

New data on yttrocrasite from the Clear Creek pegmatite, Burnet County, Texas

WILSON W. CROOK, III

Department of Geology and Mineralogy
The University of Michigan
Ann Arbor, Michigan 49109

Abstract

X-ray diffraction data for non-metamict yttrocrasite from the Clear Creek pegmatite, Burnet County, Texas, shows it to be orthorhombic, space group *Pbcn*, $a = 12.862(7)$, $b = 4.810(2)$, $c = 4.571(3)$ Å, $V = 282.79$ Å³. The mineral is biaxial (–) with $\alpha = 2.131(2)$, $\beta = 2.137(2)$, $\gamma = 2.142(2)$, $2V_x = 60\text{--}70^\circ$. The strongest diffraction lines are 2.147(100)(600), 6.455(90)(200), 4.331(90)(110), and 3.121(30)(310). The calculated formula, based on $AB_2(O,OH)_6$, is $(Y_{0.601}RE_{0.141}Th_{0.118}U_{0.029}Mn_{0.007}Ca_{0.104}Pb_{0.006})(Ti_{1.838}Fe_{0.092}W_{0.062}Ta_{0.002})(O_{5.058}OH_{0.942})$. X-ray, optical, and chemical analysis suggests that yttrocrasite is the titanium-rich end-member of the euxenite group of rare-earth multiple oxides.

Introduction

Yttrocrasite, an oxide of titanium, thorium, and the yttrium-group rare earths was discovered by Hiddén and Warren in 1906. The original description included an incomplete wet chemical analysis and a few physical properties. The type locality, a granite pegmatite two miles east of the famous Barringer Hill rare-earth pegmatite, was inundated during the construction of Lake Buchanan in 1936. Additional data on yttrocrasite have not been obtained because of the combination of scarcity of material and its characteristic metamict state.

Occurrence

The pegmatites of the Llano Uplift region of central Texas are well known as sources of a large variety of primary and secondary rare-earth minerals. In May 1976 the author discovered three crude crystals of yttrocrasite at the Clear Creek pegmatite, Burnet County, Texas (Crook, 1977). Associated minerals include gadolinite, behoite, rowlandite, tenerite, yttrilite, allanite, samarskite, fergusonite, bastnaesite, cyrtolite (zircon), uraninite, thorite, "gummite", thorogummite, and texasite.

Yttrocrasite is found in perthitic blocky microcline and biotite associated with hematite staining within the inner intermediate zone of the pegmatite. Small areas within the perthite are vuggy and are filled with smoky quartz, hematite, biotite, and fergusonite. Clear Creek yttrocrasite is clearly associated with

fergusonite and cyrtolite intergrown within biotite plates. Three distinct crystals were found, megascopically distinguishable from the other rare-earth species by their color (green-brown) and their shape (orthorhombic-dipyramidal).

Physical properties

Yttrocrasite occurs as prismatic crystals with observed forms {100}, {010}, and {001}. Fracture is uneven to subconchoidal, and there is no observable cleavage. The color is green-brown and the crystals are typically opaque but are transparent in thin fragments. A dull exterior alteration coating is common. The streak is pale-brown to greenish-gray and the hardness is 5½–6. The specific gravity (21°C) was determined by repeated measurements using a Berman balance to be 5.315(5) on unaltered material, 4.624(5)–5.149(5) on metamict specimens, and 4.260(5) on alteration coatings. The habit is prismatic, the morphology being similar to polycrase, a member of the euxenite group. Although a tabular habit has been reported for specimens from the Southern Pacific Silica Quarry, Nuevo, California (Murdoch and Webb, 1956), it was not observed on those from Clear Creek.

The mineral is biaxial (–) with $\alpha = 2.131(2)$, $\beta = 2.137(2)$, $\gamma = 2.142(2)$, $2V_x = 60\text{--}70^\circ$ (Na light). Pleochroism is $X =$ colorless, amber to pale brown, $Y =$ brown, $Z =$ brown, green-brown to opaque with absorption $X > Y > Z$.

