Structural Investigation of Pure and N-doped Cerium Oxygen Apatite ($Ce_{4.67}[SiO_4]_3O$) by Neutron Diffraction

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ABSTRACT

The site occupancy of nitrogen atoms were studied in a sample of 4800 ppm N-containing cerium oxygen apatite with neutron diffraction. The atomic parameters and occupancy factors for different oxygen sites of the apatite lattice were refined by Rietveld analysis. Cerium oxygen apatite was confirmed to have a space group of $P6_3/m$. The so-called "free" oxygen sites (0,0,1/4 and 0,0,3/4) were found to be the most likely sites for nitrogen substitution rather than the silicon-bonded sites.

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INTRODUCTION

The apatite-type compound, $Ce_{4.67}[SiO_4]_3O$, has recently been shown[1] to be able to absorb nitrogen in its crystal structure (hexagonal, a = 9.657 Å, c = 7.118 Å) when it was prepared from nitrogen containing starting materials (such as Si_3N_4) or even after heating in nitrogen bearing gas atmospheres. The presence of small amounts of nitrogen in the structure could be identified with XRD by a significant increase in the unit cell volume, as compared to the pure form of the compound, mainly provided by a larger increase in the c-axis dimension of the cell[1,2].

Considering all atomic sites per unit cell, the structure of cerium oxygen apatite might best be described [3] by the formula $^{IX}(Ce_{3.33}\ \square_{0.67})\ ^{VII}(Ce_6)[^{IV}Si^{IV}O_4]_6\ ^{III}O_2$. One possibility regarding the nature of nitrogen substitution for oxygen in this structure is the replacement of 3-coordinated "free" (i.e., not-bonded to the silicons of tetrahedra) oxygens, which are found at the 0,0,1/4 and 0,0,3/4 positions on the 6_3 axis, with nitrogen. Such a substitution would require more and more ceriums to occupy the cation vacancies in the 9-coordinated sites up to a maximum of 14100 ppm of nitrogen present in the material, leading to a formula for a defect-free and nitrogen-bearing cerium apatite as $Ce_{10}[SiO_4]_6N_2$. Using powder x-ray diffraction, chemical analysis and weight loss data, in a cerium apatite sample containing about 16600 ppm nitrogen, Gaude[4] proposed the substitution of oxygen with nitrogen to take place in the distorted silicate tetrahedra according to the formula : $Ce_{10}[SiO_{3.61}N_{0.39}]_6O_{1.83}\square_{0.17}$ leading to the formation of vacancies in the 3-coordinated oxygen sites. Gaude[4] also reported

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the collapse of the hexagonal apatite structure in samples containing 21700 and 24400 ppm according to the XRD data.

The purpose of the present study was to investigate the site occupancy of nitrogen atoms with neutron diffraction, which would be more sensitive in distinguishing nitrogen from oxygen as compared to x-rays, in cerium apatite samples doped with ppm-level nitrogen.

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EXPERIMENTAL PROCEDURE

To facilitate the conduct of a comparative study on the possible effects of nitrogen presence on the crystal structure of cerium apatite, pure and 7050 ppm nitrogen (in the unfired powder mixture) containing samples have been prepared. The pure sample was synthesized by combining appropriate quantities of CeO_2 (99.87% pure, Cerac) and fumed SiO_2 (99.98% pure, Sigma) in ethanol in an agate mortar and then wet mixing (in ethanol) in plastic jars with alumina balls for 24 hours followed by overnight drying at 80°C. The nitrogen doped sample was prepared by mixing the appropriate quantities of CeO_2 , fumed SiO_2 , and Si_3N_4 (>98% pure, Shin-Etsu) in a similar manner. Powders were first pressed uniaxially into pellets in a tungsten carbide-lined steel die at about 20 MPa and then cold isostatically pressed in latex bags at 200 MPa. Pellets were heated in platinum crucibles in a vertical Al_2O_3 tube furnace at 1560°C in a prepurified (O_2 < 50 ppm) flowing argon ("pure" sample) or nitrogen ("N-doped" sample) atmosphere for 6 hours ("pure") or 40 hours ("N-doped"), followed by quenching in water. The laser source mass spectroscopy analysis of a typical, heated "pure" cerium oxygen apatite sample has previously been reported [1]. The inert gas fusion analysis carried out for the determination of nitrogen level revealed the presence of only about 4800 ± 500 ppm nitrogen in the heated doped sample. The density measurements (via Archimedes method) of both the "pure" and "doped" samples yielded 5.52 ± 0.06 gm/cm^3 which well conformed to the XRD density calculated (5.47 gm/cm^3) for the samples of cerium oxygen apatite stoichiometry described by the above mentioned formula. The neutron diffraction

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experiments of the powder samples were performed on the HIPD instrument at the Los Alamos Neutron Scattering Center. Rietveld analyses of the two samples were processed with GSAS[5] on a DEC-Station 5000 computer.

