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DETERMINATION OF THE DEGREE OF CRYSTALLINITY OF METAMICTIC EUXENITE AND FERGUSONITE

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Abstract. Taking euxenite (Y,Ce...) (Nb, Ta, Ti)₂ (O, OH)₆ and fergusonite Y(Nb, Ta)O₄ as examples, quantitative changes occurring during recrystallization of metamictic minerals were investigated using X-ray quantitative analysis. An interpretation was given of the inhibition or even a regression of the process of ordering of the structure observed in certain temperature ranges. Also, the fact that polymorphic transformation of euxenites was attended by an exothermic peak was accounted for. It has been found that the heating time does not affect essentially the rate of ordering of the structure. Changes in the crystallite size occurring during recrystallization of metamictic minerals were determined.

INTRODUCTION

The metamictic state is characterized by structural disorder (amorphous to X-rays) while the crystal habit is frequently well developed. The essential features of this state were discussed by Pabst (1952). The metamictic state can be changed by appropriate heating of such mineral at temperatures higher than 400°C, leading to their recrystallization. This procedure finds wide application in crystallochemical studies of those substances. The processes occurring in the course of heating of metamictic minerals were generally explained from the viewpoint of polymorphic transformations involved.

This paper is an attempt at quantitative evaluation of the increase in the crystalline phase content during recrystallization of metamictic minerals. The method of Ohlberg and Strickler (1962) was adopted, involving measurements of the intensity of coherent X-ray scattering on glasses for the defined value of 2θ . X-ray diffraction patterns of amorphous substances show an increase in the background intensity at small angles of 2θ . This phenomenon, referred to as amorphous halo, is the effect of the intensified noncrystalline scattering. Its intensity is reduced as the degree

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of ordering of the structure increases. Measured at one point of the glass, crystalline and partly crystalline substance, this intensity can become a measure of crystallinity. This is expressed by Ohlberg's and Strickler's equation:

$$C_i = \frac{I_g - I_x}{I_g - I_c} \cdot 100 (\%),$$

where:

I_g , I_x , I_c are the scattering intensity of amorphous substance, partly recrystallized sample and crystalline components, respectively.

This method has certain limitations arising from the assumption that the intensity measured at one point is proportional to the total amorphous scattering. According to Ohlberg and Strickler, it is not convenient to have a content of crystallites less than 10%, as slight changes in non-crystalline scattering cannot be measured accurately. For the same reason, in the author's opinion, the sensitivity of this method diminishes when the content of the glassy phase is less than 10%.

EXPERIMENTAL

From the amply represented group of silicates and niobotantalates occurring in metamictic state, euxenites from Arendal and Lindesnas (Norway) and fergusonite from Llano County, Texas (USA) were selected for analyses. All the specimens were taken from the collections of the Museum of Mineralogy of the Wrocław University. Crystalline standards were obtained by heating the samples at 1000°C for 2 h. X-ray diffraction pattern of the heated samples is characterized by the presence of sharp and intensive peaks. Due to recrystallization, the density of minerals has increased, e.g. 5.09 and 5.24 resp. for metamictic and crystalline euxenite from Lindesnas.

Intensity measurements of amorphous X-ray scattering were carried out in a DRON-2.0 diffractometer with a scintillation counter, using $\text{CuK}_\alpha/\text{Ni}$ radiation and time constant 2s. The relative statistical reading error did not exceed 1%. Considering the high mass absorption coefficient of the minerals studied, exceeding 150 cm^2/g , powder samples were very carefully ground. The absorption coefficient is lower for non-heated metamictic glasses. The experimentally determined mass absorption coefficient for metamictic euxenite from Lindesnas is 96.8 cm^2/g (CuK_α radiation).

To measure the scattered intensity, a point of a value of $28^\circ 2\theta$ was selected for euxenites and one of 24° for fergusonite. These points exhibited a considerable scattering intensity and no overlapping of diffraction lines produced by the crystalline phase occurred. In order to change the metamictic state, the samples were heated at temperatures from 400 to 1000°C, every 100°C, for different lengths of time. After each run, the intensity of scattered radiation was measured. The intensity of amorphous scattering was calculated as an average of 10 point measurements. The error of calculation of the degree of crystallinity was $\pm 5\%$. The size of error was determined by measuring the scattered intensity for three artificial mixtures of metamictic minerals and their crystalline phases.

