P28

HIGH-PRESSURE STUDY OF α AND β POLYMORPHS OF GERMANIUM NITRIDE

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The family of nitrides of group IV has become more widely known since 1989 [1] when the shortest and strongest covalent bond in C_3N_4 [2] was predicted; the prediction was followed by numerous experimental studies. Other theoretical predictions concerning the existence of spinel-type structure (the γ polymorph) have also been successfully experimentally confirmed [3, 4]. The members of this family crystallise with several structures at ambient pressure. At high pressures, spinel- and olivine-type phases as well as an amorphous one have been reported. In this study the pressure behaviour of two polymorphs of a representative of this family, α- and β-Ge_3N_4 is presented.

Ge_3N_4 is a prospective material for application, *e.g.*, in photodiodes, amplifiers, optic fibres and protective coatings [5], it has been considered for applications as metal-insulator-semiconductor field effect transistors (MIS FET) [6], as a possible negative electrode material for Li-ion batteries [7], and as photocatalysts [8-10], in particular for water decomposition [9, 10]. The structure of basic polymorphs is understood since the work of Ruddlesden and Popper [11] who have confirmed that the hexagonal ($P6_3/m$) β phase has reduced phenacite-type unit cell, and the trigonal ($P3_1c$) α phase is structurally a closely related one. Both, α and β Ge_3N_4 polymorphs have recently been studied by synchrotron X-ray diffraction at high pressures in a diamond anvil cell [12]. The cited study shows that in the pressure range 22 to 25 GPa, the β-Ge_3N_4 phase undergoes a 7% reduction in unit-cell volume, leading to the new δ-Ge_3N_4 polymorph.

A Raman spectroscopy study of polymorphic transitions occurring in compressed Ge_3N_4 has provided an evidence of a new transition at 20 GPa [13]. A change of compressibility at about 20 GPa for nanocrystalline spinel-type Ge_3N_4 has been attributed to the surface energy contributions to the shell layers of nanoparticles [14]. First-principles investigation of the properties of various polymorphs of Ge_3N_4 including the olivine one have been performed in Ref. [15].

Preparation of pure α and β phases is very difficult. Ruddlesen and Popper were successful in preparation of α and β dominant samples by reaction of germanium and germanium oxide with ammonia, respectively [10]. The sample studied (ALDRICH) in the present work was a mixture of α and β polymorphs of Ge_3N_4 and contained minor amounts of germanium and germanium oxide. The weight proportion of these four phases was: 27.1(0.8)%, 72.1(1.1)%, 0.07(0.04)%, 0.69(0.15)% accordingly. The refined lattice parameters at room temperature are $a = 8.2006(3)$ Å, $c = 5.9317(3)$ Å for α phase and $a = 8.0319(2)$ Å, $c = 3.0771(1)$ Å for the β one.

The high-pressure study was performed at the MAX80 diffraction press, F2.1 beamline (Hasylab, DESY). NaCl was used as a pressure standard. The pressures ranged up to 5 GPa. Energy-dispersive diffraction method at diffraction angle of 4.521° was used. To determine the lattice parameters of the component phases, the Le Bail method was chosen. For calculations the Fullprof 2k (v. 2.70) program was applied. Examples of fitted spectra collected at the ambient and 5.0 GPa pressures are shown in Fig. 1. The obtained bulk moduli, 208.0(6.6) for α phase and 192.5(3.5) for β phase will be discussed and compared to those reported for other Ge_3N_4 phases (see Table 1).

Table 1. Bulk moduli of basic Ge_3N_4 phases. Theoretical values are given in italics.

B [GPa] α phase	B [GPa] β phase	B [GPa] γ phase	Reference
	218		[3]
		381(2) (a) 268(4) (b)	[14]
165(10)	185(7)		[12]
208.0(6.6)	192.5(3.5)		This work
	185		(LDA) [16]
	166		(CGA) [16]
219.8	*219.8*	*232.5*	[5]
	214	*266*	[17]

(a) below 20 GPa, (b) above 20 GPa.

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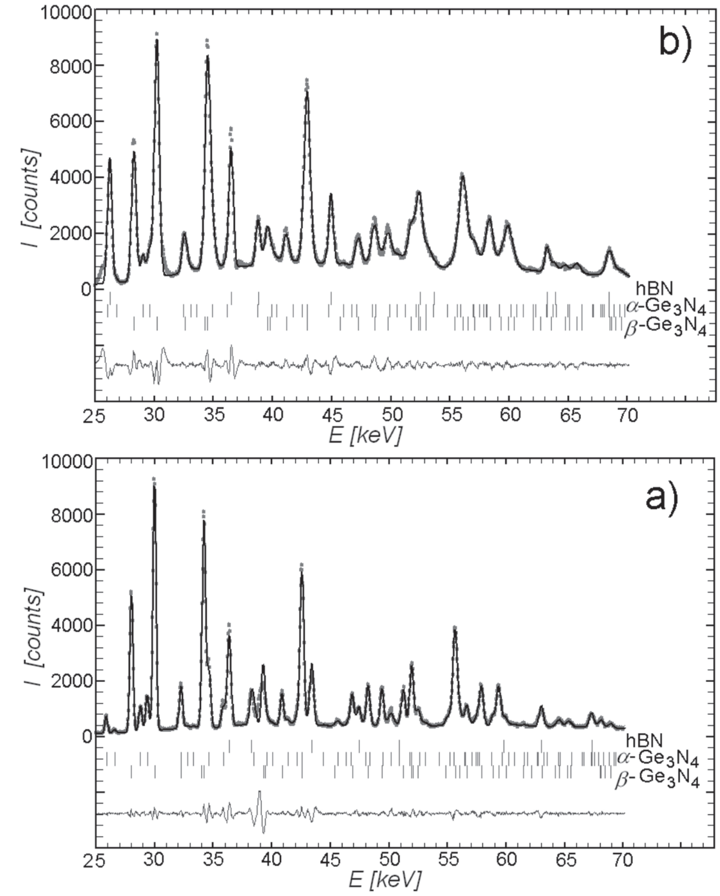

Figure 1. Examples of spectra collected at the ambient (a) and 5.0 GPa (b) pressures, fitted using the Le Bail method.

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