

STRONTIUM IN THE APATITE STRUCTURE: STRONTIAN FLUORAPATITE AND BELOVITE-(Ce)

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ABSTRACT

Strontium is one of the most common substituents in apatite; the presence and behavior of Sr in apatite-group phases are of considerable significance in geology, materials science and biology. The atomic arrangements in strontian fluorapatite (1.18 Sr atoms per 10 Ca sites) and belovite-(Ce) [ideally $\text{Sr}_6(\text{REE}_2\text{Na}_2)(\text{PO}_4)_6\text{F}_2$] have been refined to R values of 0.016 and 0.014, respectively, in order to examine the incorporation of Sr in apatite and apatite-group minerals. In strontian fluorapatite, Sr is ordered at the Ca(2) site, and no dissymmetrization from $P6_3/m$ results from the substitution; expansion of the Ca(2) site accommodates the Sr. In belovite-(Ce), the symmetry of the atomic arrangement degenerates to $P\bar{3}$ as the apatite Ca(1)-equivalents split to form separate sites for Na and the REE; Sr is ordered at the apatite-equivalent Ca(2) sites. The symmetry reduction results principally from shifts in O(3) apatite equivalents [which are split to O(3) and O(4) in belovite] to accommodate Na and REE in distinct sites, sites that are equivalent to Ca(1) sites in $P6_3/m$ apatite. The ordering of Sr and REE in belovite suggests that it may be possible to tailor the emission characteristics of apatite phosphors and lasers by controlling the distribution of luminescence-activating lanthanides between the two Ca sites with Sr codoping.

Keywords: apatite, strontian fluorapatite, belovite-(Ce), strontium, rare-earth elements.

SOMMAIRE

Le strontium est un des éléments les plus couramment incorporés dans l'apatite; la présence et le comportement du Sr ont donc une grande importance à la fois en géologie, en sciences des matériaux et en biologie. Nous avons déterminé l'agencement des atomes dans la fluorapatite strontifère (1.18 atomes de Sr par 10 sites Ca) et la bélovite-(Ce) [idéalement, $\text{Sr}_6(\text{REE}_2\text{Na}_2)(\text{PO}_4)_6\text{F}_2$] jusqu'à un résidu R de 0.016 et 0.014, respectivement, afin de déterminer le mode de substitution du Sr dans l'apatite et les minéraux du groupe de l'apatite. Dans la fluorapatite strontifère, le Sr se loge dans le site Ca(2) site, et aucun écart de la symétrie $P6_3/m$ en résulte; l'expansion du site Ca(2) accommode le Sr. Dans le cas de la bélovite-(Ce), la symétrie de la structure dégénère à $P\bar{3}$ parce que l'équivalent du site Ca(1) de l'apatite devient deux sites, un pour le Na et l'autre pour les terres rares. Le Sr est incorporé dans l'équivalent du site Ca(2). La réduction de la symétrie résulte surtout des déplacements de l'équivalent de l'atome O(3) dans la structure de l'apatite [qui devient O(3) et O(4) dans la bélovite] pour accommoder le Na et les terres rares dans des sites distincts, équivalents à Ca(1) dans l'apatite $P6_3/m$. La mise en ordre du Sr et des terres rares dans la bélovite mène à la possibilité de prédéterminer les émissions caractéristiques de phosphors et de lasers faits de ce matériau en ajustant la distribution des terres rares responsables de la luminescence entre les deux sites Ca par codopage avec le Sr.

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Mots-clés: apatite, fluorapatite strontifère, bélovite-(Ce), strontium, terres rares.

INTRODUCTION

Apatite is known for its extensive compositional variation, and the nature of the substituents and their influence on the apatite structure have been widely studied (Elliott 1994). Strontium is one of the most common substituents in apatite. A complete solid-solution exists between Ca and Sr in synthetic apatite (Khattech & Jemal 1997), although the Sr end member has not been found in nature.

