

Theoretical study of thermodynamic mixing properties and local structure of $(\text{Ca,Sr})_{10}[\text{PO}_4]_6\text{F}_2$ solid solution

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Apatite is a common phosphate mineral of industrial importance, typical for igneous, sedimentary and metamorphic rocks. Cation substitution and isomorphism are distinctive characteristics of all naturally occurred minerals. Natural fluorapatite includes Sr^{2+} , Ba^{2+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , Pb^{2+} , etc. as impurities of Ca^{2+} ions. Presence of substituent influences structural parameters and physical properties of minerals and as a result their possible applications. In addition to well known apatite applications in fertilizing soils and catalysis [1], this mineral is also considered to be a good candidate for radioactive waste immobilization [2], in which various foreign cations play an important role.

Fluorapatite crystallizes in the hexagonal system $P6_3/m$. There are two distinct cation sites: 9-fold coordinated $4f$ site (M1) and 7-fold coordinated $6h$ one (M2). While the M1 cation associates only with oxygen atoms, the cation M2 has six bonds with oxygen atoms and one bond with a fluorine anion. There were numerous contradictory experimental [3, 4, 5, 6] and theoretical [7] results concerning the distribution of substituent over M1 and M2 sites in mixed calcium strontium apatite.

Our work is focused on theoretical investigation of thermodynamic mixing properties of $(\text{Ca,Sr})_{10}[\text{PO}_4]_6\text{F}_2$ solid solution and thorough analysis of its local structure. The distribution of Sr and Ca over M1 ($4f$) and M2 ($6h$) cation sites and its influence on thermodynamic and structural parameters are considered in particular. The thermodynamic mixing properties were computed for $4 \times 4 \times 4$ supercell (2688 atoms) within the semi-empirical approach using previously elaborated interatomic potentials [8]. The calculations were carried out with the program GULP [9] using the high-performance computer at Moscow State University [10].

The mixing properties were calculated over the entire range of compositions for six different $4f:6h$ site ratio of occupancy by Sr cations. According to the obtained thermodynamic data, 7-fold coordinated $6h$ site is more preferable for large Sr cations. The compounds with the most energetically preferable ratio were used for further simulations. In order to analyze the local structure of fluorapatite solid solution in detail, distribution histograms of M-O and M-F interatomic distances and coordination polyhedron volumes were plotted. The distribution of Sr2-F bond lengths in the investigated solid solution turned out to be deviant. Instead of expected decrease of Sr2-F bonds, their average value in solid solution tends to be higher than in pure Sr-apatite compound.

Undertaken analysis of bond sums backed up the preference for Sr ions to occupy smaller sized $6h$ sites. Strontium ions at geometrically larger $4f$ sites are found to be over bonded (their bond valence sums are greater than the formal charge of Sr ion). Moreover influence of second coordination sphere on Ca and Sr cations furthers ordering of higher charged Sr into $6h$ site. M1 and M2 cations are surrounded by six and five P^{5+} ions respectively. Thus being over bonded at M1 site and surrounded by six high charged P^{5+} , Sr ions preferentially occupy M2 position. This preference is in agreement with the experimental studies [6].

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