Vickers Hardness and Reflectance Determinations for Metamict \( \text{AB}_2\text{O}_6 \)-Type Rare Earth Ti–Nb–Ta Oxides

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Abstract

Orthorhombic, metamict, \( \text{AB}_2\text{O}_6 \)-type rare earth Ti–Nb–Ta oxides have VHN\(_{\text{w}} \) values ranging from 633 to 746. VHN\(_{\text{w}} \) 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\(_2\)O\(_5\), or Ta\(_2\)O\(_5\). A symmetric correlation matrix is calculated for all data.

Introduction

The orthorhombic, often metamict, Ti–Nb–Ta oxides of the type formula \( \text{AB}_2\text{O}_6 \) (\( A = \text{RE, Fe, Mn, Ca, U, Th}; B = \text{Nb, Ta, Ti} \)) include euxenite, polycrase, priorite-blomstrandine, and aeschynite. Present mineralogic systematics are contradictory, but euxenite and aeschynite are ideally defined as \( \text{YNbTiO}_6 \) and \( \text{CeNbTiO}_6 \). 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\(_2\)O\(_5\), and Ta\(_2\)O\(_5\). 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 \( \mu \)m 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\(_2\)O\(_5\), and Ta\(_2\)O\(_5\) 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\(_2\)O\(_5\) is \( \pm 2.5 \) percent; Ta\(_2\)O\(_5\), \( \pm 5.0 \) 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\(_2\)O\(_5\), or Ta\(_2\)O\(_5\). VHN shows a negative correlation with Nb\(_2\)O\(_5\) and a positive correlation with Ta\(_2\)O\(_5\). Despite the calculated correlation coefficients, one should note that the large standard deviations
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. The expected inverse correlation of TiO₂ with Nb₂O₅ 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 TiO₂, Nb₂O₅, and Ta₂O₅. 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 TiO₂, Nb₂O₅, and Ta₂O₅ indicates that B-cations are similarly affected by alteration.

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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 Wambcke, 1970).

In summary, variation in reflectance in the oxides studied is due more to alteration than to variation in TiO\(_2\), Nb\(_2\)O\(_5\) or Ta\(_2\)O\(_5\) contents. VHN shows a negative correlation with Nb\(_2\)O\(_5\) and a positive correlation with Ta\(_2\)O\(_5\); the variation does not allow the determination of composition from VHN data. As metamictization increases, VHN decreases until totally metamict specimens have a VHN of approximately 1000. 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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**References**


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