RESULTS

Heating of metamictic euxenite gives rise to two, low- and high-temperature, polymorphic modifications of this minerals. Seifert and Beck (1965) have shown that the low-temperature modification corresponds in its structure to aeschynite, $(\text{Ce}, \text{Th} \dots) (\text{Ti}, \text{Nb}, \text{Ta})_2\text{O}_6$, whereas at 750°C pseudomonotropic transformation of aeschynite into euxenite takes place. Euxenite and aeschynite show close similarity in chemical composition and have the same atomic coordination, but their structure differ slightly (Graham, Thornber 1974).

Figure 1 shows the dependence of the calculated degree of crystallinity of euxenites on the temperature and time of heating. As appears from the plot, recrystallization of euxenite starts at 400°C, but this process is actually reflected only by a reduction in the intensity of the amorphous halo. Between 400 and 500°C the content of crystalline phase increases up to 40%. This increase is attended by an exothermic peak on DTA curves (Fig.

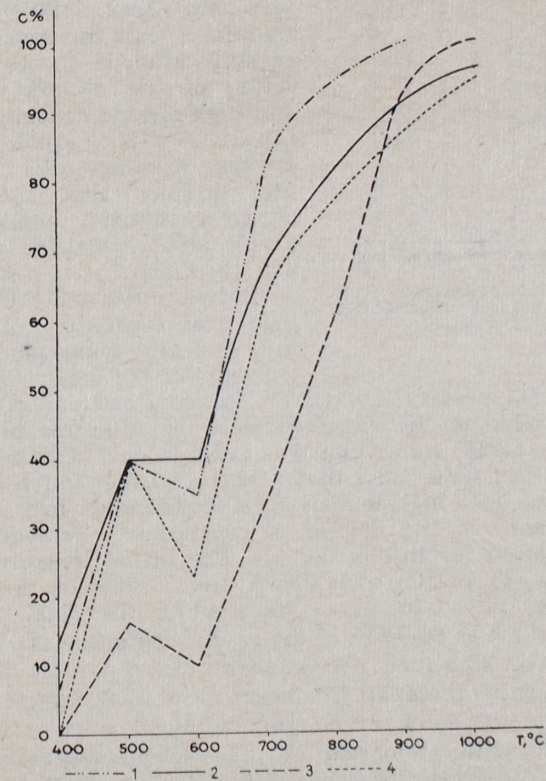


Fig. 1. Plot of the degree of crystallinity (C) of euxenites vs. heating time and temperature
Euxenite from Lindesnas heated at different temperatures for: 1 - 2 h, 2 - 1 h, 3 - 15 min.,
4 - euxenite from Arendal - 20 min.

2) and two broad peaks of equal intensity (29.9° and $30.75^\circ 2\theta$) appearing in X-ray diffraction patterns. This is the stage of partial recrystallization, when the crystalline phase has an aeschnitic structure. At this point, instead of further increase in the content of the crystalline phase, the inhibition of the process or even a regression has been noted. This fact can be accounted for as follows: In the first stage of recrystallization there is only 40% of crystalline phase in the system; therefore, further condensation of atom groupings must take place in order that the recrystallization be complete.

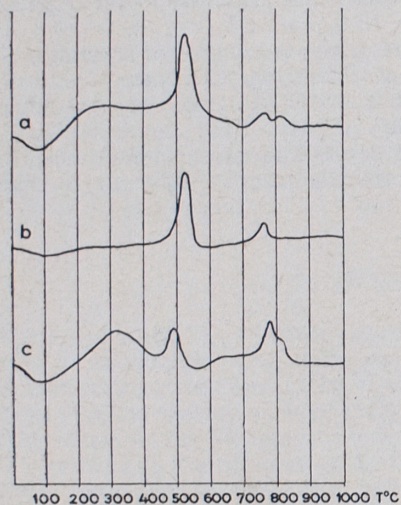


Fig. 2. DTA curves of euxenites from a — Arendal, b — Arendal (after Seifert, Beck 1965), c — Lindenas

