CHARACTERIZATION OF SYNTHETIC VOLTAITE ANALOGUES

István E. Sajó[a]

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Recently new NH_4- and Mg-containing minerals of the voltaite group have been discovered. As they were found in minute amounts and are intimately intergrown with their associated minerals, a number of their properties could not be measured and characterized properly. The four pure end members of the solid solution series were synthesized and characterized, that made possible the reliable identification of natural solid solutions within the boundaries of this phase composition range.

* Corresponding Authors
Fax: +36-1-3257554
E-Mail: sajo.istvan@ttk.mta.hu
[a] Institute of Materials and Environmental Chemistry, Research Center for Natural Sciences Hungarian Academy of Sciences, Pusztaszeri út 59-67. H-1025 Budapest, Hungary

Introduction

Voltaite, $K_2Fe^{2+}{}_5Fe^{3+}{}_3Al[SO_4]_{12}\cdot 18H_2O$, an inorganic framework structure featuring a large cubic unit cell (space group Fd3c) occurs as a mineral[1]. Due to the large unit cell size (a_0 ~ 27.25 Å) the structure is not highly sensitive to cationic sizes. Substitution at the K^+ and Fe^{2+} sites results in a variety of structural analogues with similar cell constants[2]

The newly discovered ammoniomagnesiovoltaite $(NH_4,K)_2(Mg,Fe^{2+})_5Fe^{3+}{}_3Al[SO_4]_{12}\cdot 18H_2O$[3] is a rare mineral intimately intergrown with its associated minerals (eg tschermigite, sabieite, kieserite, etc.). Therefore preparation of phase pure natural specimens was not feasible for the necessary investigations. Having a cubic structure, its unit cell is characterized with a single a_0 cell parameter, resulting in powder diffraction data insufficient for the extraction of two compositional coordinates. Additionally the synthetic analogues were characterized with their IR spectra, density and index of refraction.

Materials and methods

Synthesis: Voltaite analogues were prepared according to Mereiter.[4] Strongly acidic solution of the appropriate salts was prepared with the molar ratio $K_2SO_4 : FeSO_4 : Fe_2(SO_4)_3 : Al_2(SO_4)_3 : H_2SO_4 : H_2O = 0.08 : 0.44 : 0.15 : 0.12 : 1.66 : 40$ and evaporated at 80°C for about 2-3 days to the half of its original volume. The well developed crystals were filtered from the mother liquor and immediately rinsed with 10% H_2SO_4 then thoroughly dried. The isomorphous analogues were prepared with the same procedure, replacing K_2SO_4 for $(NH_4)_2SO_4$ and/or $FeSO_4$ for $MgSO_4$, as required. The resulting products were phase pure voltaite analogues, stable at room temperature and atmospheric conditions.

X-ray powder diffraction measurements were done on a Model PW 3710 / PW 1050 Bragg-Brentano diffractometer, using Cu Kα radiation (λ=1.541862Å), secondary beam graphite monochromator and proportional counter. Synthetic fluorophlogopite mica (NIST SRM 675) and silicon powder (NIST SRM 640) were used as internal two theta standards. Lattice parameters were determined with Le Bail whole pattern decomposition method[5] using the Fullprof Rietveld[6] software suite. Infrared spectra were taken on a Thermo Nicolet Avatar 320 FT–IR spectrometer in the 4000–400 cm^{-1} range using KBr discs. Density values were determined with the sink-float method with a pycnometer and acetone-bromoform mixture. Indices of refraction were determined at 546 nm light wavelength. Theoretical indices of refraction were estimated from the chemical composition and density values for each member using the Gladstone-Dale relationship with the new series of Gladstone-Dale constants (GDCs) as determined by Mandarino and Eggleton.[7] The experimental and estimated indices of refraction were then compared to see if inconsistencies exist.

Discussion

Mg substitution at the Fe^{II} site results in a decrease of the cell parameter of 0.11Å, while NH_4 subtitution of the K increases the cell size about the same amount. As the structure allows the formation of continuous solid solution between the four end members, owing to the opposite effect of the two substituents, a given cell size may represent a range on the two-dimensional composition map. Full substitution at both sites results in a unit cell size close to the un-substituted voltaite, as a consequence of the nearly identical but opposite effect the two substituents (cf. *tab. 1*). The cell constant determined by Gossner and Fell[2] for K-Mg-voltaite is fairly different from our values (27.42 Å vs. 27.26 Å). However it is not surprising considering the precision of the XRD technique of those times. Mereiter[4] and Schwarte and Fischer[8] determined the cell constants from single crystal measurements, that were aimed at structure determination and not for precise lattice parameter measurement. The deviations of their values from ours are well within the error boundaries of the single crystal method.

