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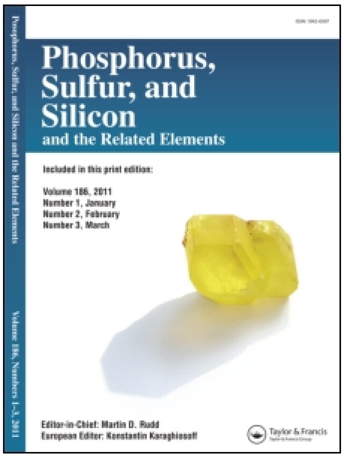

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Cation Distribution Studies in Double Orthophosphates with Whitlockite Structure

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CATION DISTRIBUTION STUDIES IN DOUBLE ORTHOPHOSPHATES WITH WHITLOCKITE STRUCTURE

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The structure of β-$Ca_3(PO_4)_2$ is known to be similar to that of whitlockite (R3c, Z = 21). The cations are distributed in five different positions, the position Ca(4) being only half occupied. The whitlockite network is stable while the filling of the Ca(4) position changes from 0 to 1. The presence of vacancies allows to provide heterovalent substitutions $3Ca^{2+} = 2M^{3+} + \square$ and $Ca^{2+} + \square = 2Me^{+}$ with limits of compositions $Ca_9M\square(PO_4)_7$ and $Ca_{10}Me(PO_4)_7$ respectively. The possible cation size can be changed from 0.55 Å (Fe^{3+}) to 1.51 Å (K^+). In order to check these suggestions we have synthesized $Ca_9M(PO_4)_7$ (M = rare earth element, Y, Bi, Fe, Al, In, Sc) compounds. The double phosphates were studied by luminescence, infrared spectroscopy and X-ray diffraction. All these compounds are isostructural to β-$Ca_3(PO_4)_2$. The cell parameters gradually decrease for M = La - Ho, Y and remain constant for M = Er - Lu. This divergence can be attributed to the change of the coordination number of the rare earth element. A considerable decrease of parameters is observed for the compounds of small-size trivalent elements, their IR spectra show more bands. By luminescence it was found that rare earth elements and Y, Bi occupy Ca(1), Ca(2), Ca(3) positions. The study of $Ca_{9.18}Fe_{0.88}(PO_4)_7$ structure shows that Fe^{3+} occupies octahedral Ca(5) site. The considerable decrease of lattice parameters and changes in IR spectra of compounds with M = Fe, Al, In, Sc result from the occupation of Ca(5) site with trivalent cations and from redistribution of charges in the cation sublattice of the β-$Ca_3(PO_4)_2$ type structure.