# NOTES

Is There a Continuous Cation Migration in Calcium–Strontium Hydroxyapatites?

Heijligers et al. (1) have recently reported evidence for an expansion of the unit cell of stoichiometric calcium hydroxyapatite when strontium is included in the apatitic lattice. In this note we study the infrared spectra of the same series as worked out by Heijligers et al., i.e.,

$$Ca_{10-x}Sr_x(PO_4)_6(OH)_2,$$
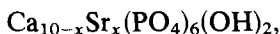
where the compositional parameter x runs from 0 to 10.

Syntheses were made 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. Absorption cells were built up using the KBr disk technique. Deuteration was carried out by heating the samples at around 300°C in a D_2O atmosphere.

In Table I we give the values of the frequencies associated with the ir OH bands in each of the compounds we have

synthesized. The OH groups in apatites possess two bands: one originating from the OH stretching vibration, and the other associated with the librational vibration arising from the hindered rotation of the OH group around the c apatite axis (3). As in the compounds we are dealing with, the librational bands overlap with those of the stronger ν_4 modes of the PO_4^{3-}, in order to detect these bands, deuteration was carried out on each sample. The values of the OH librational frequencies in the table have been calculated in the following way: we have first recorded the ir spectra of a series of apatites in which the librational band of the OH group does not overlap with the ν_4-PO_4 modes; by measuring then the librational frequency of the OD group in these apatites, it has been possible to find the frequency ratio $\nu_{LOH}/\nu_{LOD} = 1.34$ which is practically constant in all the tested samples. Assuming then this ratio to hold also in the calcium–strontium apatites, the ν_{LOH} frequencies in the ir spectra of these last compounds were immediately computed.

Since the OH groups in apatites form linear hydrogen bonds with the nearest oxygen belonging to the surrounding PO_4 groups (4), the increase of the $\nu_s(OH)$ frequency with the value of x is indicative of an expansion of the a and b unit-cell parameters which was noted by Heijligers et al. (1). The decrease of the ν_{LOH} frequency with the increase of x is also concordant with this kind of lattice effect, provided that the libration of the OH is associated with an OH hindered rotation.

TABLE I

STRETCHING AND LIBRATIONAL FREQUENCIES OF THE OH GROUP IN CALCIUM–STRONTIUM HYDROXYAPATITES[a]

x	$\nu_s(OH)$	$\nu_s(OD)$	$\dfrac{\nu_s(OH)}{\nu_s(OD)}$	$\nu_L(OH)$	$\nu_L(OD)$
2	3580	2642	1.355	610	455
4	3583	2644	1.355	559	417
5	3585	2645	1.355	552	412
6	3587	2647	1.355	545	407
8	3595	2651	1.356	537	402

[a] All the frequencies in the table are given in cm^{-1} and were measured using the OH standard frequency of $Ca(OH)_2$ which is situated at $3644\ cm^{-1}$.

It is worth noting the presence in Table I of only one OH stretching band and only one librational band for the OH group. This is indicative of an isotropic distribution of Ca and Sr throughout the apatite lattice. Any distribution in which the Ca and/or Sr cations would be independently ordered would give rise to the existence of more than one $\nu_s(OH)$ band (and, consequently, more than one ν_{LOH} band). However, the distribution of cations, whatsoever it is, cannot be static because, if so, one would also obtain two or more ir OH stretching bands and two or more ir OH librational bands. We suggest then the existence of a continuous migration mechanism for the cations in such a way that the OH groups in the lattice encounter along their rotation motion a fully symmetric three-degenerated itinerary in all the cases. This requires simultaneous migrations of both the Ca and Sr cations from one reticular plane to another and, at the same time, migrations of the same cations between different positions belonging to the same reticular plane. This mechanism is certainly related to the equilibrium $Ca(I) + Sr(II) \rightleftarrows Ca(II) + Sr(I)$ stated by Heijligers et al. (1), so that the final conclusion that may be drawn from the present ir data is that the solid solutions of calcium–strontium apatites are close to ideal in the thermodynamical sense, as was found from X-ray diffraction measurements.

References

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