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# Solid and Liquid Synthetic Routes of Vanadium, Niobium and Titanium Nano-metal Borides

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**Abstract**

The synthetic comparison between the solid and liquid phases of metal borides was subjected to empirical investigation. The solid phase direct reaction of $V_2O_5$, $Nb_2O_5$, $Ta_2O_5$ with excess elemental boron in a muffle furnace at 500, 700 and 1000°C for 2, 2 and 15 hours respectively, produced a mixture (as it could be seen from the xrd patterns) of MB2 and $M_2O_5$ (minimal oxides). SEM shows a superparamagnetism and Magnetic hysteresis proved that. The liquid phase reaction of Vanadium trichloride, $VCl_3$, with sodium borohydride, $NaBH_4$ (1:3 ratio), produced pure black nanocrystals and nanorods of $VB_2$ as it is proved by xrd. Due to some ordering difficulties of Niobium and Tantalum salts liquid phase reactions couldn't be carried out.

**Keywords:** Nanocompounds; Metalborides; Nanowires; Nanocrystals

## Introduction

Due to special characters including high hardness, high melting points, high-temperature strength, corrosion resistance, chemical stability, wear resistance and electrical properties [1-6], a great number of transition metal borides were synthesized. Metal borides like $VB_2$, $CrB_2$, $TiB_2$, $W_2B_5$ and others have been used as a coating to strengthen carbon steels to resist electronic heating with high power density in vacuum, in one case layers of vanadium boride $VB_2$ are coated on steel surface [7]. Niobium borides due to their high melting temperature, high strength, high thermal and electrical conductivity, high strength and high chemical stability they have been considered as an excellent candidates for high temperate applications [8,9]. Superconductivity at 39 K of diborides metals $MB_2$ (M=Mg, Be, AL, Nb, Mo, Ta, Ti, Hf, V, and Cr) were investigated [10-14]. It is reported that the $NbB_2$-$CrB_2$ composite has a high hardness and resist oxidations [15]. Five niobium borides are known by a wide range of atomic ratios ($Nb_2B$, $Nb_3B_2$, NbB, $Nb_3B_4$ and $NbB_2$) are known to have high melting points and good electrical and thermal conductivities [16-18]. Compared with other transition metal borides there are relatively few studies available on the synthesis of niobium borides. The main reported preparation methods of niobium boride are the solid state reaction between niobium metal and elemental boron and molten salt electrolysis under temperature above 1500°C [19-24].

Five tantalum borides TaB, $TaB_2$, $Ta_3B_4$, $Ta_2B$ and $Ta_3B_2$ have received an intensive investigation due to their remarkable structures stability and bonding [25]. Tantalum borides like other transition metals they have excellent properties such as high melting point, high hardness, high elastic modulus, good thermal and electrical conductivity, excellent oxidation resistance, and considerable chemical stability

Almost none of the previous studies proved a pure production of metal borides rather a mixture of boride compounds was formed [22,23]. In the present work two different methods have been carried out in synthetic process of vanadium, niobium and tantalum borides, namely, solid states and wet reaction.

## Experimentation/Empirical Analysis

### Reagents

Unless otherwise specified, reagent grade chemicals were employed. The precursor materials were Vanadium (V) Oxide ($V_2O_5$, BDH), Niobium (V) Oxide ($Nb_2O_5$, Alfa Aesar), Tantalum (V) Oxide ($Ta_2O_5$, Alfa Aesar). Boron Powder (Amorphous) (B, Loba Chemie). Sodium Borohydride ($NaBH_4$, BDH). Vanadium (III) Chloride ($VCl_3$, Fluka AG), Hydrochloric acid (HCl, Sigma-Aldrich, fuming >37%).