Of particular interest in environmental and materials sciences is the use of apatite to sequester radionuclides such as U and ^{90}Sr , a common product in spent nuclear fuel (Weber *et al.* 1995). Because of the high affinity of Sr for the apatite structure, ^{90}Sr bioaccumulates in bone and teeth and poses a particular radiological risk to humans. Moreover, the physicochemical behavior of apatite has led to its consideration as a solid waste form for many radionuclides (Ewing *et al.* 1995, Weber *et al.* 1995) including ^{90}Sr , and researchers are

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actively investigating this potential (Wronkiewicz *et al.* 1996). A further consideration in the storage of ^{90}Sr is the behavior of the radiogenic daughter product, ^{90}Y (also radioactive), in the solid waste form. In the case of apatite, Y is highly compatible and is another common substituent for Ca in natural samples (Rakovan & Reeder 1994).

The apatite structure and its tolerance for a wide range of substituents also provide an excellent overall mix of the optical, thermal and mechanical properties required for an efficient laser source (Gruber *et al.* 1999). Simultaneous substitutions involving elements other than the lasing ion can affect the performance and characteristics of the laser, and cosubstitution of lanthanides and Sr (end-member strontium-apatite) for Ca has led to lasers with certain desired characteristics (Payne *et al.* 1994).

Geologically, Sr in apatite has been used as a petrogenetic indicator (*i.e.*, Faure & Powell 1972, Kistler & Peterman 1973) and for dating *via* the Rb–Sr geochronometer (*i.e.*, Kruger *et al.* 1998).

Understanding the structural response of apatite to a wide range of Sr concentrations is important in assessing the use of apatite as a possible host for radioactive ^{90}Sr contamination, in engineering novel and better lasing and phosphor materials, and in understanding the behavior of Sr in geological systems where apatite is present. In this paper, we present the results of crystal-structure refinements of Sr-rich fluorapatite and belovite-(Ce) from the Lovozero Massif, Kola Peninsula, Russia. In comparison to the previous study by Hughes *et al.* (1991a), we explore here the structural response of apatite to much higher loading of Sr.

PREVIOUS STUDIES OF SITE OCCUPANCIES

Sr incorporation in Ca-dominant apatite-group minerals

Continuous solid-solution between Ca and Sr end-members has been established (Khattech & Jemal 1997, Khudolozhkin *et al.* 1972), and many compositions along this join are found in nature. Numerous experiments, with contradictory results, have addressed the ordering of substituent Sr between the two nonequivalent Ca sites [Ca(1), Ca(2)] in apatite. In a structure analysis of synthetic $\text{Sr}_3\text{Ca}_2(\text{PO}_4)_3\text{F}$, Klevcova (1964) demonstrated that the symmetry of the compound degenerates to $P6$ from the $P6_3/m$ of end-member fluorapatite, and that the Sr atoms are distributed between the degenerate equivalents of both $P6_3/m$ sites. In a predictive study on the basis of energy analysis of cation ordering in apatite, Khudolozhkin *et al.* (1972) synthesized a series of Sr-substituted hydroxylapatite samples. They determined the degree of order of Sr over the two cation sites on the basis of intensity ratios derived from

