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Synthesis, crystal structure and properties of $Mg_3B_{36}Si_9C$ and related rare earth compounds $RE_{3-x}B_{36}Si_9C$ (RE=Y, Gd–Lu)

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ABSTRACT

We report on the synthesis and characterisation of $Mg_3B_{36}Si_9C$. Black single crystals of hexagonal shape were yielded from the elements at 1600 °C in h-BN crucibles welded in Ta ampoules. The crystal structure (space group $R\bar{3}m$, a=10.0793(13) Å, c=16.372(3) Å, 660 refl., 51 param., $R_1(F)$=0.019; w$R_2(F^2)$=0.051) is characterized by a Kagome-net of B_{12} icosahedra, ethane like Si_8-units and disordered SiC-dumbbells. Vibrational spectra show typical features of boron-rich borides and Zintl phases. $Mg_3B_{36}Si_9C$ is stable against HF/HNO_3 and conc. NaOH. The micro-hardness is 17.0 GPa (Vickers) and 14.5 GPa (Knoop), respectively. According to simple electron counting rules $Mg_3B_{36}Si_9C$ is an electron precise compound. Band structure calculations reveal a band gap of 1.0 eV in agreement to the black colour. Interatomic distances obtained from the refinement of X-ray data are biased and falsified by the disorder of the SiC-dumbbell. The most evident structural parameters were obtained by relaxation calculation. Composition and carbon content were confirmed by WDX measurements. The small but significant carbon content is necessary by structural reasons and frequently caused by contaminations. The rare earth compounds $RE_{3-x}B_{36}Si_9C$ (RE=Y, Dy–Lu) are isotypic. Single crystals were grown from a silicon melt and their structures refined. The partial occupation of the RE-sites fits to the requirements of an electron-precise composition. According to the displacement parameters a relaxation should be applied to obtain correct structural parameters.

1. Introduction

Boron rich borides are in a class of compounds for their own because they contain a great variety of boron polyhedra and show a unique structure chemistry [1–3]. Furthermore they are of growing interest for a number of applications in material sciences. Examples are high temperature materials [4], abrasives [5], composites [6], HT-semiconductors [7] and HT-thermoelectrics [8]. The remarkable tendency of polyhedra formation is frequently connected to the incorporation of small amounts of foreign elements to stabilize the polyhedra by the additional electrons [3]. Foreign elements are metals and non-metals as well. According to their lower electronegativity metal atoms transfer their electrons to the boron polyhedra and form cations which are placed between the polyhedra. Non-metal atoms like C, N, and Si have a higher number of valence electrons. They can form larger units between the polyhedra and can also be a part of them. Therefore many boron rich borides show partial and/or mixed occupations that demands special attention in synthesis, structure determination (displacement parameters, residual electron density) and analytical characterisation (i.e. Na_2B_{29} [9a]/NaB_{15} [9b]; KB_5C [10a]/KB_6 [10b]; Mg_5B_{44}/ScB_{15}/$Sc_4Cu_{2-x}B_{90}$ [11]). These topics must be taken into account for the application of electron counting rules and the discussion of chemical bonding in boron-rich borides [3]. Furthermore there are prominent examples where on the first sight remarkable physical properties were found. Recently HT-ferromagnetism was reported for CaB_6 [12] and CaB_2C_2 [13]. But in both cases the unexpected ferromagnetism (and publication in "visible" places) was probably caused by Fe contamination because pure samples turned out to be diamagnetic [14]. On the other hand very exciting physical properties are known for boridecarbides. Examples are the superconductivity in quarternary compounds like YPd_2B_2C and $LuNi_2B_2C$ [15] and ferromagnetism in $U_2ScB_6C_3$ [16]. Finally, small amounts of foreign elements or deviations from the ideal composition can have a great influence on the conductivity or optical properties. Recent examples are $LiB_{12}P_{2-x}C_x$ [17] and $Mg_{4-x}B_{50}C_8$ [18].