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RESULTS AND DISCUSSION

The main structural features of the "pure" sample are displayed in Figure 1. This structure was refined to a residual R = 5.3%. The atomic parameters corresponding to cell dimensions a = 9.652(2) Å and c = 7.112(1) Å are listed in Table 1. The unit cell did have the centrosymmetric $P6_3/m$ space group. The parameters given in Table 1 only slightly differed from those given by Belokoneva et al.[6] for $Ce_{4.67}[SiO_4]_3O$ with the cell dimensions a = 9.736 Å and c = 7.116 Å. There was no reasonable explanation for the mismatch seen in the value of the a dimension, except for the possible variations in the purity of the samples and the method of evaluating the experimental data. The atomic distances and angles observed in the structure of pure sample were tabulated in Table 2. Cerium ions at the Ce(1) positions are surrounded by 9 oxygens which are all silicon-bonded. The refined value of the occupancy factor (i.e., 0.84(2)) for those ceriums showed that Ce(1) sites were occupied only by about 3 1/3 Ce^{3+} cations out of a possible of 4. Therefore, 2/3 vacant sites per cell would be statistically distributed on these lattice sites. This finding makes it possible for us to assume the above-mentioned defect formula for this compound. The average of the Ce(1)-O distances in the 9-coordinated polyhedra was found to be 2.609(5) Å in this sample. The other distinct cerium positions, Ce(2), were surrounded by 7 oxygens; 6 of those silicon - bonded, the other being the "free" oxygen, O(4). In these 7-pointed polyhedra of ceriums, 4 of the 6 silicon-bonded oxygens were those that occupied the O(3)-sites. The ceriums found at these

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Figure 1. Crystal structure of pure cerium oxygen apatite ($Ce_{4.67}[SiO_4]_3O$) based on the atomic coordinates listed in Table I

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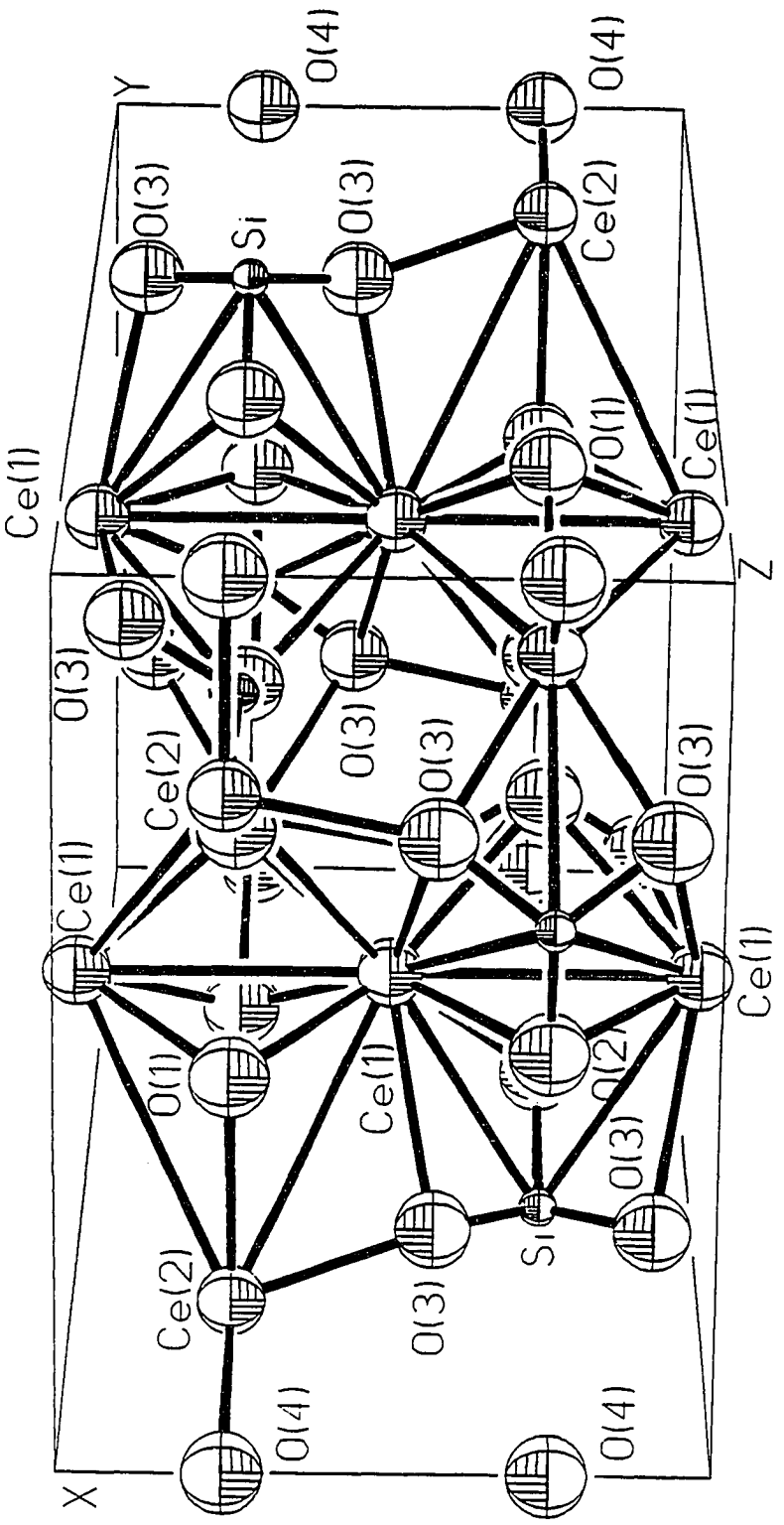

