

c-BN color change with bonded water added into the h-BN–Mg system

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Abstract

Cubic boron nitride (c-BN) crystals were synthesized in conditions of high temperature and high pressure (HTHP) when different kinds of bonded water were respectively added into the system of h-BN–Mg. All bonded water used in this work could reduce the temperature of growing c-BN compared to that in the system of h-BN–Mg. The c-BN color could change from black to yellow when certain amounts of bonded water, such as $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$, were added. However, c-BN color remained black no matter how much bonded water, such as $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, was added. The bonded water can be classified into Chlorine-containing bonded water (Cl-BW) and Chlorine-free bonded water (ClF-BW) according to their different characters and effects on the synthesized c-BN color.

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1. Introduction

Cubic boron nitride (c-BN) has been applied in many fields because of its outstanding properties. c-BN is the second hardest material. Its high hardness and high thermal conductivity make it useful as a cutting tool and as an abrasive. In addition, its high thermal conductivity and the possibility of appropriate doping make it a potential material for applications in electric fields.

At HTHP conditions, c-BN crystals can be synthesized from hexagonal boron nitride (h-BN) with the catalysts such as the alkali metals, alkaline earth metals, their nitrides, and their boric nitrides [1–6]. The color of the synthesized c-BN crystals varies according to the types of the catalysts used. Generally, black c-BN crystals are synthesized from h-BN when alkali metals or alkaline earth metals are used. With their nitrides or their boric nitrides as the catalysts, the color of synthesized c-BN is yellow [1,4]. Also, the color may be white when water, boric acid, or urea is used [7]. If M' (M' = Al, B, Si, Ti) is doped into the mixture of h-BN and M_xN_y ($\text{M}_x\text{N}_y = \text{Ca}_3\text{N}_2$, Li_3N , Mg_3N_2),

the synthesized c-BN color can change from yellow to black with increasing proportions of M' [4,8].

The effect of bounded water on the c-BN transformation from h-BN in the presence of magnesium (Mg) has been heavily studied [9–15]. It was reported that when the amount of bonded water increased in the mixture of h-BN and magnesium, the synthesized c-BN color would change from black to yellow [9]. However, our work demonstrates that only ClF-BW can make the color change. When Cl-BW is added into the mixture of h-BN and Mg, the synthesized c-BN color remains black, regardless of the amount.

2. Experiment

The c-BN crystal was synthesized at HTHP in a cubic anvil high-pressure apparatus. The pressure was estimated by an oil press load, which was calibrated by the pressure-induced phase transitions of bismuth, thallium, and barium metals. The temperature was estimated by the relationship between applied electrical power and temperature, which was measured by using the platinum–rhodium thermocouple. The assembly used in this work is shown in Fig. 1. In sample column A, the mixture of h-BN, Mg and different kinds of bonded water such as $\text{NiSO}_4 \cdot$

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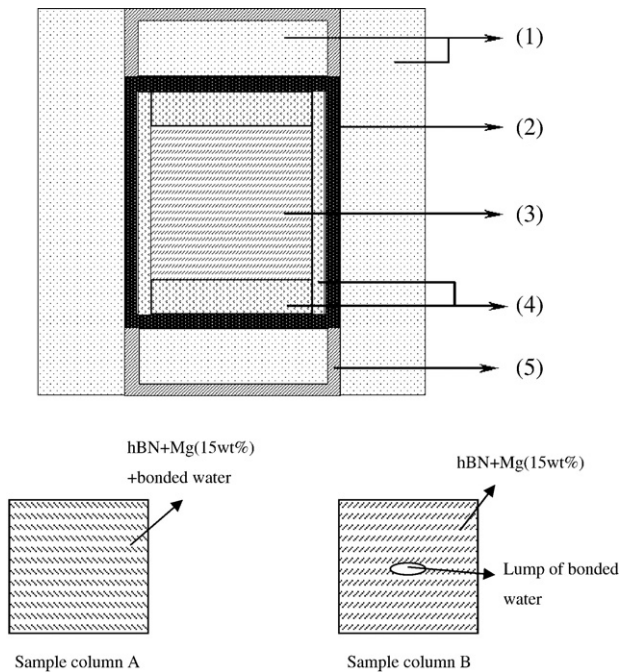


Fig. 1. High pressure cell assembly of c-BN crystal synthesis. (1) pyrophyllite; (2) graphite (3) sample column; (4) h-BN; (5) steel ring.