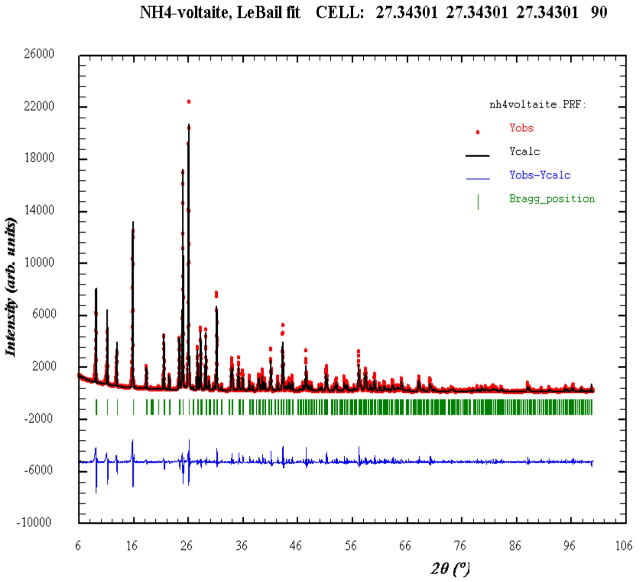
Table 1: Unit cell parameters and physical properties of the synthetic voltaite analogues.

	formula	a_0 [Å]	D_x g/cm^3	D_m g/cm^3	n* GDC	n exp.	Ref.
Voltaite	$K_2Fe^{2+}{}_5Fe^{3+}{}_3Al[SO_4]_{12}\cdot 18H_2O$	27.25	2.664	-	1.5955	-	[4]
Voltaite	$K_2Fe^{2+}{}_5Fe^{3+}{}_3Al[SO_4]_{12}\cdot 18H_2O$	27.232	2.669	2.667	1.5955	1.596	this study
Mg-Voltaite	$K_2Mg_5Fe^{3+}{}_3Al[SO_4]_{12}\cdot 18H_2O$	27.121	2.492	2.495	1.569	1.571	this study
Mg-Voltaite	$K_2Mg_5Fe^{3+}{}_3Al[SO_4]_{12}\cdot 18H_2O$	27.225	2.464	-	1.569	-	[8]
Ammoniovoltaite	$[NH_4]_2Fe^{2+}{}_5Fe^{3+}{}_3Al[SO_4]_{12}\cdot 18H_2O$	27.343	2.582	2.585	1.5975	1.598	this study
Mg-ammoniovoltaite	$[NH_4]_2Mg_5Fe^{3+}{}_3Al[SO_4]_{12}\cdot 18H_2O$	27.260	2.400	2.395	1.571	1.572	this study
Mg-ammoniovoltaite	$[NH_4]_2Mg_5Fe^{3+}{}_3Al[SO_4]_{12}\cdot 18H_2O$	27.42	2.357	2.375	1.571	-	[2]

Calculated densities (D_x) are given for the nominal formula and measured unit cell size. *Estimated indices of refraction (n, GDC) are based on Gladstone-Dale relationship, nominal chemical composition and measured density.

Their FTIR spectra do not show striking differences. Some of the absorption bands exhibit a minor shift corresponding to the difference of the atomic masses of the substituents. The only major difference is the presence of a well defined absorption band at 1428 cm^{-1} in the NH_4 containing analogues, which is completely missing inthe K containing ones. It is suggested, that in the lack of other reliable analytical technique, the relative intensity of the 1428 cm^{-1} absorption band can be used for the estimation of NH_4 – K substitution ratio.

Fig 1: Whole pattern decomposition of the NH_4-voltaite powder XRD scan.



The measured and calculated densities exhibit a good correlation, referring to that real structures may well correspond to the theoretical formulas. Furthermore, the range of density values is relatively broad (2.40 ~ 2.67 g/cm^3) allowing a more sensitive differentiation. The excellent compatibility of the experimental and estimated indices of refraction corroborates the theoretical compositions and gives a further way to navigate in the coordinates of the solid solution map.

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