

High-pressure / High-temperature Synthesis in Materials Chemistry

60 years ago, very little was known about chemistry at high pressures and temperatures. Today, an increasing number of experimental devices and techniques have become available which open entirely new areas in which solid state chemistry under elevated pressure can be studied. An increasing number of publications dedicated to the topic pressure testify to the great interest in basic and applied fields of high-pressure research. Remembering the pioneering work of P.W. Bridgman just over one hundred years ago, this issue of *Zeitschrift für Naturforschung B – Chemical Sciences* collects 16 papers, which deal with preparative solid state chemistry under high-pressure or solvothermal conditions.

A general overview on recent aspects of high-pressure chemistry in Materials Science is given by Demazeau *et al.* (Bordeaux / France). High pressure is important either for stabilizing new structural modifications of materials previously prepared only at ambient pressure, or for preparing entirely new materials. The review describes the main factors induced by the parameter pressure that lead to new structural varieties or novel materials. Two different approaches become evident: (i) for a given composition with characteristic chemical bonds, high pressure can induce structural transformations, (ii) high pressure can lead to the formation of novel materials from different precursors through the formation of new chemical bonds.

A new filled skutterudite $\text{TbFe}_4\text{P}_{12}$ was prepared at around 4 GPa and 1050 °C (Shirotani *et al.*, Murorashi / Japan). Several of the filled skutterudites are only accessible through high-pressure techniques. Metallic $\text{TbFe}_4\text{P}_{12}$ is a ferromagnet at 10 K.

The TiNiSi type normal-pressure modifications of the stannides REPtSn ($\text{RE} = \text{La}, \text{Pr}, \text{Sm}$) transform to metastable ZrNiAl -type phases under multianvil high-pressure (9–14 GPa) high-temperature (1050–1400 °C) conditions (Riecken *et al.*, Münster / München / Germany). The magnetic properties of these phases change drastically on going from the normal- to the high-pressure modifications.

Yamanaka *et al.* (Higashi-Hiroshima / Japan) report on the preparation and structure determination of a new silicide BaSi_6 . A detailed bonding analysis of iso-

typic SrSi_6 by Schwarz *et al.* (Dresden / Germany) reveals that SrSi_6 does not belong to the class of classical Zintl phases, but represents a member of the group of electron-excess intermetallic compounds which are frequently labelled as metallic Zintl phases.

Demazeau *et al.* (Bordeaux / France) report on a novel synthetic strategy for a long known compound, RhO_2 . Reaction of anhydrous RhCl_3 with Na_2O_2 at 600 °C under an oxygen pressure of 200 MPa yields crystalline, rutile-type RhO_2 , avoiding partial oxygen substitution by hydroxyl groups.

Two new series of metastable oxides, namely REMn_2O_5 and $\text{RECu}_3\text{Mn}_4\text{O}_{12}$, prepared under moderate pressure conditions are reviewed by Alonso *et al.* (Madrid / Spain). A novel series of ferrimagnetic oxides with comparatively high Curie temperatures were obtained by replacing Mn^{3+} by Fe^{3+} in the parent REMn_2O_5 compounds ($\text{RE} = \text{Y}, \text{Dy–Yb}$).

Recent results on high-pressure / high-temperature synthesis of new transition metal oxide perovskites are reviewed by Rodgers *et al.* (Edinburgh / United Kingdom). Their focus is on perovskite and related Ruddlesden-Popper type transition metal oxides, which were synthesized during the last decade. Special attention is paid to the multiferroic bismuth-based perovskites and the manganite materials revealing colossal magnetoresistance and charge ordering.

High oxygen pressure is a key tool for the stabilization of transition metals in highest formal oxidation states, by securing to strong chemical bonds through improvement of the $\text{M}^{n+}\text{–O}$ bond covalency. Using this approach, Demazeau *et al.* (Bordeaux / France) review different electronic phenomena in ^{57}Fe -doped RENiO_3 nickelates ($\text{RE} = \text{rare earths}, \text{Y and Tl}$) and ^{119}Sn -doped AEFeO_3 ferrates ($\text{AE} = \text{Ca}, \text{Sr}$). Phenomena like unusual electronic configurations, orbital ordering, charge disproportionation, and insulator-metal transitions in the perovskites series can easily be monitored via Mössbauer spectroscopy.

Platinum nanoparticles and nanorods can be synthesized by a microwave-assisted solvothermal technique (Komarneni *et al.*, Pennsylvania / USA). By changing the reaction conditions a controlled particle size (*ca.* 3 nm) and morphology could be obtained. Such

nanoparticles have technical importance in the catalysis of hydrosilylation, oxidation, and hydrogenation reactions.

Dubitsky *et al.* (Moscow / Russia) present an interesting approach for superhard, superconducting ($T_C = 10.5 - 12.6$ K) materials which can be obtained by high-pressure / high-temperature sintering of synthetic diamond powders coated with a niobium film and in 50% – 50% composition with superhard C_{60} fullerite. Composite materials with $T_C = 36.1 - 37.5$ K were obtained in the systems diamond – MgB_2 and cubic boron nitride (*c*-BN) – MgB_2 . Another class of superhard materials can be obtained through pressure-induced (15 GPa, 520–1820 K) polymerization of solid fullerenes C_{60} and C_{70} in a toroid type apparatus (Blank *et al.*, Moscow / Russia)

Solvothermal techniques can be used for stabilizing *c*-BN nanocrystals under moderate conditions. Considering the instability of BN nanoparticles, Lai *et al.* (Jinan / China) investigated the structural transformation of BN nanoparticles in benzene and found that a large proportion of *h*-BN nanoparticles can be converted into *c*-BN and *w*-BN (wurtzite type BN) at 280 °C and 50 MPa. These results may open up new synthetic routes for the large-scale synthesis of other superhard nanomaterials under moderate conditions, such as diamond and cubic carbon nitride. The article by Dubrovinskaya *et al.* (Bayreuth / Germany) also deals with hard materials. Direct reaction of boron

carbide with graphite in a multianvil apparatus under high-pressure / high-temperature conditions led to bulk samples of boron-doped diamond.

In a series of *in situ* experiments in an externally heated diamond anvil cell, Kurnosov *et al.* (Bayreuth / Germany) studied the melting phase relation of methane clathrate hydrates up to 3 GPa. Interestingly, the melting is not significantly affected by the presence of ammonia. Such systems are important for understanding the nature of Titan's atmosphere.

Holbig *et al.* (Bayreuth / Germany) report on the compression behaviour of zircon-doped nano anatase, which was synthesized by sol-gel methods and investigated with the help of a diamond anvil cell up to a pressure of 13 GPa. *Ab initio* electronic structure simulations indicate a clustering of the Zr atoms. Furthermore, the effect of the chemical substitution on the mechanical properties is discussed.

By bringing together diverse topics of current high-pressure chemistry which utilize different experimental approaches (autoclaves, multianvil, and diamond-anvil-cell techniques), this issue of *Zeitschrift für Naturforschung B – Chemical Sciences* tries to underline the importance of the parameter pressure as a thermodynamic variable equal to the temperature and the chemical potential in modern Materials Chemistry.

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