Although the situation seems to be clear the reality is more complex. The hardness and high thermal and chemical stabilities make the synthesis and a clear characterisation of boron rich borides more difficult. Because of the slow diffusion at low

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temperatures equilibrium conditions are not easy to reach. By use of molten metals as solvents and reactants we were able to synthesize and characterize single crystals of new borides [19] and especially boron-rich borides [17–28]. Furthermore we have shown that a simultaneous quantitative analysis of light elements down to boron is possible by WDX and EDX measurements on single crystals [11,18,21,24,28].

Motivated by the recent discovery of superconductivity in MgB_2 [29], the excellent thermal stability of Si/B based ceramics [30] and the growing importance of Mg containing alloys [31] we have investigated the ternary system B/Mg/Si. In this way we obtained yellow transparent single crystals of $MgB_{12}Si_2$ as the first stoichiometric ternary compound in the system B/Mg/Si [19]. First as a by-product and later on as a main product we obtained black single crystals of $Mg_3B_{36}Si_9C$. By combination of detailed X-ray investigations of single crystals with WDX measurements we developed a structure model for the quaternary compound $Mg_3B_{36}Si_9C$ containing B_{12}-icosahedra, Si_8 units and disordered SiC dumbbells. Similar compounds of *RE* elements were already described by Kanatzidis et al. ($RE_{3-x}B_{36}Si_8C_2$ [32]) and Tanaka et al. ($RE_{1-x}B_{12}Si_{3.3-\delta}$ [33]) but the problem of the disordered SiC unit was not discussed properly.

Preliminary results on $Mg_3B_{36}Si_9C$ were already presented [28] which may have led to a modified interpretation of the data of the rare earth compounds by Tanaka et al. [34].

2. Synthesis and characterisation

2.1. Synthesis $Mg_3B_{36}Si_9C$

B, Mg and Si were mixed in molar ratios 1:2:4 and pressed into a pellet (total mass: 500 mg). The pellet was put into a BN-crucible and sealed in a Ta-ampoule. In an atmosphere of argon it was heated up to 1600 °C, held for 40 h, cooled down to 1400 °C with a ratio of 10 K/h and then cooled to room temperature with 600 K/h. The excess of the melt was removed with a mixture of HF/HNO_3. The residue consists of black hexagonal platelets which were identified as $Mg_3B_{36}Si_9C$ [28]. As a by-product we observed black needle-shaped crystals of $Mg_{1.13}B_{12}Si_2$ [28] and in some cases yellow transparent platelets of $MgB_{12}Si_2$ [19] as shown in Fig. 1. Subsequent syntheses have shown that the yield of $Mg_3B_{36}Si_9C$ depends on the amount of added carbon. The highest content of $Mg_3B_{36}Si_9C$ was obtained with a carbon share close to the observed B:C ratio. But even in case of carbon-free batches some crystals of $Mg_3B_{36}Si_9C$ were observed because commercial boron usually contains more or less carbon. Depending from the reaction conditions small amounts of binary borides were observed (MgB_7 [27], MgB_{12} [35], α-SiB_3 [36], SiB_6 [37]). Syntheses were done in a high temperature furnace equipped with graphite heater (Astro 1000-3500-FP20, Thermal Technologies) and an optical pyrometer for temperature measurement (ET2LTCFC, Raytek).

2.2. X-ray powder diffraction

Some of the black crystals were crushed and used for an X-ray powder diffractogram (STOE STADI-P, Mo$K\alpha_1$-radiation, Ge-monochromator). All reflections observed were indexed with the hexagonal unit cell ($a=10.106(3)$ Å, $c=16.431(9)$ Å). The measured intensities showed excellent agreement to the calculated values on the basis of the refined crystal structure (Fig. 2).

