

C. HIGH-PRESSURE SYNTHESIS

A review of high-pressure synthesis, as illustrated by studies on compounds with the chemical formula ABX_3 or $(AX)_n(ABX_3)$, has been prepared for publication as a chapter entitled "High-Pressure Syntheses" in Preparative Methods in Solid State Chemistry, edited by P. Hagenmuller (Academic Press, New York). The Introduction is given below.

"High-pressure synthesis has a practical as well as a scientific interest, since many high-pressure products are either stable or metastable at atmospheric pressure to temperatures well above 300°K. To illustrate the strategy and present-day techniques of high-pressure synthesis, we have chosen to review the high-pressure studies - through June 1970 - performed on compounds having the chemical formula ABX_3 or $(AX)_n(ABX_3)$, where cation A is always larger than cation B. At atmospheric pressure, these compounds crystallize in a variety of different structures, or do not form at all. High pressures stabilize preferentially the more dense phase. The most dense ABX_3 phase has the cubic-perovskite structure, and if the

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Section II

A cation is not too small, pressures obtainable in the laboratory are generally sufficient to stabilize it. In the case of oxides, fluorides and chlorides, these high-pressure perovskites, as well as the intermediate-pressure polymorphs, are generally stable at atmospheric pressure and room temperature.

After a brief description in Sec. II of general preparative techniques, several ABX_3 and $(AX)_n(ABX_3)$ structures are compared in Sec. III, special attention being given to cation-site coordinations and relative densities. The experimental summary is divided into three operational groupings:

- (1) High-pressure transformations of compositions prepared at atmospheric pressure
- (2) Composition formations requiring elevated pressures
- (3) Syntheses greatly facilitated by pressure

Within the first grouping, the relative stabilities of five hexagonal-perovskite polytypes are determined by the relative ionic sizes and the pressure. These polytypes are distinguished from the other polymorphs, since extensive data on the relationships between them are now available. The relative stabilities of other ABX_3 polymorphs depend upon the outer-electron configurations at the cations as well as on relative ionic sizes and pressure. Some general features of these inter-relationships are presented. They permit classification of the second grouping into six distinguishable groupings, each representing a different set of conditions, modifiable by high pressure, that inhibit composition formation at atmospheric pressure. In all cases, high pressure stabilizes preferentially a more dense phase. This classification is not intended to be exhaustive, but to illustrate, from available data on ABX_3 compounds, considerations pertinent to the choice of high pressure as a tool for chemical synthesis. The final section merely calls attention to the fact that high pressure may also alter the kinetics of a reaction so as to greatly facilitate synthesis of a composition stable at atmospheric pressure."

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