point symmetry D_{2h} preserved. On DTA curves a pronounced exothermic peak appears instead of the expected weak endothermic peak (Fig. 2). Seifert and Beck (1965) think that this peak is due to recrystallization. They suggest at the same time that a chemical reaction leading to the change of the low- into high-temperature modification may occur. However, measurements of the degree of crystallinity provide a slightly different explanation for this behaviour. The initial temperature of the exothermic peak (T_i 750°C) corresponds to 65—70% of the crystalline (low-temperature) phase in the system while the final temperature (T_f 820°C) to as much as 85—90% of the crystalline phase. At 770°C phase with the euxenitic structure recrystallizes directly from the glass as a high-temperature modification. The heat of euxenite recrystallization can be used to change the aeschnitic structure (designated as $\alpha - \text{AB}_2\text{O}_6$), which is unstable at this temperature, into the euxenite structure ($\beta - \text{AB}_2\text{O}_6$). Thus the recrystallization effect coincides with that of polymorphic transformation of the low- into high-temperature modification. The answer to the question whether the heat energy of euxenite recrystallization is sufficient to convert 70% of $\alpha - \text{AB}_2\text{O}_6$ into $\beta - \text{AB}_2\text{O}_6$ is

positive because the transformation of these structures requires only slight displacements of atoms, mainly oxygens, resulting in the change of coordination numbers of A ions from 8 to 4 (Graham, Thornber 1974). Besides, this energy can be used just to initiate the transformation, which will then proceed as an avalanche process. It is worth noting, however, that this process does not lead to the transformation of all $\alpha - \text{AB}_2\text{O}_6$ into $\beta - \text{AB}_2\text{O}_6$, but the aeschnitic structure is partly preserved (metastable) at high temperatures. This statement is substantiated by the analysis of X-ray diffractograms and, specifically, by the double exothermic peak recorded on DTA curves. The first peak corresponds to recrystallization of the bulk of metamictic euxenite and the second to crystallization of euxenite on the relics of the aeschnitic structure. Complete recrystallization of the mineral does not depend on the heating time (Fig. 1). Prolonged heating (e.g. 2 h) results in that complete crystallinity is attained at 900°C whereas polymorphic transformation is effected at

Between 700 and 750°C polymorphic transformation of aeschnite into euxenite takes place, involving a change of the space group with the

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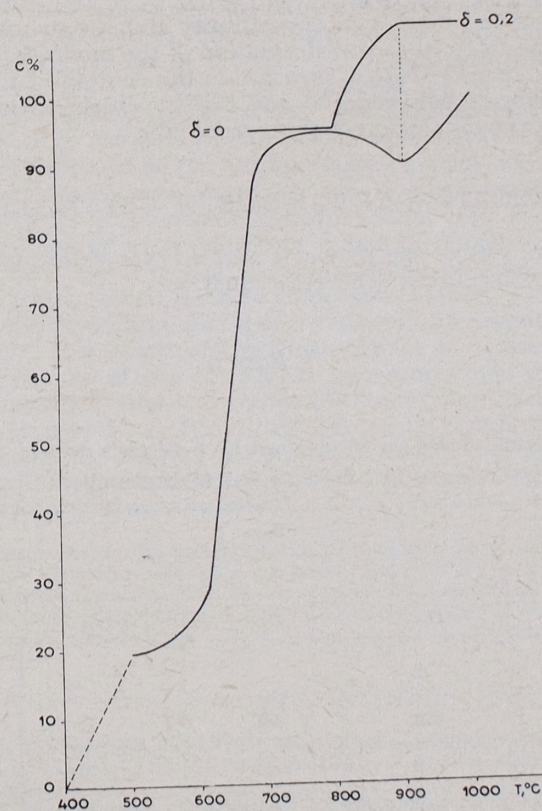


Fig. 3. Plot of the degree of crystallinity of fergusonite from Llano County vs. heating temperature

At the top: Komkov's plot (1957) of the difference of lattice constants a and b vs. temperature

lower temperatures. On the other hand, it depends on the heating time whether a pure phase with the euxenitic structure will be formed or relics of the α - AB_2O_6 structure will be preserved.

