JOURNAL OF SOLID STATE CHEMISTRY **26**, 383–387 (1978)

Cation Ordering in $Ca_2La_8(SiO_4)_6O_2$

L. W. SCHROEDER AND M. MATHEW

American Dental Association Health Foundation Research Unit, National Bureau of Standards, Washington, D.C. 20234.

Received February 17, 1978

The distribution of La^{3+} and Ca^{2+} over the cation sites in $Ca_2La_8(SiO_4)_6O_2$ was determined by single-crystal X-ray diffraction. $Ca_2La_8(SiO_4)_6O_2$ has the apatite structure, and all available evidence indicates that the space group is $P6_3/m$, thus precluding a completely ordered structure. The $6h$ lattice sites are occupied by La^{3+}. In contrast, the $4f$ sites are occupied equally by La^{3+} and Ca^{2+} ions. Consideration of the properties of the La^{3+} and Ca^{2+} ions suggests that this distribution is thermodynamically favored for this composition. A simple Ising model suggests ordered columns. These would not be precluded by space group $P6_3/m$, if the correlation between adjacent columns were random.

Introduction

The incorporation of foreign cations in the apatite structure is of considerable interest, because it is expected to change the bulk properties of the apatite. Unfortunately, it is currently not possible to predict the distribution of the various cations over the two nonequivalent crystallographic sites in apatite *a priori*. Felsche (*1*) has made inferences about the cation distribution in rare earth silicates on the basis of changes in unit cell dimensions. More recently, a preliminary energy analysis of cation ordering has been made (*2*) which suggests that the type of cation–anion bond is more important than the size of the cation.

The oxyapatite $Ca_2La_8(SiO_4)_6O_2$ is an interesting compound to study, because Ca^{2+} and La^{3+} are about the same size and the composition would allow a completely ordered structure to occur in space group $P6_3$. Hence we have studied the cation distribution in $Ca_2La_8(SiO_4)_6O_2$ by means of single-crystal X-ray diffraction.

Experimental

A 1-cm section from a single-crystal boule grown by the Czochralski method was kindly supplied by R. A. Hopkins (*3*). Several pieces were cut from the boule and ground into spheres. A sphere of diameter 100 μm, mounted in a general orientation, was used for the data collection. The cell parameters of a = 9.651(1) and c = 7.155(1) Å (hexagonal system) used in this study were obtained by a least-squares fit of thirty $\pm 2\theta$ values measured using a four-circle diffractometer equipped with Mo$K\alpha_1$ ($\lambda = 0.70930$ Å) radiation and a graphite monochromator. The diffractometer control program was written by Lenhert (*4*).

Four equivalents ($\pm hk \pm l$) of data up to $2\theta = 60°$ and one from hkl up to $2\theta = 80°$ were collected using θ–2θ scans. The scan rate was 0.5° min^{-1} and backgrounds were counted for 40 sec at both ends of the scan range. Four standard reflections measured at intervals of 30 showed insignificant variation in intensity during the data collection. An absorption

0022–4596/78/0264–0383$02.00/0

TABLE I

ATOMIC PARAMETERS ($\times 10^4$) IN $Ca_2La_8(SiO_4)_6O_2$[a]

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$M(1)$[b] (4*f*)[c]	3333	6667	35(1)	74(1)	U_{11}	94(1)	$U_{11}/2$	0	0
$M(2)$[b] (6*h*)	2458(1)	147(1)	2500	61(1)	58(1)	64(1)	23(1)	0	0
Si (6*h*)	3729(1)	4031(1)	2500	48(3)	53(3)	63(3)	26(3)	0	0
O(1) (6*h*)	4692(4)	5965(4)	2500	62(11)	82(11)	373(20)	25(9)	0	0
O(2) (6*h*)	4907(4)	3281(4)	2500	101(11)	153(12)	123(11)	105(10)	0	0
O(3) (12*i*)	2553(3)	3422(5)	697(4)	145(9)	491(18)	106(9)	197(11)	−56(7)	−135(11)
O(4) (2*a*)	0	0	2500	74(11)	U_{11}	448(39)	$U_{11}/2$	0	0

[a] The thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Parameters without estimates of standard deviations (in parentheses) are fixed by symmetry.

