Infrared Spectra of Calcium–Strontium Phosphate Apatites

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The ir spectra of calcium–strontium phosphate apatites were studied and the OH, PO_4, CO_3, and cation–oxygen fundamental frequencies were assigned. Furthermore, X-ray diffraction patterns were obtained and lattice parameters were calculated.

Introduction

In order to confirm the results advanced elsewhere (*1*), the series $Ca_{10-x}Sr_x$ $(PO_4)_6(OH)_2$ was studied in this paper by ir spectroscopy. Assignments of the OH, PO_4, and cation–oxygen vibrational bands were made.

Experimental

Samples of $Ca_{10-x}Sr_x(PO_4)_6(OH)_2$, where the compositional parameter x runs from 0 to 10, were synthesized using $Sr(NO_3)_2$ and $Ca(NO_3)_2$ according to the method described elsewhere (*2*). Mid-ir absorption spectra were recorded on a Perkin–Elmer 457 spectrophotometer, using the KBr disk technique. Deuteration was carried out by heating the samples in a glass at around 300°C in a D_2O atmosphere for 4 hr.

X-Ray diffraction patterns were obtained with a Philips PV 1130/00 diffractometer and PV 1050/20 goniometer with a Cu anticathode (40 kV, 20 mA).

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Results and Discussion

The results of chemical analysis of the samples are given in Table I. The values of the metal/phosphorus ratios are consistent with the formation of homogeneous solid solution. This will be confirmed further by the ir absorption spectroscopy and X-ray diffractograms.

Infrared absorption spectra for $x = 2, 5, 8$ are shown in Fig. 1. The positions (in cm^{-1}) and assignments of the bands for all the samples are given in Table II.

OH Bands

The OH vibration band in all the spectra are situated in the region 3.500–3.600 cm^{-1}. That band appears as a symmetrical and generally narrow absorption, whose position is indicative of an OH lattice attractive interaction, which has been attributed to the existence of hydrogen bonding between the OH and the nearest Os of PO_4^{3-} ions (*3*).

It can be observed in Table II that the position of the $\nu_s(OH)$ mode increases continually with x. Over the complete range of x values this increase is comparable to the difference between the stretching frequen-

TABLE I

CHEMICAL ANALYSES OF CALCIUM–STRONTIUM HYDROXYLAPATITES: $Ca_{10-x}Sr_x(PO_4)_6(OH)_2$

		x								
		1	2	3	4	5	6	7	8	9
Ca/P	Theor.	1.50	1.33	1.17	1.00	0.83	0.67	0.50	0.33	0.17
	Exper.	1.51	1.34	1.17	1.00	0.83	0.68	0.51	0.33	0.16
Sr/P	Theor.	0.17	0.33	0.50	0.67	0.83	1.00	1.17	1.33	1.50
	Exper.	0.16	0.33	0.49	0.67	0.83	0.99	1.16	1.34	1.51

cies of the OH groups in $Ca_{10}(PO_4)_6$ $(OH)_2$ and $Sr_{10}(PO_4)_6(OH)_2$ (3572 and 3593 cm^{-1}, respectively). So, the interaction between the OH group and the crystal becomes weaker as the Sr amount in the structure increases.

However, these data do not allow one to ascertain the existence of an expansion of the $a(=b)$ unit-cell parameters with x, because the position of the OH ions with re-

spect to the reticular planes containing Ca^{2+} and/or Sr^{2+} could be random.

Since the libration band $\nu_t(OH)$ (4, 5) overlaps with those of the stronger ν_4 modes of PO_4^{3-} ions, except for $x = 1$ and 9, in which it is detected at 633 and 544 cm^{-1}, respectively, in order to know the position of the libration band for $1 < x < 9$ deuteration was carried out on each sample.

