Supplementary Information

Synthesis of size-selective MnB crystals in tens of seconds

Junqi Liu, Ruifeng Qi,Xiaohua Qiao, Qingsong Huang*

School of Chemical Engineering, Sichuan University, Chengdu 610065, China.

E-mail: qshuang@scu.edu.cn

1. Image of bulk MnB

Fig. S1 Image of synthesized MnB(left) and precursor(right) block. The unit of the ruler is 1 inch.

2. Preparation time of other methods

Table S1 Preparation time of TMBs

Sample	Method	Time	Ref
Bulk MnB, MnB_2, Mn_3B_4	HIP	20-60 min	1–3
Nano MnB	Metal Borohydride Reduction	3 h	4
Nano MoB_2	Solid-State Metathesis	24 h	5
Bulk Fe_2B, Co_2B, Ni_3B etc.	BI3 Reduction	24 h	6
Nano FeB, CoB, NiB etc.	Sn Substitution	4-8 h	7
Nano CrB	Metal Borohydride Reduction	10 h	8
Nano NbB_2	Metal Borohydride Reduction	6 h	9
MnB, MnB_2, NiB	RDMF	15-30 s	This work

3. The gain size of HTHP-synthesized TMBs

Table S2 The gain size of HTHP-synthesized TMBs

Sample	Methods	Ref
MnB	15-20 μm	3
Mn3B4	4-6 μm	1
MnB2	6-12 μm	2
MnB	1-2 μm	This work