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Table 1. Atomic Parameters of Pure $Ce_{4.67}[SiO_4]_3O$

Atom	Occ. factor	x	y	z	U_{ISO}
Ce (1)	0.84(2)	0.6667	0.3333	0.0001(9)	0.9 (2)
Ce (2)	1	0.9880(6)	0.2297(5)	0.2500	0.7 (1)
Si	1	0.3726(5)	0.4025(5)	0.2500	0.02 (7)
O (1)	1	0.4850(5)	0.3230(4)	0.2500	1.9 (1)
O (2)	1	0.4726(5)	0.5968(4)	0.2500	1.49 (9)
O (3)	1	0.2548(4)	0.3448(4)	0.0685(3)	2.12 (8)
O (4)	1	0.0000	0.0000	0.2500	3.5 (2)

sites (three of which surround one O(4) on the 6_3 axis) exhibited a significantly short distance of 2.28 Å to the "free" oxygens which are at the 0,0,1/4 and 0,0,3/4 positions which was even less than the sum of the ionic radii. This behaviour, as previously reported by Felsche[3] for Gd-oxygen apatite, represents the strong polarizing forces exerted by the rare earth cation on the oxygen which is not silicon bonded. The average Ce(2) - O distance in the 7-coordinated polyhedra was 2.506(6) Å. Taking the average oxygen radius as 1.38 Å, the effective Ce^{3+} ionic radii would be 1.23 and 1.13 Å for the 9- and 7-coordinated polyhedra, respectively. From these, one could calculate the mean value of the Ce^{3+} ionic radius in the apatite structure as 1.177 Å. An exactly similar analysis carried out by Felsche[3], for the gadolinium

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Table 2. Interatomic Distances and Angles in Pure $Ce_{4.67}[SiO_4]_3O$

Vector	Length (Å)	Angle	Degrees
Ce(1)-Ce(1)	3.556(13)	Ce(1)-Ce(1)-O(1)	136.2(1)
Ce(1)-Si	3.282(5)	Ce(1)-Ce(1)-O(2)	135.0(1)
Ce(1)-O(1)	2.464(5)	O(1)-Ce(1)-O(1)	73.7(2)
Ce(1)-O(2)	2.516(5)	O(1)-Ce(1)-O(2)	153.7(1)
Ce(1)-O(3)	2.848(3)	O(2)-Ce(1)-O(2)	75.6(2)
Ce(2)-Ce(2)	3.944(7)	O(2)-Ce(2)-O(3)	70.5(2)
Ce(2)-Si	3.220(6)	O(2)-Ce(2)-O(4)	150.3(2)
Ce(2)-Si	3.322(6)	O(3)-Ce(2)-O(3)	135.4(2)
Ce(2)-O(1)	2.733(6)	O(3)-Ce(2)-O(4)	83.9(1)
Ce(2)-O(2)	2.492(6)	O(1)-Si-O(2)	113.4(3)
Ce(2)-O(3)	2.437(3)	O(1)-Si-O(3)	111.0(2)
Ce(2)-O(3)	2.583(5)	O(2)-Si-O(3)	107.8(2)
Ce(2)-O(4)	2.277(4)	O(3)-Si-O(3)	105.4(3)
Si-O(1)	1.612(5)	Ce(1)-O(1)-Si	128.0(1)
Si-O(2)	1.625(6)	Ce(2)-O(2)-Si	123.8(3)
Si-O(3)	1.623(4)	Ce(1)-O(2)-Si	102.7(2)
		Ce(2)-O(3)-Si	142.1(2)
		Ce(2)-O(4)-Ce(2)	120.0(0)