Table 1. X-ray powder data for yttrocrasite

hkl	d_{obs}	d_{calc}	I
200	6.455	6.431	90
110	4.331	4.310	90
310	3.121	3.126	30
211	2.954	2.944	20
002	2.401	2.403	20
102	2.369	2.363	20
510	2.241	2.241	30
600	2.147	2.144	100
420	1.865	1.863	30
022	1.658	1.656	10
912	1.189	1.186	5
11,10	1.132	1.133	10
414	1.094	1.093	10

CuK α radiation, Phillips-Norelco diffractometer.
Intensities visually estimated.

X-ray crystallography

Single crystals were studied using oscillating crystal, Weissenberg, and precession methods. Unit-cell parameters from a least squares refinement are $a = 12.862(7)$, $b = 4.810(2)$, $c = 4.571(3)\text{Å}$, $a:b:c = 2.674:1:0.950$, $V = 282.79 \text{ Å}^3$. Extinctions observed were: $\{0kl\}$, $k = 2n + 1$; $\{h0l\}$, $l = 2n + 1$; $\{hk0\}$, $h + k = 2n + 1$. The space group $Pbcn$ is proposed. Powder data from a Phillips diffractometer (Table 1) were indexed using refined lattice parameters from the single-crystal study.

The space group, $Pbcn$, is consistent with members of the rare-earth multiple oxides, and Strunz (1970) has tentatively classified yttrocrasite as a member of the euxenite group. All three of the cell parameters are consistently shorter than euxenite and do not match any of those reported for group species. However, axial ratios are similar, with those of yttrocrasite being almost identical to samarskite (2.75:1:0.949).

Chemical analysis

An electron microprobe analysis (Table 2), conducted with 150 nA specimen current and 15 kV excitation voltage, helped identify yttrocrasite. Water was measured by weight loss on ignition. The iron is assumed to be present as Fe^{3+} , because this is the valence of iron reported in the originally-described yttrocrasite material (Hidden and Warren, 1906). Corrections were made using Rucklidge's EMPADR VII program (J. Rucklidge and E. L. Gasparrini, Department of Geology, University of Toronto, written communication, 1969).

Electron microprobe analyses were normalized to 3

total cations, consistent with the euxenite group, $AB_2(\text{O},\text{OH})_6$. There is considerable substitution in all sites, and the chemical formula of the analyzed material is $(\text{Y}_{0.601}\text{La}_{0.003}\text{Ce}_{0.013}\text{Pr}_{0.002}\text{Nd}_{0.0007}\text{Sm}_{0.017}\text{Gd}_{0.0039}\text{Tb}_{0.001}\text{Dy}_{0.018}\text{Ho}_{0.002}\text{Er}_{0.029}\text{Tm}_{0.002}\text{Yb}_{0.005}\text{Lu}_{0.003}\text{Th}_{0.118}\text{U}_{0.029}\text{Mn}_{0.007}\text{Ca}_{0.104}\text{Pb}_{0.006}) (\text{Ti}_{1.838}\text{Fe}_{0.092}\text{W}_{0.062}\text{Ta}_{0.002}) (\text{O}_{5.058}\text{OH}_{0.942})$. Thus the formula is ideally $AB_2(\text{O},\text{OH})_6$ with $A = \text{Y}, \text{Th}, \text{Ca}, \text{U}, \text{RE}$; $B = \text{Ti}, \text{Fe}^{3+}$, and W . Both metamict and non-metamict material were found to have essentially the same composition.

