THE AMERICAN MINERALOGIST, VOL. 50, SEPTEMBER, 1965

EFFECT OF NEUTRON BOMBARDMENT ON THE KINETICS OF SOME RECONSTRUCTIVE PHASE TRANSFORMATIONS[1]

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INTRODUCTION

Several authors have reported anomalous polymorphic behavior attributable to structural disorder induced by neutron bombardment. Chapman, Warren and Dienes (1953) reported the reaction black phosphorous→red phosphorous as being caused, to a small extent, by neutron bombardment. Two years later, in 1955, Fleeman and Dienes studying the first order gray tin→white tin transformation, normally slow below 13° C., reported that the transition had occurred as a result of neutron irradiation of $10^{18}n/cm^2$ total flux, under low temperature conditions. The effect of neutron irradiation on the monoclinic→cubic ZrO_2 transformation was, for several years, the subject of investigations—Wittels and Sherrill (1959a, b) and Adam and Cox (1959). It is now thought that, while pure monoclinic ZrO_2 does not transform to the cubic phase under neutron bombardment, in the presence of small amounts of impurities stabilizing the cubic phase (V, Cr, Ta, etc.) transformation does occur under moderate irradiation conditions. The marked influence of neutron bombardment on structure and properties of the silica polymorphs has been demonstrated on several occasions, and has been reviewed briefly by the authors in a previous communication (Roy and Buhsmer, in press).

In order to determine whether neutron bombardment measurably affected various solid-solid phase transformations it was decided to determine qualitatively the influence of such irradiation on the kinetics of several selected reconstructive transformation. Materials exhibiting both normal and reverse volume relationships, including devitrification reactions were chosen.

EXPERIMENTAL APPROACH

For irradiations, performed at the Brookhaven National Laboratory (BNL) reactor, quartz and cristobalite samples were sealed in reactor-grade 2-S aluminum vials, and the exposure was determined as the sum of the thermal neutron flux and flux greater than 1 mev; the latter being determined on the basis of the (n, p) reaction with nickel wire, while the

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former is taken from the approximate flux level of the reactor and the total exposure time. Samples of PbO, γ-Ca_2SiO_4 and SiO_2-glass were irradiated in the Pennsylvania State University (PSU) reactor to a total flux of about 10^{17} n/cm^2 determined solely from the operating level of the reactor and the exposure time.

For the high pressure experiments a sample was pelletized inside a nickel ring, covered on top and bottom by platinum foil, and pressurized in the uniaxial device described by Roy and Dachille (1960). For the high temperature runs the sample was sealed in a platinum tube and heated in a platinum wound furnace. For the lower pressure runs (in the region of one Kbar) the samples were sealed dry in a gold tube as described by Roy and Tuttle (1956). Extent of conversion, in all cases, was determined from the *x*-ray diffraction patterns using the ratio-of-peak-heights method. Since the conclusions drawn are entirely qualitative, all tables and figures are omitted since they are available to the interested reader in the thesis (see first footnote).

Results

Transformations Having Positive Volume Change.

1) SiO_2 quartz→SiO_2 cristobalite

The quartz samples were heated for 12 hours at temperatures ranging from 1150° to 1530° C. From the results it is apparent that no marked change was observed in the rate of the quartz→cristobalite transition after neutron irradiation to a total flux of 2.4×10^{19}n/cm^2. In view of Primak's work (1958) this result is not entirely surprising since he demonstrated that at these temperatures the damage in quartz could be rapidly annealed out.

2) SiO_2 quartz→SiO_2 coesite

Quartz was reacted in the stability field of coesite at 75 Kbar pressure and 477° C. The reaction was continued for 15 hours. Although the data are insufficient to propose a meaningful neutron flux-per cent transformation dependence, it is apparent that irradiation produced defects have a marked effect on the reconstructive quartz→coesite transition in that conversion proceeds approximately twice as fast after exposure of the quartz to a total flux of 2×10^{19}n/cm^2. This could mean that islands of disordered material convert faster to coesite, although at this flux the quartz (by *x*-ray) appears to be well crystallized.

The reverse reaction was also attempted by placing unirradiated and irradiated coesite in the quartz field at 22 kbar and 493° C. for 18 hours. The *x*-ray diffraction pattern of the unirradiated sample showed no detectable transformation to quartz, while the irradiated material revealed about 35% quartz present after reaction. Comparison with the data for the forward reaction shows about equal conversion for the irradiated samples, but the unirradiated material exhibited a very different amount of reaction. This may be evidence that the effect of neutron bombardment is similar to that of increase in temperature of the system since the kinetics is increased in both directions.

Transformations Having Negative Volume Change.

