# A new facile method for preparing $M_3B_7O_{13}I$ boracites (M = Mn, Fe, Co, Ni, Cd)

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## 1. Experimental Section

All reactants were used without further purification. The purities of the starting oxides were checked by powder X-ray diffraction data. Amorphous boron powder (95–97%, Dan Dong Chemical Industry), Iodine (>99.8%, Shanghai Shi Yi Chemical Reagent CO., Ltd), $B_2O_3$ (98.0%), MnO (99.5%), $Mn_3O_4$ (>98.6%), $Fe_3O_4$ (97%), CoO (99.99%) and NiO were purchased from Aladdin Chemistry CO.,Ltd, $Fe_2O_3$ (>99.8%, Tianjin Fu Chen chemical reagent works), $Co_3O_4$ (99%, Shanghai Reagent General factory), CdO (99.95%, 325 mesh, Alfa Aesar China (Tianjin) Co., Ltd.).

In brief, the reported approach is a two crucible method, i.e., two silica crucibles were placed into a silica tubing, the top one contains stoichiometric metal oxide, $B_2O_3$, which were mixed and ground for 3 minutes in a mortar before loading. The bottom one contains stoichiometric element B, and $I_2$, which were mixed and ground for 3 minutes in a mortar before loading. The reaction assembly was flame sealed under vacuum and then heated in a furnace to the designated reaction temperature in 2 h, dwelled there for 3 days, and then cooled to the room temperature by switching off furnace.

In a typical experiment, MnO (255 mg, 3.6 mmol), $B_2O_3$ (278 mg, 4.0 mmol), elemental B (8 mg, 0.8 mmol) and $I_2$ (167 mg, 0.66 mmol) were weighed and loaded. Extra amount of B and $I_2$ according to the stoichiometry (reaction **1**, Table 1) were loading to ensure the complete reaction. The assembly was heated to 450 °C for 3 days. After the reaction, the excess B and $I_2$ remained in the bottom crucible, no corrosion on the inner surface of the crucibles as well as the silica jacket was found. The products were crushed and ground in a mortar and washed with ethanol several times to remove the unreacted $I_2$, B. The experimental conditions and some details for M = Mn, Fe, Co, Ni, Cd were summarized in Table 1.

For comparison, a reaction without loading B was carried out. MnO (255 mg, 3.6 mmol), $B_2O_3$ (278 mg, 4.0 mmol) and $I_2$ (167 mg, 0.66 mmol) were loaded, and heated according to the corresponding profiles, i.e., 450 $^oC$ and 600 $^oC$ for 3 days, the products were mainly $Mn(BO_2)_2$, together with $I_2O_4$, desired boracite was not formed at all. (Fig. S6)

**Powder X-ray Diffraction:** X-ray powder diffraction data were recorded on a Rigaku D/MiniFlex Ⅱ diffractometer at 15 kV, 30 mA for Cu Kα. Data were collected in

the range $2\theta$ = 5−75° with scan step of 0.02°. The cell parameters of $M_3B_7O_{13}I$ were obtained by the cell refinement with the aid of JADE 5.0 software package.

Table S1 Cell parameters (Å) calculated from the XRD patterns of $M_3B_7O_{13}I$ (M = Mn, Fe, Co, Ni, Cd)

| reaction | formula | experimental | ref |
|---|---|---|---|
| **1** | $Mn_3B_7O_{13}I$ | *a* = 12.326 (3) | *a* = 12.3404(3)[1] |
| **2** | $Fe_3B_7O_{13}I$ | *a* = 12.2589(6) | *a* = 12.22869(2)[2] |
| **3** | $Co_3B_7O_{13}I$ | *a* = 12.093(4) | *a* = 12.110(1)[3] |
| **4** | $Ni_3B_7O_{13}I$ | *a* = 11.998(5) | *a* = 12.0368(8)[4] |
| **5** | $Cd_3B_7O_{13}I$ | *a* = 8.868(3),<br>*b* = 8.874(2),<br>*c* = 12.507(4) | *a* = 8.890,<br>*b* = 8.890,<br>*c* = 12.530 (~~JCPDS~~PDF-2 No: = 26–0247) |
| **6** | $Mn_3B_7O_{13}I$ | *a* = 12.365(2) | *a* = 12.3404(3)[1] |
| **7** | $Fe_3B_7O_{13}I$ | *a* = 12.205(3) | *a* = 12.22869(2)[2] |
| **8** | $Co_3B_7O_{13}I$ | *a* = 12.110(3) | *a* = 12.110(1)[3] |
| **10** | $Mn_3B_7O_{13}I$ | *a* = 12.331(2) | *a* = 12.3404(3)[1] |
| **11** | $Mn_3B_7O_{13}I$ | *a* = 12.363(3) | *a* = 12.3404(3)[1] |
| **13** | $Mn_3B_7O_{13}I$ | *a* = 12.364(1) | *a* = 12.3404(3)[1] |
| **14** | $Mn_3B_7O_{13}I$ | *a* = 12.338(1) | *a* = 12.3404(3)[1] |
| **15** | $Mn_3B_7O_{13}I$ | *a* = 12.336(1) | *a* = 12.3404(3)[1] |

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**Scanning Electron Microscope**: The SEM images were obtained by using a JSM 6700F scanning electron microscope equipped with a field emission gun operating at 10 kV.

**Magnetic Susceptibility:** The DC (direct current) magnetic susceptibility of $Mn_3B_7O_{13}I$ was measured on a Quantum Design MPMS-XL magnetometer in the temperature range of 2–300 K. The as-synthesized polycrystalline sample was ground to a fine power to minimize possible anisotropic effects and loaded into a gelatin capsule. The data were corrected for the susceptibility of the container and for the diamagnetic contribution from the ion core.