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counterpart of this compound, generated the effective ionic radii of 1.15 and 1.02 Å in both types of polyhedra, and a mean value of Gd^{3+} ionic radius as 1.08 Å in the structure. This decrease in ionic radius (from Ce to Gd) should be regarded as a perfect example for the "lanthanide contraction" observed in the lanthanide series of elements. Felsche[3] predicted the ionic radius of Ce^{3+} in the apatite structure as 1.17 Å from a plot of apatite cell volumes (for the other lanthanide oxygen apatites) versus the cube of ionic radii of the lanthanides. This early prediction has also been experimentally confirmed by this study.

The initial amount of nitrogen (in the form of Si_3N_4) we added to the powder mixture of the "doped" sample corresponded to about 7050 ppm elemental nitrogen in the compound, assuming all of the nitrogen end up substituting oxygens at the O(4)-sites. This amount and type of nitrogen incorporation in the apatite structure would then be denoted by the following formula; $Ce_{9.667}[SiO_4]_6O_{1.00}N_{1.00}$. If we had added 14100 ppm nitrogen, this formula would have changed to $Ce_{10}[SiO_4]_6N_2$. However, the chemical analysis we performed on the final, heat treated sample indicated the presence of only 4800 ppm elemental nitrogen in the doped compound. This amount of nitrogen would lead to a formula as $Ce_{9.553}[SiO_4]_6O_{1.341}N_{0.659}$. The site occupancy of the O(4) positions (by nitrogen) calculated from this formula would then correspond to about 33%.

Apparently, we have lost about 32 wt% of nitrogen, that has been present in the initial powder mixture, during the heating stage to synthesize the compound. One possible explanation for the loss of nitrogen at high temperatures might be the formation of gaseous N_2 during solid state reaction of the individual Si_3N_4 particles with CeO_2 and SiO_2. Another

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possibility could be the presence of significant amounts of SiO_2 in Si_3N_4 that might have adversely affected the initial assumed N levels in the powder mixtures. The relatively low atmospheric pressures exerted by the flowing (100 ml/min) N_2 gas in our tube furnace did clearly not suffice to compensate for the apparent nitrogen losses as one would expect from using higher pressures. Another drawback of our experimental technique might be pointed out as our use of CeO_2 rather than Ce_2O_3 in the initial powder mixture. CeO_2 would evolve gaseous O_2 during its transformation to Ce_2O_3 at temperatures above 1400° C in inert atmospheres. This O_2 to be supplied by CeO_2 might then cause, especially at the particle-to-particle interfaces as a surface phenomenon, the initial silicon nitride phase to convert into a family of silicon-oxynitride phases whose compositions would be determined mainly by factors such as the distance from the interface which supplies the oxygen , the magnitude of P_{O2} in the vicinity of the particles, the temperature and, of course, the time in which such adverse conditions had persisted. The last factor, time, would mainly be controlled by the rate of flushing off of unsought O_2 by the flowing nitrogen atmosphere. Every step of the conversion of silicon nitride to silicon oxynitride would accompany a certain amount of gaseous nitrogen evolution, which would then only be expected to be replaced back by the nitrogen atmosphere.

