Synthesis and Magnetic Properties of BaCe*Ln*(O,N)$_4$, *Ln* = La, Ce

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The CaFe$_2$O$_4$-type oxidenitrides BaCe*Ln*(O,N)$_4$ (*Ln* = La, Ce) have been synthesized by reaction of perovskite-type BaCeO$_3$ with *Ln*N at 800°C. X-ray powder diffraction and magnetic data are presented. Composition data for BaCe*Ln*(O,N)$_4$ and observed magnetic moments which are smaller than would be expected for only a Ce^{3+} electronic configuration suggest a mixed-valence state for cerium. Ca Ce$_2$(O,N)$_4$ and BaThCe(O,N)$_4$ could not be synthesized by this procedure. © 1990 Academic Press, Inc.

Introduction

Pseudoternary transition metal oxidenitride perovskite- and scheelite-type compounds have received moderate attention in the past decade because of their potential applications as dielectric materials (*1–3*). Most extensively studied have been the perovskite-related *AB*(O,N)$_3$ species in which *A* is an alkali, alkaline earth, Y, or lanthanoid cation; *B* is W, Mo, V, Nb, Ta, or Ti; and either *A* or *B*, or both, typically have a lower than maximum oxidation state (*4–8*). Scheelite-type *AB*(O,N)$_4$ compounds have been studied less extensively (*9–11*). A few lanthanoid oxidenitrides are known to be ferromagnetic semiconductors, conductors (*12*), or superconductors (*13*). Since mixed valences, uncommon stoichiometries, and new structures might be achieved by effectively substituting N^{3-} for O^{2-}, pseudoternary lanthanoid-containing oxidenitrides appeared to be potentially interesting magnetic and electrical materials. We therefore decided to investigate selected lanthanoid-containing oxidenitrides.

Because cerium can exhibit multiple valency its nitride and oxidenitride systems seemed of special interest. Room temperature magnetic susceptibility data suggest the Ce^{4+} content in CeN may be as high as 89% (*14*); Ce^{4+}, as expected, has also been reported in both Li$_2$CeN$_2$ and Ce$_2$N$_2$O (*15*). These observations suggest that some cerium ions tend to be in their highest oxidation state even in the presence of reducing N^{3-} ions. On the other hand, cerium forms calcium ferrite-type BaCe$_2$O$_4$ that presumably contains Ce^{3+} ions (*16*) and is probably stabilized by lattice energy. Effectively substituting N^{3-} for O^{2-} in BaCe$_2$O$_4$ by fusing CeN with BaCeO$_3$ thus might both lead to a stable compound and introduce Ce^{4+} into the lattice to give a mixed valence compound. We thus synthesized and examined BaCe*Ln*(O,N)$_4$ (*Ln* = La and Ce) compounds and present the results of these studies.

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Experimental

CeN and LaN were prepared by heating 5–6 g of metal chips (typical purity 99.9%; Research Chemicals, Phoenix, AZ) in a slowly flowing ammonia gas (Matheson) stream at 700°C for 12 hr. Ground powdered CeN was dark brown and contained ~10% CeO$_2$ by mass; LaN was black and contained ~5% La$_2$O$_3$. Perovskite-type Ba CeO$_3$ and BaThO$_3$ were synthesized by heating intimately ground 1 : 1 molar mixtures of BaCO$_3$ and MO$_2$ (M = Ce, Th) at 950°C for 24 hr, then quenching them; the products were monophasic by X-ray powder diffraction. A 0.8–1.0 g intimately ground and nominally stoichiometric mixture of BaCeO$_3$ and LnN was sealed into an outgassed quartz tube under vacuum or an argon atmosphere, heated at 800°C for 24 h, then quenched by removal from the furnace.