1) $PbO_{litharge} \rightarrow PbO_{Massicot}$

The two polymorphs of PbO; red tetragonal litharge and yellow orthorhombic massicot, are related by a slow reconstructive transformation under the proper temperature-pressure conditions. The transformation is unusual in that the high temperature form, massicot, has a slightly higher density than the low temperature form, litharge (White *et al.*, 1961). Pure samples of litharge and massicot were formed from reagent grade PbO (a mixture of the two forms) by hydrothermal (I) and thermal (II) synthesis. After irradiation of the PbO samples to about $10^{17}n/cm^2$ in the PSU reactor, it was found that no litharge→massicot transformation (detectable by *x*-ray diffraction) had been effected. The results of the thermal treatments show that although the kinetics of the polymorphic reaction are complicated, the massicot polymorph seems favored by the effects of neutron bombardment.

2) γ-$Ca_2SiO_4 \rightarrow \alpha^1 Ca_2SiO_4$

A second example of a negative transition volume is found in calcium orthosilicate. The gamma form was prepared from silica (Cab-$\overline{o}$sil) in two steps at a maximum temperature of 1385° C.; *x*-ray diffraction of the sample showed γ-Ca_2SiO_4 with trace amounts of the beta polymorph. After irradiation to $10^{17}n/cm^2$ in the PSU reactor, the *x*-ray diffraction pattern shows peak broadening and an increase in the amount of the beta form present, indicating considerable neutron bombardment induced structural disorder and the transformation to the denser beta polymorph much below its transition temperature. Comparison with the PbO results shows that neutron induced disorder does not simply favor the lower density form.

DTA patterns were run on the γ form after irradiation, and the $\gamma \rightarrow \alpha^1$ peak was not detected even up to 950° C.; *x*-ray diffraction indicated almost complete transformation of the irradiated sample to the beta form, while the unirradiated sample still contained a substantial amount of the gamma form.

3) Crystallization reactions:

The devitrification reactions were performed in the high pressure uniaxial device mentioned above, and the SiO_2 glass samples were irradiated to a flux of about $10^{17}n/cm^2$ in the PSU reactor.

a) *SiO_2 glass→SiO_2 coesite transformation:* The data from several runs indicate a marked but very complicated influence on neutron irradiation of the rate of devitrification under the pressure-temperature conditions of the coesite stability field. The appearance of quartz in runs of less than 18 hours suggests its presence as a reaction intermediate, but more data are needed to speculate on the mechanism involved. Nevertheless, it can be said that in the early stages of the crystallization process irradiation to as low as $10^{17}n/cm^2$ total flux affects the glass structure enough to increase the rate of coesite formation.

b) *SiO_2 glass→SiO_2 quartz transformation:* At pressures as high as 25 kbar and temperatures as high as 500° C. for reaction times of up to two days this reaction was not detected by *x*-ray diffraction for either the irradiated or unirradiated glass.

Conclusions

It is evident that structural disorder introduced into the crystalline solid by irradiation in a nuclear reactor has a most important effect on the rate of the polymorphic transformations in that substance. The survey and qualitative nature of the approach in this work does not permit unique interpretations of the mechanism involved, but rather serves to demonstrate that most reconstructive transformations occurring in a temperature region where extensive annealing is not likely to take place were affected measurably by neutron irradiation. Each transformation behaved differently after irradiation in most cases increasing the rate of reaction, but in some cases favoring a particular structural state, not necessarily the lower density state.

Acknowledgments

This research was supported by the NSF under Grant *G-419231*. We are also indebted to Dr. G. J. Dienes for making available access to the reactor facilities at Brookhaven.

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THE AMERICAN MINERALOGIST, VOL. 50, SEPTEMBER, 1965

SPESSARTITE-QUARTZ ROCKS (COTICULES) FROM NOVA SCOTIA[1]

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Introduction

In mainland Nova Scotia, metasedimentary rocks of the Lower Ordovician Halifax Formation contain beds, lenses and nodules composed chiefly of spressartite and quartz. Renard (1878) called similar rocks, from the Ardennes region of Belgium, "coticules." This word is derived from coticula, the feminine diminutive form of the Latin cos, cotis, meaning "any hardstone, flintstone, whetstone, hone or grindstone." Emerson (1898) used the term to describe quartz-garnet rocks in southeastern New England and its use was revived by Clifford (1960) for similar rocks in western New Hampshire. The term gondite (Fermor, 1909) has been applied to similar rocks but appears to embrace a broader group of manganese-bearing rocks than coticule. Take (in Trost, 1958) used the name gondite for spessartite-garnet rocks from Lazy Head, Nova Scotia. These are probably coticules.[2]

Slates and schists of the Halifax Formation are known to contain coticule beds or lenses at several widely separated localities. Good exposures of coticules are present near Port Felix South of Lundy and near Sandford.

Lithology and Chemical Composition

The coticules occur interbedded with and in pelitic rocks that have undergone regional metamorphism of greenschist grade. Locally, near

[1] Published by permission of the Director, Geological Survey of Canada.

[2] The authors acknowledge the assistance rendered by Dr. J. E. Sanders in securing reference material on coticule terminology.