Measurements of the degree of crystallinity of fergusonite from Llano County are presented in Figure 3. It has been found (Komkov 1957, 1959; Wolten, Chase 1967; Graham, Thornber 1974) that from 750°C the low-temperature fergusonite of tetragonal symmetry (*T*) changes after cooling into the monoclinic modification (*M*) and this, in turn, converts at 1200°C into its modification (*M'*). On the plot of the degree of crystallinity against heating temperature (Fig. 3), the transformation of *T*-into *M*-fergusonite is attended by a slight increase in the content of glassy phase (by about 5%). From Graham's considerations (1974) it appears that the change of *T*-into *M*-fergusonite requires slight atomic displacement and, as follows from Figure 3, this process occurs in the virtually recrystallized substance. A correlation of the plot discussed with that of Komkov (1957), presenting the relationship between the difference of lattice constants $\sigma = b - a$ and recrystallization temperature (Fig. 3), yields some interesting data. A steady increase in the value of σ and, simultaneously, a deterioration in the degree of crystallinity due to structural changes corresponds to the interval of transformation of the modification *T* into *M*. It has been noted that the rate of increase in the content of the crystalline phase becomes slower between 500 and 600°C, which, as in the case of euxenite, is due to condensation of atom groupings.

DETERMINATION OF THE SIZE OF CRYSTALLITES

The crystallite size of the minerals studied was determined by X-ray approximation method using Scherrer's equation:

$$D_{hkl} = \frac{K\lambda}{B_i \cos \theta}$$

Table 1

Crystallite size (in Å) obtained by Scherrer's method
a — euxenite, b — *T* — and *M*-fergusonite

T, °C	D_{hkl}				
	a	b			
	D_{sr}	D_{211}	D_{203}	$D_{\bar{1}\bar{3}1}$	D_{007}
600		70			
700	99	210	460		250
800	110	220	480		280
900	560	310	710		360
1000	1450			200	

where D_{hkl} is the crystallite thickness measured along the normal to *hkl* planes; *K* is a constant depending on the shape of crystallites and the method of determination of the diffraction line breadth; B_i is the integral breadth of a diffraction line free from non-diffraction broadening. Klug and Aleksander (1974) recommend the value of $K = 1.05$ for calculation of the integral breadth.

The results of calculations are presented in Table 1. A comparison of these results with the degree of crystallinity of the minerals studied reveals that the smallest increase in the crystallite size (the interval between 700—800°C) corresponds to a decrease in the rate of ordering of the structure due to polymorphic transformation of *T*-into *M*-fergusonite and α -into β -euxenite.

DISCUSSION

When heated progressively at temperature higher than 400°C, metamictic minerals assume a crystal structure, undergoing simultaneously polymorphic transformation. The exothermic peak associated with the polymorphic transformation of the low- into high-temperature modification of euxenite at 750—770°C can be accounted for by crystallization of the remaining (about 30%) glassy phase. The emitted heat of crystallization is used to change the aeschynitic (low-temperature) into euxenitic structure. This thesis could be proved by making a DTA analysis of completely nonmetamictic aeschynite, in which case a weak endothermic peak will correspond to its polymorphic transformation into euxenite. A deterioration in the degree of crystallinity noted for euxenite in the range between 500 and 600°C is due to condensation of atom groupings of the amorphous phase, which leads to disproportionation. The inhibition of the increase in the crystalline phase content noted for fergusonite in the range of 800—900°C is a result of the displacement of atoms (mainly oxygens) during the change of the tetragonal into monoclinic modification. Polymorphic transformations of the minerals studied are attended by a decrease in the rate of growth of crystallites. The achievement of perfect crystallinity depends on the heating temperature alone. Prolonged heating results in that crystalline perfection is achieved at a lower temperature and polymorphic transformation is complete.

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Janusz JANECZEK

OKREŚLENIE STOPNIA KRystalICZNOŚCI METAMIKTYCZNEGO EUXENITU I FERGUSONITU

Streszczenie

Posługując się metodą Ohlberga i Stricklera (1962) rentgenograficznego określania stopnia krystaliczności szkielek, prześlędzono zmiany przyrostu fazy krystalicznej w trakcie ogrzewania minerałów metamiktycznych: euxenitów z Norwegii i fergusonitu z Teksasu. Wyniki przedstawiono na figurze 1 i 3. Minerale te w trakcie ogrzewania w temperaturach wyższych od 400°C rekrytalizują podlegając jednocześnie przemianom polimorficznym.

