A NEW MINERAL—ANKANGITE

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Received March 28, 1988.

Key words: new mineral, ankangite, oxide.

Ankangite is a new mineral containing Ba, Ti and V. It was named after the discovery of locality, Ankang County, Shaanxi Province. Ankangite has been approved by the Commission on New Minerals and Mineral Names of the I. M. A.

I. GENERAL DESCRIPTIONS

1. *Occurrence*

Ankangite occurs in a quartz vein, associates and intergrows with quartz (over 95%), barite, barytocalcite, barium roscoelite, diopsite, etc.

2. *Physical and Optical Properties*

Ankangite occurs as a black euhedral or subhedral tetragonal prismatic crystal, with size of 0.2—0.5 × 0.2—0.5 × 0.5—1 mm^3, and complete prismatical faces can be seen (Fig. 1). (100) grows more perfect than (110). No complete faces of bases or pyramids are found on ankangite crystals. Its streak is greyish-black and luster is vitreous to adamantine. It is brittle. The VHN (50 g load) is 874 kgf/mm^2. Ankangite tends to produce the uneven fractures nearly perpendicular to the *c*-axis. The measured

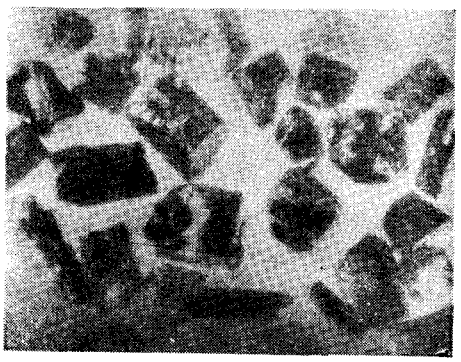

Fig. 1. Crystal habit of ankangite.

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density is 4.44 g/cm^3 by the JN-A-25 torsion balance, using CCl_4 as the medium. The calculated density is 4.389 g/cm^3. Ankangite is not magnetic and not soluble in HCl (solution).

In reflected light, ankangite is rose-reddish grey-white. Under crossed polars, it exhibits distinct anisotropism. Bireflectance ranges from weak to distinct and reflection pleochroism ranges from pinkish-grey (R_p) to light pink (R_g), with $R_g // c$. No internal reflections are observed. The reflective dispersion of rotation is $v > r$. The measured reflectivities (589 nm): R_e 20.1%, R_o 12.8%.

3. *Thermal and Infrared Analyses of Ankangite*

The infrared spectrum of ankangite, as shown in Fig. 2, has been measured by a Perkin-Elmer 577 bibeam grating spectrophotometer with the KBr press-piece method. Between 350—650 cm^{-1} in the spectrum, there is a wide gentle slope zone; at each of 314 and 760 cm^{-1}, there is an absorption peak. Ankangite does not have water and hydroxy groups, as indicated by infrared analyses.

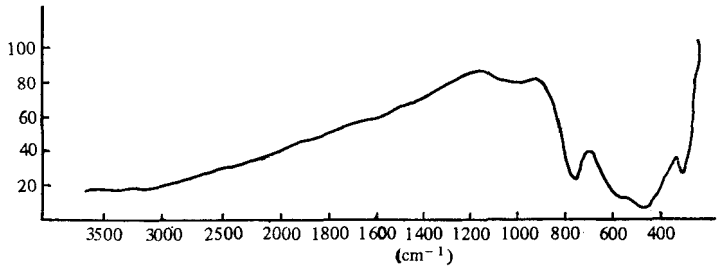

Fig. 2. Infrared spectrum of ankangite.

The DTA and TG curves of ankangite are shown in Fig. 3. There is a distinctive endothermic valley at 588℃ and an exothermic peak at 643℃ on the DTA curve. With the exothermic action, the weight increases by 2.8%. There is an inference that the exothermic action and the increase in weight are caused by vanadium oxidation.

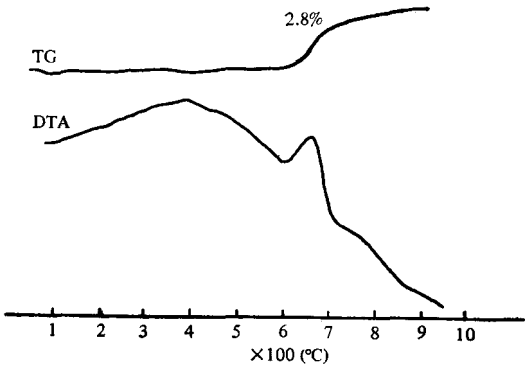

Fig. 3. DTA and TG curves of ankangite.

II. Chemical Composition and Vanadium Valence of Ankangite

To determine the chemical composition of ankangite, electron microprobe and chemical techniques have been utilized. The standard substances used in the microprobe analyses are benitoite, chromite and lead orthogermanate divanadate (synthetic). The chemical composition of ankangite, obtained by the electron microprobe technique, is TiO_2 54.0891%, BaO 20.5927%, V_2O_3 22.3242% and Cr_2O_3 2.0792%. In calculating the formula, the microprobe analysis results have been used. The formula, calculated on the basis of 16 oxygens, is $Ba_{1.087}(Ti_{5.482}V_{2.412}Cr_{0.222})_{8.116}O_{16}$. The ideal formula is Ba(Ti, V, Cr)$_8$O$_{16}$ with Ti > V > Cr.

