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Recovery of the original samarskite structure by heating in a reducing atmosphere

Yoshinori Sugitani, Yoshihisa Suzuki and Kozo Nagashima

Institute of Chemistry, University of Tsukuba
Sakura-mura, Ibaraki 305 Japan

Abstract

The original samarskite structure was recovered by heating metamict samples in a reducing atmosphere (H_2) at 550°C. The X-ray diffraction pattern of the recovered phase is quite different from those of samples heated in an oxidizing atmosphere. Lattice parameters have been calculated from the diffraction data, and the axial ratio has been found to be in good agreement with the reported data obtained by morphological observation.

Introduction

Samarskite, (Y,Er,Ce,U,Ca,Fe,Pb,Th) (Nb,Ta,Ti, Sn)$_2$O$_6$, occurs naturally in the metamict state due to the presence of significant amounts of radioactive elements such as uranium and thorium (Palache et al., 1952; Lima de Faria, 1964). Consequently, previous studies of this mineral have been carried out on samples which have been recrystallized in an attempt to restore the original lattice structure (Berman, 1950; Komkov, 1965; Nilssen, 1970; Nudel'man and Sidorenko, 1963; Sugitani et al., 1980; Van Wambeke, 1960). Recrystallization of the mineral has been attempted by controlled heating in an oxidizing atmosphere (generally in air or an inert atmosphere (e.g., N_2). However, the results for samarskite obtained from this procedure differ from sample to sample and from study to study depending upon the locality of the sample and/or the method of heat treatment adopted by the investigators (e.g., Lima de Faria, 1964). Complete understanding of either the explicit chemical formula or the crystal structure of samarskite has not yet been achieved.

Results and discussion

Generally, samarskites recrystallized in air or N_2 show complicated powder X-ray patterns. This has been ascribed to the formation of a number of different crystalline phases during the heating, only one of which can be regarded as the original samarskite phase.

We have found, however, that natural samarskite which has been recrystallized at high temperatures (400~1200°C) in a reducing (H_2) gas flow will yield a relatively simple X-ray powder pattern. If indeed a single crystalline phase now predominates it may be postulated that this is, in fact, the original samarskite.

Figure 1 shows powder X-ray diffractograms of a natural samarskite sample from Kawabe, Fukushima Pref., Japan, heated at various temperatures in air (left side of Fig. 1) and in H_2 atmosphere (right side of Fig. 1). The sample treated at 580°C in air shows peaks characteristic of the synthetic Nb_3UO_{10} phase. At increased temperatures different diffraction patterns appear (e.g., that at 800°C), and finally at 1200°C the results obtained correspond well with those reported by Nilssen (1970). This diffraction pattern can be ascribed to the formation of several new crystalline phases including pyrochlore, fergusonite, and ixiolite-like $FeNbO_4$.

The results obtained from heating this metamict sample in a reducing atmosphere, however, differ significantly from those described above and reported elsewhere which have all employed an oxidizing or inert atmosphere during heating. As can be seen from the right hand side of Figure 1, two distinct phases can be obtained by heating in a reducing atmosphere. The first, or low temperature phase, is obtained by heating at 550°C for 16 hr. On heating to 950°C, a high temperature phase forms as is indicated by the splitting of the main peak in the diffraction pattern into a doublet. It was found, in addition, that both the low and high temperature phases can be treated so as to give exactly the same diffraction patterns as those shown on the left hand side of Figure 1, simply by heating in air at the requisite temperature.

These results would indicate that the original phase of samarskite is formed only in a reducing atmosphere and that it cannot be recovered from the metamict state by heating in air. Attempts to recover the original phase of samarskite by heating in N_2 atmosphere were not successful for the samples in the present study. These would seem reasonable if the original samarskite, like many other complex Nb–Ta–Ti oxide minerals, contains a proportion of its iron and/or uranium in lower oxidation states e.g., Fe(II), U(IV) etc. at the time of its formation. Natural samarskites might have been oxidized to some extent by weathering, hydrothermal influence, or radioactivity. In order to confirm this hypothesis, a synthetic study using a variety of starting oxide materials contain-

