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State of Art and recent trends in bulk carbon nitrides synthesis

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Abstract

Light element-based materials are of relevant interest because of their specific physico-chemical properties mainly dependent on the involved strong chemical bonds. Among them, diamond and c-BN are still today the most representative materials especially concerning super hardness property. Nevertheless, since the prediction by Liu and Cohen (on the basis of ab initio calculation) of theoretical materials with C_3N_4 composition exhibiting low compressibility, many efforts have been devoted to the synthesis of carbon nitrides.

The first part of this review deals with the brief description of the different predicted C_3N_4 polymorphs exhibiting either a dense network or a graphitic one. In addition, predicted carbon nitrides with different stoichiometry are also described.

The second part presents the analysis of the processing routes described in the literature for the synthesis of carbon nitrides as bulk materials. If many attempts have been devoted to high-pressure processes (direct synthesis, direct conversion from the graphitic form, flux-assisted conversion or solvothermal processes), some experiments performed in moderate experimental conditions have also been investigated and appear as really promising. A comparison with the different processes developed for diamond and c-BN is associated.

As a conclusion, a discussion about the promising routes related to bulk carbon nitrides synthesis is given.

Keywords: C_3N_4; Carbon nitride; Synthesis; Hard materials; High pressure; Solvothermal synthesis

Contents

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1. Introduction

Light element-based materials which associate 2p and 3p elements mainly from columns III to V are of great interest due to their various physicochemical properties: because of the chemical bond strength induced by the short atomic distance they exhibit very high hardness (H), high chemical inertia, good thermal conductivity, optical transparency on a wide wave number range, highly refractory character (if atmosphere does not induce a chemical degradation) and electronic insulator behaviour with high band gap values.

Among all these properties, hardness is the most representative. It represents the ability of a solid to resist the penetration of a hardest material. As a consequence ultrahard materials will undergo slight deformations. On the microscopic level, for ideal solids, hardness (H) can be evaluated by the bulk modulus (B), superhard covalent materials necessarily exhibiting high B values. The excessive hardness and bulk modulus in light element-based materials as diamond are induced by two main factors: the short interatomic distances, inducing a high covalency of the chemical bonds and the three-dimensional crystalline network. To date, diamond is the hardest known material which makes it particularly suitable for applications such as cutting, drilling, grinding or polishing tools. Nevertheless its chemical reactivity in presence of ferrous metals or oxygen at high temperature leads to the formation of iron carbide or carbon oxide, respectively. These experimental restrictions involve that the research of new superhard materials has become a world-wide challenge [1,2].

In 1956, cubic boron nitride with blende-type structure has been synthesized under high pressure [3]. While isoelectronic and isostructural with diamond, it is nevertheless less impressive from mechanical and thermal point of view due to the heteropolar B–N bond. It appears however interesting because it is less chemical reactive in presence of ferrous metals.

In 1989, Liu and Cohen have proposed an empirical model to define the bulk modulus of covalent solids as a function of average coordination number N_c, ionicity parameter λ and bond length d: $B = 1/4N_c\ (1971–220\lambda)\ d^{-3.5}$ [4,5]. According to this formula and on the basis of the β-Si_3N_4 structure, the authors have claimed the existence of an hypothetic material β-C_3N_4 which expected mechanical properties were of relevant interest. Then, many efforts have been devoted to the study of this promising material and other derived polymorphs. Theoretical and experimental studies have been performed in order to determine and elaborate superhard carbon nitrides of general CN_x formula with high mechanical performances.

Concerning the elaboration, two main preparation routes have been developed: carbon nitrides have been obtained either as thin films or as bulk materials. Many publications devoted to CN_x thin film elaboration have allowed concluding that the existence of crystalline stoichiometric C_3N_4 has not been clearly evidenced yet. To date, the so-obtained deposits are generally mainly amorphous and can eventually contain nanometric CN_x crystallites [6,7]. However, these amorphous thin films seem to present interesting mechanical, tribological and optical properties [8–11].

We propose here a State of Art devoted to the elaboration of bulk carbon nitrides. The first part briefly reminds the various polymorphs predicted either with C_3N_4 stoichiometry or not. In the second one, a description of processes involved for the synthesis of diamond and cubic boron nitride is first given. We then analyze experimental results obtained concerning the elaboration of carbon nitrides according to different routes and in softer conditions. In this way, promising trends are finally discussed.