4. Schematic of the magnetism and vortex current coupling growth (RDMF) technique

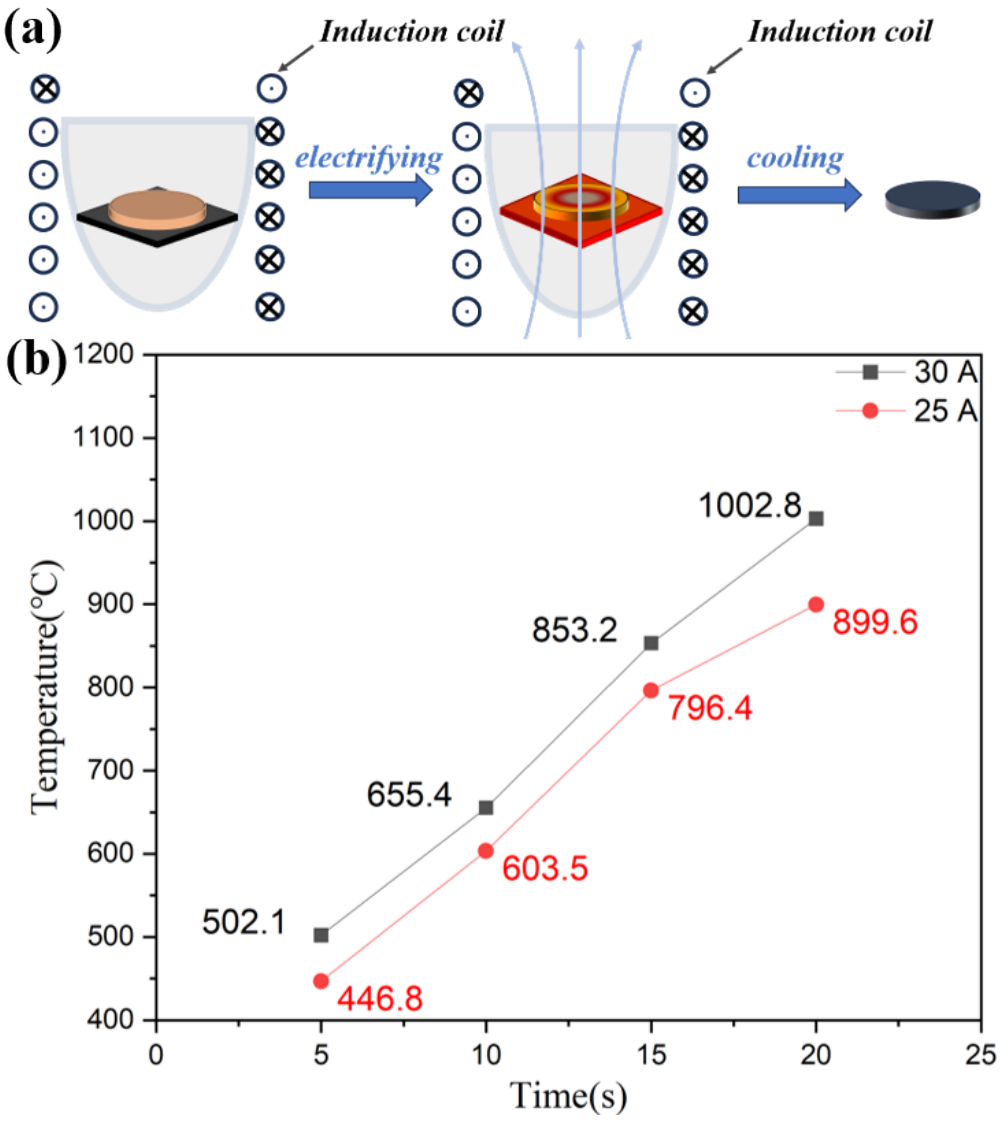

Fig. S2 (a)Schematic of the magnetism and vortex current coupling growth (DMF) technique for preparation of the MnB. (b) Temperature of carbon paper under 30 A and 25 A in air atmosphere.

5. The hardness and relative density of RDMF-MnB and TF-Mn-B sample

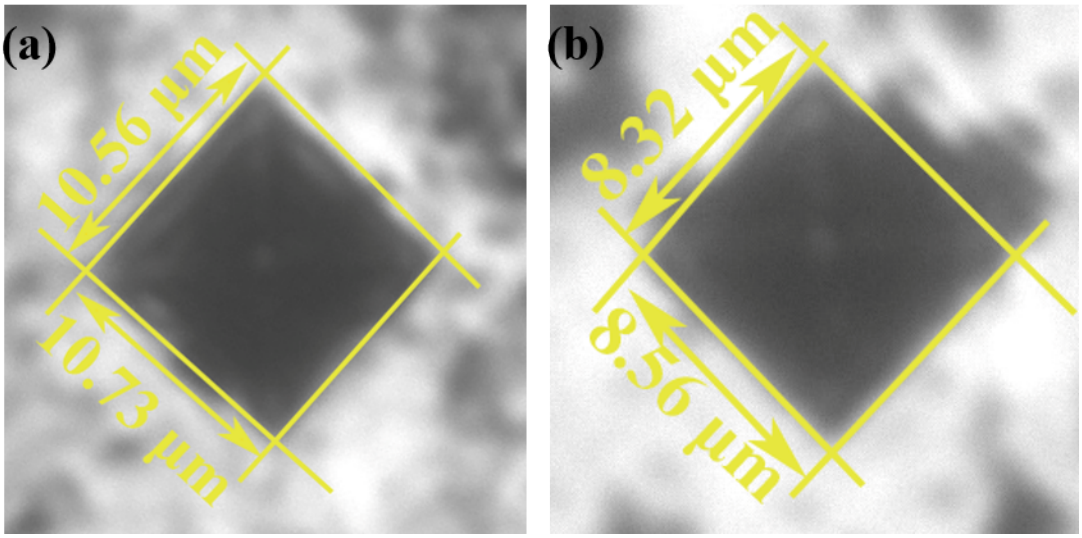

Fig S3 (a) and (b), Typical optical images of the indentation of Furnace Mn-B and RDMF-MnB sample at the applied load of 0.05 kg. d1 and d2 was measured on the images, respectively.

The Vickers hardness values at the different applied loads are determined based on the following equation:

$H_V = 1854.4P/d^2$

where d is the arithmetic mean length of the two diagonals of indentations (in mm), P is the applied load (in N), and HV is the Vickers hardness (in GPa).

Therefore, we can calculate the Vickers hardness of Tube Furnace Mn-B and DMF-MnB sample.

H_V(TF-MnB)=8.02 Gpa and H_V(DMF-Mn-B)=12.77 Gpa.

Table S3. Comparison of the relative density of TF-Mn-B and DMF-MnB.

