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A. A. Belik^a; F. Izumi^a; B. I. Lazoryak^b; S. Yu. Stefanovich^b; T. Kamiyama^c; K. Oikawa^c

^a National Institute for Materials Science, Japan ^b Moscow State University, Russia ^c Institute of Materials Structure Science, Japan

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STRUCTURE AND PROPERTIES OF $\text{Ca}_9\text{FeD}(\text{PO}_4)_7$

A. A. Belik,^a F. Izumi,^a B. I. Lazoryak,^b S. Yu. Stefanovich,^b
T. Kamiyama,^c and K. Oikawa^c

National Institute for Materials Science, Japan,^a Moscow State
University, Russia;^b and Institute of Materials Structure
Science, Japan^c

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A new phosphate, $\text{Ca}_9\text{FeD}(\text{PO}_4)_7$, with a whitlockite-like structure was synthesized from $\text{Ca}_9\text{Fe}(\text{PO}_4)_7$ by reducing it in D_2 at 820 K. Its structural, physical, and chemical properties were studied by X-ray and neutron diffraction, IR and Mössbauer spectroscopy, second harmonic generation, and thermal analysis in different atmospheres. Neutron diffraction experiments at 10 K (space group $R\bar{3}c$; $a = 10.3505(1)$ Å and $c = 37.0420(3)$ Å) and 300 K (space group $R\bar{3}c$; $a = 10.3691(1)$ Å and $c = 37.1291(3)$ Å) made it possible to locate D atoms and propose a mechanism of reducing $\text{Ca}_9\text{Fe}(\text{PO}_4)_7$. Its reduction accompanies changes in orientation of PO_4 tetrahedra and formation of O11–D–O21 bonds with distances of 0.976(9) Å and 1.754(10) Å, respectively. Mössbauer spectroscopy indicated that $\text{Ca}_9\text{FeD}(\text{PO}_4)_7$ contains only Fe^{2+} ions. The IR spectrum of $\text{Ca}_9\text{FeD}(\text{PO}_4)_7$ showed a broad absorption band due to O–D stretching at 2240 cm^{-1} in addition to P–O stretching and bending bands in a wavenumber range of $450\text{--}1700\text{ cm}^{-1}$. Second harmonic generation in $\text{Ca}_9\text{FeD}(\text{PO}_4)_7$ ($I_{2\omega}/I_{2\omega}(\text{SiO}_2) \approx 0.15$) was by an order of magnitude less than that in $\text{Ca}_9\text{Fe}(\text{PO}_4)_7$ ($I_{2\omega}/I_{2\omega}(\text{SiO}_2) \approx 2.5$). $\text{Ca}_9\text{FeD}(\text{PO}_4)_7$ was stable in an Ar atmosphere up to 840 K. Above this temperature, it decomposed to a whitlockite-like phase and $\text{Ca}_2\text{P}_2\text{O}_7$ with releasing D_2O and without changing the oxidation state of Fe. In air, $\text{Ca}_9\text{FeD}(\text{PO}_4)_7$ lost D_2O without destruction of the whitlockite-like structure to form $\text{Ca}_9\text{Fe}(\text{PO}_4)_7$.

Address correspondence to F. Izumi, Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
E-mail: Izumi.Fujio@nims.go.jp