Structure of synthetic Li$_2$(Mg,Cu)Cu$_3$[Si$_2$O$_6$]: A unique chain silicate related to pyroxene

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ABSTRACT

A unique Cu-bearing chain silicate, Li$_2$(Mg,Cu)Cu$_3$[Si$_2$O$_6$], was synthesized, and the structure was determined by single-crystal X-ray diffraction techniques. The structure was found to be triclinic, space group $P1$, with unit-cell parameters $a = 5.7068(7)$, $b = 7.4784(9)$, $c = 5.2193(3)$ Å, $\alpha = 99.911(8)$, $\beta = 97.436(8)$, $\gamma = 84.52(1)^\circ$, and $Z = 1$. The arrangement of two single chains, [Si$_2$O$_6$], differs significantly from chain arrangements in the pyroxene and pyroxenoid structures, and the “I-beam” description of the pyroxene structure is not applicable. The structure may be classified as a new derivative type of the pyroxene structure, with an “oblique I-beam”. Cu atoms are coordinated by four O atoms in a square-planar arrangement with 1.94–2.00 Å for Cu-O and two O atoms with longer Cu-O distances of 2.41–2.92 Å, consistent with the crystal-field stabilization of the $d^9$ electronic structure of Cu$^{2+}$. The square-planar CuO$_4$ units form a [CuO$_{n=2}$] ribbon with $n = 3$ in the structure, which is also found in Cu-bearing chain silicates such as shattuckite and plancheite with $n > 3$. Mg is octahedrally coordinated by O atoms, but the configuration is affected by the partial replacement by Cu.

INTRODUCTION

Co- and Ni-bearing silicates have been studied mainly for the purpose of simulating the structural behavior of ferromagnesian silicate minerals under the high-temperature and high-pressure conditions prevailing in the Earth’s interior. However, the crystal-chemical behavior of Cu-bearing silicates is different, possibly because of the electronic configuration of Cu$^{2+}$. Most of these naturally occurring minerals are hydrous or hydrated silicates and some are chain silicates. The following are examples of Cu-bearing chain silicates that have chain structures: shattuckite, Cu$_2$[Si$_2$O$_6$](OH)$_2$ (Mrose and Vlisdis 1966; Kawahara 1976; Evans and Mrose 1966, 1977); plancheite, Cu$_3$[Si$_2$O$_6$](OH)$_2$·xH$_2$O (Evans and Mrose 1966, 1977); and liebauite, Cu$_2$Cu$_2$[Si$_2$O$_6$] (Zöller et al. 1992). Liebauite is one of the few anhydrous Cu-bearing minerals. The layer silicate cuprorivinite, CaCu[Si$_2$O$_6$] (Mazzi and Pabst 1962), is another example of a natural anhydrous Cu-bearing phase. On the other hand, most synthetic Cu-bearing chain silicates are anhydrous. Typical examples include Na$_2$Cu$_2$[Si$_2$O$_6$] (Kawamura and Kawahara 1976), Na$_2$Cu$_2$[Si$_2$O$_6$] (Kawamura and Kawahara 1977), CuMg[Si$_2$O$_6$] (Breuer et al. 1986), and CaBa$_2$Cu[Si$_2$O$_6$] (Angel et al. 1990). However, synthetic Cu-bearing chain silicates related to pyroxene are rare in comparison with silicates containing Co, Ni, or Zn (e.g., Morimoto et al. 1970, 1974, 1975). Nevertheless, knowledge of the phase stabilities and Cu configurations of Cu-bearing silicate structures is important for understanding the mineralogy and geochemistry of transition metals.

Examples of Cu-bearing silicates with single-chain structures are also quite rare. The mineral shattuckite and synthetic CuMg[Si$_2$O$_6$] and Na$_2$Cu$_2$[Si$_2$O$_6$] are the only known examples. CuMg[Si$_2$O$_6$] was reported to be analogous to the clinopyroxene structure with space group $P2_1/c$, with an ordered arrangement of Mg and Cu as determined by the semiquantitative comparison of observed and calculated X-ray powder diffraction intensities (Breuer et al. 1986). However, the detailed structure is unknown. The configuration of the [Si$_2$O$_6$] chain of shattuckite is similar to that of pyroxene with straight chains, but the cation arrangement is different from that of pyroxene. The structure of plancheite is a derivative structure of shattuckite but with amphibole-type double chains instead of single chains. The [Si$_2$O$_6$] unit of Na$_2$Cu$_2$[Si$_2$O$_6$] is a single chain; however, it is different from that of pyroxene but similar to that of haradaite (Takéuchi and Joswig 1967).

Thus, Cu-bearing pyroxene or pyroxene-derivative structures are very rare, even though the ionic radius of Cu$^{2+}$ is similar to that of other transition metal ions. In the present paper, a new Cu-bearing silicate structure with straight single chains is described and the crystal-chemical behavior of Cu$^{2+}$ in the structure is discussed.

EXPERIMENTAL METHOD

Sample preparation and chemical analysis

The crystalline phase of Li$_2$(Mg,Cu)Cu$_3$[Si$_2$O$_6$] was synthesized in an oxide-flux mixture, which was primarily prepared for the synthesis of Cu-bearing pyroxene.