Preparations which involved nitrides and oxidenitrides were handled in an argon-filled glove box whose water content was typically 3–8 ppm, and oxygen content 2000–3000 ppm. Nitrogen content was determined by Galbraith Laboratories. Every specimen was examined by X-ray powder diffraction in a Guinier camera with monochromatic Cu $K\alpha_1$ ($\lambda\alpha_1$ = 1.54050 Å) radiation. NBS certified Si (a = 5.43082(4) Å) served as internal standard. The following programs were utilized: for indexing interplanar d-spacings, TREOR (17); for lattice parameter refinement, APPLEMAN (18); and for powder intensity calculations, POWD12 (19). Magnetic susceptibilities measured with a Quantum Design SQUID magnetometer at various magnetic fields between 1000 and 20,000 G were extrapolated to zero reciprocal field to eliminate ferromagnetic impurity contributions. A diamagnetism correction was found to be negligible and not applied.

For electrical conductivity measurements ~1.5-g specimens of each product were inserted into thin-walled 6.35-mm i.d. Ta cy-
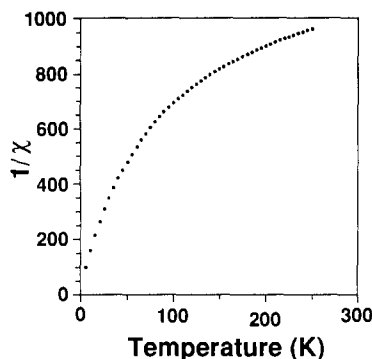

FIG. 1. Plot of reciprocal of BaCeLa(O,N)$_4$ magnetic susceptibility (emu mol^{-1}) against temperature.

lindrical crucibles whose ends were crimped closed. The containers were then heated to 1200–1300°C for ~2 h in a ~10^{-5} Torr vacuum to sinter the material. Conductivity was checked with a digital ohmmeter.

Results and Discussion

Reddish-colored BaCeLn(O,N)$_4$ (Ln = La, Ce) powders were obtained both by quenching and upon slow cooling. They gave similar X-ray powder diffraction patterns, decomposed quickly upon contact with water, and evolved ammonia gas that was easily detected both by its smell and by moist $pHydrion$ paper. They also decomposed slowly in air with a weight gain and a color change first to light yellow and eventually to brown.

Both oxidenitrides are strongly paramagnetic between 10 and 300 K. At temperatures greater than ~40 K they obey the Curie law. A plot of the reciprocal magnetic susceptibility of BaCeLa(O,N)$_4$ against T is presented in Fig. 1. For BaCeLa(O,N)$_4$ the presence of Ce^{3+} is thus clear. Observed magnetic moments are lower than those calculated on the basis of an f^1 localized configuration for Ce^{3+}, indicative that the cerium ions exhibit mixed valency. The observed magnetic moments of 1.83 and

TABLE I

LATTICE PARAMETERS FOR SELECTED (*Pbnm*, Z = 4) $CaFe_2O_4$-TYPE
OXIDES AND OXIDENITRIDES

Formula	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$V(\text{Å}^3)$	Ref.[a]
$BaCe_2O_4$	12.584	10.641	3.676	492.2	(16)
$BaCe_2(O,N)_4$	12.565(1)	10.644(1)	3.6593(4)	489.4	
$BaCeLa(O,N)_4$	12.573(3)	10.637(3)	3.657(1)	489.1	
$BaLa_2O_4$	12.652(2)	10.686(2)	3.7077(6)	501.3	
	12.662	10.675	3.705	500.8	(16)

[a] This work, except as noted.

1.70 μ_B at 300 K for $\frac{1}{2}$ $BaCe_2(O,N)_4$ and Ba
$CeLa(O,N)_4$, respectively, correspond to
about 1.44 Ce^{3+} in $BaCe_2(O,N)_4$ and 0.68
Ce^{3+} in $BaCeLa(O,N)_4$. Approximately
70% of the cerium ions in each compound
are in the trivalent state.

