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Vickers Hardness and Reflectance Determinations for Metamict AB_2O_6-Type Rare Earth Ti–Nb–Ta Oxides

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Abstract

Orthorhombic, metamict, AB_2O_6-type rare earth Ti–Nb–Ta oxides have VHN_{50} values ranging from 633 to 746. VHN_{50} increases to approximately 1000 for annealed specimens. Reflectances measured in air vary from 11.9 to 15.6 (470 nm), 11.7 to 15.6 (546 nm), 11.0 to 15.0 (589 nm) and 11.6 to 15.0 (650 nm). Variations in reflectance are due more to alteration than variation in weight percent TiO_2, Nb_2O_5 or Ta_2O_5. A symmetric correlation matrix is calculated for all data.

Introduction

The orthorhombic, often metamict, Ti–Nb–Ta oxides of the type formula AB_2O_6 (A = RE, Fe, Mn, Ca, U, Th; B = Nb, Ta, Ti) include euxenite, polycrase, priorite-blomstrandine, and aeschynite. Present mineralogic systematics are contradictory, but euxenite and aeschynite are ideally defined as $YNbTiO_6$ and $CeNbTiO_6$. Polycrase and blomstrandine are considered titanium rich varieties. Priorite (= aeschynite-(Y) following Levinson, 1966) is the low temperature dimorph of euxenite (Mitchell, 1972) and isostructural with aeschynite (Komkov, 1959). Limited VHN and reflectance data have been available (Bowie and Taylor, 1958; Hutchinson, 1955; Vlasov, 1966) but are not accompanied by the determination of weight percentages of TiO_2, Nb_2O_5 and Ta_2O_5. The effect of metamictization and alteration on VHN and reflectance of minerals in this group has not been determined previously.

Analytical Techniques

VHN was measured on a Leitz Miniload Microhardness Tester with a fifty gram load on polished billets and polished thin sections (25 to 30 μm thick). VHN values on billets and polished thin sections of the same specimen were always within less than three percent of one another. Reflectance was measured in air for the four wavelengths 470 nm, 546 nm, 589 nm, and 650 nm, using a Zeiss continuous interference-filter monochromator and a Zeiss MPM microscope photometer. The silicon carbide standard had reflectances of 20.90 percent, 20.30 percent, 20.00 percent, and 19.65 percent in air for the respective wavelengths. Ten measurements of VHN and reflectance for each of the four wavelengths were made on each specimen. Chemical analysis of TiO_2, Nb_2O_5 and Ta_2O_5 was determined using an ARL electron microprobe using five analyzed specimens (Nos. 4, 5, 7, 12, 13 in Table 1) as standards. Relative error for TiO_2 and Nb_2O_5 is $\pm$2.5 percent; Ta_2O_5, $\pm$5.0 percent.

Results and Discussion

The results for 17 specimens are summarized in Table 1, and the calculated standard deviation for each group of ten measurements is given in parentheses. VHN varies from 633 to 746; reflectance varies from 11.9 to 15.6 (470 nm), 11.7 to 15.6 (546 nm), 11.0 to 15.0 (589 nm), and 11.6 to 15.0 (650 nm). A symmetric correlation matrix was computed using program BMDO2D (Dixon, 1971) and is summarized in Table 2 for all data. The five percent probability significance level is 0.482; hence correlation coefficients with absolute values greater than 0.482 indicate at most only five chances in 100 that the correlations are coincidental. The reflectances at each wavelength show a strong positive correlation with one another but none with the weight percent TiO_2, Nb_2O_5, or Ta_2O_5. VHN shows a negative correlation with Nb_2O_5 and a positive correlation with Ta_2O_5. Despite the calculated correlation coefficients, one should note that the large standard deviations

TABLE 1. VHN and Reflectance Data for Orthorhombic Metamict AB_2O_6-Type Rare Earth Ti-Nb-Ta Oxides