Measurements of Powder X-ray diffraction (XRD) were carried out with a Bruker D8 Advance diffractometer (CuKα λ=1.54Å; Ni filter; 40 KV, 40 mA; Divergence slit: 1mm, LynxEye one-dimensional detector, Detector slit: 8 mm). Scanning Electron Microscope and Transmission Electron Microscope (SEM and TEM) were performed by employing a microscope of model Titan 80-300 CT from FEI Company (Hillsboro, OR), which was equipped with a field emission gun (FEG) and a charged-Couple Devices (CCD) camera of 4k × 4k pixels. Furthermore, the analyses of all samples were performed by operating the microscope at 300 kV accelerating voltage in order to take full advantage of the highest spatial resolution possible from this microscope. An aperture of 100 microns was also inserted into the back-focal plane (BPF) of the objective lens, to improve the image contrast. The Magnetization measurement was carried out in an ever-cool Squid-Vibrating Sample Magnetometer (SVSM), from the manufacturer Quantum Design, USA.

### Synthesis

#### Solid phase

***Preparation of metal borides using metal oxide and boron powder***

*Vanadium boride:* Mixing of 7.2752 g of Vanadium Oxide (10 mmol) and 2.3784 g Amorphous Boron Powder (10 mmol), in a porcelain crucible and placed in a muffle furnace with a gradual raising the temperature starting 500°C for two hours than 700°C for two hours

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and finally 1000°C for 15 hours. After cooling to the room temperature in a muffle furnace, the mixture was leached with 1 N HCl at 100°C for three hours under magnetic stirring. Solution was filtered and washed with distilled water and ethanol. The precipitate was then treated with 1 N $NH_4Cl$ at 100°C for three hours under magnetic stirring. Solution was filtered and washed with distilled water and ethanol and dried in a vacuum oven at 150°C for 3 hours. The yield is 64%.

$$4\ V_2O_5 + 22\ B \xrightarrow[500\text{-}1000^{\circ}C]{\Delta} 6\ VB_2 + V_2O_5 + 5\ B_2O_3$$

*Niobium boride:* 10.6324 g of Niobium Oxide (10 mmol) and 2.3784 g Amorphous Boron Powder (10 mmol), were mixed in a porcelain crucible and placed in a muffle furnace. Temperature gradually raised starting 500°C for two hours then 700°C for two hours and finally 1000°C for 15 hours. After cooling to the room temperature in a muffle furnace, the mixture was leached with 1 N HCl at 100°C for three hour under magnetic stirring. Solution was filtered and washed with distilled water and ethanol. The precipitate was then treated with 1 N NH4Cl at 100°C for three hours under magnetic stirring. Solution was filtered and washed with distilled water and ethanol and dried in a vacuum oven at 150°C for 3 hours. The yield is 57%.

$$4\ Nb_2O_5 + 22\ B \xrightarrow[500\text{-}1000^{\circ}C]{\Delta} 6\ NbB_2 + Nb_2O_5 + 5\ B_2O_3$$

*Tantalum boride:* 17.6757 g of Tantalum Oxide (10 mmol) and 2.3784 g Amorphous Boron Powder (10 mmol), were mixed in a porcelain crucible and placed in a muffle furnace. Temperature gradually raised starting 500°C for two hours then 700°C for two hours and finally 1000°C for 15 hours. After cooling to the room temperature in a muffle furnace, the mixture was leached with 1 N HCl at 100°C for three hours under magnetic stirring. Solution was filtered and washed with distilled water and ethanol. The precipitate was then treated with 1 N $NH_4Cl$ at 100°C for three hours under magnetic stirring. Solution was filtered and washed with distilled water and ethanol and dried in a vacuum oven at 150°C for 3 hours. The yield is 48%.

$$4\ Ta_2O_5 + 22\ B \xrightarrow[500\text{-}1000\ ^{\circ}C]{\Delta} 6\ TaB_2 + Ta_2O_5 + 5\ B_2O_3$$

