

Reports

Spherulitic Recrystallization of Metamict Polycrase

Abstract. *Spherulites occur in the metamict matrix of the rare earth AB_2O_6 -type niobium-tantalum-titanium oxide, polycrase. Microprobe analyses show that the spherulites are similar in composition to the metamict polycrase except for a fivefold increase in calcium oxide. X-ray examination suggests that the spherulites are a titanium-rich rare earth fersmite.*

Spherulites are not uncommon features of natural glasses (1), but this report is the first description of the crystallization of spherulites from the amorphous matrix of a metamict mineral.

The spherulites occur in the metamict matrix of an orthorhombic AB_2O_6 -type oxide (A = rare earths, Ca, U, Th, Fe^{2+} , Mn; B = Nb, Ta, Ti, Fe^{3+}), polycrase, from Hitterö (Hidra), Norway (No. 473 in the Stanford University Mineral Collection). Although the specimen is labeled "aeschnite," microprobe analysis confirmed its polycrase composition. Because of confusion in the early nomenclature, it is not uncommon that museum specimens of aeschnite from Hitterö are found to have a polycrase composition (2).

In thin section, the spherulites occur as pale-yellow circles 30 to 150 μm in

diameter against a honey-yellow background of metamict polycrase. Under crossed Nicol prisms the spherulites exhibit a moderate birefringence which

Table 1. Partial electron microprobe analysis of metamict polycrase matrix and crystalline spherulites. Percentages are by weight; $\Sigma Ce_{RE} = Ce_2O_3 + Nd_2O_3 + Sm_2O_3$; $\Sigma Y_{RE} = Y_2O_3 + Gd_2O_3 + Dy_2O_3 + Er_2O_3 + Yb_2O_3$.

Metal oxide	Metamict matrix (%)	Spherulite (%)
TiO ₂	37.40	37.00
Nb ₂ O ₅	12.80	12.53
Ta ₂ O ₅	4.20	4.30
CaO	0.39	1.80
U ₃ O ₈ *	3.30	3.23
ThO ₂	7.50	7.50
Fe ₂ O ₃ *	0.71	0.76
ΣCe_{RE}	3.23	3.10
ΣY_{RE}	22.26	20.78

* Oxidation state is not determined by microprobe analysis.

increases in the center region. The surrounding polycrase is isotropic. The individual fibrils of the spherulites are seldom distinct and the extinction uniaxial isogyre characteristic of spherulites is observed in only a few instances. The spherulites occur throughout the specimen but are more concentrated along the numerous microfractures, where they coalesce, forming alteration zones parallel to the microfractures. At this stage of development, individual fibrils cannot be distinguished.

Results of partial electron microprobe analysis of the metamict matrix and the crystalline spherulites are tabulated in Table 1. The spherulites are similar in composition to the surrounding metamict polycrase except for a fivefold increase in CaO content. X-ray examination by Debye-Scherrer camera gives a faint diffraction pattern, but the lines can be matched with those of rare earth fersmite (3).

The x-ray data and the higher Ca content suggest that the crystallizing phase is a rare earth fersmite, an intermediate member of the euxenite-fersmite isomorphous series (4). These spherulites differ from the rare earth fersmite described by Makarochkin *et al.* (3) in their lower CaO content (1.80 compared to 8.23 percent by weight) and their much higher TiO₂ content (37.00 compared to 16.85 percent by weight). If the spherulites are fersmite, this is the first description of a rare earth fersmite analog to polycrase.

The formation of the spherulites was probably initiated by a thermal (for

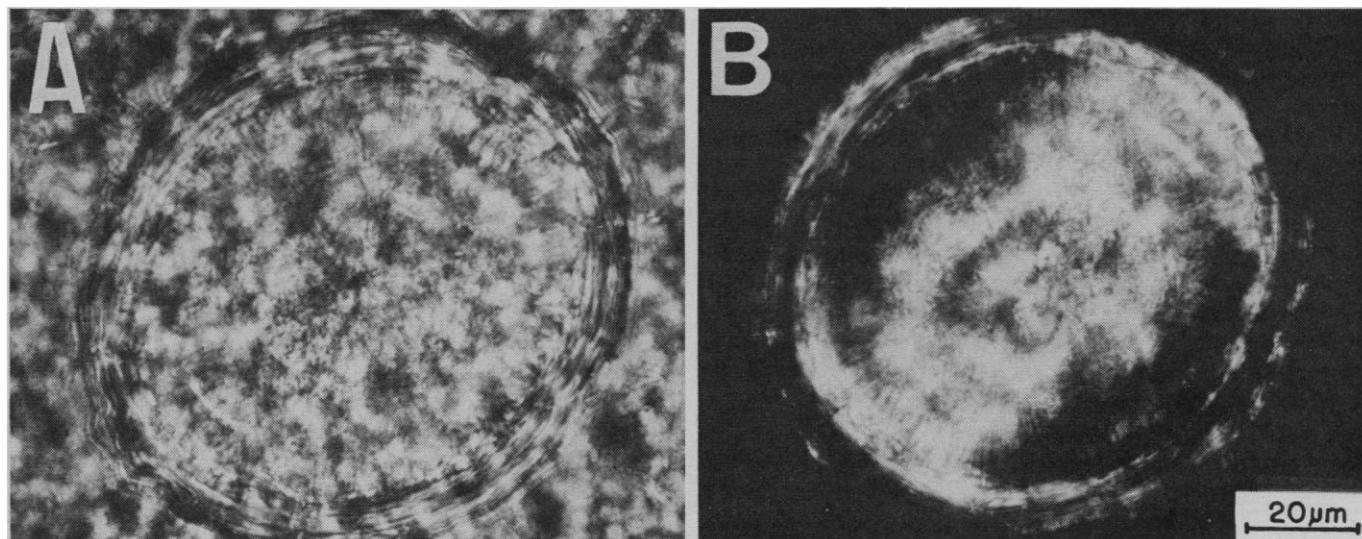


Fig. 1. (A) Spherulite in transmitted light, individual fibrils barely distinct; (B) spherulite under crossed Nicol prisms; the metamict matrix is isotropic.