[b] La^{3+} occupancy of $M(1)$ is 0.520(1) and $M(2)$ is 0.986(1). In each case, Ca^{2+} occupancy is one minus La^{3+} occupancy.

[c] Wyckoff notation for sites in $P6_3/m$.

correction ($\mu R = 1.075$) was applied using the equation of Rouse and Cooper (*5*). The data were then merged into a set of 1221 independent reflections of which 1181 had $F > 2\sigma(F)$ and were considered observed. The index, $\sum_i^m \sum_j^n (F_{ij} - \langle F_i \rangle)/F_{ij}$, where n is the number of equivalents and m the total number of independent reflections, is 0.013 over 2688 observations.

An initial F_0 Fourier synthesis was phased by calculating the structure factors for a La atom in the $4f$[1] position of $P6_3/m$. The remaining atoms were located by reiterating Fourier syntheses and least-squares refinements. Scattering factors including anomalous dispersion terms for the neutral atoms were taken from "International Tables" (*6*). Program RFINE4 (*7*) was used to refine atomic parameters; the quantity minimized was $\sum w(|F_0| - |F_c|)^2$, where $w = (\sigma(F_0))^{-2}$. In the final cycles the distribution of Ca and La over sites $6h$ and $4f$ was refined. At convergence (maximum parameter shift to error ratio of 0.06) the values of $R = \sum ||F_0| - |F_c|| / \sum |F_0|$ and $R_w = [\sum w(|F_0| - |F_c|)^2 / \sum w |F_0|^2]^{1/2}$ were 0.025 and 0.042, respectively.

As a check the structure was refined in space group $P6_3$ using remerged data. A slightly lower R factor was achieved, but physically unreasonable thermal parameters were obtained, e.g., the rms for the Si atom was <0.01 Å. A piezoelectric test (*8*) gave a negative result. Hopkins *et al.* (*3*) reported that the pits showed the presence of a mirror plane perpendicular to c. Hence, all available evidence indicates that the space group is $P6_3/m$.

Results and Discussion

Structure parameters are given in Table I, and a list of observed and calculated structure amplitudes is available.[2] Selected interatomic distances and angles are given in Table II.

Results from our refinements indicate that

---

[1] Numbers 1 and 2 refer to apatite cations in the sites with Wyckoff notation $4f$ and $6h$, respectively; $4f$ refers to the column cation sites, $6h$ to the triangle sites.

[2] See NAPS document No. 03269 for 11 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiche are \$3.00. Outside the United States and Canada, postage is \$3.00 for a photocopy or \$1.50 for a fiche.

only La^{3+} ions occupy the 6*h* sites (occupancy = 0.986(1) La^{3+}, 0.014 Ca^{2+}), and that the 4*f* sites are occupied nearly equally by La^{3+} and Ca^{2+} ions (occupancies 0.520 and 0.480, respectively). Although refinement with fixed occupancies of cations (6*h* site by La^{3+} only and 4*f* sites by equal amounts of La^{3+} and Ca^{2+}) gave a slightly higher *R* factor (significant according to Hamilton's *R*-factor ratio test (*9*)) the values of the associated thermal parameters changed in a compensating manner. For example, the thermal parameter associated with the 6*h* site increased by as much as three times their error when the site occupancy of La increased from 0.986 to 1.000 (1.4%). Thus the difference between these two values for the La^{3+} occupancy of the 6*h* site has little or no crystal chemical significance.

For oxyapatites of the formula $Ca_2RE_8(SiO_4)_6O_2$ (RE = rare earth), the cell constant *c* changes continuously with the radius of the rare earth ion, whereas *a* shows a discontinuity around Gd (radius 1.08 Å) (*1*). This discontinuity in variation has been interpreted as due to change in distribution of Ca ions from 4*f* to 6*h* sites. However, no detailed structure analysis is available for any rare earth ion with radius less than that of Gd. For rare earths larger than Gd, the variation of both *a* and *c* axes is quite similar. Although a random distribution of Ca could account for this similarity, our experimental results show that Ca is essentially distributed over the 4*f* sites, which is also in agreement with Felsche's interpretation.