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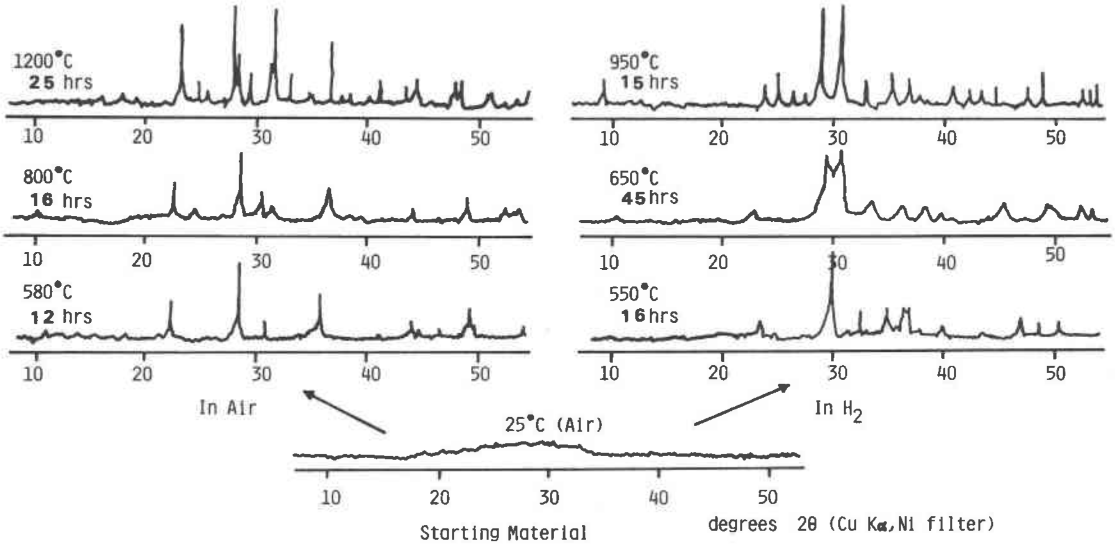

Fig. 1. X-ray powder patterns of samarskite, Kawabe, Fukushima Prefecture, Japan, heated in oxidizing and in reducing atmospheres. Heating time and temperature are indicated on the diffractograms.

Table 1. X-ray power diffraction data for Samarskite, Kawabe, Fukushima Prefecture, Japan, heated in H_2 gas flow at 550°C for 16 hours*

h k l	d_{cal}	d_{obs}	I/I_o
1 1 0	3.723	3.728	15
0 1 1	3.579	3.589	5
1 1 1	3.029	3.030	100
2 0 0	2.844	2.843	15
0 0 2	2.605	2.603	15
2 0 1	2.496	2.495	10
2 1 0	2.463	2.463	5
0 2 0	2.462	2.461	5
1 1 2	2.135	2.136	5
2 0 2	1.921	1.920	10
2 2 0	1.861	1.863	10
3 1 0	1.769	1.767	10
0 3 1	1.566	1.567	5
1 3 1	1.510	1.511	5
3 1 2	1.464	1.463	5

* CuK_α radiation, diffractometer method, 2°/min in 2θ, Si standard.

ing different oxidation states of Fe + U would be necessary.

The peaks for the low temperature phase have been indexed as shown in Table 1. The lattice parameters and axial ratios of the recrystallized samarskite have been calculated by least squares and are shown in Table 2, along with results for other samarskite samples from different localities in Japan. The data on the axial ratios in Table 2 do not directly coincide with the data described elsewhere, e.g., 0.5456:1:0.5173 and 0.5547:1:0.5173, Palache et al. (1952); and Brögger (1906) respectively. However, if we take half of their *b* parameters as our new *b* parameters, their axial ratios can be recalculated to be

1.0912:1:1.0346 (Dana)

and

1.1094:1:1.0346 (Brögger).

These values are in good agreement with our calculated data except for Samekawa samarskite which has a doubled *b* dimension compared to the others. The reason for this doubling is not known. It might be ascribed to some form of ordering of metal ions.

Analysis of the high temperature phase of natural samarskite as well as a synthetic study of samarskite is in progress.

Table 2. Lattice parameters of natural samarskite from several localities in Fukushima Prefecture, Japan. Figures in parentheses are standard deviations*

	Temperature treated (H_2 atmosphere)	a(Å)	b	c	β(°)	a : b : c
Kawabe	550°C	5.687(4)	4.925(2)	5.210(8)	90.02(8)	1.155:1:1.058
Ishikawa	550	5.664(6)	4.940(3)	5.173(7)	90.0(2)	1.147:1:1.047
Utsumine	600	5.64(2)	4.98(4)	5.18(2)	90.0(4)	1.133:1:1.040
Samekawa	600	5.71(3)	9.80(3)	5.20(1)	90.5(3)	0.583:1:0.531 (1.165:1:1.061)

* Numbers of reflections used and rejected in the calculation of lattice parameters are 14 and 1 for Kawabe, 8 and 0 for Ishikawa, 11 and 0 for Utsumine, and 10 and 3 for Samekawa Sample.

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