Sample	Relative Density
TF-Mn-B	3.59
DMF-MnB	3.88

6. A typical non-in-situ process of the 30A-20s powder MnB synthesis

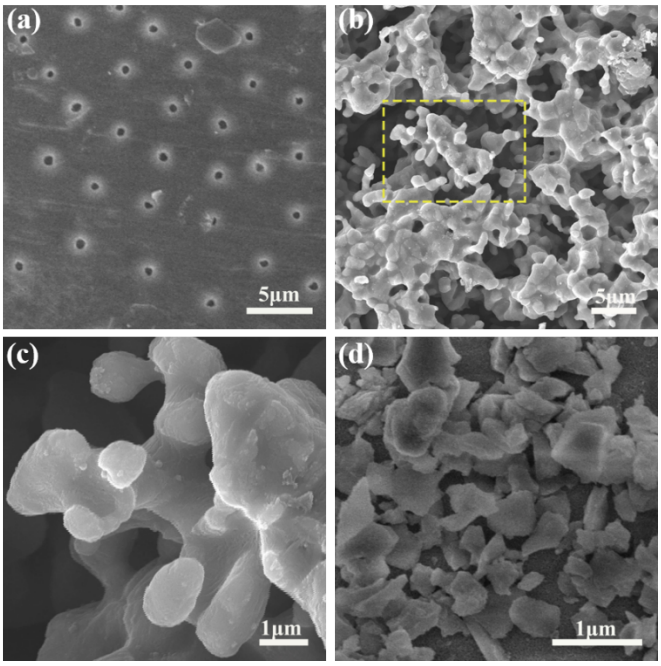

Fig S4 SEM images of powder MnB synthesis. (a) Sintered block with boron oxides coated and there are uniform blow-holes in it. (b) Sintered block with alcohol ultrasonic washed, boron oxides were removed and the porous structure of block was exposed. (c) Partial enlarged image of (b), (d) Crushed porous block which partly possessed small size below 1 μm.

7. Grain size of 30A-20s powder sample with alcohol washed.

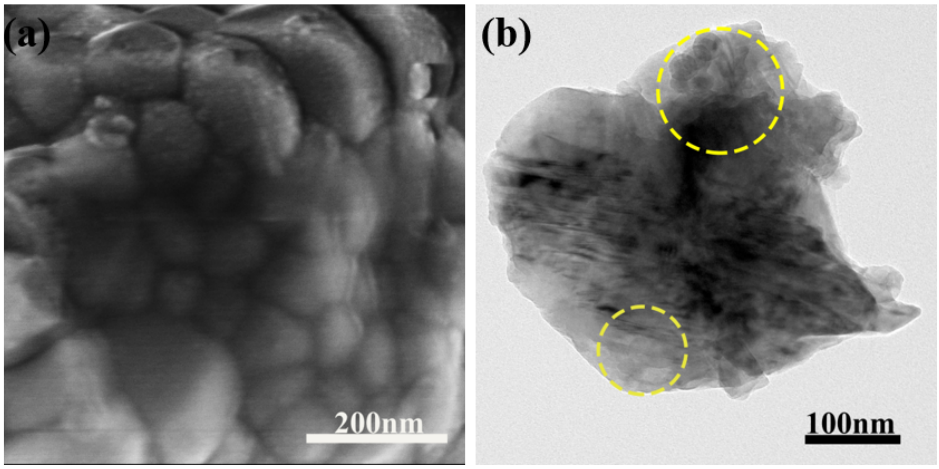

Fig S5 SEM(a) and TEM(b) images of 30A-20s powder sample with alcohol washed.