**Liquid phase**

*Preparation of vanadium boride using vanadium chlorides and sodium borohydride:* Dissolving 3.1459 g of Vanadium (III) Chloride (10 mmol) in 100 ml distilled water, stirred on a magnetic stirrer and 2.2698 g (10 mmol) of sodium borohydride dissolved in 50 ml distilled water and dropwise added from separator funnel. The mixture was stirring for 30 minutes at room tempeture. The precipitate was filtered and carefully washed with dilute hydrochloric acid then with distilled water. $VB_2$ Precipitate was dried in the oven (open air) at 400°C for five hours. Yield was 65%.

$$2\ VCl_3 + 6\ NaBH_4 + 6\ H_2O \longrightarrow 2\ VB_2 + 6\ NaCl + 15\ H_2 + 2\ B(OH)_3$$

## Results and Discussion

In order to reach the most proper way to produce nanocrystals of metal borides, Solid and liquid phases were tried.

### Solid phase

Direct reaction of vanadium metal oxide, $V_2O_5$, with elemental boron in muffle furnace. Leaching, filtering and drying the product yielded mixed black nanorod crystals of $VB_2$ along with $V_2O_5$ as it could be seen in XRD (Figure 1a) and TEM (Figure 1b). Magnetic hysteresis of the product (Figure 1c) indicates superparamagnetic crystals [26] which reflects the presence of nanocrystals.

Niobium oxide, $Nb_2O_5$, reacted with elemental boron in muffle furnace under a blanket of argon for 15 hours. Leaching, filtering and drying the product yielded a mixed black nanorod crystals of $NbB_2$ and $Nb_2O_5$ as it could be seen in XRD (Figure 2a) and TEM (Figure 2b). Magnetic hysteresis of the product (Figure 2c) indicates superparamagnetic crystals* which reflects the presence of nanocrystals.