Figure 2 shows the spectral regions of in-

TABLE II

FREQUENCIES (IN cm^{-1}) AND ASSIGNMENTS OF THE BANDS IN THE ir SPECTRUM OF $Ca_{10-x}Sr_x(PO_4)_6(OH)_2$

Mode	1	2	3	4	5	6	7	8	9
$\nu_3(PO_4)$	1091	1088	1088	1085	1085	1082	1082	1077	1080
	1070	1048	1060	1060	1057	1055	1055	1040	1040
	1030	1028	1025	1024	1025	1020	1020	1027	1030
$\nu_1(PO_4)$	962	958	960	955	954	952	951	949	977
									952
$\nu_4(PO_4)$	603	600	600	600	600	599	600	599	597
	580	575	580	580	580	575	575	575	575
	572	570	570	570	570	566	566	567	565
$\nu_2(PO_4)$	475	472	472	468	468	465	462	462	466
	460	460	460	460	460	460	455	455	455
$\nu_s(OH)$	3579	3580	3581	3583	3585	3587	3588	3591	3593
$\nu_t(OH)$	633								544
$\nu(CO_3)$	~1450	~1465?		1465	1465	1470		1465	
		1445		1450	1450			1445	
	~1415	1415		1415	1415	1415		1415	
		~880		~880	875	~875		~875	
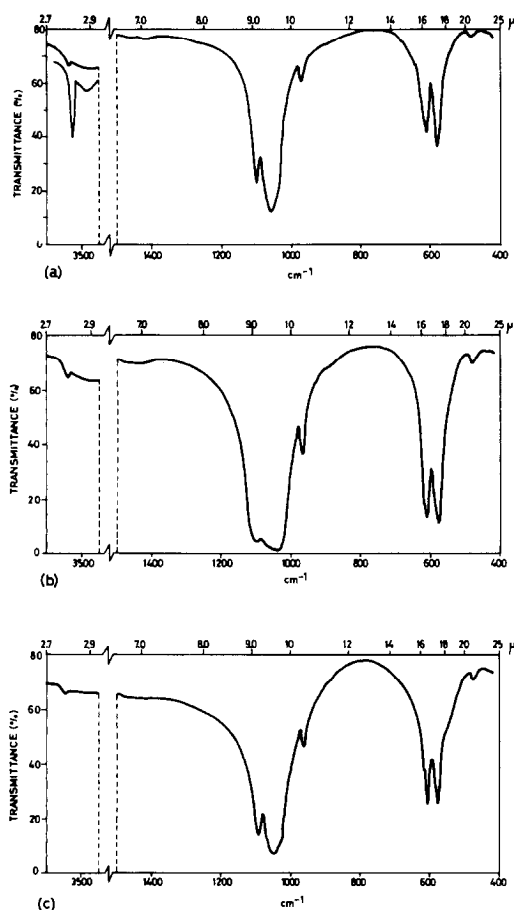
FIG. 1. Infrared spectra of $Ca_{10-x}Sr_x$ $(PO_4)_6(OH)_2 \cdot$ (a) $x = 2$, (b) $x = 5$, (c) $x = 8$.

TABLE III

LIBRATIONAL FREQUENCIES (cm^{-1}) OF THE OH AND OD GROUP IN CALCIUM–STRONTIUM HYDROXYLAPATITES

x	$\nu_L(OH)^a$	$\nu_L(OD)$
1	610	455
2	610	455
3	596	445
4	559	417
5	552	412
6	545	407
7	543	405
8	539	402
9	539	402

^{a} These values are calculated from the rate $\nu_L(OH)/\nu_L(OD) = 1.34$.

except for $x = 9$. This decreasing indicates that the hydrogen bond formed between the OH group and the nearest PO_4^{3-} ions becomes weaker as the Sr amount rises, which is in agreement with the observed values of $\nu_s(OH)$ frequencies.

From the above analysis of the $\nu_s(OH)$ and $\nu_t(OD)$ absorptions it is not possible to confirm with full certainty the results advanced elsewhere (1) with respect to the process of cationic migration. However, the fact that the bands $\nu_s(OH)$ and $\nu_t(OD)$

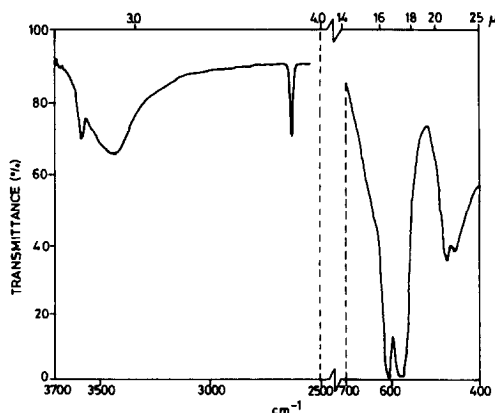terest for the sample $x = 2$, partially deuterated. The remaining compounds show a similar behavior. It can be observed that: (i) the absorption at 3580 cm^{-1} is maintained while the band $\nu_s(OD)$ appears at 2642 cm^{-1}, and (ii) the existence of a new band at 455 cm^{-1} which has no correspondence in the ir spectrum of the undeuterated sample.