eight reflections measured using a powder diffractometer, and concluded that Sr preferentially occupies the Ca(2) sites in apatite with ~10% Sr incorporation, but that the degree of order decreases as the Sr content increases. Urusov & Khudolozhkin (1975) suggested that the “medium” preference of Sr for the Ca(2) site in fluor- and hydroxylapatite results from the differing electronegativity of the ligands of the two sites, *i.e.*, Ca(1)O_9 versus Ca(2)O_6X (where X represents F, OH). Heijligers *et al.* (1979) and Andrés-Vergés *et al.* (1980) suggested, on the basis of powder X-ray and infrared spectra, respectively, that the Sr occupies both Ca sites in Sr-substituted synthetic hydroxylapatite, but the ratio $\text{Sr}_{\text{Ca(1)}}/\text{Sr}_{\text{Ca(2)}}$ varies as a function of composition. Hughes *et al.* (1991a) presented results of high-precision crystal-structure refinements of two natural apatites containing 3.83 and 2.7 wt.% Sr, and found that in this compositional range Sr strongly favors the Ca(2) site. In a Rietveld study of synthetic apatite-group phases containing 5, 20, and 60% Sr atoms in the Ca sites, Bigi *et al.* (1998) found that the strontium preference for the Ca(2) site increases with increasing Sr concentration. Sudarsanan & Young (1974) refined the structure of synthetic $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$. It was found to be isostructural with $P6_3/m$ fluorapatite except for the Cl ions that lie at $(0,0,1/2)$, midway between the triangles defined by Sr at $z = 1/4, 3/4$. This is in contrast to end-member chlorapatite, in which Cl lies at $(0,0,0.44)$ (Mackie *et al.* 1972), space group $P2_1/b$. It is unusual that in this structure, the Cl ions above and below the Sr(2) site are equidistant, yielding 8-coordination of the Sr(2) site rather than the 7-coordination of this site in other apatites. In a study of chlorapatite with varying degrees of replacement of Ca by Sr, Sudarsanan & Young (1980) found that the preference of Sr to partition into the Ca(2) site decreases with increasing Sr. Furthermore, the coordinates of the Cl atom depend on the amount of Sr present. In chlorapatite, Cl lies at $(0,0,0.44)$, but shifts to $(0,0,1/2)$ at or before 48% of the Ca is replaced by Sr.

Belovite

Several groups, with differing results, have studied the structure and composition of belovite. In the first description of the belovite structure, Klevcova & Borisov (1964; $R = 0.13$) concluded that the Sr is ordered solely at the Ca(2) sites, and ordering of the Na and Ce atoms reduces the symmetry from $P6_3/m$ to $P\bar{3}$. Nadezhina *et al.* (1987; $R = 0.048$) refined the structure of belovite-(Ce) in space group $P\bar{3}$. Pekov *et al.* (1995) reported space group $P3$ for belovite-(Ce), on the basis of peak positions from powder data. The La-rich analog was reported by Pekov *et al.* (1996) to have $P\bar{3}$ symmetry (again on the basis of powder data), whereas Kabalova *et al.* (1997) determined, in a Rietveld study, that the space group is $P3$ ($R_{wp} = 0.045$).

EXPERIMENTAL

Chemical analysis

The strontian fluorapatite was analyzed using the University of Colorado's JEOL 8600 Superprobe. For Sr, strontianite (NMNH, R10065) was employed as a standard; for Ca, P, and F, fluorapatite (NMNH 104021) was used. The recalculated formula from the average result of five analyses is $(\text{Ca}_{8.91}\text{Sr}_{1.09})\text{P}_{5.85}\text{O}_{12}[\text{F}_{1.88}(\text{OH})_{0.12}]$ on the basis of $(\text{Ca} + \text{Sr}) = 10$, OH by difference.

Belovite-(Ce) was analyzed on a Cameca SX-100 electron microprobe at the New Mexico Bureau of Mines and Mineral Resources, Socorro, New Mexico. For Ca, F and P, apatite was employed as a standard; for Na, albite; for Si, orthoclase; for S, pyrite; for Cl, marialite; for Ba, barite; for Sr, synthetic SrTiO_3 ; for Y, La, Ce and Nd, synthetic phosphates of the respective element were used. The microprobe was operated at 15 kV and 19.9 nA.

Crystal structure

Strontian fluorapatite and belovite-(Ce) from the Lovozero Massif, Kola Peninsula, Russia were prepared for crystal-structure examination. Because of the high linear-absorption coefficient of the rare-earth-element-bearing belovite, the crystal of belovite-(Ce) was ground to a sphere. An Enraf-Nonius CAD4 single-crystal diffractometer was used for crystal orientation and data collection for both crystals; unit cells were determined from the least-squares refinement of the setting angles of 25 reflections, each measured in four positions.