As opposed to the pure, oxygen apatite sample we used for neutron diffraction studies, the N-doped sample had significant quantities of CeO_{2-x} and monoclinic, high-temperature form of $Ce_2Si_2O_7$ in it which were then needed to be accounted for and excluded in the structural refinements of the major apatite phase. As we have shown recently [7], in a study of

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the high temperature phase relations in the system Ce_2O_3 - $Ce_2Si_2O_7$, cerium oxygen apatite phase is stable as a line compound in the temperature range 1200° to its melting point 1950°C in inert atmospheres such as purified argon and vacuum, or in reducing atmospheres like argon + 10% H_2. Although we did not study its behaviour specifically in nitrogen atmospheres, we still would not expect it to decompose into CeO_{2-x} and $Ce_2Si_2O_7$ in pure nitrogen at 1560°C. We have shown that there were no solid solubility between $Ce_2Si_2O_7$ and $Ce_{9.33}[SiO_4]_6O_2$. The only possibility that remains to explain the observation of these minor phases in this sample is that the CeO_{2-x} phase appears to be unreacted and also tended to be isolated in distinct CeO_{2-x}-rich pockets all over the sample pellet. As a consequence of that, some SiO_2 -rich regions (as compared to the line compound stoichiometry of the apatite phase) have developed which would then shift the overall composition of those from apatite towards $Ce_2Si_2O_7$. The presence of these two minor phases in the N-doped sample could be regarded as a unique adverse condition that might still affect the accuracy of the structural refinement presented below.

Being the major question that needs to be answered, the determination of the site(s) that would be preferred by nitrogen in substituting for oxygen was the main concern of this part of the study. We have based the Rietveld refinement of the N-doped sample on the atomic coordinates that were obtained in the first part for the "pure" sample of cerium oxygen apatite. The tetrahedral oxygen sites that were silicon-bonded (i.e., O(1) and O(3)) as well as the "free" oxygen site (O(4)) were refined to a residual R = 4.3%. In each of these refinements nitrogen was placed in those sites as if it was sharing the same site with oxygen. These did not

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Table 3. Atomic Parameters of 4800 ppm N-doped $Ce_{4.67}[SiO_4]_3O$

Atom	Occ. factor	x	y	z	U_{ISO}
Ce(1)	0.85(2)	0.6667	0.3333	0.0007(19)	3.3 (3)
Ce(2)	1	0.9871(9)	0.2287(8)	0.2500	1.5 (1)
Si	1	0.3731(8)	0.4017(9)	0.2500	1.2 (1)
O(1)	1	0.4850(9)	0.3186(8)	0.2500	3.3 (2)
O(2)	1	0.4744(9)	0.5965(7)	0.2500	2.9 (2)
O(3)	1	0.2526(7)	0.3392(6)	0.0681(6)	3.5 (1)
O(4)	0.61(12)	0.0000	0.0000	0.2500	5.6 (7)
N(4)	0.39	0.0000	0.0000	0.2500	5.6 (7)

result in any significant changes in the atomic coordinates of the structure. The new lattice constants were found to be a = 9.6585(3) Å and c = 7.1139(4) Å. They showed a very slight but definite increase in both axes when compared to those of the pure sample . The atomic parameters of the doped sample, while the nitrogen being placed at the O(4) site, are shown in Table 3. The occupancy factor of Ce(1) sites (0.85(2)) is in good agreement with the one predicted by the formula; $Ce_{9.553}[SiO_4]_6O_{1.341}N_{0.659}$ as 0.88. The occupancy factor refined as 0.39 for the nitrogens sharing the O(4)-sites with oxygen was predicted by the above formula as 0.33. On the other hand, when we put the nitrogens into O(3)-sites and O(1)-sites

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separately, the occupancy factors for nitrogen were found to be 0.23 and 0.10, respectively, which were much less than that of predicted by the chemical formula. The temperature factors were found to be 4.3 and 3.7 when the nitrogens were put into O(3) and O(1) sites together with oxygens, respectively.

The response of the interatomic distances and angles to the introduction of 4800 ppm N into the lattice were displayed in Figure 2. Although the slight changes observed in the interatomic distances between the central silicon and four oxygens occupying three different sites may be regarded as insignificant, one could still detect the presence of a geometrical rearrangement and the tendency of the atoms toward the ideal symmetry of a perfect tetrahedra (i.e., equal interatomic distances and angles of 109.28°) in going from "pure" to "N-doped" sample. We believe that the motivation for this movement was mainly the elimination of vacancies at the Ce(1) sites (caused by N substitution in the oxygen sites of the lattice). It would have been quite interesting to see what would happen to the tetrahedra upon the complete elimination of vacancies, i.e., for a sample of $Ce_{10}[SiO_4]_6N_2$. As a further observation, the interatomic distances and angles displayed in Fig. 2 for the "N-doped" sample were virtually the same, after each refinement cycle, for all three candidate sites we examined for N, namely, the O(1)- , O(3)- and O(4)-sites. This means that the presence of N in the lattice does not directly affect the tetrahedral coordination between Si and oxygens. However, if the large nitrogens (1.71 Å) were really substituting for the tetrahedral oxygens then one would expect to see more pronounced changes in the interatomic distances of individual tetrahedra, especially in the comparison of, for instance, tetrahedral O(3)- and non-tetrahedral

