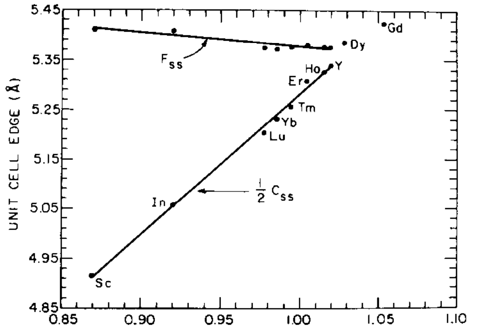

FIG. 3. Plot of the F_{ss} and C_{ss} cell constants in the (F_{ss} + C_{ss}) region of the systems CeO_2–RE_2O_3 as a function of RE^{3+} radius.

increasing RE^{3+} radius. As the difference in unit cells decreases, the fcc-type lines of the F_{ss} and C_{ss} within the (F_{ss} + C_{ss}) region would tend to merge to the point where they may not be resolvable by routine XRD techniques. The points for Dy and Gd do not lie on the plot since, as previously mentioned, the cell constants for the solid solutions in these systems are larger than those of the end members. The combined (and related) effects of a shrinking (F_{ss} + C_{ss}) phase field and convergence of the cell constants with increasing RE^{3+} radius with the resulting effects on the XRD patterns is therefore a likely explanation for the claim of a complete solid solution series in the systems CeO_2–RE_2O_3 and the proposal of a continuous structural transition.

An attempt to reproduce the results of Bevan *et al.* (*17*) was undertaken as part of the second half of this study. Samples in the system CeO_2–Y_2O_3 were prepared at 5 mole% Y_2O_3 increments from 0 to 35% Y_2O_3. The samples were fired at 1600°C in air for 4 days and cooled to room temperature in about 1 hr by turning off the furnace. The fired samples were observed to be well sintered with little visible surface porosity hence reaction of the bulk sample with air while cooling can be discounted. Powder diffraction examination of the samples revealed the presence of a F_{ss} plus bcc-type lines indexable using the doubled cell constants calculated from the fcc lines in samples from 10 to 35% Y_2O_3. The (222) F_{ss} reflections were not observed to split in any of the 1600°C patterns and none of the peaks were diffuse. The results of the 1600°C firings were nearly identical to those of Bevan *et al.* who also observed fcc plus bcc reflections in samples containing 11 to 38% Y_2O_3. In contrast, samples of identical compositions fired at 1200°C, showed a pure F_{ss} for compositions from 0 to 17% Y_2O_3 and (F_{ss} + C_{ss}) for compositions richer in Y_2O_3. The C_{ss} had a cell constant such that it was easily observed in the presence of the F_{ss}.

An explanation for the observation of weak bcc-type reflections in diffractograms of specimens supposedly within the pure F_{ss} region of the systems CeO_2–RE_2O_3 was suggested by the work of Tuller and Nowick (*23*). They demonstrated that the electrical conductivity of fcc $(CeO_2)_{0.95}$–$(Y_2O_3)_{0.05}$ solid solutions changed from purely ionic conductivity at low temperatures (<900°C) and high oxygen partial pressures ($>10^{-3}$ atm) to a mixed ionic–electronic mechanism at higher temperatures (>900°C) and lower oxygen partial pressures ($<10^{-3}$ atm). Ionic conduction was attributed to conduction via oxygen vacancies. The onset of electronic contributions was attributed to Ce^{4+} reduction to Ce^{3+}, resulting in the liberation of electrons. The transition point was found to be a function of temperature, occurring at lower oxygen partial pressures with increasing temperature. At 1150°C the transition point was found to approach the air–oxygen isobar ($10^{-0.68}$ atm). Similar phenomena in other CeO_2–RE_2O_3 systems over a broader range of compositions within the fcc CeO_2-rich regions has been observed by Kudo and Obayashi (*21, 22*).

Because Bevan *et al.* (*17*) prepared their specimens at 1600°C in air, some Ce^{4+} reduction to Ce^{3+} would have occurred resulting in compositions within the ternary system CeO_2–RE_2O_3–Ce_2O_3. Ce^{3+} formation on firing at high temperatures has been observed in other systems in which Ce^{4+} is present as a starting material. Frederikse *et al.* (*30*), in a study of the system "CeO_2"–ZrO_2 over the temperature range 1100–1600°C in air, show that fluorite-structure-type solid solutions of $(Ce,Zr)O_{2-x}$ form in which the value of x increases quite rapidly with firing temperature. It is interesting to note that at constant temperature the solid solutions are characterized by a larger value of x than the pure cerium oxide end member (*30, 31*). To explore the possibility of Ce^{3+} formation in the "CeO_2"–Y_2O_3 samples fired at 1600°C, consider the system CeO_2–Y_2O_3–Nd_2O_3 in which Nd^{3+} is used as a crystal chemical stand-in for Ce^{3+} (Fig. 4). Nd^{3+} and Ce^{3+} have very similar ionic radii (1.109 and 1.143 Å, respectively, in eightfold coordination (*29*)) and Nd_2O_3 and Ce_2O_3 have the same A-type structure. The proposed system at 1200°C has been constructed by interpolation from known phase relations (*27*). Taking advantage of the fact that this system can be studied using an air atmosphere (at 1200°C Ce is present almost entirely as 4+), we have examined compositions along the 5 mole% Y_2O_3 composition section, ranging from 0 to 40 mole% Nd_2O_3 in 5 mole% increments as indicated in Fig. 4. All samples were prepared and characterized as previously described. X-Ray powder diffractograms of samples at 10 mole% Nd_2O_3 intervals are presented in Fig. 5. The phases observed are in agreement with the interpolated phase diagram.