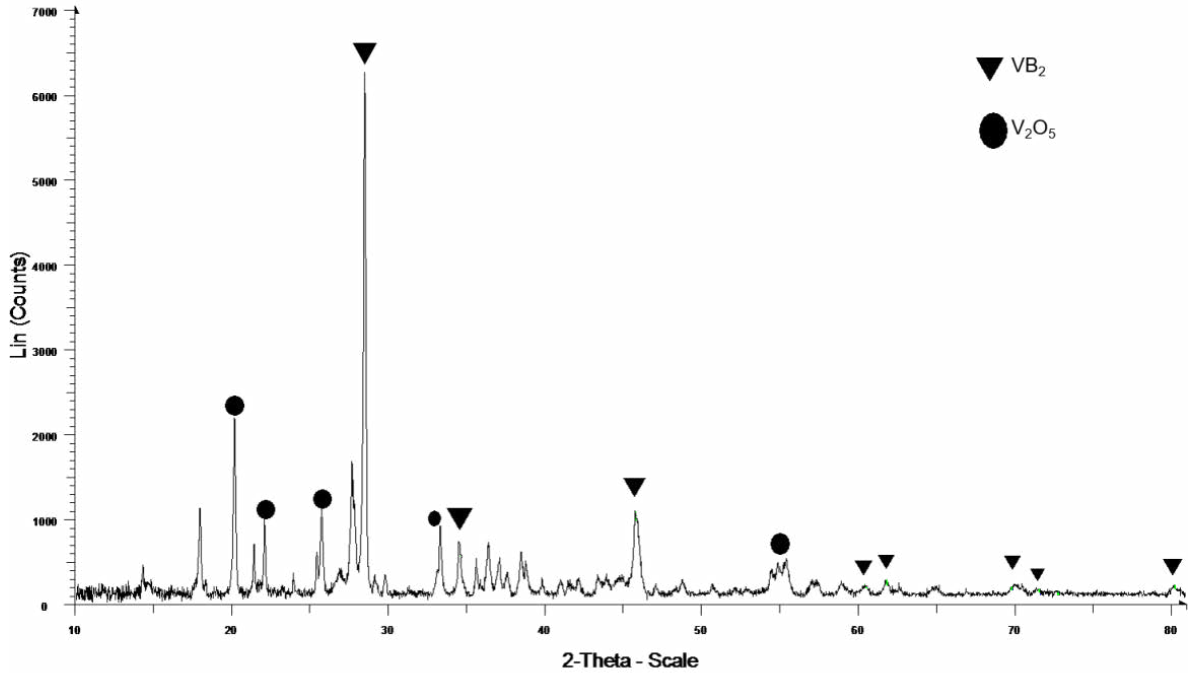


**Figure 1a:** XRD pattern indicating a mixture of $VB_2$ and $V_2O_5$ yielded by reaction of $V_2O_5$ with B.

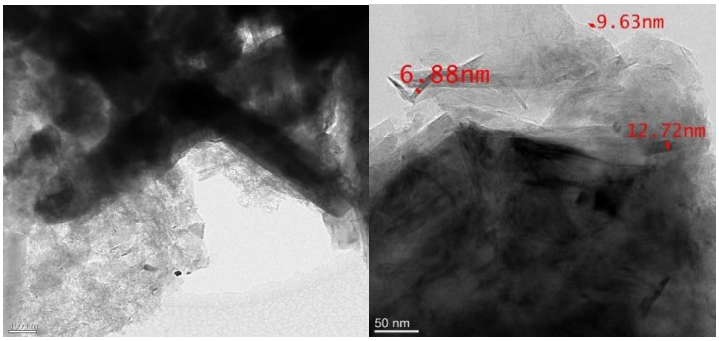


**Figure 1b:** TEM image of mixed nanocrystals of $VB_2$ and $V_2O_5$.

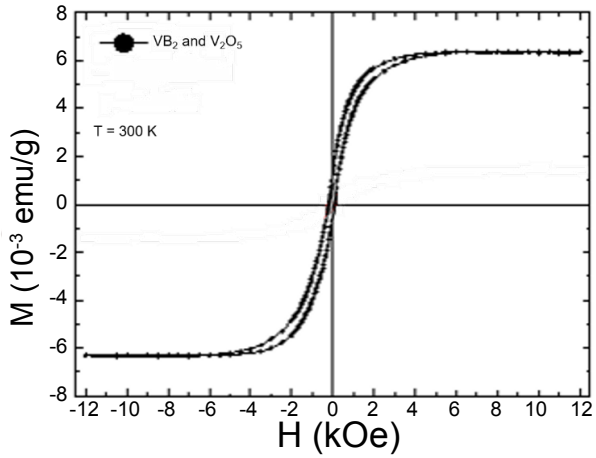


**Figure 1c:** Magnetic hysteresis shows superparamagnetism of $VB_2$ and $V_2O_5$.

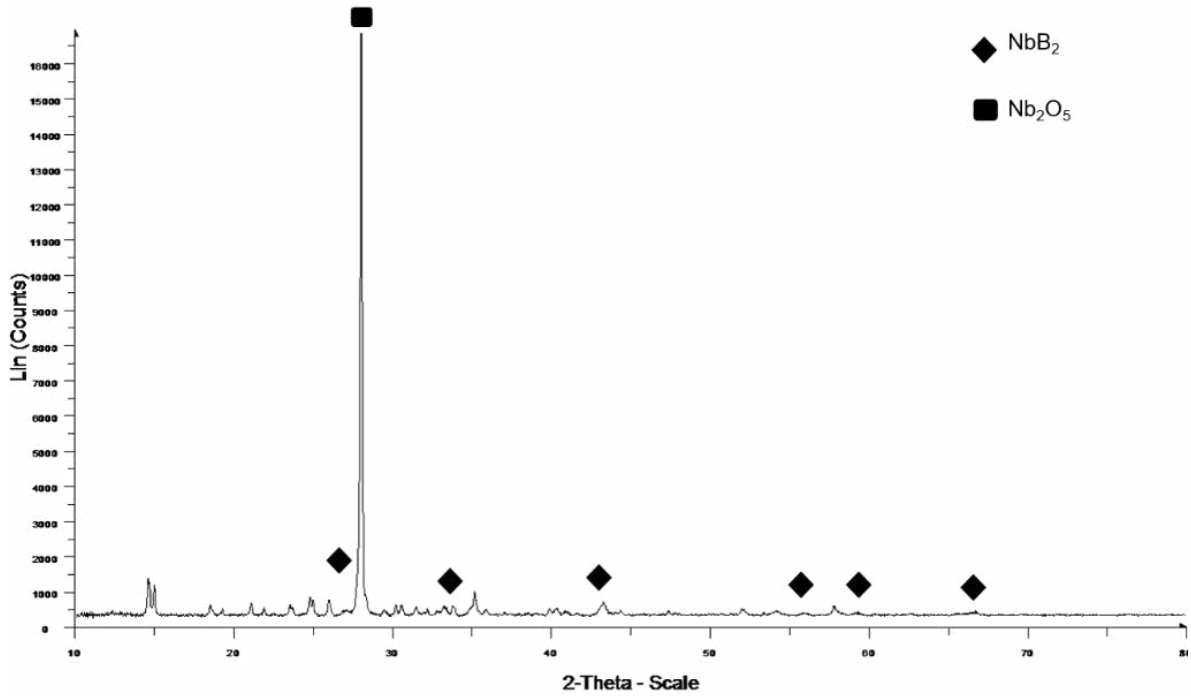