Intensity data were collected using the parameters in Table 1, and reduced to structure factors using the SDP for Windows package of programs (Frenz 1997). Absorption was corrected using $360^\circ \Psi$ -scan data, and, subsequent to structure refinement, the absorption-surface method as implemented in program DIFABS (Walker & Stuart 1983). A weighting scheme with weights proportional to σ^{-2} was employed, with a term to downweigh intense diffraction-maxima.

The atomic arrangement of the strontian fluorapatite was routinely refined from the apatite starting model (Hughes *et al.* 1991a) in space group $P6_3/m$. The occupants of the Ca(1) and Ca(2) sites were constrained with the assumption $\text{Ca} + \text{Sr} = 1$. For belovite-(Ce), the putative space-group $P\bar{3}$ and the starting model of Nadezhina *et al.* (1987) were employed; the successful refinement of the structure in this space group, coupled with the presence of numerous non-positive-definite atoms when refinements were attempted in $P\bar{3}$, confirmed $P\bar{3}$ as the correct space-group. For both experiments, neutral-atom scattering factors with terms for anomalous dispersion were employed. For belovite-(Ce), data with $I > 6\sigma_I$ were used, whereas for strontian fluorapatite, $I > 5\sigma_I$ data were employed.

In belovite-(Ce), the penultimate difference-map revealed a large ($>1 e^-/\text{\AA}^3$) peak that was several times larger than all other peaks; examination of the stereochemistry of that site suggested that it is occupied by Cl. The presence of minor chlorine in the belovite crystal was confirmed by electron-probe micro-analysis, and the parameters of a partial Cl atom assigned to that site refined routinely; this Cl site was previously unrecognized in belovite.

CRYSTAL-STRUCTURE RESULTS

The unit-cell parameters and crystal data are listed in Table 1. Table 2 contains positional parameters and equivalent isotropic B values for both minerals, and Table 3 contains anisotropic thermal parameters. Selected bond-lengths for the two structures are given in Table 4, and observed and calculated structure-factors for strontian fluorapatite and belovite-(Ce), in Table 5. Tables 3 and 5 may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada. For ease of comparison, the equivalent nomenclature of atoms for belovite-(Ce) as in the apatite *sensu stricto* is used in Table 2. Table 6 contains the results of electron-microprobe analyses of the strontian fluorapatite and belovite-(Ce) samples. The low total (97.86 wt.%) for the belovite-(Ce) most likely results from poor polish of the sample. The recalculated formula based on the average

TABLE 1. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENT FOR STRONTIAN FLUORAPATITE (SrAp) AND BELOVITE-(Ce) (Blv)

Unit cell			
SrAp, $P6_3/m$:			
a (\AA)	9.416(1)	c	6.924(1)
Blv, $P\bar{3}$:			
a (\AA)	9.659(2)	c	7.182(2)
θ limit	(SrAp) 1.0 - 30.0 $^\circ$	Scan type	$\theta 2\theta \leq 60$ s
	(Blv) 1.0 - 30.0 $^\circ$	Scan type	$\theta 2\theta \leq 70$ s
Standards (SrAp, Blv)			
Orientation:	3/300 reflections	Intensity:	3 per 4 hrs
Data collected (SrAp)	3633, $-h$ to h , $-k$ to k , $-l$ to l		
	(Blv) 4224, $-h$ to h , $-k$ to k , -2 to l		
Unique data	(SrAp) 559	R_{merge}	0.017
	(Blv) 1106	R_{merge}	0.022
(SrAp)	Data $> 5\sigma_I$	Variables	50
(Blv)	Data $> 6\sigma_I$	Variables	72
GooF	(SrAp) 1.016	(Blv)	0.834
R	(SrAp) 0.016	R_w	0.022
	0.028 (all data)		
	(Blv) 0.014	R_w	0.019
	0.037 (all data)		
Largest peaks on difference map ($e^-/\text{\AA}^3$)			
(SrAp)	(+)	(-)	0.315
(Blv)	(+)	(-)	0.546