2.3. $RE_{3-x}B_{36}Si_9C$ (*RE*=Y, Gd–Lu)

Single crystals of $RE_{3-x}B_{36}Si_9C$ (*RE*=Y, Gd–Lu) were obtained from mixtures of Si, *RE* and B in a ratio 30:1:20 to 40:1:25. The

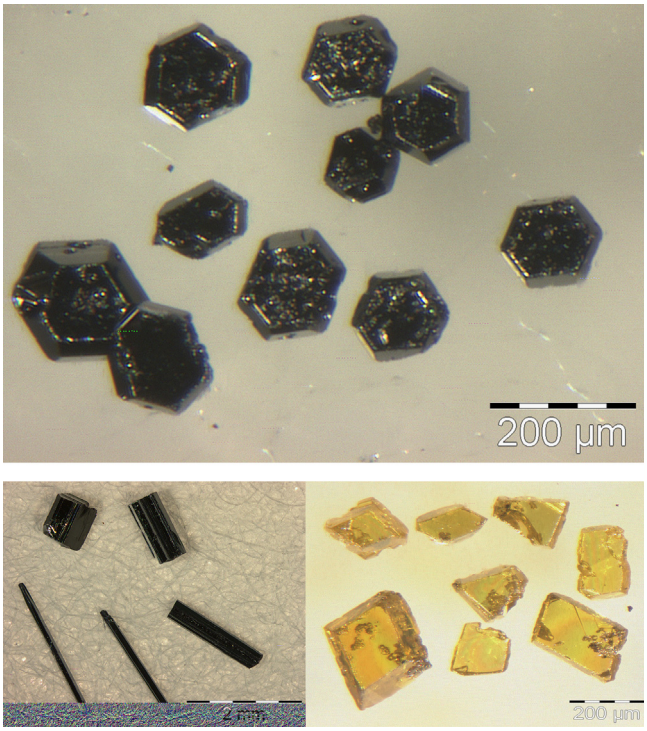

Fig. 1. Single crystal of $Mg_3B_{36}Si_9C$ (top), $Mg_{1.13}B_{12}Si_2$ (bottom, left) and $MgB_{12}Si_2$ (bottom, right).

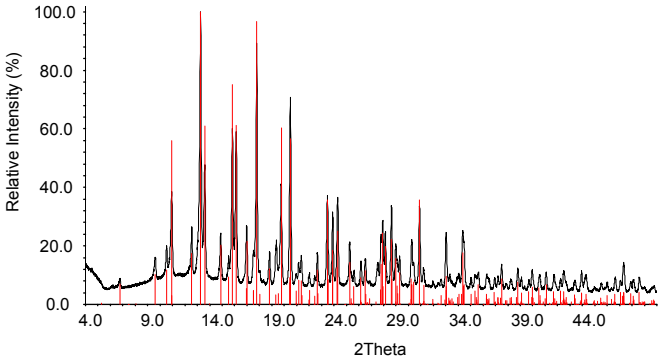

Fig. 2. Observed and calculated X-ray powder pattern of $Mg_3B_{36}Si_9C$.

synthesis was similar to $Mg_3B_{36}Si_9C$, but the temperature was increased to 1700 °C. Because of the higher melting point of *RE* metals the enclosure of the BN-crucibles in Ta-ampoules was not necessary. In contrast to the communication of Kanazidis et al. [30] the synthesis of the Sc-compound was not possible. As we used a furnace with graphite heater this might explain the carbon content of the products. Furthermore, commercial samples of elemental boron unsually contain small amounts of carbon. By-products were $SiB_{\sim 6}$ (*Pnnm*, oP340.6) [37], α-SiB_3 (hR42, $R\bar{3}m$) [36], B_4C (hR45, $R\bar{3}m$) [38] and REB_{50} (or $REB_{37.8}Si_{2.7}$) (*Pbam*, oP332 [39,40]) which were characterized by single crystal investigations. Usually, the distinction was done according to crystal colour and shape.

2.4. Structure analysis

One of the black hexagonal platelets was selected for the structure analysis. Measurements were done using a diffractometer equipped with an image plate detector (IPDS II, Fa. STOE, Darmstadt, Germany [41]). The reflections were indexed with a rhombohedral cell. After refinement values of $a=10.0793(13)$ Å