$6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, was directly pressed into the column. In sample column B, when the mixture powder of h-BN and Mg was pressed into the column, a lump of bonded water was packed into it. Then, the assembled cell was treated for 5 min at a high pressure (5.0 GPa) and a high temperature (1300 °C). After being quenched, sample column A was measured by X-Ray diffraction, and sample column B was observed by an optical microscope.

3. Results

c-BN crystals were synthesized from the mixture of h-BN, Mg and bonded water at HTHP. Table 1 shows that the synthesized c-BN color would change from black to yellow when the amount of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ increases, while the synthesized c-BN color is independent of the amount of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.

Fig. 2 (a), (b) shows the photographs of synthesized c-BN crystals when $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (10 wt.%) and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (10 wt.%) are added into the mixture of h-BN and Mg (15 wt.%), re-

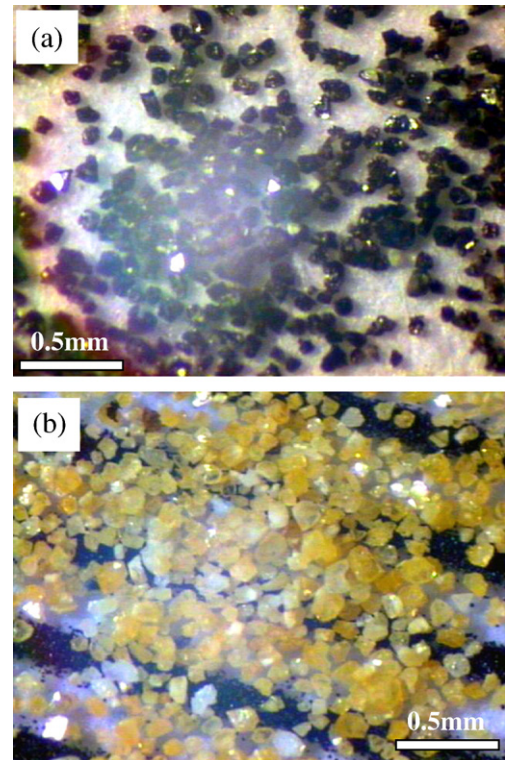


Fig. 2. (a), (b) Photographs of c-BN crystals synthesized with the mixture of h-BN, Magnesium (15 wt.%) and bonded water at 5.0 GPa and 1300 °C. (a) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (10 wt.%); (b) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (10 wt.%).

spectively. The c-BN color is black when $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (10 wt.%) is added and is yellow when $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (10 wt.%) is added.

Fig. 3 shows the sketch map of samples with a lump of different bonded water packed into it, after these samples are quenched at HTHP. When the lump of ClF-BW is packed into the mixture of h-BN and Mg, the quenched sample would have three sections shown in Fig. 3 (a). Section A is close to the lump, in which c-BN crystals exist and their color is yellow. Section B is near section A, in which black c-BN grains exist. The outer place is section C and no c-BN crystals are synthesized there. If the lump of Cl-BW is packed into it, then the quenched sample would have two sections: a growing black

Table 1
Content of bonded water dependence of the c-BN crystal color in the h-BN–Mg and bonded water system

h-BN (wt.%) (content of Mg is fixed at 15 wt.%)	c-BN crystal color
(a) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (wt.%)	
80: 5	Black
75: 10	Yellow
65: 20	No c-BN forms
(b) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (wt.%)	
80: 5	Black
75: 10	Black
65: 20	No c-BN forms

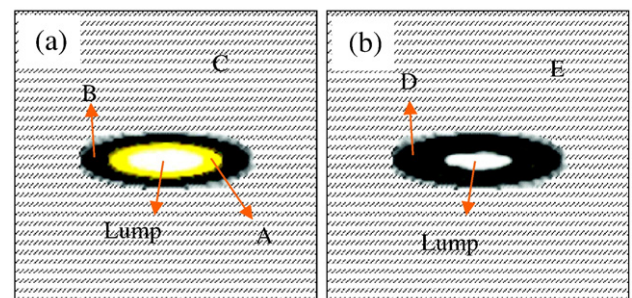


Fig. 3. (a), (b) Sketch map of samples with a lump of different bonded water packed into, after these samples are quenched at 5.0 GPa and 1300 °C. (a) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$ was packed into respectively; (b) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was packed into respectively.

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