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Figure 2. Changes observed in the interatomic distances and angles of the silicate tetrahedra upon doping as opposed to constant Ce(2) - O(4) distances in both samples

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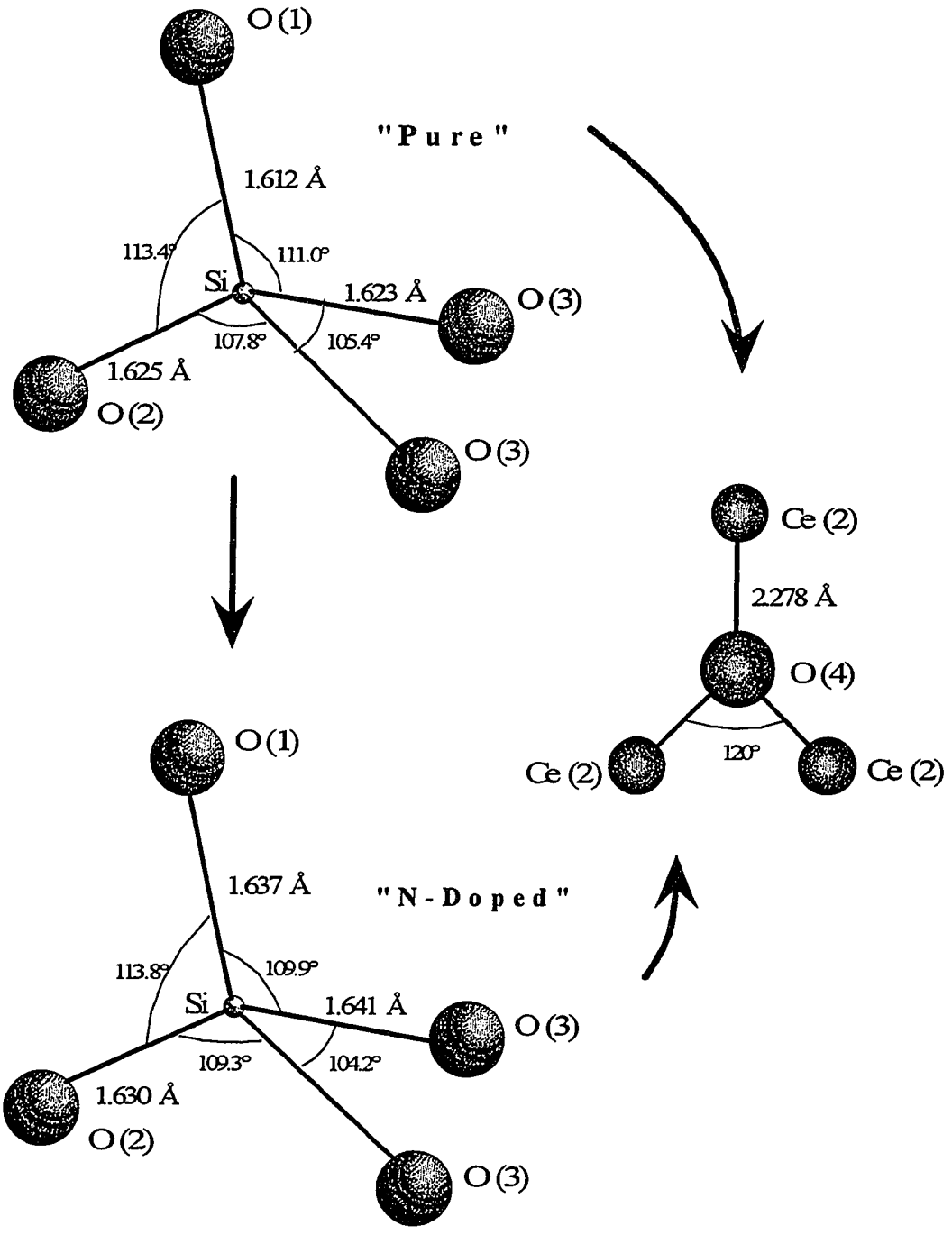

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O(4)-sites. The filling up of the vacancies in the 9-coordinated (all being silicon-bonded oxygens) Ce(1) positions seemed to have a more definite influence in the geometric rearrangements to be observed within the silicate tetrahedra.

