HIGH PRESSURE, HIGH TEMPERATURE SYNTHESES OF RARE EARTH DIANTIMONIDES AND Th_3P_4 TYPE POLYMORPHS OF RARE EARTH SESQUISULFIDES

Abstract of

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ABSTRACT

The rare earths form series of compounds which are known for several elements but end abruptly or undergo a change of structure at some member of the series. The diantimonides are one such series. Sb-Sb repulsion becomes stronger as the rare earth size decreases and the previously known series ended at Sm. It was felt that high pressure would overcome the Sb-Sb repulsion and allow bonding to form stable or metastable compounds not possible by ordinary techniques.

Synthesis studies were carried out on mixtures of antimony with all the rare earths except Pm and with Sc and Y. The known diantimonide series was extended two elements to $GdSb_2$ and $TbSb_2$. A new orthorhombic structure was found in the series for $GdSb_2$, $TbSb_2$, $DySb_2$, $HoSb_2$, $ErSb_2$, $TmSb_2$ and YSb_2. Attempts to synthesize diantimonides of Sc, La, Ce, Eu and Lu were not successful.

Reaction products for one to two molar mixtures of rare earth to antimony were determined for all the elements studied as a function of pressure and temperature up to 70 kilobars and 1800 ^{o}C. Products were identified by their X ray diffraction patterns. Only Sb plus the rare earth oxide were found for La, Ce and Eu. The oxygen apparently

migrated into the sample from the pyrophyllite tetrahedrons. For Sc and Lu only the monoantimonides plus Sb were found. Only $LaSb_2$ type diantimonides were found for Pr, Nd, Sm and Yb. Complex reaction product diagrams were obtained for mixtures of Gd, Tb, Dy, Ho, Er and Tm with Sb. Two different orthorhombic structures were found for $GdSb_2$ and $TbSb_2$.

All compounds in the rare earth - antimony systems were silver-grey and metallic in appearance. All reacted almost the same with acids, H_2O and NH_4OH but did not react with organic reagents. They were stable to the atmosphere. The density of each compound was determined.

Most of the heavy rare earth sesquisulfides are known in a monoclinic form except Yb_2S_3 which is orthorhombic and Lu_2S_3 which is rhombohedral. The light rare earth sesquisulfides are commonly found in a Th_3P_4 type cubic structure. Dy_2S_3 is found in both cubic and monoclinic forms. Since the cubic form is more dense and higher coordinated it seemed probable that the monoclinic form of the heavy rare earth sesquisulfides could be converted to the cubic form by high pressure techniques. Dy_2S_3, Ho_2S_3, Er_2S_3, Tm_2S_3, Yb_2S_3 and Y_2S_3 were all converted to the cubic form at 77 kilobars and 2000 °C in a cubic press. Lu_2S_3 was about 50 per cent converted to the cubic form at these conditions.

The results of this investigation suggest that other series of rare earth compounds could be extended by high pressure techniques and several possibilities are discussed.