In Table III we give the frequencies associated with the librational mode of the OH and OD groups in calcium–strontium hydroxylapatites. The values of the OH torsional frequencies were calculated using the frequency ratio $\nu_t(OH)/\nu_t(OD) = 1.34$ (1). It can be seen how $\nu_t(OH)$ decreases with x

FIG. 2. Infrared spectrum of $Ca_8Cr_2(PO_4)_6(OH)_2$ partially deuterated.

are symmetric in these heterocationic compounds points toward the possibility the such a process may take place. Dynamic proofs are necessary in order to ratify this hypothesis.

PO_4 Bands

The assignments of the fundamental modes of PO_4 anions are given in Table II. In all the cases, except for $x = 9$, we detect three ν_4 modes, three ν_3 modes, two ν_2 modes, and one ν_1 mode. As a consequence, for Ca–Sr hydroxylapatites, the PO_4^{3-} ions belong to the C_s point group as observed in the separate hydroxylapatites of Ca and Sr (5). However, for resolving the two ν_2 modes, it has been necessary to make highly concentrated absorption cells.

For $x = 9$, two ν_1 modes at 979 and 959 cm^{-1} can be detected. This suggests that the PO_4^{3-} ions are perturbed by two fields of different strength.

CO_3 Bands

The group of bands around 1400 cm^{-1} must be attributed to vibrations of CO_3^{2-} ions, probably introduced during the process of synthesis.

An explanation of this phenomenon may be offered: The pH required for the formation of stoichiometric apatites is very high and decreases locally when the compound is formed. Consistently, for pure calcium phosphate apatites, the PO_4^{3-} and OH^- ions are replaced by PO_4H^- and H_2O, respectively (6). However, this is not the case for Sr apatites (7), where stabilization is reached by incorporating CO_3^{2-} ions instead of the monoacid phosphates. In the present cases, we think that the positions occupied by the CO_3^{2-} ions inside the structure are close to those of AB carbonate apatite.

Ca–O and Sr–O Bands

The group of bands situated between 400 and 250 cm^{-1} could be tentatively attributed to either Ca–O and Sr–O stretching mo-

FIG. 3. Cation–oxygen stretching bands for: (a) $x = 2$, (b) $x = 5$, (c) $x = 8$.

FIG. 4. Cation–oxygen stretching bands for: (b) $Ca_5Sr_5(PO_4)_6(OH)_2$, (d) $Ca_5Sr_5(PO_4)_6F_2$.

$(PO_4)_6F_2$ and $Ca_5Sr_5(PO_4)_6(OH)_2$. It can be observed that, except for the absorptions near 250 cm^{-1}, all the bands disappear as fluorine is introduced in the structure. In this way, it can be affirmed that these bands correspond to vibrations Sr–O and Ca–O, or more concretely, M_3O, where the oxygen atoms belong to the OH groups and M may be Ca or Sr. The bands at around 250 cm^{-1} in the unfluorinated spectrum should be assigned to lattice vibrations.

Approximate positions of the most apparent M_3O bands are given in Table IV.

Cations in the apatitic lattice display as shown in Fig. 5 (8–11). The cations and the oxygen involved in the resulting M_3O vibrations around 300 cm^{-1} must be situated on the same τ plane, since any other relative situation would yield much lower stretching frequencies. The group M_3O (M being Ca and/or Sr) originates either one symmetric and one antisymmetric stretching band (whenever the Ms are either all Ca or all Sr), or one symmetric and two antisymmetric stretching bands in any other case.

The cation distribution in planes σ and τ of Fig. 5 can be deduced from spectral analysis on the grounds that the unit cell is formed by two τ planes and one σ plane.

Lattice Parameters

X-Ray diffraction patterns of $Ca_{10-x}Sr_x$ $(PO_4)_6(OH)_2$ show (Fig. 6) that the samples

tions or lattice vibrations (Fig. 3) (5). In order to decide which of these two assignments holds true in our cases, we operated in the two following ways: (a) under deuteration, the position of the different bands undergoes small displacements (around 10 cm^{-1}); this suggests that these vibrations are associated to systems containing protons; (b) definitive evidence is obtained from the ir spectra of the fluorinated samples. Figure 4 shows the spectral region 400–250 cm^{-1} for the samples Ca_5Sr_5
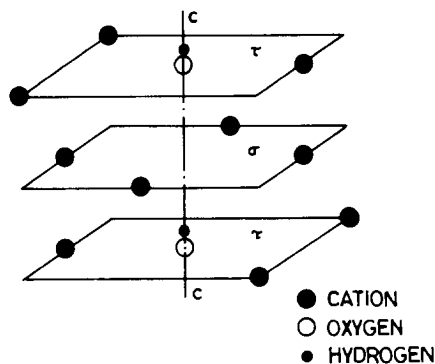

FIG. 5. Cation distribution in the apatitic unit cell.