**Figure 2a:** XRD spectra of $NbB_2$ and $Nb_2O_5$ produced by direct reaction of $Nb_2O_5$ and B to produce.

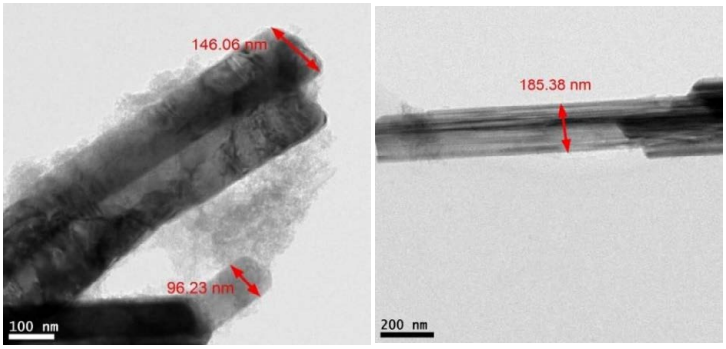


**Figure 2b:** TEM image of beautiful nanorods crystals of $NbB_2$ and $Nb_2O_5$.

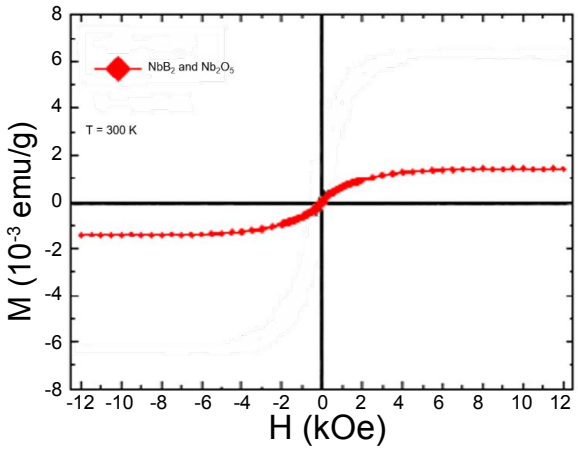


**Figure 2c:** Magnetic hysteresis shows superparamagnetism of $NbB_2$ and $Nb_2O_5$ Nanocrystals.

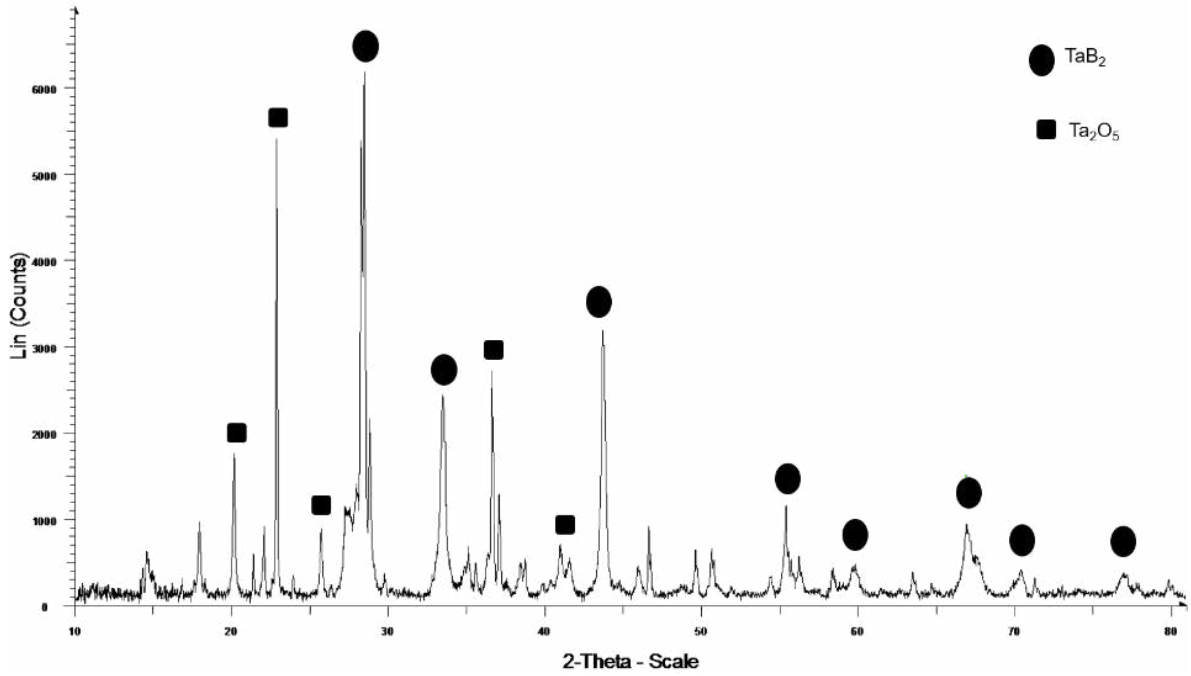