No.	Name*	Location	VHN_{50}	Reflectance (%) 470nm	546nm	589nm	650nm	Weight Percent TiO_2	Nb_2O_5	Ta_2O_5	Source**
1	aeschynite	Hitterö, Norway	665(42)	12.9(.9)	12.7(.8)	13.6(.2)	13.5(.2)	37.4	12.8	4.2	SD #473
2	aeschynite	Miask, Urals, USSR	645(29)	15.0(.5)	14.6(.1)	14.1(.2)	14.2(.2)	24.6	40.1	0.8	C.O.H.
3	aeschynite	Hitterö, Norway	683(26)	12.9(.6)	13.9(.3)	13.6(.3)	13.3(.3)	27.2	28.0	5.0	C.O.H.
4	polycrase	Minas Geraes, Brazil	713(42)	15.5(.4)	14.6(.2)	13.4(.3)	13.9(.2)	31.2	12.9	8.2	C.O.H.
5	polycrase	Minas Geraes, Brazil	733(30)	15.0(.3)	14.2(.3)	13.8(.4)	13.5(.2)	31.7	11.5	7.4	C.O.H.
6	polycrase	Minas Geraes, Brazil	746(40)	15.2(.2)	14.6(.3)	14.1(.4)	14.4(.4)	31.4	15.9	8.9	SD #25946
7	blomstrandine	Kåbuland, Iveland, Norway	735(42)	14.4(.6)	13.0(.4)	11.3(.4)	12.9(.4)	29.5	16.4	4.7	C.O.H.
8	blomstrandine	Morefjaer, Arendal, Norway	705(40)	14.5(.2)	13.6(.3)	13.0(.3)	13.4(.1)	31.9	19.0	2.0	C.O.H.
9	blomstrandine	Slobrekka, Iveland, Norway	674(39)	11.9(.7)	11.7(.6)	11.0(.2)	11.6(.7)	33.8	13.9	4.0	C.O.H.
10	blomstrandine	Hitterö, Norway	727(37)	15.0(.3)	14.0(.2)	13.5(.2)	14.2(.2)	37.3	14.8	1.9	C.O.H.
11	blomstrandine	Morefjaer, Norway	672(66)	13.6(.5)	14.1(.9)	13.4(.3)	14.0(.3)	28.8	25.0	4.5	C.O.H.
12	euxenite	Iveland, Norway	692(40)	15.6(.2)	14.8(.3)	13.8(.1)	14.2(.2)	24.5	24.2	3.0	C.O.H.
13	euxenite	Voandekaka, Madagascar	655(50)	13.8(.7)	13.0(.4)	12.5(.3)	12.5(.4)	25.6	24.8	7.7	SD #6363
14	euxenite	Sjaen, Krajerö, Norway	679(37)	13.7(.6)	13.6(.5)	12.4(.3)	12.4(.4)	26.0	27.2	3.4	SD #6364
15	euxenite	Minas Geraes, Brazil	673(46)	15.0(.1)	14.6(.1)	13.7(.2)	13.7(.1)	34.5	15.2	1.1	SD #25950
16	euxenite	Betsiboka Val., Madagascar	658(39)	15.3(.4)	14.7(.4)	14.2(.3)	14.1(.3)	24.5	27.4	2.5	C.O.H.
16***	euxenite	Betsiboka Val., Madagascar	627(26)	13.6(.5)	12.9(.4)	12.2(.2)	11.9(.6)	22.7	26.2	2.4	C.O.H.
17	euxenite	Betsiboka Val., Madagascar	633(38)	15.6(.8)	15.6(.4)	15.0(.3)	15.0(.2)	28.5	31.4	1.8	SD #6361
17***	euxenite	Betsiboka Val., Madagascar	611(41)	13.9(.4)	13.4(.3)	12.9(.2)	12.9(.2)	24.4	31.4	1.7	SD #6361

*As given at time of acquisition
**SD = Mineralogy Collection Stanford University; C.O.H. = private collection of Dr. C. O. Hutton
***Altered areas

(±26 to ±66) in measurements on single specimens preclude the use of VHN in the determination of composition. The negative correlation of Nb_2O_5 and positive correlation of Ta_2O_5 with VHN rests heavily on the values for only two specimens (Nos. 2 and 17). Indeed, considering the variation of cations in the *A*-site, one may only suggest that an increase in Nb or decrease in Ta will lower the VHN for any particular specimen. The expected inverse correlation of TiO_2 with Nb_2O_5 is demonstrated.