TABLE 2. POSITIONAL PARAMETERS AND ISOTROPIC B VALUES FOR ATOMS IN BELOVITE-(Ce) AND STRONTIAN FLUORAPATITE

Atom	x	y	z	B(\AA^2)	Occ.
Strontian Fluorapatite					
Ca(1)	2/3	1/3	0.0004(1)	0.842(8)	Ca _{0.9741(5)} Sr _{0.0259}
Ca(2)	0.24967(5)	0.01007(5)	1/4	0.912(8)	Ca _{0.8229(7)} Sr _{0.1771}
P	0.02937(7)	0.63066(7)	1/4	0.66(1)	P _{1.00}
O(1)	0.4849(2)	0.3278(2)	1/4	1.16(4)	O _{1.00}
O(2)	0.4129(2)	0.8794(2)	1/4	1.30(4)	O _{1.00}
O(3)	0.0836(2)	0.7422(2)	0.0721(2)	1.50(3)	O _{1.00}
F	0	0	1/4	2.68(6)	F _{1.00}
Belovite-(Ce)					
Ce[Ca1]	1/3	2/3	0.48227(6)	0.767(5)	Ce _{0.9167(4)}
Na[Ca1]	1/3	2/3	0.9881(3)	0.88(2)	Na _{1.502(2)}
Sr[Ca2]	0.23726(4)	-0.01866(4)	0.75818(5)	1.065(7)	Sr _{1.012(1)}
P[1]	0.5970(1)	-0.3730(1)	0.2534(2)	0.79(2)	P _{1.00}
O(1)[O1]	0.1501(3)	-0.3415(3)	0.7299(4)	1.40(6)	O _{1.00}
O(2)[O2]	0.8764(3)	0.4157(3)	0.7756(4)	1.45(6)	O _{1.00}
O(3)[O3]	0.7274(4)	0.0981(3)	0.5656(4)	1.56(7)	O _{1.00}
O(4)[O3']	0.3132(4)	0.2558(3)	0.9018(5)	2.04(7)	O _{1.00}
F[F]	0	0	0.289(1)	3.2(1)	F _{1.00}
Cl[Cl]	0	0	1/2	2.68	Cl _{0.021(1)}

Anisotropically refined atoms are given in the form of the isotropic equivalent as calculated by the method of Hamilton (1959).

For belovite-(Ce), the apatite *sensu stricto* atom nomenclature is included in brackets.

result of three analyses is (Sr_{5.74}Ba_{0.22})Σ_{5.96}Na_{2.12}(Ce_{1.18}La_{0.64}Nd_{0.34})Σ_{2.16}(P_{6.06}Si_{0.22})Σ_{6.28}O₂₄[F_{1.96}(OH)_{0.02}Cl_{0.02}].

Strontian fluorapatite

The Sr²⁺ ion is significantly larger than the Ca²⁺ ion. Shannon (1976) reported effective ionic radii of 1.31 Å for ⁹¹Sr²⁺ and 1.21 Å for ⁷¹Sr²⁺; these values compare with 1.18 Å and 1.06 Å for ⁹¹Ca²⁺ and ⁷¹Ca²⁺, the coordination of the apatite Ca(1) and Ca(2) sites, respectively.

The apatite formula can be written as Ca(1)₄Ca(2)₆(PO₄)₆(OH,F,Cl)₂, illustrating the two Ca sites of differing rank in space group *P6₃/m* for apatite *sensu stricto*. As noted above, numerous studies have been undertaken to determine the degree of order of substituents for Ca over the two sites, with discordant results. For the strontian fluorapatite described herein, virtually all Sr is ordered at the Ca(2) sites, in accord with the earlier studies of Sudarsanan & Young (1980), Hughes *et al.* (1991a), and Bigi *et al.* (1998). The site refinement gave (Ca_{0.975}Sr_{0.025}) at Ca(1) and (Ca_{0.82}Sr_{0.18}) at Ca(2), which yields a total of 1.18 Sr atoms per formula unit (*apfu*), in good agreement with 1.09 *apfu* determined by chemical analysis.