The $BaCe_2(O,N)_4$ powder X-ray diffrac-
tion pattern can be indexed on orthorhombic
symmetry with figures of merit, $F(20) = 26$
and $F(31) = 23$ (20). Lattice parameters of
both $BaLn_2(O,N)_4$ compounds are listed in
Table I. (The X-ray powder diffraction pho-
tograph of $BaCe_2(O,N)_4$ contained a trace
unidentified impurity—two very weak re-
flections.) Systematic extinctions consistent
with space groups *Pbnm* (No. 62, centro-
symmetric) or *Pbn2₁* (No. 33, noncentro-
symmetric) suggest the $CaFe_2O_4$-type struc-
ture (21). Intensities calculated using the
atomic parameters for $CaSc_2O_4$ (22) and iso-
tropic temperature factors of 1.5, 1.0, and
0.9, respectively, for O^{2-}, Ba^{2+}, and
$Ce^{3+ \text{ and } 4+}$ agree well with observed values.
Miller indices and observed and calculated
interplanar d-spacings and intensities for
$BaCe_2(O,N)_4$ are presented in Table II.

Duplicate nitrogen analyses were per-
formed on two identical but separately pack-
aged (i.e., A,B) $BaLaCe(O,N)_4$ specimens.
Found for A: 1.60, 1.55%; for B: 1.62,
1.49%. (The second member of each pair
is lower than the first as would happen if
hydrolysis occurred between analyses and

may indicate a slightly low analysis result.)
Combining all four results yields %N = 1.56
± 0.05. If all anion sites are occupied, the
formula is $BaCeLaO_{3.47(2)}N_{0.53(2)}$. The actual
nitrogen content is slightly higher than this;
as is indicated below, the specimen con-
tained ~10% $BaLa_2O_4$.

Duplicate nitrogen analyses were also
performed on comparably packaged Ba
$Ce_2(O,N)_4$ specimens. Found for A: 1.23,
1.56%; for B: 2.35, 2.41%. In lieu of the data
on the Ln = La compound, the disparity
between the two A results, and the magnetic
data, the A set is rejected. The remaining
analytical data suggest the formula
$BaCe_2O_{3.18(1)}N_{0.82(1)}$.

Magnetic data suggest the formulas Ba
$CeLaO_{3.68}N_{0.32}$ and $BaCe_2O_{3.44}N_{0.56}$, again
on the assumption of complete anion site
occupancy. They support the mixed anion
composition, partial reduction of Ce^{4+} in
both CeN and $BaCeO_3$ by N^{3-} when the
latter reacts with CeN at 800°C, and a
greater Ce^{3+} ion content in the oxidenitride
than in the reactant CeN. For BaCeLa
$(O,N)_4$ the magnetic data also underestimate
the N-content because of the $BaLa_2O_4$ im-
purity.

The product of the $BaCeO_3$–LaN reaction
is a mixture of two $CaFe_2O_4$-type structures:
$BaCeLa(O,N)_4$ and $BaLa_2O_4$ (16). The data
compiled in Table I illustrate the close rela-
tionship between the lattice parameters of

TABLE II

MILLER INDICES AND CALCULATED AND OBSERVED INTERPLANAR d-SPACINGS AND INTENSITIES FOR $Pbnm$ CaFe$_2$O$_4$-TYPE BaCe$_2$(O,N)$_4$