The distribution of Ca^{2+} and La^{3+} over the cation sites in $Ca_2La_8(SiO_4)_6O_2$ can better be understood in terms of the ionic properties of Ca and La. Since La^{3+} is somewhat larger than Ca^{2+} (radii of 1.10 and 1.00 Å, respectively (*10*)) it might be expected that it would completely fill the larger 4*f* column sites. Instead, the La^{3+} ion fills the 6*h* sites, which suggests that the following considerations are important:

(i) Placing all of the La^{3+} ions closest to the O^{2-} ion provides for more electrostatic binding and lowers the crystal energy.

(ii) The oxide ion is more polarizable than the oxygen of SiO_4^{4-}, judging from Fajans' rules (*11*). Since La^{3+} is somewhat more polarizable than Ca^{2+} (*12*) the crystal energy can be lowered by dispersion forces if La^{3+} and O^{2-} are nearest neighbors.

(iii) If some Ca^{2+} were in the 6*h* sites, then there would be some $La^{3+} \cdots La^{3+}$ pairs in the columns and this would increase the energy due to electrostatic repulsion because the cation–cation distance in the columns is only 3.5 Å compared to 4.1 Å in the 6 *h* sites.

(iv) The 6*h* cation sites are surrounded by four SiO_4 groups and the 4*f* sites by six, so the $La^{3+} \cdots Si^{4+}$ repulsion energy is minimized by placing the fewest La^{3+} ions in the 4*f* position.

The observed $La^{3+} \cdots O^{2-}$ distance of 2.305(1) Å which is 0.16 Å shorter than the sum of the ionic radii (*9*) certainly indicates

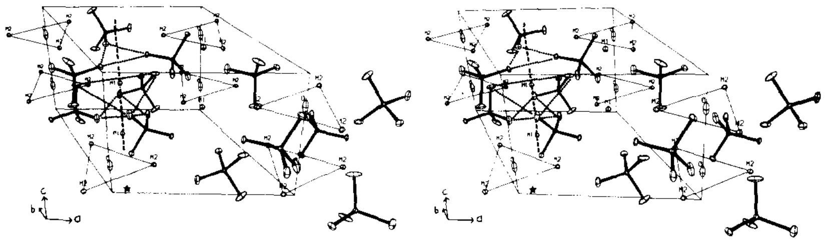

FIG. 1. Unit cell of $Ca_2La_8(SiO_4)_6O_2$. Cation sites 6*h* and 4*f* are indicated by *M*2 and *M*1, respectively. The dotted line shows one of the cation columns. Some SiO_4 ions have been omitted for clarity.

that the $La^{3+} \cdots O^{2-}$ binding is very strong in the crystal. Models having one-half oxide ion displaced on either side of the cation triangles were tried, but the oxide ion shifted to the midpoint of the cation triangles. Thus the short $La^{3+} \cdots O^{2-}$ distance is not an artifact. The strong $La^{3+} \cdots O^{2-}$ binding may also account for the fact that this material is significantly harder than fluorapatite. A very short $Gd–O^{2-}$ distance was observed in the compound $Gd_{9.33}\square_{0.67}(SiO_4)_6O_2$ (*13*), which also supports the idea that the rare earth cations polarize the oxide ion.

The question of cation ordering in the $4f$ column sites remains. Space group $P6_3/m$ requires the same occupancy in each $4f$ site, but this does not in itself provide any information about ordering in a given column since position $4f$ includes two columns (at $\frac{1}{3}$, $\frac{2}{3}$, z and $\frac{2}{3}$, $\frac{1}{3}$, z). A simple Ising model would suggest on the basis of electrostatic and nonelectrostatic repulsion that a given column is ordered. Different columns could have different origins, i.e., the cation at $\frac{1}{3}$, $\frac{2}{3}$, ~0 need not always be the same for adjacent columns. Thus, there would not be perfect order in directions perpendicular to c. The cation–cation distances in a given column are $c/2 \sim 3.5$ Å compared to 5.5 Å between columns, indicating that the effect of cation repulsion within a column is more important than the effect between columns.

The oxide ion lies on the 6_3 axis and in the plane defined by the triangle of three La^{3+} ions as in the compound $Gd_{9.33}\square_{0.67}(SiO_4)_6O_2$ (*13*). However, this need not always be the case if space group restrictions do not exist. For example, the samarium oxynitrides, $Sm_{10}Si_6N_2O_{24}$ (*14*) and $Sm_8Cr_2Si_6N_2O_{24}$ (*15*), have oxyapatite structures in space group $P6_3$, which lacks the mirror plane. In these compounds the oxide ion is about 0.20 Å from the midpoint of the triangle of cations.

