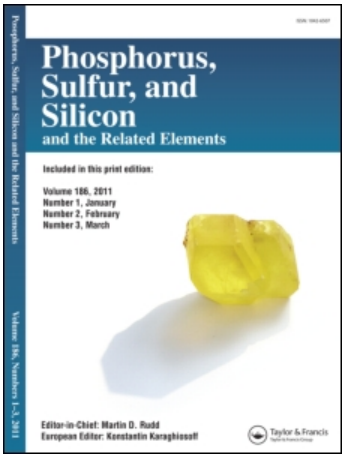

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Online publication date: 27 October 2010

To cite this Article Belik, A. A. , Izumi, F. , Lazoryak, B. I. , Stefanovich, S. Yu. , Kamiyama, T. and Oikawa, K.(2002) 'Structure and Properties of Ca 9 FeD(PO 4) 7', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 8, 2233
To link to this Article: DOI: 10.1080/10426500213363
URL: http://dx.doi.org/10.1080/10426500213363

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:2233

1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290095278

STRUCTURE AND PROPERTIES OF $Ca_9FeD(PO_4)_7$

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(Received July 29, 2001; accepted December 25, 2001)

Keywords: Crystal structure; deuterium; neutron diffraction; tricalcium phosphate; whitlockite

A new phosphate, $Ca_9FeD(PO_4)_7$, with a whitlockite-like structure was synthesized from $Ca_9Fe(PO_4)_7$ 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 $R3c$; $a = 10.3505(1)$ Å and $c = 37.0420(3)$ Å) and 300 K (space group $R3c$; $a = 10.3691(1)$ Å and $c = 37.1291(3)$ Å) made it possible to locate D atoms and propose a mechanism of reducing $Ca_9Fe(PO_4)_7$. Its reduction accompanies changes in orientation of $P1O_4$ 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 $Ca_9FeD(PO_4)_7$ contains only Fe^{2+} ions. The IR spectrum of $Ca_9FeD(PO_4)_7$ 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 450–1700 cm^{-1}. Second harmonic generation in $Ca_9FeD(PO_4)_7$ ($I_{2\omega}/I_{2\omega}(SiO_2) \approx 0.15$) was by an order of magnitude less than that in $Ca_9Fe(PO_4)_7$ ($I_{2\omega}/I_{2\omega}(SiO_2) \approx 2.5$). $Ca_9FeD(PO_4)_7$ was stable in an Ar atmosphere up to 840 K. Above this temperature, it decomposed to a whitlockite-like phase and $Ca_2P_2O_7$ with releasing D_2O and without changing the oxidation state of Fe. In air, $Ca_9FeD(PO_4)_7$ lost D_2O without destruction of the whitlockite-like structure to form $Ca_9Fe(PO_4)_7$.

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