example, hydrothermal) event postdating metamictization. The chemical changes are quite similar to primary pseudomorphic alteration of complex Nb-Ta-Ti oxides (5) and the natural recrystallization of the metamict Nb-Ta-Ti oxide, pyrochlore (6). The formation of spherulites during primary alteration and recrystallization may be a temporary feature which becomes obscured as the recrystallization progresses and spherulites coalesce and themselves recrystallize. Their transitory nature may explain why spherulites have not been previously observed in altered metamict Nb-Ta-Ti oxides.

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Monoclinic Sulfur: Heat Capacity Anomaly at 198°K Caused by Disordering of the Crystal Structure

Abstract. *The entropy of disorder of the idealized crystal structure of monoclinic sulfur at high temperatures is equal to the extra entropy change in the lambda-type (second order transformation type) heat capacity anomaly found at 198°K. The extrapolated entropy is zero at 0°K. The partially disordered crystal structure gradually becomes ordered as the temperature is lowered.*

The crystal structure of monoclinic sulfur (the form which is stable over a 20° temperature range just below the melting point at normal pressure) was found by Sands (1) to be partially disordered, in that one-third of the S₈ molecules which make up the structure can assume either of two orientations. The heat capacity measurements described below indicate that this disorder disappears as the temperature is lowered, resulting in a lambda-type (second order transformation type) heat capacity anomaly peaking at about 198°K.

The heat capacities of monoclinic and orthorhombic sulfur were measured separately from 12°K to the tempera-

ture T_e where they were in equilibrium with each other. In this temperature range, orthorhombic sulfur is the stable form at normal pressures. The heat of transformation (ΔH_e) was determined at T_e. A heat capacity anomaly was found at 198°K. The data are accurate enough to permit reliable calculations of entropy differences pertinent to the crystal structure.

Orthorhombic sulfur has an ordered crystal structure and its entropy is conventionally defined as zero at 0°K. From a third-law calculation comparing orthorhombic and monoclinic sulfur, the entropy of the monoclinic form at 0°K is 0.007 ± 0.020 cal °K⁻¹ g-atom⁻¹. This calculation was made with only the new heat capacity data obtained in the study reported here. If the disordered crystal structure determined by Sands (1) were maintained down to 0°K, the zero point entropy would be (R/24)ln 2 per gram atom (R is the gas constant), or 0.057 cal °K⁻¹ g-atom⁻¹, calculated according to statistical thermodynamics. This entropy is not present at 0°K and the crystal structure at very low temperatures is therefore ordered.

The obvious place to look for the

missing entropy is in the lambda anomaly shown in Fig. 1. The experimental data (average heat capacities and temperature ranges) are shown by the horizontal bars; the solid curve was derived from them. Except for this anomaly, the heat capacities were smooth, monotonically increasing functions of temperature.

To find the extra entropy change in this anomaly, it was necessary to determine what the heat capacity would have been in the absence of an anomaly. Conveniently, the heat capacity difference between monoclinic and orthorhombic sulfur was the same linear function of temperature over ranges below and above the anomaly. This linear function could be used to interpolate the "normal" heat capacity through the anomalous region. A smooth interpolation of this type is reasonable because of the similarity between orthorhombic and monoclinic sulfur and the very slight effects to be expected from introducing complete ordering into the monoclinic structure.

Figure 2 shows the extra entropy, ΔS, calculated by integrating the difference between the actual and interpolated heat capacities of monoclinic sulfur between 70° and 300°K. The uncertainty of integration from 120° to 220°K is estimated as ± 0.005 cal °K⁻¹ g-atom⁻¹ in addition to any error of interpolation. The agreement between the data in Fig. 2 and the theoretical entropy of disorder of the high-temperature crystal structure is quite reasonable. The heat capacity anomaly is most likely caused by the gradual acquisition of disorder as the temperature is raised, and the data in Fig. 2 reflect the degree of this disorder at each temperature. The entropy at 0°K is not significantly different from zero within the experimental uncertainty, but it is worth noting that the total of this entropy and the maximum ΔS from Fig. 2 agrees almost perfectly with the entropy calculated by Sands (1).

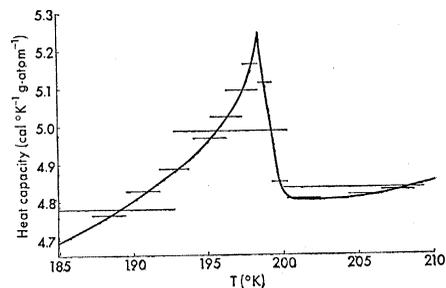


Fig. 1. Heat capacity of monoclinic sulfur near 198°K.

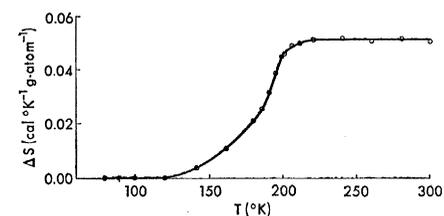


Fig. 2. Extra entropy in the heat capacity anomaly of monoclinic sulfur.