TABLE 4. SELECTED BOND LENGTHS (Å) IN STRONTIAN FLUORAPATITE AND BELOVITE-(Ce)

Strontian fluorapatite					
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ca(1)-	O(1) (x3)	2.414(2)	Ca(2)-	O(1)	2.688(2)
	O(2) (x3)	2.464(1)		O(2)	2.404(3)
	O(3) (x3)	2.821(2)		O(3) (x2)	2.366(2)
Mean =		2.566	O(3) (x2)	2.526(1)	
			F	2.3047(5)	
			Mean =	2.454	
P-	O(1)	1.535(2)			
	O(2)	1.536(2)			
	O(3) (x2)	1.532(2)			
Mean =		1.534			
Belovite-(Ce)					
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ce-	O(1)(x3)	2.483(3)	Na-	O(1)(x3)	2.537(3)
	O(2)(x3)	2.560(3)		O(2)(x3)	2.451(3)
	O(3)(x3)	2.638(4)		O(4)(x3)	3.207(4)
Mean =		2.560	Mean =		2.732
Sr-	O(1)	2.802(3)	P-	O(1)	1.536(3)
	O(2)	2.532(4)		O(2)	1.531(3)
	O(3)	2.525(3)		O(3)	1.557(3)
	O(3)	2.805(3)		O(4)	1.515(3)
	O(4)	2.491(3)	Mean	1.535	
	O(4)	2.585(3)			
F	2.411(1)				
Mean		2.593			
	Cl	3.0227(4)			

Although the Sr is almost completely ordered at the Ca(2) sites, there is no dissymmetrization of the *P6₃/m* apatite structure associated with the substitution. The main response to the incorporation of Sr is seen in the Ca(2) polyhedron. Ca(2) bonds to seven ligands [Ca(2)O₆F] in a distorted polyhedron, and expands con-

TABLE 6. CHEMICAL ANALYSES OF BELOVITE-(Ce) AND STRONTIAN FLUORAPATITE

Strontian fluorapatite*		Belovite-(Ce)[†]	
Oxide/element	Wt. %	Oxide/element	Wt. %
CaO	47.14(64)	CaO	0.61(9)
P ₂ O ₅	10.67(20)	P ₂ O ₅	27.5(16)
SrO	39.15(17)	SrO	38.1(18)
F	3.37(35)	BaO	2.15(21)
-O = F	1.42	Na ₂ O	4.19(47)
Total	98.91	La ₂ O ₃	6.67(24)
		Ce ₂ O ₃	12.47(19)
		Nd ₂ O ₃	3.74(32)
		SiO ₂	0.9(15)
		OH	0.1(1)
		F	2.39(26)
		Cl	0.03(1)
		-O = F	1.01
		Total	97.86

*Formula: (Ca_{8.91}Sr_{1.09})P_{3.85}O₁₂[F_{1.88}(OH)_{0.12}]

†Formula: (Sr_{5.74}Ba_{0.22})Na_{2.12}(Ce_{1.18}La_{0.64}Nd_{0.34})P_{6.06}Si_{0.22}O₂₄F_{1.96}(OH)_{0.02}Cl_{0.02}

siderably with substitution of Sr. Figure 1 displays the response of several Sr–ligand bond lengths to increasing incorporation of Sr; clearly the Ca(2) polyhedron can expand sufficiently to incorporate the 18% substitution in the present study.

In addition to Sr, the apatite structure is known to incorporate large amounts of rare-earth elements (*REE*), particularly the lighter ones (*LREE*). Hughes *et al.* (1991b) and Fleet & Pan (1995, 1997) have demonstrated a strong site-preference for Ca(2) among the *LREE*. The sample of belovite studied here presents an interesting case in which both Sr and *LREE* compete for the Ca(2) sites, and illustrates the dissymmetrization that occurs because both cannot occupy Ca(2).