The average Si–O bond length is 1.623(2) Å, in excellent agreement with the value of 1.625 Å reported by Baur (*16*). Table II shows that the SiO_4 ion is somewhat distorted. The major part of the distortion seems to be a compression along the c axis. There is little interaction between the oxide ion and the oxygens of the SiO_4 ion, as all distances are greater than 3.240 Å.

TABLE II

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Cation–cation	
La(6*h*)–*M*(4*f*)[a]	4.0934(3)[b]
M(4*f*)–*M*(4*f*)	3.6278(9)
M(4*f*)–*M*(4*f*)	3.5271(9)
La(6*h*)–La(6*h*)	3.9918(4)
Cation–oxygen	
M(4*f*)–O(1)	2.485(2)
M(4*f*)–O(2)	2.468(2)
M(4*f*)–O(3)	2.870(4)
La–O(1)	2.506(3)
La–O(2)	2.754(3)
La–O(3), O(3)′	2.437(3)
La–O(3)″, O(3)‴	2.609(3)
La–O(4)	2.305(1)
SiO_4 ion	
Si–O(1)	1.616(4)
Si–O(2)	1.624(3)
Si(O(3), O(3)′	1.622(3)
O(1)–Si–O(2)	112.9(2)
O(1)–Si–O(3)	108.2(2)
O(2)–Si–O(3)	110.9(2)
O(3)–Si–O(3)′	105.4(2)

[a] Wyckoff notation for cation sites.

[b] Numbers in parentheses are estimated standard deviations.

In summary, the structure of $Ca_2La_8(SiO_4)_6O_2$ shows that cation ordering in apatites can be understood in terms of the properties of the constituent ions.

Acknowledgments

We thank R. A. Hopkins for the crystal of $Ca_2La_8(SiO_4)_6O_2$. P. Kingsbury provided technical assistance. Figure 1 was drawn using a local version of C. K. Johnson's ORTEP program. This investigation was supported in part by Research Grant DE00572 to the American Dental Association Health Foundation from the National Institute of Dental Research and is part of the dental research program conducted by the National Bureau of Standards in cooperation with the American Dental Association Health Foundation.

References

1. J. Felsche, *J. Solid State Chem.* **5**, 266 (1972).
2. V. S. Urusov and V. O. Khudolozhkin, *Geochem. Int.* **10**, 1048 (1974).
3. R. H. Hopkins, G. W. Roland, K. B. Steinbruegge, and W. D. Partlow, *J. Electrochem. Soc.* **118**, 637 (1971).
4. P. G. Lenhert, *J. Appl. Crystallogr.* **8**, 568 (1975).
5. K. D. Rouse and M. J. Cooper, *Acta Crystallogr. A* **26**, 682 (1970).
6. "International Tables for X-Ray Crystallography," Vol. IV, pp. 99–101, 149–150, Kynoch Press, Birmingham (1974).
7. L. W. Finger and E. Prince, *Nat. Bur. Stand. (U.S.) Tech Note* 854, 1–733 (1975).
8. R. J. Blume, *Rev. Sci. Instrum.* **32**, 598 (1966).
9. W. C. Hamilton, "Statistics in Physical Science," pp. 158–161, Ronald Press, New York (1964).
10. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. B* **25**, 925 (1969).
11. K. Fajans, *Naturwissenschaften* **11**, 165 (1923).
12. J. R. Tessman, A. H. Kohn, and W. Shockley, *Phys. Rev.* **92**, 890 (1953).
13. Yu. I. Smolin and Yu. F. Shepelev, *Izv. Akad. Nauk. SSSR Neorg. Mat.* **5**, 1823 (1969).
14. I. Gaude, P. L'Horidon, C. Hamon, R. Marckland, and Y. Laurent, *Bull. Soc. Fr. Mineral. Crystallogr.* **98**, 214 (1975).
15. M. Maunoye, C. Hamon, P. L'Horidon, and Y. Laurent, *Bull. Soc. Fr. Mineral Crystallogr.* **99**, 203 (1976).
16. W. H. Baur, *in* "ACA Program and Abstracts, Summer Meeting, 1976," Abstract G7, p. 60.