8. Size distribution of 30 A-20 s powder MnB

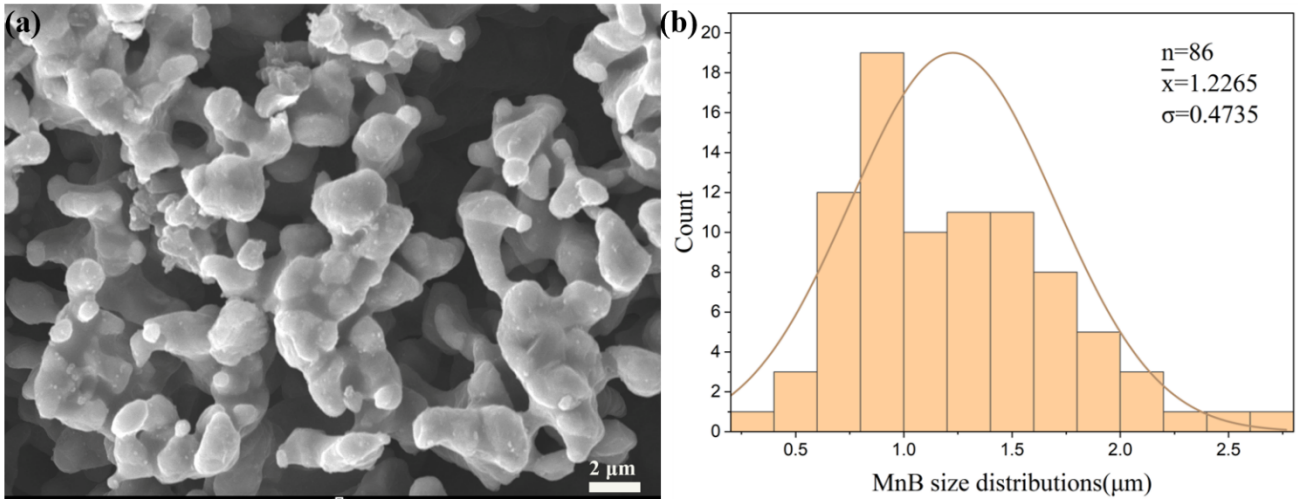

Fig S6 SEM image (a) and its size distribution (b) of 30 A-20 S powder MnB

9. SEM image and mapping of 25A-20s powder sample with alcohol washed.

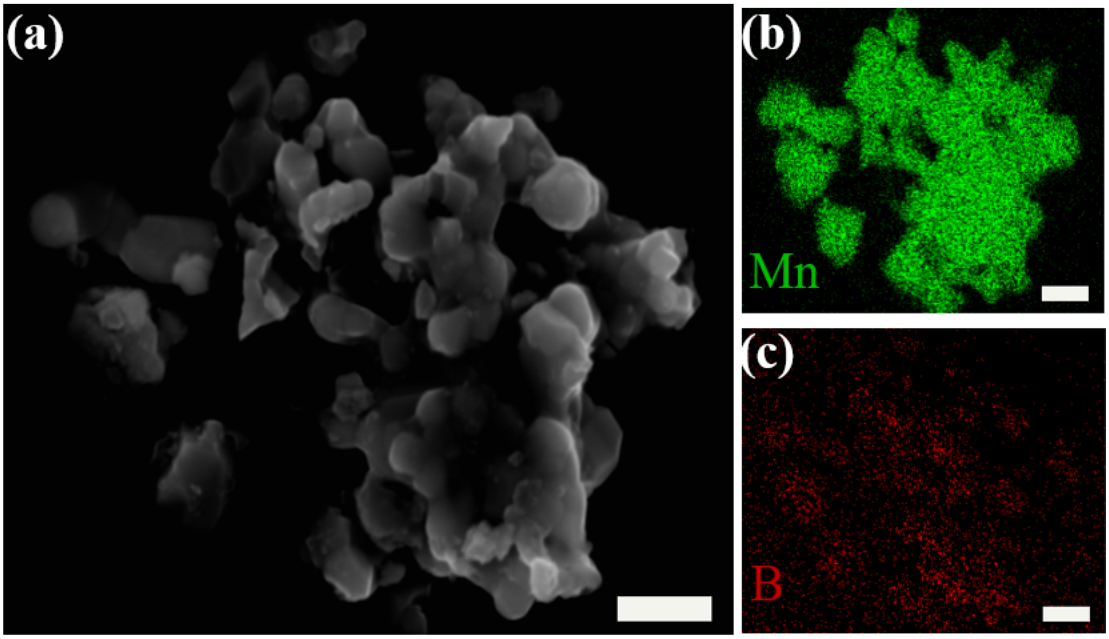

Fig S7 (a) SEM image and(b), (c) Mn and B elements mappings, the bar is 1 μm.