Belovite-(Ce)

The ideal formula for belovite is $\text{Sr}_6(\text{Na}_2\text{REE}_2)(\text{PO}_4)_6\text{O}_{24}(\text{OH},\text{F},\text{Cl})_2$, equivalent to apatite *sensu stricto* with the following substitutions: $\text{Ca}(2)_{-6}\text{Sr}_{+6}$ and $\text{Ca}(1)_{-4}\text{Na}_{+2}\text{REE}_{+2}$. The present study confirms the previous findings that Sr overcomes the *REE* in competition for the Ca(2) sites of apatite. Optimization of the site assignments for the Sr, Na, and Ce sites using the method of Wright *et al.* (2000) yields Sr: ($\text{Sr}_{0.85}\text{Ce}_{0.06}\text{Na}_{0.05}\text{Ba}_{0.02}\text{Nd}_{0.02}$), Na: ($\text{Na}_{0.84}\text{Nd}_{0.12}\square_{0.04}$), and Ce: ($\text{Ce}_{0.38}\text{La}_{0.31}\text{Sr}_{0.22}\text{Ba}_{0.09}$). Thus each of the three Ca substituents (Sr, Na, *REE*) dominates one site, which has modified its topology to accommodate the specific ion.

In belovite, Sr substitutes into the Ca(2)-equivalent sites of the apatite structure. Thus Sr effectively precludes *REE* from occupying the Ca(2)-equivalent sites. The remaining Ca sites, the sites equivalent to Ca(1) of apatite, must respond to occupation by essentially equal amounts of Na and *REE*, ions with distinctly different ligation requirements. Unlike the single Ca(1) site in apatite *sensu stricto*, loss of symmetry in $P\bar{3}$ yields two Ca(1) subequivalents, one dominated by Na and the other by *REE*.

The Ca(1) site in apatite *sensu stricto* bonds to nine atoms of oxygen [$3 \times \text{O}(1)$, $3 \times \text{O}(2)$, and $3 \times \text{O}(3)$] in the topology of a tri-capped trigonal prism. The Na and Ce equivalents to Ca(1) in belovite-(Ce) display significantly different bond-lengths to the oxygen atoms of their respective polyhedra; $\langle \text{NaO}_9 \rangle = 2.732 \text{ \AA}$, $\langle \text{CeO}_9 \rangle = 2.560 \text{ \AA}$ (Table 4). The principal difference lies in the bonds to the apatite-equivalent O(3) sites, termed O(3) and O(4) in belovite-(Ce). The oxygen atoms that are O(3) equivalents in apatite are separated by 0.55 \AA in belovite-(Ce), allowing the Ce–O(3) bond length of 2.638 \AA and an Na–O(4) bond length of 3.207 \AA ; the bonds would be equivalent in the $P6_3/m$ apatite structure. Indeed, with an Na–O bond length of 3.207 \AA , the Na coordination is probably more appropriately considered a NaO_6 trigonal pyramid; the long bonds through the prism faces each contribute only 0.02 valence units.

In all previous investigations of the structure of belovite, Cl was not recognized as a column anion. As

noted above, the penultimate Fourier-difference map revealed a large positive peak at $(0,0,\frac{1}{2})$, and the ligation of that site showed that it is occupied by the small amount of Cl reported. Thus, unlike apatite *sensu stricto*, the Sr atoms adjacent to Cl column anions are 8-coordinated as SrO_6Cl_2 .