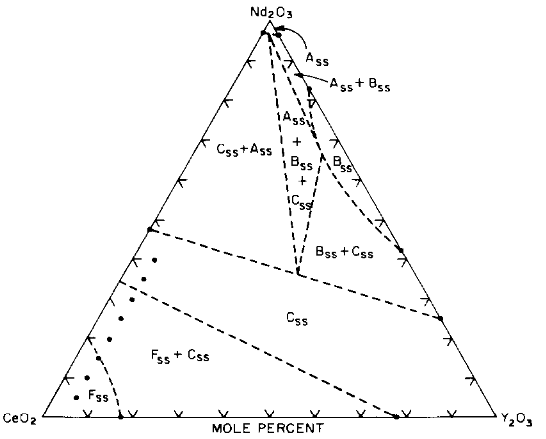

FIG. 4. Predicted subsolidus phase relations in the system CeO_2–Y_2O_3–Nd_2O_3 based on extrapolation from known binary relations at 1200°C. The compositions fired in this study are indicated on the diagram. A_{ss} and B_{ss} are solid solutions based on the A- and B-type RE_2O_3 structures, respectively.

While the diagram is drawn based on phase relations at 1200°C in air, it is expected to resemble relations over a temperature range of up to 1800°C. A number of workers reporting work in systems involving end members of this type have shown that there are no order–disorder transformations or compounds formed in this temperature range. The only change of phase

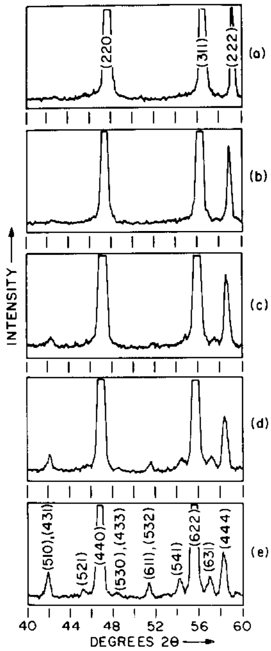

FIG. 5. Portions of X-ray diffractograms of samples fired in the system CeO_2–Y_2O_3–Nd_2O_3 at 1200°C in air. Linear intensity scale; Cu*Kα* radiation.

relations with temperature appears to be a slight shift of the phase boundaries such that single-phase regions are expanded at the expense of multiphase regions. It is assumed, therefore, that Fig. 4 represents approximate phase relations in the system CeO_2–Y_2O_3–Nd_2O_3 over a broad temperature range.

An examination of Fig. 5 shows that the sample containing zero mole% Nd_2O_3 (a) produces only Bragg reflections characteristic of the fcc structure. This sample is phase-pure F_{ss}. As the amount of Nd_2O_3 is increased, the fcc lines remain present but bcc-type lines begin to appear (c–e). The bcc lines are of low intensity and are not diffuse. The intensity of the bcc lines does increase, however, relative to the F_{ss} reflections, indicating that these samples lie within a region of (F_{ss} + C_{ss}). The combined (222) and (444) reflections of the F_{ss} and C_{ss} do not split in any of the samples. These observations concur with the results of the 1600°C firings in the CeO_2–Y_2O_3 system. Because of this similarity, it is suggested that the extra bcc reflections observed by Bevan *et al.* were due to the actual presence of a C-type phase containing some Ce^{3+} produced during their high-temperature syntheses, and not structural ordering of defects.

As a further argument against the domain theory, it should be noted that the samples of composition 10 to 35% Y_2O_3 fired at 1600°C produced sharp bcc reflections in addition to the F_{ss} pattern. Samples of 0 to 18% Y_2O_3 fired at 1200°C produced only reflections of F_{ss}. Since these results contradict the usual observation that ordering is enhanced by slow cooling or equilibration at low temperatures, we consider this further evidence for our contentions.