h	k	l	d_c(Å)	d_o(Å)	I_o^a	I_c	h	k	l	d_c(Å)	d_o(Å)	I_o^a	I_c
0	2	0	5.322	5.331	vw	3	3	3	4	1.9142	—		2
2	2	0	4.061	4.065	w	9	0	0	2	1.8297	1.8283	w	20
1	0	1	3.513	3.513	w	11	1	5	1	1.8207	1.8210	vw	1
1	1	1	3.336	3.338	w	9	6	3	0	1.8035	1.8031	w	14
4	0	0	3.141	3.142	m	45	6	1	1	1.7916	1.7911	w	17
2	3	0	3.089	3.086	vs	100	4	4	1	1.7754 }	1.7734	m	20
2	1	1	3.031	3.029	s	67	0	6	0	1.7740 }			12
0	2	1	3.015 }	3.013	m	32	2	5	1	1.7659 }	1.7651	w	14
4	1	0	3.013 }			8	4	5	0	1.7623 }			4
1	2	1	2.932	2.932	w	7	6	2	1	1.7200	1.7202	w	6
2	2	1	2.718	2.711	w	2	3	5	1	1.6847	1.6846	vw	2
3	1	1	2.6677	2.6677	m	26	2	2	2	1.6681	1.6687	vw	2
1	3	1	2.4965	2.4963	w	9	6	4	0	1.6457	1.6459	vw	3
2	4	0	2.4503 }	2.4483	w	4	5	4	1	1.6346		—	4
3	2	1	2.4471 }			2	7	1	1	1.5934	1.5931	vw	3
2	3	1	2.3606		—	3	1	6	1	1.5836 }	1.5806	w	2
4	1	1	2.3259	2.3257	w	8	4	0	2	1.5810 }			14
3	3	1	2.1764 }	2.1748	m	11	2	3	2	1.5743 }	1.5731	m	33
4	2	1	2.1753 }			31	8	0	0	1.5706 }			2
0	4	1	2.1521	2.1510	w	21	4	1	2	1.5639	1.5638	vw	3
1	4	1	2.1212	2.1208	w	12	8	1	0	1.5538	1.5536	vw	5
5	0	1	2.0716	2.0713	vw	6	4	6	0	1.5447 }	1.5442	w	12
2	4	1	2.0360	2.0344	vw	2	7	2	1	1.5424 }			1
6	2	0	1.9487	1.9486	w	12	8	2	0	1.5064 }	1.5012	vw	1
5	2	1	1.9305	1.9301	w	5	6	4	1	1.5009 }			5

^{a} v = very; w = weak; m = moderate; s = strong.

BaCeLn(O,N)$_4$ (Ln = La, Ce) and BaLn_2O$_4$. The unit cell volume of BaCe$_2$(O,N)$_4$ is slightly less than that of BaCe$_2$O$_4$. This result would not be expected from oxidation number and ionic radii considerations. The Ce^{3+}, La^{3+}, and Ce^{4+} CN VI ionic radii are 1.01, 1.03, and 0.87 Å, respectively; O^{2-} and N^{3-} CN IV ionic radii are 1.38 and 1.46 Å (23). If the compounds are considered ionic the number of N^{3-} and Ce^{4+} ions must be equal. The volume of a N^{3-} ion is 2.028 Å^3 larger than that of the O^{2-} ion while a Ce^{4+} ion is 1.557 Å^3 smaller than a Ce^{3+} ion. We would thus expect a unit cell volume increase of 0.470 Å^3/N atom. The volume decrease therefore must reflect either more efficient lattice packing (which is unlikely), a smaller size for the nitrogen atom than its

'ionic' radius indicates, or the presence of a greater quantity of Ce^{4+} than is required for charge balance. Magnetic and analytical data suggest a nitrogen atom smaller than predicted by its ionic radius.

Specimens prepared for resistance measurements were ~6 mm in diameter and 10 mm long. Unidentified impurity reflections were observed in the X-ray powder diffraction patterns of both sintered specimens. Their resistances at room temperature exceeded 2 megohms. These resistivities are so large that even in the presence of a small impurity level the products must be insulators. Although precise resistivities could not be obtained, these data suggest localized trivalent and tetravalent cations.

The oxygen needed to substitute for loss of nitrogen came from the small amount of La_2O_3 or CeO_2 present in the reactants. In reactions which involved CeN this contaminant disappeared during reaction. In those which involved LaN the product contained a $BaLa_2O_4$ impurity, an indication of insufficient La_2O_3 to allow the reaction to go to completion. The reaction can typically be illustrated by Eq. (1),

$$6BaCeO_3(s) + 4LnN(s) + Ln_2O_3(s) \xrightarrow{800°C}$$
$$6BaCeLnO_{3.5}N_{0.5}(s) + \tfrac{1}{2}N_2(g) \quad (1)$$
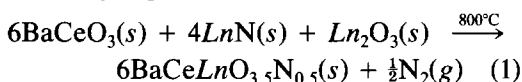
Gas evolution indeed occurred; quartz tubes which contained the products were pressurized when they were opened in the glove box. When research was initiated the reaction was envisioned a $1:1$ $BaCeO_3:LnN$ combination and oxide was not considered necessary. The results indicate that the (Ba Ce_2O_3N) $3:1$ $O:N$ product is less stable than less nitrogen-rich compounds; additional oxide is therefore necessary for reaction.