The interatomic distances between the 3-coordinated "free", non-tetrahedral oxygens (O(4)-sites) and the Ce(2) atoms did not show any changes after doping with N and remained constant at 2.28 Å as also indicated in Figure 2. This exemplifies the significantly electropositive character of the heavy cerium atoms and the extent of strong polarizing forces exerted by them on the oxygens or nitrogens that would occupy the 0,0,1/4 or 0,0,3/4 positions which would keep those equal interatomic distances at a value even less than the sum of the individual ionic radii. These positions which are surrounded only by ceriums form the main tunnels along the 6_3 axes of the cerium apatite lattice (Figure 3) and they would be the most favourable oxygen sites for nitrogen to substitute for. At nitrogen levels below 14100 ppm (the level of nitrogen dictated by the formula $Ce_{10}[SiO_4]_6N_2$), we believe, it would be more unlikely for N to replace O in the silicon tetrahedra since this would mean the formation of oxygen vacancies in the "free" oxygen sites surrounded by three highly electropositive cerium atoms. At higher nitrogen levels such as 21700 and 24400 ppm, as reported by Gaude[4], the apatite structure was no longer stable, and it decomposed to Ce_2SiO_5 and $Ce_2Si_2O_7$. We believe that it would be quite unlikely to be able to ascertain the exact positions occupied by N in the apatite lattice just by thermogravimetric analysis and powder XRD as attempted for cerium apatite by Gaude[4] and recently for yttrium apatite by Veyret et al.[8].

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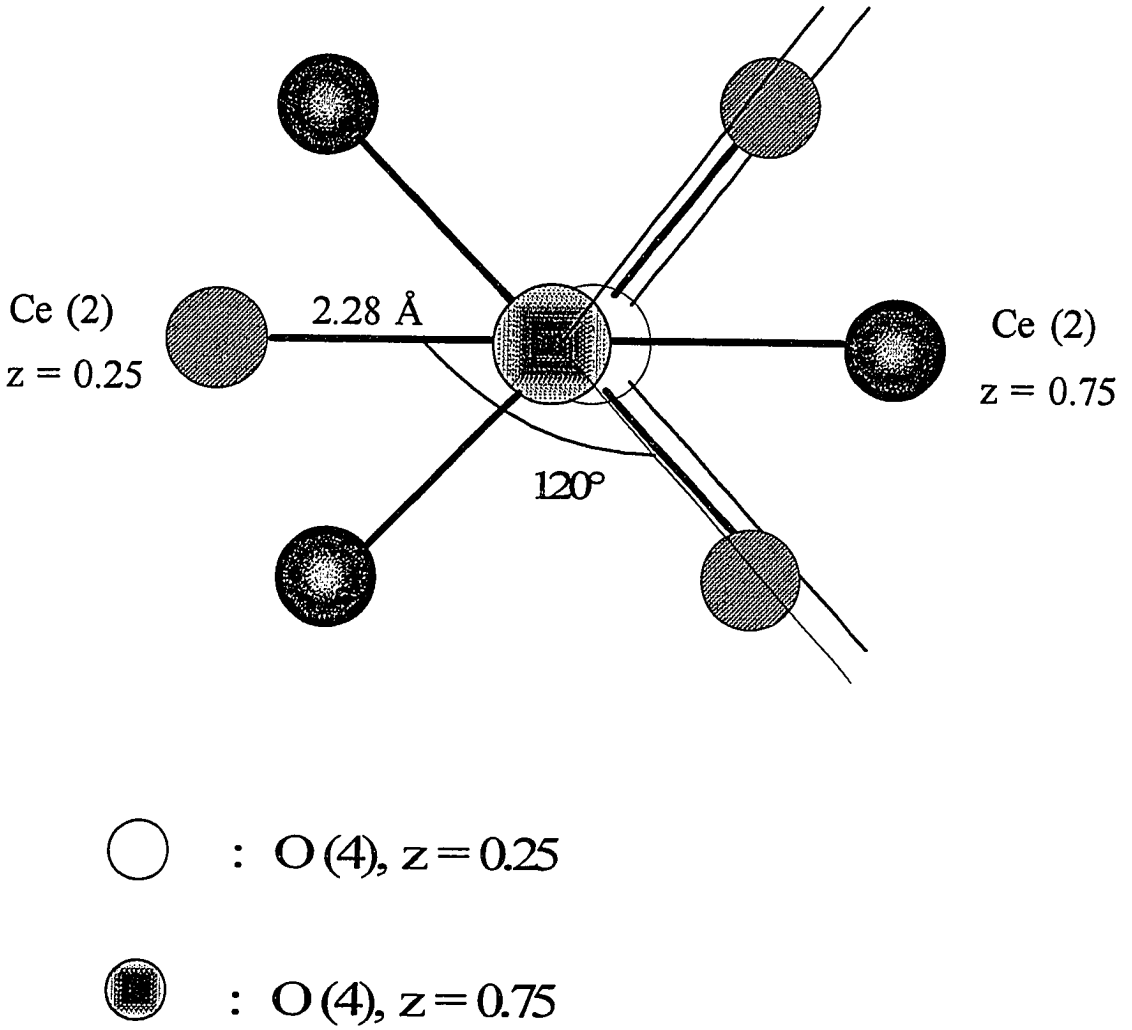