10. XRD pattern of DMF-synthesized powder MnB_2 and NiB

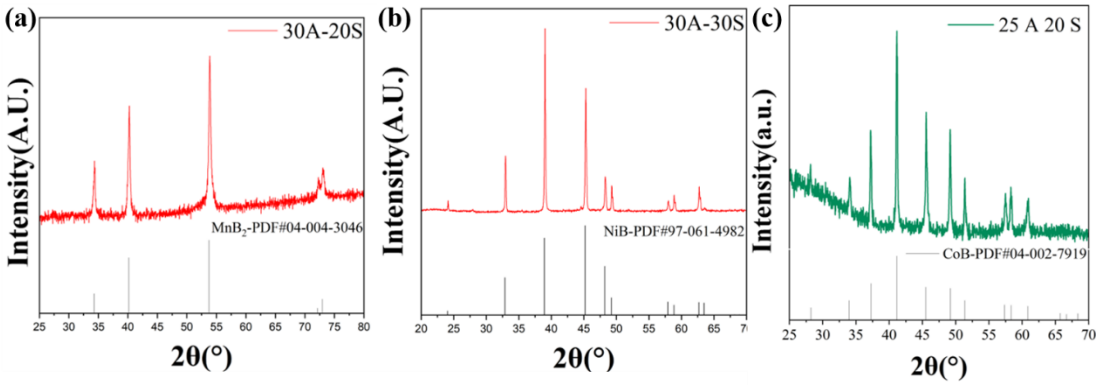

Fig S8 XRD spectra of the DMF-synthesized powder MnB_2 (a) and NiB (b) CoB (c)

11. Elemental composition of synthesized metal borides by ICP-OES analysis.

Table S4. ICP-OES analysis

Sample	Starting composition	ICP-OES
n=0.8 bulk MnB	Mn:B=0.8	Mn:B=0.996
30 A powder MnB	Mn:B=0.5	Mn:B=1.00

12. The correlation between powder size and coercive force (Hc)

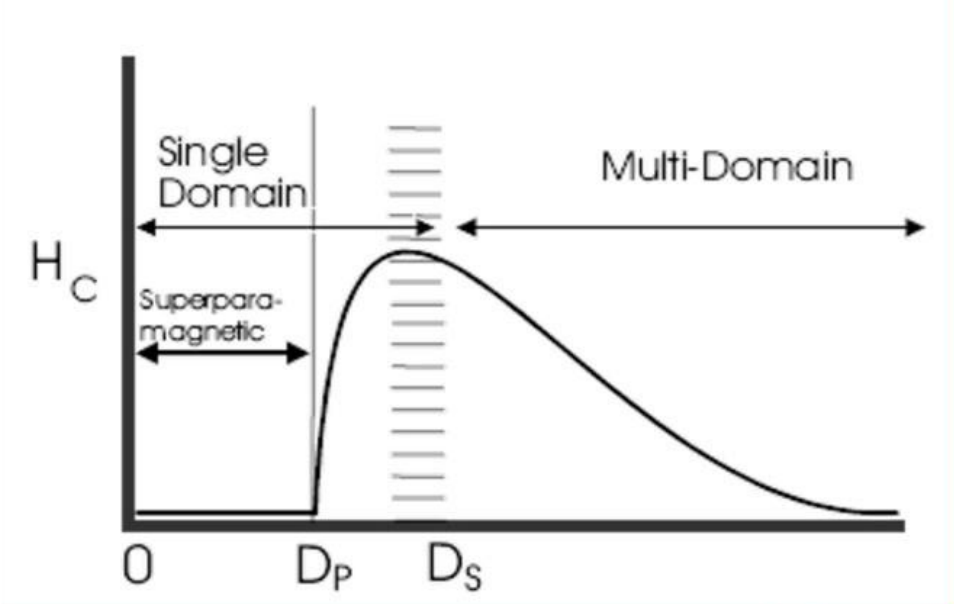

Fig S9 The correlation between powder size and coercive force (Hc).
As the powder size decreases, the multi-domain powders convert to single-domain, the Hc would be increased into a maximum value. Single domain size of soft magnetic materials is ranging from several nano to 100 nm, so the increased Hc indicates the decease of powder size.