Reduction of Ce^{4+} by N^{3-} also occurred in the $CaO-CeO_2-CeN$ system when we attempted to prepare $CaCe_2(O,N)_4$ at 950°C. The quartz tubes again contained a gas under pressure and a Ce_2O_3-like phase (presumably $Ce_2(O,N)_3$) resulted; $CaCe_2(O,N)_4$ did not form. The Ca^{2+} ionic radius is presumed too small to stabilize the compound.

Efforts to synthesize $BaThCe(O,N)_4$ using the difficult to reduce Th^{4+} to substitute for Ce^{4+} in $BaCeO_3$ were unsuccessful even though perovskite-type $BaThO_3$ was prepared (24). The 0.94-Å Th^{4+} ionic radius is very close to that of Ce^{4+} (0.87 Å) and reasonably close to that of Ce^{3+} (1.01 Å) (23), suggesting that a mixed valence Ce-compound might form. However, a Ba ThO_3-CeN reaction did not occur even at 950°C, a temperature higher than that for the $BaCeO_3-CeN$ reaction (800°C)—the only product was again a Ce_2O_3-like phase which resulted from reaction between CeN and the CeO_2 impurity. This observation

suggests mixed valence to be an important factor for the formation of $BaM_2(O,N)_4$-type oxidenitrides—for cerium to exhibit both $3+$ and $4+$ oxidation states the related central cation must exhibit some degree of trivalency.

It is noteworthy that the cerium oxidenitrides characterized so far have structures and lattice parameters closely related to those of their oxide counterparts. The X-ray diffraction pattern previously reported for the (Ce^{4+}-containing) oxidenitride, Ce_2N_2O (15), said to be isostructural with Th_2N_2O, is almost identical to that of Ce_2O_3 prepared by H_2 reduction of CeO_2 at 1200°C (25). This similarity can be demonstrated better by a comparison of their hexagonal lattice parameters; "Ce_2N_2O": $a = 3.880$ Å, $c = 6.057$ Å vs. Ce_2O_3: $a = 3.891$ Å, $c = 6.063$ Å. Given the essentially identical X-ray scattering powers of N^{3-} and O^{2-}, the small size difference between them, and the counter-balancing size difference between Ce^{4+} and Ce^{3+}, it is difficult to distinguish Ce_2N_2O (Ce^{4+}), Ce_2O_3 (Ce^{3+}), and Ce_2NO_2 (Ce^{3+} and Ce^{4+}) and other mixed valence states by X-ray diffraction. Similarly, the possibility that the reported Li_2CeN_2 (15) with Ce^{4+} could be a mixed valent Li_2 $Ce(O,N)_2$ cannot be dismissed. Since anion ordering has been observed in the cerium oxidenitride CeO_xN_{1-x} (26), the true symmetries of these oxidenitrides may differ from predictions based upon X-ray diffraction data. Further studies, e.g., neutron diffraction, appear necessary to characterize these compounds definitively.

ACKNOWLEDGMENT

References

1. R. Marchand, F. Pors, Y. Laurent, O. Regreny, J. J. Lostec, and J. M. Haussonne, *J. Phys. Colloq.* **C1**, 901 (1986).
2. *Chem. Abstr.* **109**;P77252y (1987).

3. *Chem. Abstr.* **110;**P126935s (1989).