Table 2. Microprobe analysis of yttrocrasite (1) and samarskite (2), Burnet County, Texas

	1	2
CaO	1.71	3.08
MgO	--	0.08
MnO	0.14	--
Na_2O	--	0.10
K_2O	--	0.05
Fe_2O_3	1.63	10.88
TiO_2	49.56	2.17
Al_2O_3	--	0.15
WO_3	1.79	--
SiO_2	--	0.93
PbO	0.38	1.62
Ta_2O_5	0.06	6.04
Nb_2O_5	0.02	41.29
ThO_2	9.12	1.95
U_3O_8	2.36	16.26
ZrO_2	--	0.21
RE_2O_3	29.05	12.53
H_2O	5.07	--
TOTAL	100.89	98.70
Y_2O_3	19.92	7.69
La_2O_3	0.14	0.02
Ce_2O_3	0.63	0.18
Pr_2O_3	0.13	trace
Nd_2O_3	0.34	0.19
Sm_2O_3	0.88	0.63
Gd_2O_3	2.09	0.66
Tb_2O_3	0.07	0.26
Dy_2O_3	2.55	0.64
Ho_2O_3	0.10	0.13
Er_2O_3	1.63	0.68
Tm_2O_3	0.14	0.05
Yb_2O_3	0.26	1.36
Lu_2O_3	0.17	0.04

Discussion

These data suggest that yttrrocrasite is the titanium-rich, niobium-, tantalum-poor end-member of the euxenite group of rare-earth multiple oxides. Optical and physical properties are generally consistent with other members of the series. Metamict yttrrocrasite differs from non-metamict material only by its lower specific gravity, isotropism ($n = 2.14$), well-developed conchoidal fracture, and alteration coatings. Chemical composition is apparently identical for both states. X-ray data show yttrrocrasite to have space group *Pbcn*, consistent with the euxenite group. However, all three lattice parameters are significantly smaller than any of those reported for euxenite, polycrase, samarskite, fersmite, etc. The reduction in cell size is proportional for all three axes, and the axial ratio of yttrrocrasite is very similar to all members of the $AB_2(O,OH)_6$ series.

Consideration of the ionic radii of substituting elements in either the *A* or *B* site alone does not account for the significantly smaller cell size in yttrrocrasite. Members of the euxenite group crystallize in a columbite-like layer structure in which the *A* cations occur every third layer. This layering is parallel to closest-packed planes of zig-zag chains of *B* octahedra (Graham and Thornber, 1974). Slight adjustments in the oxygen atoms change the coordination number of the *A* ions to eight. However, all members of the series are characterized by extensive substitution in the *A* site, which results in variable bond lengths and

charge distribution for the *A* polyhedra. Ideally the *A* sites are eight-coordinated, but variation in the *A*-site ionic radii causes distortion of the octahedra, and smaller cations (Y^{3+}) are more stable in six-fold coordination. Thus the *A* site is *x*-coordinated, the coordination number depending on the elements present.

Assuming a fersmite-like structure, the zig-zag chains of *B*-site octahedra are joined by common corners to form two-dimensional double layers. These are interlinked by eight-coordinated large (RE) cations (Alexandrov, 1960). The shortened cell parameters in yttrrocrasite must be due to considerable corrugation of the zig-zag chains of *B* (Ti) octahedra, resulting in an overall contraction of the structure.

References

- Alexandrov, V. B. (1960) The crystal structure of fersmite. *Dokl. Akad. Nauk. USSR*, 132, 669–672.
- Crook, W. W., III (1977) The Clear Creek pegmatite: a rare-earth pegmatite in Burnet County, Texas. *Mineral. Record*, 8, 88–90.
- Graham, J. and M. R. Thornber (1974) The crystal chemistry of complex niobium and tantalum oxides. I. Structural classification of MO_2 phases. *Am. Mineral.*, 59, 1026–1039.
- Hidden, W. E. and C. H. Warren (1906) On yttrrocrasite, a new yttrium–thorium–uranium–titanite. *Am. J. Sci.*, 22, 515–519.
- Murdoch, J. and R. W. Webb (1956) Minerals of California. *Calif. Bur. Mines, Bull.*, 173, 351.
- Strunz, H. (1970) *Mineralogische Tabellen*. Akademische Verlagsgesellschaft, Leipzig.

Manuscript received, July 30, 1976; accepted for publication, May 24, 1977.