Lattice Constant of Digenite

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Digenite, $Cu_{1.8}S$, was first discovered by Buerger[1] in copper-sulfur system. The crystal structure of this phase is known as a cubic lattice of anti-fluorite type, in which half of the copper atoms are statistically distributed in the interstices of the sulfur atoms, forming so-called *averaged structure*[1,2]. Ramdohr[3] has thereafter discovered the naturally occurring mineral of this composition, and named it *Neodigenite*.

The Buerger's phase diagram of copper-sulfur system shows that the digenite phase has no range of solid solution at room temperature. However, some investigators[4] have maintained that this is not the case but that the digenite has some range of solid solution.

In this communication, the lattice constant of digenite at room temperature is measured using the samples of various compositions, and it is confirmed that the digenite has a range of solid solution.

The sample used was synthesized from electrolytic copper and thoroughly-distilled sulfur. The stoichiometric Cu_2S and CuS were first prepared by heat-treatment of copper and a corresponding amount of sulfur sealed in a vacuum Pyrex tube for about two hundred hours at 400°C. Then, these materials were mixed in appropriate ratio, sealed in vacuum, and heat-treated by the same procedure as above, with gradual cooling to the room temperature. Thus the samples of desired compositions were obtained.

X-ray powder photographs were obtained for these samples using Straumanis-type camera of 90 mm. diameter and $CuK\alpha$ radiation. The line of (551) (711) is very suitable to determine the lattice constant, since its Bragg angle for $CuK\alpha$ is about 81°, although its intensity is very weak. Sometimes, (440) line was measured by focusing backreflection camera and $FeK\alpha$ radiation. The Bragg angle of this case is about 80°. As the wave lengths of X-rays, the values of Siegbahn's table[5] were used.

In the Figure, the lattice constants observed are plotted against the composition, and it is shown that these vary from 5.554 to 5.544 kX with the increase of sulfur content. The accuracy for the measurement of the lattice constant is estimated to be ±0.001 kX, and that of the composition to be ±0.2 atomic percent of sulfur.

From this result, it is obvious that the digenite has a range of solid solution, though it is relatively narrow, at room temperature. The range seems to cover the compositions from 35.7 to 36.1 atomic percent of sulfur, but more sufficient experimental points are necessary to determine it precisely. The fact

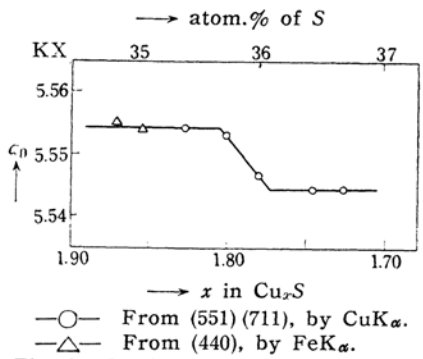

Fig. 1. Lattice constant of digenite.

that the lattice contracts when the atomic fraction of cation is decreased suggests that the variation of composition may be caused by the escape of cations from their lattice sites.

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