Dixenite, Cu$^{1+}$Mn$^{2+}_{14}$Fe$^{3+}_{3}(\text{OH})_{6}(\text{As}^{5+}O_{3})_{5}(\text{Si}^{4+}O_{4})_{2}(\text{As}^{3+}O_{4})_{2}$: metallic [As$^{3+}$Cu$^{1+}$] clusters in an oxide matrix

Takaharu Araki and Paul B. Moore

Department of the Geophysical Sciences
The University of Chicago, Chicago, Illinois 60637

Abstract

The crystal structure of dixenite was analyzed using a crystal from the type and sole locality at Långban, Sweden. The end-member formula Cu$^{1+}$Mn$^{2+}_{14}$Fe$^{3+}(\text{OH})_{6}(\text{As}^{5+}O_{3})_{5}(\text{Si}^{4+}O_{4})_{2}(\text{As}^{3+}O_{4})_{2}$ is proposed. Dixenite is rhombohedral, $a = 8.233(4)$, $c = 37.499(1)$Å, space group $R3$, $Z = 3$. Twenty-eight atoms occur in the asymmetric unit including two disordered Cu$^{1+}$ cations, $R = 0.064$ for 2507 independent reflections.

The structure is related to but distinct from that of hematolite, (Mn$^{2+}$,Mg,Al)$_{15}$ (OH)$_{23}$(AsO$_4$)$_6$(AsO$_4$)$_2$. Three kinds of anionic radicals occur: (As$^{5+}O_4$)$_{3}$ trigonal pyramids; and (Si$^{4+}O_4$) and (As$^{5+}O_4$) tetrahedra. Three of the five nonequivalent layers along [001] are similar in hematolite and dixenite. One layer in dixenite, however, contains a disordered cluster, idealized as [Cu$^{1+}$As$^{3+}_2$] where a tetrahedron of As$^{5+}$ ions surrounds a Cu$^{1+}$ ion. All lone pair electrons from As$^{3+}$ point into the central cavity which houses Cu$^{1+}$(d$^{10}$) and this cluster is believed to be stabilized by the 18-electron rule where Cu$^{1+}$As$^{3+}_2$ forms a closed argon core.

Introduction

Dixenite is a rare mineral, originally described by Flink (1920) from the mineralogically complex Fe–Mn oxide ore deposit in Långban, Sweden. The mineral was long problematical: Wickman (1951) proposed the formula (Mn,Fe,Cu,As$^{3+})_{10}$(Si,As$^{5+})_3$(O,OH)$_{32}$. Wuenisch (1960) presented a relationship to the complex arsenosicate mcovernite, and Moore and Araki (1978) proposed Mn$^{2+}$, Mn$^{4+}$ (OH)$_6$(AsO$_4$)$_6$(SiO$_4$)$_2$ and a model for the structure derived from hematolite, (Mn$^{2+}$,Mg,Al)$_{15}$(OH)$_{23}$(AsO$_4$)$_6$(AsO$_4$)$_2$ to which it shares similarities in cell parameters and space group.

We studied dixenite’s structure in hopes of gathering more clues about the structure of mcovernite, and discovered several unusual features, including incorrectness of the proposed structure of Moore and Araki (1978), the presence of [As$^{5+}Cu^{1+}$] metal clusters, the occurrence of As$^{3+}O_3$ trigonal pyramids, and solid solution between As$^{3+}$ and Si$^{4+}$ in tetrahedral oxygen coordination.

Experimental details

On the basis of a relationship to hematolite, kraiisslite and mcovernite (Moore and Ito, 1978) we suspected that platy deep red-brown crystals of dixenite from the only recorded locality at Långban, Sweden may in fact consist of more than one structure or polypeptide. Our dixenite sample selected for this structure study was NMNH No. C-6440. We also examined Nos. B-20579, 94920, 94935 and R-5755 (all in the U.S. National Museum of Natural History) by X-ray study and found all of them to be identical. We thank Mr. John S. White, Jr. for permission to select fragments of these specimens. The crystal selected was a deep red plate measuring 0.18 mm $\parallel a_1 \times 0.23$ mm $\parallel a_2 \times 0.06$ mm $\parallel c$. With $\mu = 132.1$ cm$^{-1}$ (MoK$\alpha$), seven divisions by the Gaussian integral method (Burnham, 1966) led to significant absorption corrections, ranging from 0.148 for low angle (001) reflections to 0.458.

Cell data were obtained from calibrated precession photographs (MoK$\alpha$ radiation) and yielded $a = 8.233(4)$, $c = 37.499(1)$Å, Laue symmetry 3. Intensities were collected on a PALLRED semi-automated diffractometer with the $a_2$-axis $\parallel$ rotation and with graphite monochromatized MoK$\alpha$ radiation. Background counting time on each side of the peak was 20 sec, scan speed 1°min$^{-1}$, scan width 4.0° to 4.8°. Angular coverage maximum was $\sin \theta/\lambda = 0.80$, the