Materials and methods

Synthesis of bulk MnB. In order to prepare mono-phase bulk MnB, commercially available crystalline powders of manganese (Aladdin,99% in purity) and amorphous boron (Macklin,99% in purity) in a molar ratio of Mn: B = n: 1 were pre-mixed homogeneously together by ballmill at 500 r/min for 30min, and ball-powder mass ratios was 10:1. Then weight 2.0 g mixed powder was pressed into a Ø20 cylindrical shape by the oil press. Next the pressed block was placed in an alumina crucible and heated with graphite paper as a heating source in a magnetic suspension melting furnace which was washed three times with argon. Then the pressed block is heated for 30 s at 5 kPa(A),30.0 A by this furnace. After heating, introduce the argon immediately as a protective atmosphere and restore pressure to atmosphere, cooling for 15 min, hard bulk was obtained. Crushed into powder by hard ore pulverizer for subsequent XRD, TEM, XPS and MH measurements.

Synthesis of bulk Mn-B (Comparison sample of tube furnace). Take the same pressed block of the DMF-bulk MnB and place into alumina boat in the tube furnance in a 5 kPa pressure(A). The heating rate is set to 50 °C/min from room temperature to 1000 °C, and holding 1000 for 10 min. Then, cooling to room temperature in furnace.

Synthesis of powder MnB. In order to prepare mono-phase powder MnB, commercially available crystalline powders of manganese(II) oxide (99.16%, Bidepharm) and amorphous boron (Macklin,99% in purity) in a molar ratio of MnO: B = 1: 2, Follow-up processing is the same as bulk MnB synthesis, but the pressed block is heated for 15 s at 5 kPa(A),30.0 A by this furnace. The cooled block is soaked in alcohol for 1 h, then we can easily manually grind into powder using a grinding bowl. Centrifuge alcohol washing at 5000 r/min for 2 min, vaccum drying for 6 h of the powder for subsequent testing.

In a typical RDMF route, 2.026 g block (1.5548 g MnO+0.4478 g B) after heating the mass of block decrease to 1.9300 g. Then after alcohol washing, obtained powder mass was 1.3017g. The conversion rate of the raw materials is 90.33%.

Synthesis of powder MnB_2. In order to prepare mono-phase powder MnB, commercially available crystalline powders of manganese(II) oxide (99.16%, Bidepharm) and amorphous boron (Macklin,99% in purity) in a molar ratio of MnO: B = 1: 3, Follow-up processing is the same as bulk MnB synthesis, but the pressed block is heated for 20 s at 5 kPa(A),30.0 A by this furnace.

Synthesis of powder NiB. In order to prepare mono-phase powder NiB, commercially available crystalline powders of nickel (II) oxide (Aladdin, 99% in purity) and amorphous boron (Macklin, 99% in purity) in a molar ratio of NiO: B = 1: 1, Follow-up processing is the same as bulk MnB synthesis, but the pressed block is heated for 30 s at 5 kPa(A),30.0 A by this furnace.

Synthesis of powder CoB. In order to prepare mono-phase powder CoB, commercially available crystalline powders of cobalt (II) oxide (Aladdin, 99% in purity) and amorphous boron (Macklin,99% in purity) in a molar ratio of CoO: B = 1: 1, Follow-up processing is the same as bulk MnB synthesis, but the pressed block is heated for 30 s at 5 kPa(A),30.0 A by this furnace.

Measurements. The morphology of the collected samples was characterized by field emission scanning electron microscope (ZEISS Sigma 300, German). Use energy dispersive x-ray (EDX) to characterize the elemental composition of the material. Specimens for transmission electron microscopy (TEM) investigation were prepared by dispersing MnB powders on a carbon mesh after dilution in alcohol and ultrasonication. High-resolution transmission electron microscope (HRTEM, G2 F30, FEI., America) was used to characterize the surface and lattice details of MnB under an accelerating voltage of 200 kV. X-ray diffraction (XRD) pattern of the sample was recorded on an EMPYREAN with Cu Kα rays (λ = 1.5406 Å). The X-ray photoelectron spectroscopy (XPS) of the sample was recorded on Thermo Scientific K-Alpha with Al Kα rays (hv=1486.6 eV). Microscopic hardness was characterize by innovatest falcon507(Netherlands). Hysteresis loop curve was characterized by Quantum Design PPMS-9T (America).

Measure of relative density. Drainage method using analytical balance. Pre weigh the mass of the block, then using a string tied on the block. Immersing the entire block in a beaker with two-thirds of the water, increased mass equals drainage volume. Then, we can calculate the relative density.

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