

2. Coesite

a. Introduction

Although silicon is one of the most abundant elements of the earth and quartz or silicon dioxide is one of the most common rock-forming minerals, not until 1953 did anyone realize that a high-pressure modification of silica existed.

In 1953 a dense polymorph was synthesized by Dr. L. Coes, Jr.¹⁸ of Norton Co. This new dense form was named Coesite or silica C. This material was made at pressures of about 35 kilobars in the temperature range of 500° to 800° C. This same material was later found in nature at Meteor Crater, Arizona.

Another dense form of SiO_2 was synthesized by Stishov and Popova¹⁹ (1961) at 1200° to 1400° C at pressures above 160 kilobars. The material has been found in the Coesite bearing Coconino Sandstone²⁰ of Meteor Crater, Arizona. This dense form made at very high pressures was named Stishovite in honor of the discoverers.

b. Experimental Investigation

Fused silica was pressed at a pressure of 35 kilobars at a maximum temperature of 640° C for 5 to 10 minutes. Preliminary examination by the Becke method of determining refractive indices revealed the possible presence of Coesite which is a denser form of SiO_2 . To confirm this result, a Debye-Scherrer X-ray pattern was obtained for analysis.

Natural α -quartz was crushed and subjected to high pressure of 40 kilobars and temperature of 550° C for 20 to 65 minutes. Debye-Scherrer X-ray powder patterns were again taken of this pressed material. The "d" values obtained indicated the presence of α -quartz with two strong lines (d values of 3.10 and 3.45), corresponding to the strongest lines of Coesite. The amount of Coesite present was very small. The Coesite was formed in these experiments at the minimum pressure and temperature necessary for direct conversion of the low-density silica to the high-density silica.

B. HALIDES

NaI powder obtained from Fisher Chemicals was melted and cast into a nickel tube. After placing the sample into the high-pressure apparatus, the NaI was subjected to a pressure of 25×10^4 psi and a constant power input of 550 watts. The sample had compressed 36 percent of its original volume. The volume change caused the thermocouple to open.

These initial experiments indicated no metastable phase present as determined by X-ray diffraction.

C. RARE EARTHS

The rare earths, that is the sesquioxides, are found in three distinct structural forms. The first of these is the hexagonal or A- R_2O_3 structure which is typified by La_2O_3 . The second is the monoclinic or B- R_2O_3 structure and the third is the cubic or C- R_2O_3 structure which is the same as that of Mn_2O_3 . In general, the rare earth metal ions with the largest radii; e.g., lanthanum, form the hexagonal oxide, and those with the smallest radii form the cubic oxide. Many of the rare earths can be obtained in two modifications. Thus, samarium oxide is found in both the cubic-C and monoclinic-B forms.

Investigations of the stability limits of the various structural modifications have been carried out for a number of years. The range of stability of the three modifications as a function of cation-radius and temperature as proposed by Shafer and Roy is shown in Figure 6. It is evident from this figure that samarium oxide lies near the border between the A- and B- type fields at high temperatures. However, the A-type oxide of samarium has not been observed either in high-temperature X-ray studies nor in room-temperature examination of material quenched from high-temperatures.

In the hexagonal oxide each cation has seven nearest oxygen neighbors compared with six such neighbors in the other structures. This results in a greater density in the hexagonal modification compared with the other two forms. Thus, in the case of neodymium oxide, the relative volumes are A:B:C = 75.5:77.7:84.6 (A^3/FW). It seemed that if the A-modification of Sm_2O_3 could be formed that both high-temperature and high pressure would be required. Accordingly, the material quenched from high temperatures at pressures to 30 kilobars was examined. In no case was any trace of an hexagonal modification observed.

Experimentally, C-form (cubic) oxide ($a_0 = 10.89A$) obtained from Research Chemicals Corporation was prepressed in a steel die to approximately 50 percent of theoretical density. This compact was loaded into a nickel tube and into the high-pressure apparatus described previously. Some samples were instrumented with thermocouples, others were not. In the absence of such instrumentation the temperature of the run was estimated from the power settings as calibrated in the instrumented runs.

In eight runs (shown in Table IV) at 30 kilobars and temperatures between 575° and 925° C the C-form was converted to the more dense B-form. At the lowest temperature the conversion was incomplete. In two runs, one at 580° C and one at 925° C the monoclinic form was used as the starting material. No conversion of this oxide was observed.