4. R. MARCHAND, F. PORS, AND Y. LAURENT, *Rev. Int. Hautes. Tempér. Réfract., Fr.* **23,** 11 (1986).

5. F. PORS, P. BACHER, R. MARCHAND, Y. LAURENT, AND G. ROULT, *Rev. Int. Hautes Tempér. Réfract., Fr.* **24,** 239 (1987–1988).

6. P. BACHER, P. ANTOINE, R. MARCHAND, P. L'HARIDON, Y. LAURENT, AND G. ROULT, *J. Solid State Chem.* **77,** 67 (1988).

7. P. ANTOINE, R. MARCHAND, Y. LAURENT, C. MICHEL, AND B. RAVEAU, *Mater. Res. Bull.* **23,** 953 (1988).

8. F. PORS, R. MARCHAND, Y. LAURENT, P. BACHER, AND G. ROULT, *Mater. Res. Bull.* **23,** 1447 (1988).

9. Y. LAURENT, R. PASTUSZAK, P. L'HARIDON, AND R. MARCHAND, *Acta Crystallogr. Sect B* **38,** 914 (1982).

10. R. PASTUSZAK, P. L'HARIDON, R. MARCHAND, AND Y. LAURENT, *Acta Crystallogr. Sect B* **38,** 1427 (1982).

11. P. ANTOINE, R. MARCHAND, AND Y. LAURENT, *Rev. Int. Hautes Tempér. Réfract., Fr.* **24,** 43 (1987).

12. See, for example, (i) B. CHEVALIER, J. ETOURNEAU, AND P. HAGENMULLER, *Mater. Res. Bull.* **12,** 473 (1977); (ii) C. MOURGOUT, B. CHEVALIER, J. ETOURNEAU, J. PORTIER, P. HAGENMULLER, AND R. GEORGES, *Rev. Int. Hautes Tempér. Réfract., Fr.* **14,** 89 (1977); (iii) B. CHEVALIER, J. ETOURNEAU, P. HAGENMULLER, AND R. GEORGES, *in* "The Rare Earths in Modern Science and Technology" (G. J. McCarthy, J. J. Rhyne, and H. B. Silber, Eds.), Vol. 2, pp. 403–408, Plenum Press, New York (1980).

13. G. LIU AND H. A. EICK, to be published.

14. U. VON ESSEN AND W. KLEMM, *Z. Anorg. Allg. Chem.* **317,** 25 (1962).

15. M. G. BARKER AND I. C. ALEXANDER, *J. Chem. Soc. Dalton Trans.* 2166 (1974).

16. N. M. MAISTER AND I. M. LOPATO, *Inorg. Mater. Engl. Transl.* **9**(1), 57 (1973).

17. P. E. WERNER, L. ERIKSSON, AND M. WESTDAHL, *J. Appl. Crystallogr.* **18,** 367 (1985).

18. D. E. APPLEMAN, D. S. HANDWERKER, AND H. T. EVANS, "Program X-Ray," Geological Survey, U.S. Department of Interior, Washington, DC, (1966).

19. D. K. SMITH, M. C. NICHOLS, AND M. E. ZOLENSKY, "A FORTRAN IV Program for Calculating X-Ray Powder Diffraction Patterns: Version 10"; Pennsylvania State University, University Park (1983).

20. G. S. SMITH AND R. L. SNYDER, *J. Appl. Crystallogr.* **12,** 60 (1979).

21. R. W. G. WYCKOFF, "Crystal Structures," 2nd ed., Vol. 3, pp. 87–91, Interscience (1965).

22. H. MÜLLER-BUSCHBAUM AND H. G. SCHNERING, *Z. Anorg. Allg. Chem.* **336,** 295 (1965).

23. R. D. SHANNON, *Acta Crystallogr. Sect A* **32,** 751 (1976).

24. Powder Diffraction File card 3-1102. JCPDS: International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081.

25. Powder Diffraction File card 23-1048. JCPDS: International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081.

26. R. C. BROWN AND N. J. CLARK, *J. Inorg. Nucl. Chem.* **36,** 1777 (1974).