Figure 3. The main tunnels of the cerium apatite structure along the 6_3 axes

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CONCLUSIONS

Neutron diffraction experiments were carried out on samples of pure ($Ce_{9.33}[SiO_4]_6O_2$) and N-doped ($Ce_{9.553}[SiO_4]_6O_{1.341}N_{0.659}$) cerium apatite phase. Rietveld analyses were performed on both pure and N-doped cerium apatite. The effective ionic radius of Ce^{3+} cation in the apatite structure was found to be 1.177 Å. The interatomic distances and angles in the silicate tetrahedra were found to change slightly upon N-doping but they remained insensitive to the placement of N on the individual tetrahedral oxygen sites; O(1)- and O(3)-sites. Placing nitrogen on the non-tetrahedral O(4)-sites also produced the same interatomic distances and angles. The rearrangements observed in the structure upon N-doping could be explained by the filling up of the vacant sites in Ce(1)-sites. The density measurements were found to be inadequate in determining the levels of vacancy elimination in those sites at such low levels of N-doping investigated here. The most likely positions for nitrogen to substitute for oxygens of the lattice were deduced to be the 0,0,1/4 and 0,0,3/4 sites (O(4)-sites) at low levels of N-doping, such as 4800 ppm, since these sites are located at the center of the main tunnels of the lattice and are surrounded only by trivalent ceriums. The strongly electropositive character of Ce caused the Ce(2)-O(4) distances (in pure sample) and Ce(2)-N distances (in N-doped sample) to remain constant at 2.28 Å.

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REFERENCES

[1] A.C. Tas and M. Akinc, "Cerium Oxygen Apatite ($Ce_{4.67}[SiO_4]_3O$) X-Ray Difraction Pattern Revisited," *Powder Diffraction*, 7, 219-222 (1992).

[2] J.P. Guha, "The Silicon-cerium-oxynitride $Ce_5(SiO_4)_3N$ with Fluoroapatite Structure," *J. Mater. Sci.*, **15**, 521-522 (1980).

[3] J. Felsche, "The Crystal Chemistry of the Rare Earth Silicates ," *Structure and Bonding*, **13**, 99-197 (1973).

[4] J. Gaude, "Nouveaux Resultats sur les Apatites Azotees. I. - Le Type $Ln_{10}Si_6N_2O_{24}$ Relatif au Cerium," *Revue de Chimie Minerale*, **24**, 22-27 (1987).

[5] GSAS , A.C. Larson and R.B. VonDreele, LANSCE, MS-HB05, Los Alamos National Laboratory, Los Alamos, NM 87545, Copyright 1985-1993 : The Regents of the University California.

[6] E.L. Belokoneva, T.L. Petrova, M.A. Simonov and N.V. Belov, "Crystal Structure of Synthetic TR Analogs of Apatite $Dy_{4.67}[SiO_4]_3O$ and $Ce_{4.67}[SiO_4]_3O$," *Soviet Physics - Crystallography*, 17, 429-431 (1972).

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[7] A.C. Tas and M. Akinc, "Phase Relations in the System Ce_2O_3 - $Ce_2Si_2O_7$ in the Temperature Range 1150° to 1970°C in Reducing and Inert Atmospheres," To be published.

[8] J.B. Veyret, M. Voorde and M. Billy, "Oxidation Behavior of Silicon Yttrium Oxynitride," *J. Am. Ceram. Soc.*, 75, 3289-3292 (1992).

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