According to the principle of photoelectron energy spectra measuring electron binding energy (E_b), the E_b of V in ankangite has been measured using KRATOS ES-300 X-ray photoelectron spectrumer. It has been determined that the valence of V in ankangite should be +3.

III. X-ray Diffraction Analysis of Ankangite

1. *X-ray Powder Analysis*

The powder diffraction patterns of ankangite have been photographed by the ∅ 57.3 and ∅114.6 mm Debye cameras separately. Through measurements and indexings based on the sub-unit cell parameters obtained from the four-circle single crystal diffractometer, the main powder diffraction lines are 3.580(5)(220), 3.202(10)(310), 2.476(7)(211), 2.264(4)(420), 2.233(5)(301), 1.892(5)(411), 1.685(5)(600), 1.589(7)(521,620) and 1.397(5)(640,541).

2. *Single Crystal X-Ray Analysis*

The one-dimensional incommensurate modulation has been found along the *c*-axis of ankangite.

At first, the Weissenberg photographs of the $hk0$ and the hkl layers of the sub-unit cell have been taken, and the extinction conditions were obtained: type hkl, $h + k + l \neq 2n$. Hence the sub-unit cell of ankangite is body centred with the diffraction group $4/mI-/-$ and the possible space group $I4$, $I\bar{4}$ or $I4|m$. Then collecting the information of high angle diffraction points from the diffractometer, the precisely measured sub-unit cell parameters were obtained: $a = 10.118(1)$ Å, $c = 2.956(3)$ Å, $V = 302.62$ Å^3, and $z = 1$.

In the oscillation pattern of the *c*-axis, the layer lines made of weak diffraction points can be seen, besides those made of strong diffarction points. The weak diffraction points were once thought to be at $1/2c^*$, so that the unit cell was lengthened one time along the *c*-axis. Through careful study, it has been found that they are not at $1/2c^*$, but at about $1/2.27\ c^*$. This phenomenon has not been observed in *a* and *b* directions. It shows that there is a one-dimensional incommensurate modulation in ankangite. Analysis indicates that the structural characteristics of ankangite can be

described by the super space (Wolff et al.[11]). Its four-dimensional Bravei's class is $P^{I4/mmm}_{1\,1\,1\,1}$, and its possible super space group is $P^{I4/m}_{1\,1}$, P^{I4}_{1} or $P^{I\bar{4}}_{1}$. For details of the study about the super structure of ankangite, please refer to Ref. [2].

IV. Comparison and Discussion

The sub-unit cell parameters of ankangite are basically consistent with those of priderite, and the structure of ankangite belongs to the type of cryptomelance and hollandite. The formula of this kind of mineral can be written as $A_{2-y}B_{8-z}X_{16}$. Here A is the larger positive ions of Ba, K, Mg and Ca, or H_2O, B is the smaller positive ions of Ti, V, Mn, Cr etc., and X is O or OH with y: 0—1 and z being very small. The minerals of cryptomelance group vary widely in components and structures. New species have been found recently. Some of them are being studied. The unit cell parameters of the part of the similar minerals have been listed in Table 1 for comparison.

Table 1

Comparison Between Unit Cell Parameters of Ankangite and Similar Minerals

Mineral	Chemical Formula	Space Group	a	c	z
Ankangite	$Ba_{1.087}(Ti_{5.482}V_{2.412}Cr_{0.222})_{8.116}O_{16}$		10.118(1)[a)]	2.956(3)[a)]	1
Priderite	$(K_{0.87}Ba_{0.32}Na_{0.14})$ $(Ti_{5.48}Fe_{1.14}Al_{0.33})O_{16}$	$I4/m$	10.11	2.964	1
Redledgeite	$[Ba(H_2O)](Ti_6Cr_2)O_{16}$	$I4_1/a$	14.320	5.893	4
Mannardite	$[Ba(H_2O)]\ (Ti_6V_2)O_{16}$	$I4_1/a$	14.356(4)	5.911(3)	4

a) Sub-unit cell parameters.

Although the sub-unit cell parameters of ankangite are basically consistent with priderite, there are distinct differences in components between the two minerals. Studying the data available, it can be seen that Ba of ankangite is predominant with K not occurring in place A, while Ba of priderite is less than K. The Ti atoms of priderite are close to or more than 6, the Fe atoms are more than 1 and Mg, Al or Cr exists in little amount in place B. As regards ankangite, the Ti atoms are close to 6, V are more than 2, and a few of Cr and no Fe exist in place B.

The differences between ankangite and mannardite (a Canada's new mineral in 1982) are mainly in structure besides in components. Mannardite contains H_2O and ankangite does not. The axis of mannardite is twice in length as its sub-unit cell priderite in the c direction, but there is incommensurate modulation in this direction of ankangite.

In the process of discovery and study of ankangite, the authors accepted help from many colleagues. We thank Engineer Chen Qi-guang of the Laboratory of the Seventh Geology Team of Shaanxi Province for his profitable help in field work. Our

sincere gratitude is extended to all those who helped us in study of ankangite.

References

[1] de Wolff, P. M., Janssen, T. & Janner, A., The superspace groups for incommensurate crystal structure with a one-dimensional modulation, *Acta Crystal*, **A37**(1981), 625—636.

[2] 周 健、马喆生，安康矿不相称超晶格及相似矿物的晶体化学，现代地质，**1**(1987)，77—83.