Compositional trends in hakite, possible discrepancies from ideal structure

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Stoichiometry and site occupancies of minerals of the tetrahedrite group was suggested by simplified general formula [1] – $^{[III]}A_6{}^{[IV]}(B,C)_6{}^{[III]}X_4{}^{[IV]}Y_{12}{}^{[VI]}Z$, where A = Cu, Ag; B = Cu, Ag and C is generally divalent metal (typically Fe, Zn but also Hg, Mn, Cd etc.) in the same coordination as B; X = Sb, As, Bi, Te; Y and Z = S and Se. Hakite is Se – dominant member of tetrahedrite group. Since the experimental determination of the hakite structure is lacking the structure model based on the crystal structure of tetrahedrite with fully substituted Y and Z sites was adopted. Studied samples of hakite were found in a rich paragenesis of Ag, Hg, Pb, Cu, Sb, Cd, Tl selenides and other minerals containing As, Te, Sb, and U at the new occurrence in Příbram (uranium-base metals ore district, Czech Republic). Amount of 69 microprobe (WDS) analyses on 11 individual samples were performed. Based on different substituents detected by the microprobe study, several types of hakite were determined. A position is represented by Ag and Cu contents. At the B site Cu and at the C site Hg, Zn and lower amounts of Fe and Cd occur (Table 1). X site was occupied by Sb, minor contents of As and trace amounts of Te were detected. S-Se substitution was ascertained according to the abundant association of sulphides.

Table 1: Content of elements in Příbram hakite based on 29 apfu

	B	C			
	Cu	*Cd*	*Zn*	*Hg*	*Fe*
	3,41-4,85	0-1,05	0,01-1,82	0,01-1,95	0-0,73
mean	4,31	0,16	0,60	1,19	0,06
	A		X		
	Cu	*Ag*	*Sb*	*As*	*Te*
	5,71	0,03-1,20	3,36 - 4,18	0 - 0,67	0-0,52
mean	5,71	0,29	3,90	0,15	0,07
	Y, Z				
	S	*Se*	sum of anions		
	0,01 - 4,52	8,00 - 12,75	12,28-13,19		
mean	1,35	11,20	12,55		

According to the Table 1, it is obvious that the sum of anions is deficient compared to the ideal structure model of tetrahedrite. Mean of anions sum of 17 wds analyses on coexisted tetrahedrite gave 12,89 apfu. In spite of the rarity and small grain size of hakite, several samples were prepared for the X-ray powder diffraction study. Compared to the theoretical diffraction patterns calculated from the crystal-structure data the observed patterns of the hakite samples exhibited few additional reflections probably of the superstructure character.

Based on the chemistry and XRD results, we suppose presence of structural disorder and distortions of the hakite lattice with respect to the idealized structure adopted from tetrahedrite.

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Structure of nagelschmidtite $Ca_7Si_2P_2O_{16}$

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The metallugical properties of steelmaking slags are influenced by the formation of silicophosphates in the binary $2CaO \cdot SiO_2$ (C2S) - $3CaO \cdot P_2O_5$ (C3P) system. Silicophosphates with high concentration of phosphate in the slag are important as lime- and phosphorus-containing fertilizer. Several phase diagrams for the C2S-C3P system are found in the literatures and a wide stability region of α-C2S and $\bar{\alpha}$-C3P solid-solutions was confirmed at high temperatures above 1450°C [1,2]. In this context, nagelschmidtite $[Ca_7Si_2P_2O_{16}]$ is generally inferred to be structurally similar to α-C2S [3]. Nevertheless, structural details of nagelschmidtite have not been revealed yet.

The single crystals of nagelschmidtite were prepared from a sintered pellet with the chemical composition $CaO:SiO_2:P_2O_5:Fe_2O_3$=49.2: 25.7: 12.0: 13.1mass%). The sintered sample was first melted at 1600°C and cooled down to 1400°C at a rate of 10°C/h. Almost colourless crystal ($P6_1$; a=10.82≈2*5.4Å, c=21.46≈7.1*3Å) could be selected and the structure was analyzed by the single crystal X-ray diffraction. The structure was solved by a combination of direct-methods and difference Fourier syntheses and Fig. 1 shows the obtained structural model. The structure is constructed by Ca layer and Ca-T layer similar to that of α-C2S. Ca vacant site due to the substitution of PO_4 for SiO_4 is ordered in the Ca-T layer. The arrangement of TO_4 units (T=Si and P) is similar to that found in α–, α'$_H$-, α'$_L$- and β-C2S structures.
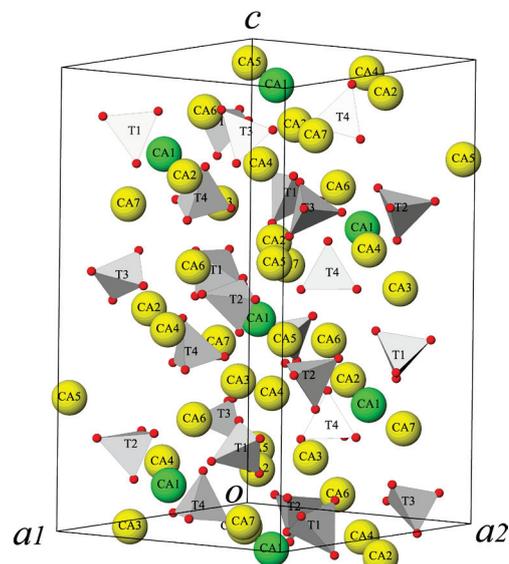
Fig. 1: Structure of nagelschmidtite $[Ca_7Si_2P_2O_{16}]$.

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