**Figure 3a:** XRD pattern of $TaB_2$ and $Ta_2O_5$ yielded by reaction of $Ta_2O_5$ with B.

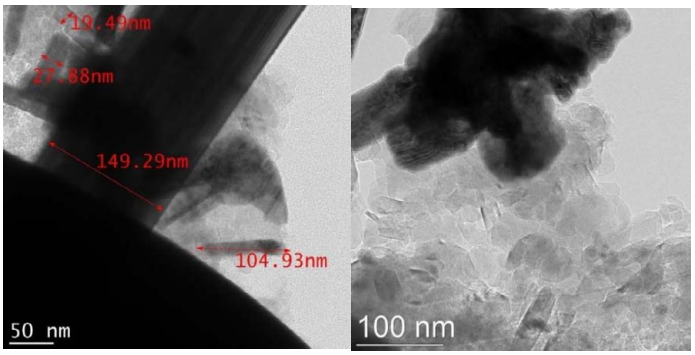


**Figure 3b:** TEM image of nanorods crystals of $TaB_2$ and $Ta_2O_5$.

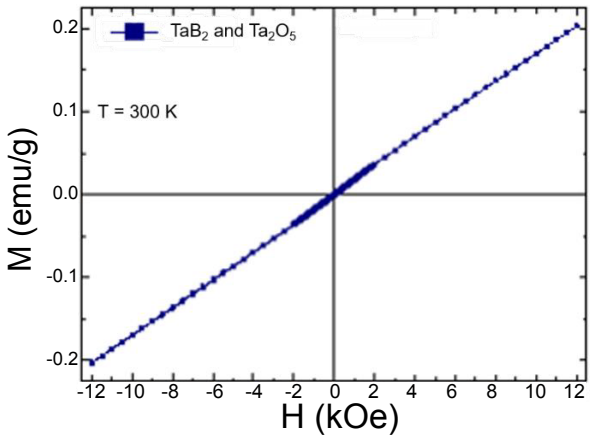


**Figure 3c:** Magnetic hysteresis of $TaB_2$ and $Ta_2O_5$ indicating normal magnetism.

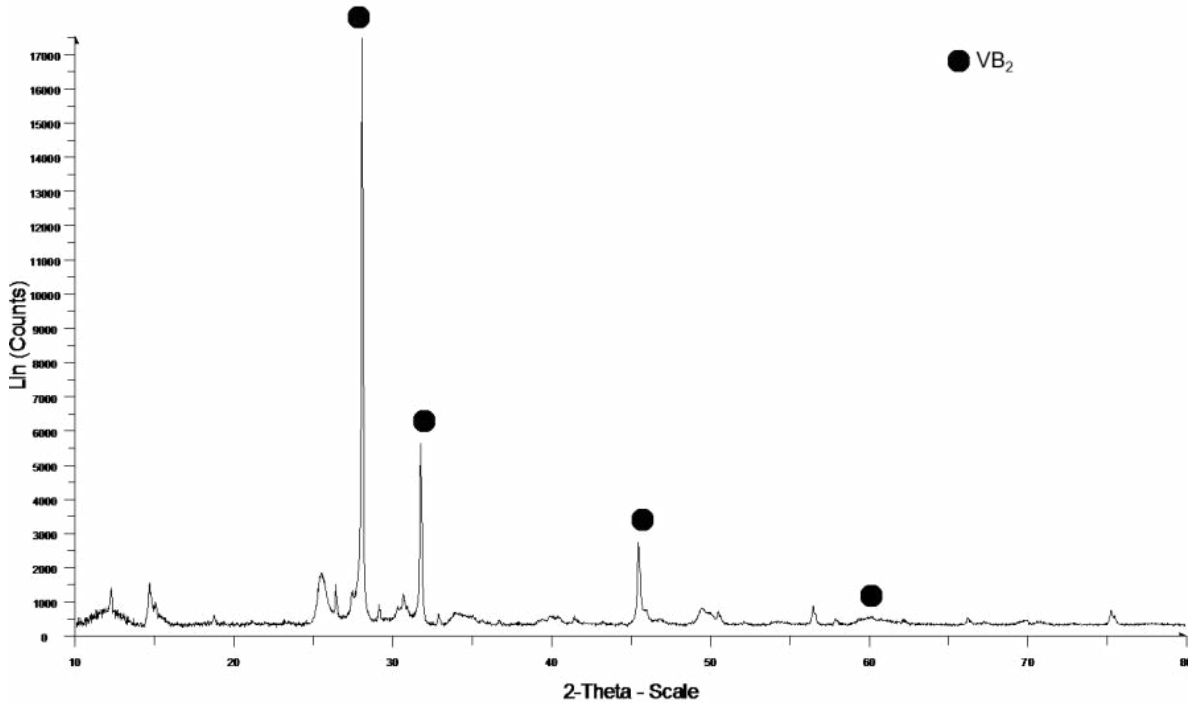


**Figure 4a:** XRD pattern of $VB_2$ yielded by reaction of $VCl_3$ with $NaBH_4$ in solution.

Going further down group five (VB) tantalum oxide, $Ta_2O_5$, reacted with elemental boron in muffle furnace at 1000°C for 15 hours. Leaching, filtering and drying the product yielded mixed black nanorod crystals of $TaB_2$ and $Ta_2O_5$ as it could be seen in XRD (Figure 3a) and TEM (Figure 3b). Figure 3c reflects regular paramagnetic properties of Tantalum compounds.