TABLE IV

FREQUENCIES (cm^{-1}) OF THE CATION–OXYGEN VIBRATIONS AND LATTICE BANDS OF $Ca_{10-x}Sr_x(PO_4)_6(OH)_2$

Mode	0^a	1	2	3	4	5	6	7	8	9	10^a
$\nu(CaO)$				360	375	355	345	340	337	334	323
	~355 sh	350	350	345	350	345					
	343	335	335	335	335	332	333	333			
						320?	320	320	320?		
			310	308	307				308	308	
$\nu(SrO)$		295	295	295	290	293	290	294		294	
		280	284	283	275	283	283	283	283	283	
		275		270	270	273	271	270	265	270	
Lattice vibration		260	260	260	258	260	258	258	258	260	
		255	253	253	253	250	250	253	252	255	

^{a} Data drawn from (4).

are well crystallized and possess a line distribution typical of the apatitic compounds, so that these compounds form a solid solution in which a given proportion of Sr replaces an equal proportion of Ca.

Table V gives the lattice parameters of these apatites derived from the X-ray diffraction data.

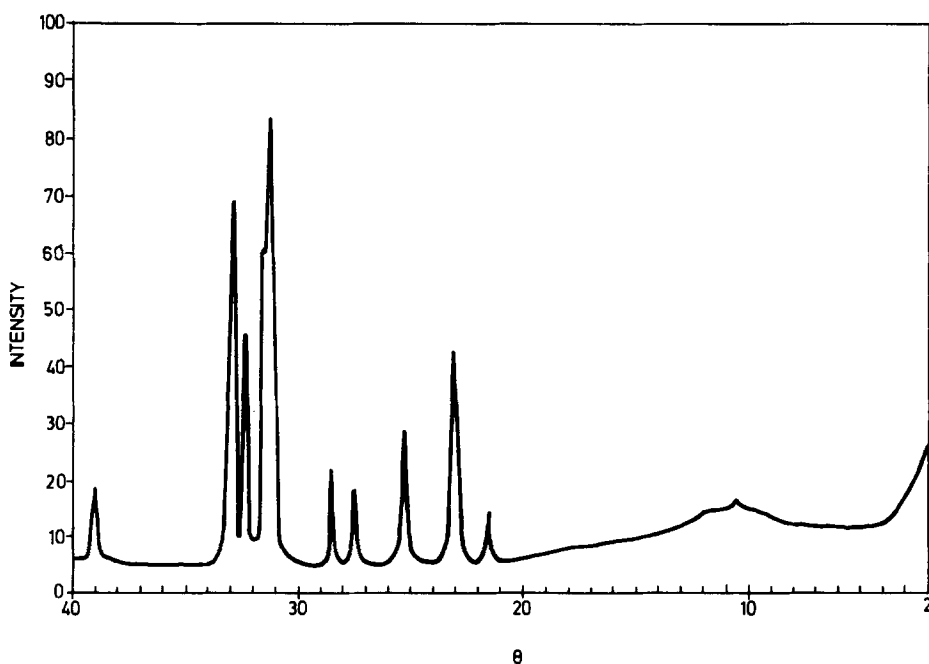An expansion of the unit cell is observed as x increases. This expansion is faster

FIG. 6. X-Ray diffraction pattern of $Ca_5Sr_5(PO_4)_6(OH_2)$.

TABLE V

Lattice Parameters (Å) for
Calcium–Strontium Apatites
$Ca_{10-x}Sr_x(PO_4)_6(OH)_2$

x	c	a(=b)	c/a	V (Å³)
1	6.91(6)	9.44(1)	0.73(3)	533.(8)
2	6.94(5)	9.45(4)	0.73(5)	537.(5)
3	6.99(4)	9.51(1)	0.73(5)	547.(9)
4	7.04(0)	9.56(2)	0.73(6)	557.(4)
5	7.08(7)	9.57(7)	0.73(9)	562.(1)
6	7.11(2)	9.62(6)	0.73(9)	570.(7)
7	7.14(8)	9.65(0)	0.74(1)	576.(4)
8	7.19(5)	9.67(3)	0.74(4)	583.(0)
9	7.23(1)	9.72(4)	0.74(4)	592.(0)

along the c axis than along the a axis, being in agreement with the largest ionic radius of strontium and with the decrease of the ν_1, $\nu_3(PO_4)$ frequencies as x increases.

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