Egzotermiczny efekt przemiany formy niskotemperaturowej w wysokotemperaturową euxenitu w 750—770°C wytłumaczono krystalizacją pozostałej (około 30%) fazy szklistej. Wydzielane ciepło krystalizacji zużywane jest do przebudowy strukturalnej istniejącej już do tego momentu formy niskotemperaturowej. Spadek stopnia krystaliczności euxenitu notowany w interwale temperatur 500—600°C wiązać należy z kondensacją ugrupowań atomów fazy amorficznej, co powoduje efekt dysproporcjonacji. Zahamowanie przyrostu fazy krystalicznej fergusonitu w przedziale 800—900°C wiąże się z przemieszczeniami atomów (głównie tlenu) w trakcie przejścia formy tetragonalnej w jednoskośną. Etapowi przemian polimorficznych badanych minerałów towarzyszy zmniejszenie tempa wzrostu krystalitów (tab. 1).

Osiągnięcie pełnej krystaliczności podczas wyprowadzania minerałów ze stanu metamiktycznego zależy wyłącznie od temperatury. Długość czasu prażenia wpływa na obniżenie temperatury osiągnięcia pełnej krystaliczności oraz na to, czy w układzie pozostaną relikty form niskotemperaturowych czy też dojdzie do całkowitej przemiany polimorficznej.

OBJAŚNIENIA FIGUR

- Fig. 1. Zależność stopnia krystaliczności (C) euxenitów od temperatury i czasu ogrzewania
Euxenit z Lindesnas prażony w poszczególnych temperaturach: 1 — 2 h, 2 — 1 h, 3 — 15 min., 4 — euxenit z Arendal — 20 min.

- Fig. 2. Krzywe DTA euxenitów
a — Arendal, b — Arendal (Seifert, Beck 1965), c — Lindesnas

- Fig. 3. Zależność stopnia krystaliczności fergusonitu z Llano County od temperatury prażenia
W górnej części przedstawiono wykres Komkova (1957) zależności różnicy stałych sieciowych a i b od temperatury

Янущ ЯНЕЧЕК

ОПРЕДЕЛЕНИЕ СТЕПЕНИ КРИСТАЛЛИЧНОСТИ МЕТАМИКТНОГО ЭВКСЕНИТА И ФЕРГУСОНИТА

Резюме

Используя метод Ольберга и Штриклера (1962) рентгенографического определения степени кристалличности стёкол, были прослежены изменения прироста кристаллической фазы во время нагревания метамикт минералов: эвксенитов из Норвегии и фергусонита из Техаса. Результаты показаны на фигурах 1 и 3. Эти минералы во время нагревания в температурах выше 400°C рекристаллизируются, подвергаясь одновременно полиморфным превращениям.

Эгзотермический эффект перемены низкотемпературной формы в высокотемпературную эвксенита при температурах 750—770°C объясняется кристаллизацией остатка (около 30%) стеклообразной фазы. Выделенные тепло кристаллизации используется для структурной перестройки существующей уже в этот момент низкотемпературной фазы. Понижение степени кристалличности эвксенита, отмеченное в интервале 500—600°C, надо связывать с конденсацией группировок атомов аморфной фазы, что вызывает эффект диспропорционации. Приторможение прироста кристаллической фазы фергусонита в интервале 800—900°C связано с перемещениями атомов (в основном кислорода) во время перехода от тетрагональной к моноклинной форме. Этапе полиморфных перемен изучаемых минералов сопутствует уменьшение скорости прироста кристаллитов (табл. 1).

Достижение полной кристалличности во время вывода минералов из метамиктичности состояния зависит лишь от температуры. Время кальцинации (прокаливания) влияет на снижение температуры достижения полной кристалличности и на то, останутся ли в системе реликты низкотемпературных форм или произойдёт полное полиморфное превращение.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Fig. 1. Зависимость степени кристалличности (C) эвксенитов от температуры и времени нагрева
Эвксенит из Линдеснас кальцинированный (прокаливаемый) в разных температурах: 1 — 2 h, 2 — 1 h, 3 — 15 min., 4 — эвксенит из Арендаль — 20 min.
- Fig. 2. Кривые дифференциального термического анализа эвксенитов
a — Арендаль, b — Арендаль (Зейферт, Бек 1965), c — Линдеснас
- Fig. 3. Зависимость степени кристалличности фергусонита из Льяно Каунти от температуры кальцинации
В верхней части показан график Комкова (1957) зависимости разности постоянных решётки a и b от температуры