## Liquid phase

Reaction of vanadium (III) Chloride, $VCl_3$, with sodium borohydride, $NaBH_4$, in solution (1:3 ratio) yielded $VB_2$ black product as it's seen in the XRD pattern (Figure 4a). SEM image (Figure 4b) shows texture of the crystals. TEM image (Figure 4c) clearly indicates nanocrystals and nanorods which is reflected on the magnetism of the product. Figure 4d reflects regular paramagnetic properties of vanadium compound.

## Conclusion

Solid phase produced mixture of metal oxides and metal borides. Solid phase no matter how careful the reaction is conducted (even under an inert atmosphere), there are always metal oxides at least as impurities; unless a good sealed sophisticated autoclave is used. On the other hand liquid phase produced pure metal boride nanocrystals. It shows that the liquid phase is much easier and produces far more pure products, even though the yield is less. TEM clearly shows nanocrystals and nanorods.

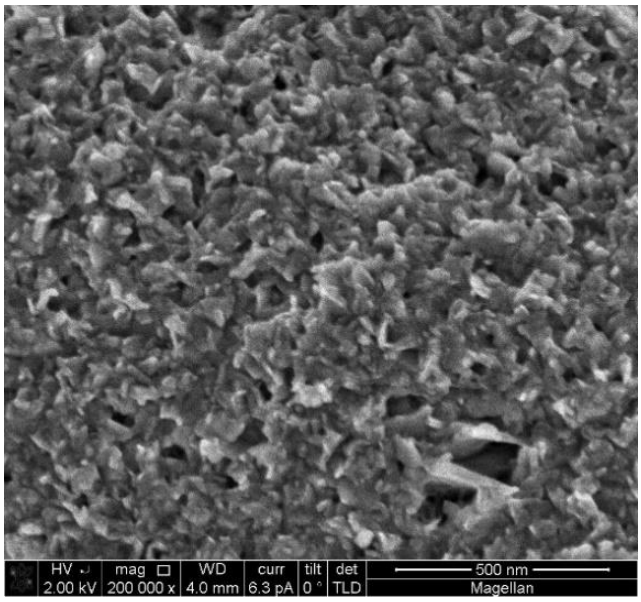


**Figure 4b:** SEM image shows nanocrystals of $VB_2$.

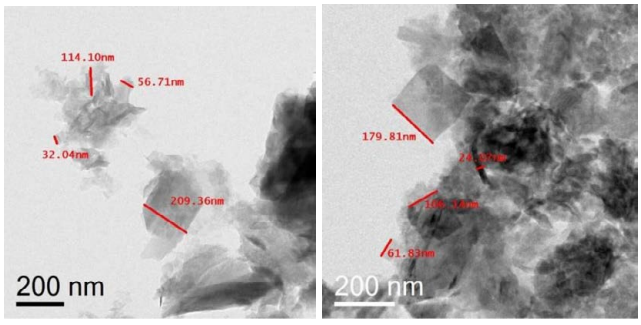


**Figure 4c:** TEM image shows nanocrystals of $VB_2$.

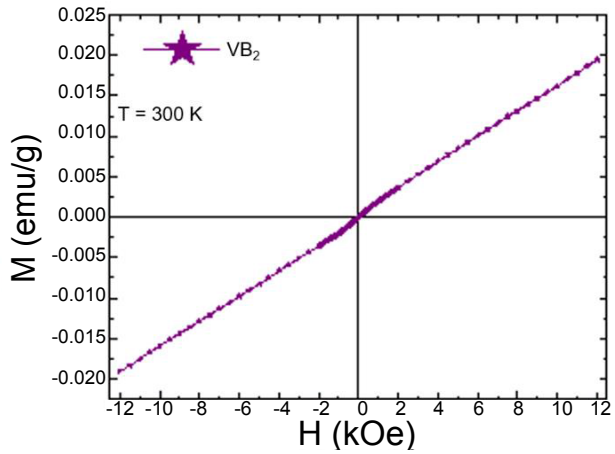


**Figure 4d:** Magnetic hysteresis of $VB_2$ indicating normal magnetism.

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