Conclusions

It has been shown that no continuous solid solution occurs in the CeO_2–RE_2O_3 systems and the conclusions of others reporting such can be explained by an inability to resolve the intense fcc-type lines of the F_{ss} and C_{ss} in the two-phase (F_{ss} + C_{ss}) region. This is due to the convergence of the cell constants of the F_{ss} and C_{ss} to an approximate 1:2 relationship with increasing rare earth ionic radius. It has also been shown that the observations of bcc-type reflections within the supposedly single-phase F_{ss} field in the CeO_2–RE_2O_3 systems fired at high temperatures at the air–oxygen isobar can be attributed to partial Ce^{4+} reduction to Ce^{3+} and the movement of the bulk sample composition into the (F_{ss} + C_{ss}) region of the CeO_2–RE_2O_3–Ce_2O_3 system.

Acknowledgments

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References

1. M. Foex and J.-P. Traverse, *Bull. Soc. Fr. Mineral. Cristallogr.* **59**, 184 (1966).
2. L. Pauling and M. D. Shappell, *Z. Kristallogr.* **75**, 128 (1930).
3. *U. S. Nat. Bur. Stand., Monogr.* **25**, *Sect. 1* (1962).
4. H. E. Swanson and E. Tatge, *Nat. Bur. Stand. U. S. Circ.* **539** (1953).
5. G. Brauer and H. Gradinger, *Z. Anorg. Allg. Chem.* **276**, 209 (1954).
6. J. D. McCullough and J. D. Britton, *J. Amer. Chem. Soc.* **74**, 5225 (1952).
7. C. Keller, H. Engerer, L. Leitner, and U. Sriyotha, *J. Inorg. Nucl. Chem.* **31**, 965 (1969).
8. H. Weitzel and C. Keller, *J. Solid State Chem.* **13**, 136 (1973).
9. L. N. Grossman, J. E. Lewis, and D. M. Rooney, *J. Nucl. Mater.* **21**, 302 (1967).
10. R. J. Beals and J. H. Handwerk, *J. Amer. Ceram. Soc.* **48**, 271 (1965).
11. C. Keller, U. Berndt, H. Engerer, and L. Leitner, *J. Solid State Chem.* **4**, 453 (1972).

12. F. Sibieude and M. Foex, *J. Nucl. Mater.* **56,** 229 (1975).
13. A. M. Diness and R. Roy, *J. Mater. Sci.* **4,** 613 (1969).
14. M. Forestier, G. Robert, M. Caillet, and C. Deportes, *Mater. Res. Bull.* **4,** 727 (1969).
15. H. T. Anderson and B. J. Wuensch, *J. Amer. Ceram. Soc.* **56,** 285 (1973).
16. C. Keller, U. Berndt, M. Debbabi, and H. Engerer, *J. Nucl. Mater.* **42,** 23 (1972).
17. D. J. M. Bevan, W. W. Barker, R. L. Martin, and T. C. Parks, *in* "Rare Earth Research" (L. Eyring, Ed.), Vol. 3, p. 441. Gordon & Breach, New York (1965).
18. R. Benz, G. Balog, and B. H. Baca, *High Temp. Sci.* **2,** 221 (1970).
19. W. A. Young, L. Lynds, J. S. Mohl, and G. G. Libowitz, "An X-Ray and Density Study of Nonstoichiometry in Uranium Oxides," NAA-SR-6765. Atomics International, Canoga Park, Calif. (1962).
20. J. Tobisch and W. Hase, *Phys. Status Solidi* **21,** K11 (1967).
21. T. Kudo and H. Obayashi, *J. Electrochem. Soc.* **123,** 415 (1976).
22. T. Kudo and H. Obayashi, *J. Electrochem. Soc.* **122,** 142 (1975).
23. H. L. Tuller and A. S. Nowick, *J. Electrochem. Soc.* **122,** 255 (1975).
24. W. W. Barker and A. F. Wilson, *J. Inorg. Nucl. Chem.* **30,** 1415 (1968).
25. F. A. Kroger and H. J. Vink, *in* "Solid State Physics" (F. Seitz and D. Turnbull, Eds.), Vol. 3, p. 307. Academic Press, New York (1964).
26. F. A. Kroger, "The Chemistry of Imperfect Crystals," Wiley, New York (1964).
27. J. G. Pepin, G. J. McCarthy, and E. R. Vance, unpublished results.
28. B. G. Hyde and L. Eyring, *in* "Rare Earth Research" (L. Eyring, Ed.), Vol. 3, p. 623. Gordon & Breach, New York (1965).
29. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
30. H. P. R. Frederikse, W. R. Hosler, and T. Negas, *in* "The Rare Earths in Modern Science and Technology" (G. J. McCarthy and J. J. Rhyne, Eds.), Vol. 1, p. 45. Plenum, New York (1978).
31. R. J. Panlener, R. N. Blumenthal, and J. E. Garnier, *J. Phys. Chem. Solids* **36,** 1213 (1975).