DISCUSSION

The results of this study support previous findings (Sudarsanan & Young 1980, Hughes *et al.* 1991a, Bigi

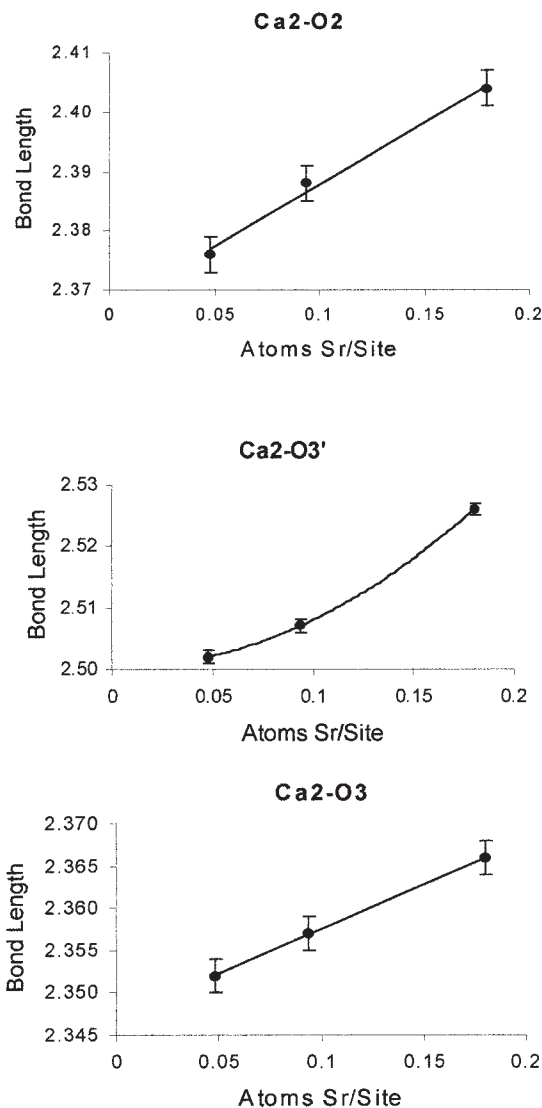


FIG. 1. Variation in the Sr–O bond length with extent of Sr incorporation in strontian fluorapatite.

et al. 1998) that Sr almost exclusively occupies the apatite Ca(2) site, even in the case of belovite, where there is competition for that site by La and Ce. This result suggests that control of the *REE* distributions between the two Ca sites in synthetic crystals of apatite can potentially be gained by concurrent doping with Sr. Because the emission characteristics of a luminescence activating ion is dependent in part on the crystal field around that ion, it thus may be possible to tailor the emission characteristics of apatite hosts by controlling the distribution of activating lanthanides between the two Ca sites with specific Sr codoping.

Hughes *et al.* (1991b) presented high-precision refinements of the structure of four natural samples of *REE*-bearing apatite. Like for Sr, they found a high preference of the light *REE* (La–Nd) for the Ca(2) site. Clearly, however, from our results for belovite-(Ce), the preference of Sr for Ca(2) is greater than that of the *LREE*, such that the *REE* are excluded from the Ca(2) site and adopt a Ca(1) site. The greater preference of Sr over the light *REE* for the Ca(2) site can be understood if the bond-valence sums for these ions in the two Ca sites of the apatite structure are considered. Hughes *et al.* (1991b) showed that the light *REE* are overbonded in both the Ca sites, but overbonding was minimized in Ca(2). The largest degree of overbonding in Ca(1) is found for La, which is as much as 0.43 valence units overbonded in the apatite samples studied. Hughes *et al.* (1991a) showed that Sr is also overbonded in both Ca sites, and to the greatest extent in Ca(1), by as much as 0.97 valence units. Thus, in competition for the Ca(2) site, Sr forces the *REE* into a Ca(1) equivalent, at least where Ca(2) is filled by Sr.

It is not clear that the Ca(2) site must be filled with Sr before the *REE* are ordered at Ca(1) equivalents. Concomitant with *REE* substitution is a charge-balancing Na substitution; in belovite, the *REE*–Na combination alters the $P6_3/m$ -equivalent Ca(1) sites to two non-equivalent sites in $P\bar{3}$, one to accommodate each of the substituents. We are planning synthesis experiments on Sr–*REE*–Na apatite to determine levels of codoping required to force the *REE* to occupy Ca(1) equivalents, and the effects of substituent level on emission characteristics in apatite-group phases.

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