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Report form of Joint Research Project at ZAIKEN (FY2023)

Title of Project	Ternary Nitride Ceramics as Superhard Materials		
Priority Area	I-Ａ(Prolongation of service Life & Processes),I-Ｂ(Prolongation of service Life & Structure)		
	New proposal		
Name of Main Applicant	Ralf RIEDEL		
Institution	Institut für Materialwissenschaft Technische Universität Darmstadt (TUDa)	**title**	Research Professor

Aim of the research project

In order to achieve prolongation of service life of various types cutting tools and sliding parts, superhard materials are extremely important.[1] Diamond is known as the hardest material, but additional superhard materials are required for their application to various fields. So far binary nitride superhard materials such as cubic boron nitride and cubic silicon nitride have been developed and their properties were reported. In addition, theoretical calculation studies predicted high hardness of binary nitrides, which have not been prepared.[2] Thus, research for finding new superhard materials is still important challenges. Although binary nitrides have attracted huge attention, research on ternary nitrides has been limited.[3]

To prepare superhard materials, high-pressure-high-temperature (HP-HT) process has been typically employed, since they are stable at a high temperature-high pressure region. It is possible to prepare high-pressure phases by the HP-HT treatment of ambient-pressure phases. On the contrary, it is also possible to prepare high-pressure phases by combining the HP-HT treatment and solid state metathesis reaction, latter of which involves the exchange of atoms between two starting compounds to form a new product. Thus, the appropriate combination of starting materials for HP-HT processes would be the key for achieving the goal, the discovery of a new superhard ternary nitride, and development of reparation methods for ternary nitrides is thus required.

In this study, we prepared $LaWN_3$ by combination of the HT-HP treatment and the solid state metathesis reactions with two sets of starting compounds by using lithium nitride, Li_3N, or sodium azide, NaN_3, as a nitrogen source and metal chlorides, $LaCl_3$ and WCl_6, as metal sources, and formed crystalline phases were analyzed.

Contents and results of the research

First, we performed the preparation of $LaWN_3$ by the reported starting materials, $LaCl_3$, WCl_6, and Li_3N based on the following reaction.[3]

$$LaCl_3 + WCl_6 + 3Li_3N \rightarrow LaWN_3 + 9LiCl$$

The starting materials were mixed in an inert atmosphere, and the mixture was placed in a belt-type high pressure apparatus. The solid state metathesis reaction was conducted at 5.5 GPa and 1300°C for 1 h. LiCl was removed by washing with hot water. The product was analyzed by XRD, and the major diffraction peaks were similar to XRD patterns of $LaWN_3$ and its solid solution, $LaWO_{0.6}N_{2.4}$. Thus, obtained phase could be expressed with a composition formula, $LaWO_xN_{3-x}$. The formation of $LaWN_3$-type compound is consistent with a previous study.[3]

Then, we tried to prepare $LaWN_3$ by the solid state metathesis reaction using sodium azide based on the following reaction.

$$LaCl_3 + WCl_6 + 9NaN_3 \rightarrow LaWN_3 + 9NaCl + 12\ N_2$$

The starting materials were mixed in an inert atmosphere, and the mixture was placed in the same belt-type high pressure apparatus as mentioned above. The solid state metathesis reaction was conducted at 5.5 GPa and 1000°C for 1 h. NaCl was removed by washing with hot water. The major phase in the XRD pattern of the product was also $LaWO_xN_{3-x}$. Thus, two different sets of starting compounds are both appropriate for the preparation of the $LaWN_3$-type compound *via* solid state metathesis reactions at high temperature and high pressure.

We will further try to synthesize ternary nitrides via solid state metathesis reactions by using lithium nitride and sodium azide as nitrogen sources.

[1] Z. Zhao *et al.*, *Annu. Rev. Mater. Res.*, **46**. 383 (2016).
[2] A. M. Tehrani and J. Brgoch, *J. Solid State Chem.*, **271**, 47 (2019).
[3] W. Sun *et al.*, *Nat. Mater.*, **18**, 732 (2019).
[4] R. E. Treece *et al.*, *Comment. Inorg. Chem.*, **16**, 313 (1995).
[5] S. Matsuishi *et al.*, *J. Solid State Chem.*, **315**, 123508 (2022).

Outputs of the project (publications, presentations, patents)

None