Alteration was apparent in all specimens and pervasive in a few. The altered areas are translucent, honey-yellow to amber, and readily apparent against the isotropic, nearly opaque unaltered areas. For two specimens (Nos. 16 and 17) measurements were made in altered areas, and the results are summarized in Table 1. There is only a slight decrease in VHN (~5%) with alteration, but there is a consistent decrease in reflectance (~15%) for all wavelengths accompanied by minor decreases in weight percent TiO_2, Nb_2O_5 and Ta_2O_5. This is consistent with the previously noted decrease of refractive index and specific gravity with alteration (Van Wambeke, 1970). Although depletion of *A*-site cations (RE, Ca, U, Th) has been reported (Van Wambeke, 1970), the decrease in TiO_2, Nb_2O_5 and Ta_2O_5 indicates that *B*-cations are similarly affected by alteration.

The decrease in VHN with alteration is not great, but one might expect VHN to vary with the degree of metamictization. The degree of metamictization is a difficult parameter to estimate, and all specimens examined in this study were amorphous to X-ray diffraction; therefore, two specimens (Nos. 14 and 17) were annealed to a maximum temperature of 1000°C to study the change in VHN with restoration of crystalline structure. The specimens were heated for two hours in increasing steps of 100°C intervals. At each interval specimens were cooled, repolished, and VHN measured. The VHN increased with anneal-

Table 2

Symmetric Correlation Matrix for AB_2O_6-Type Rare Earth Ti-Nb-Ta Oxides

	VHN_{50}	Reflectance 470 nm	546 nm	589 nm	650 nm	Weight Percent TiO_2	Nb_2O_5	Ta_2O_5
VHN_{50}	1.000							
470 nm	0.195	1.000						
546 nm	-0.086	0.843	1.000					
589 nm	-0.229	0.620	0.860	1.000				
650 nm	0.162	0.735	0.806	0.839	1.000			
TiO_2	0.376	-0.214	-0.330	-0.122	-0.005	1.000		
Nb_2O_5	-0.666	0.124	0.390	0.344	-0.071	-0.786	1.000	
Ta_2O_5	0.488	-0.080	-0.163	-0.173	-0.010	0.023	-0.428	1.000

Five percent level of significance = 0.482; correlation coefficients whose absolute value is equal or greater than 0.482 are underlined.

ing temperature, reaching a maximum of 950 at 760°C for No. 14 and 1010 at 700°C for No. 17. At higher temperatures the hardness decreased as the samples became brittle and fractured due to the repeated heating and cooling. It should be noted that the VHN measured is not a value for single grains. Metamict specimens invariably anneal to a cryptocrystalline aggregate unless some of the original structure has survived the process of metamictization. X-ray examination of No. 14 at 760°C and No. 17 at 700°C showed that both a low temperature priorite phase and a pyrochlore type cubic phase, $a_0 = 5.11$ Å, were present (Lima-de-Faria, 1964; Komkov, 1959; Van Wambeke, 1970).

In summary, variation in reflectance in the oxides studied is due more to alteration than to variation in TiO_2, Nb_2O_5 or Ta_2O_5 contents. VHN shows a negative correlation with Nb_2O_5 and a positive correlation with Ta_2O_5; the variation does not allow the determination of composition from VHN data. As metamictization increases, VHN decreases until totally metamict specimens have a VHN between 633 and 746. Annealing studies suggest that non-metamict members of this mineral group would have a VHN of approximately 1000. The standard deviations of values for VHN and reflectance for any one specimen as well as the wide range of values for all specimens are such that it is very difficult to distinguish by these means between metamict euxenite, polycrase, aeschynite, or aeschynite-(Y).

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