The susceptibility data were fit by a least-squares method to the Curie-Weiss equation $\chi_M = C/(T - q)$, where $\chi_M$ is the magnetic susceptibility, C is the Curie constant, and $q$ is the Weiss constant. The effective magnetic moment ($\mu_{eff}$) was calculated from the equation $\mu_{eff} = (7.997C)^{1/2}\ \mu_B$.[5]

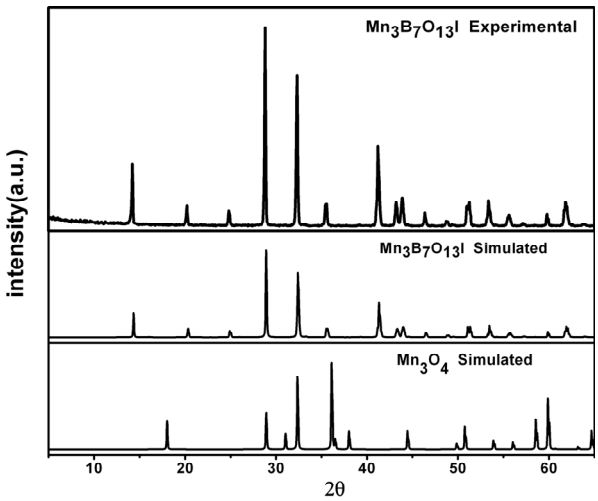


Fig. S1 X-ray powder diffraction patterns of the products of reaction **6** from $Mn_3O_4$. The pattern match well with the simulated powder pattern of $Mn_3B_7O_{13}I$ and does not show any reflection peak from either the starting $Mn_3O_4$ or other possible impurities.

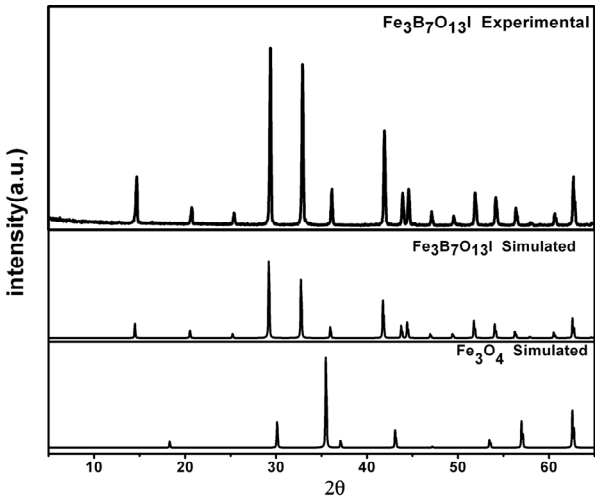


Fig. S2 X-ray powder diffraction patterns of the products of reaction **7** from $Fe_3O_4$. The pattern mach well with the simulated powder pattern of $Fe_3B_7O_{13}I$ and does not show any reflection peak from either the starting $Fe_3O_4$ or other possible impurities.

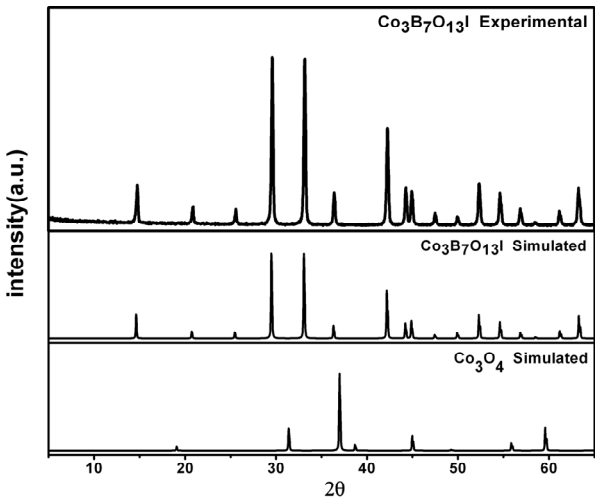


Fig. S3 X-ray powder diffraction patterns of the products of reaction **8** from $Co_3O_4$. The pattern mach well with the simulated powder pattern of $Co_3B_7O_{13}I$ and does not show any reflection peak from either the starting $Co_3O_4$ or other possible impurities.

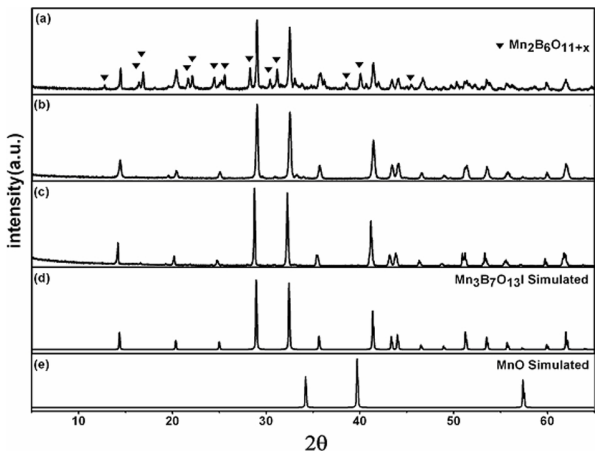


Fig. S4 X-ray powder diffraction patterns of the products of reactions of MnO at different temperatures for 3 days. (a): **9**, 400°C; (b): **10**, 500°C; (c): **11**, 600°C. Reaction **9** generates a mixture of $Mn_3B_7O_{13}I$ and $Mn_2B_6O_{11+x}$. **10** and **11** produce single phased $Mn_3B_7O_{13}I$. In these three products, no starting MnO has been observed.

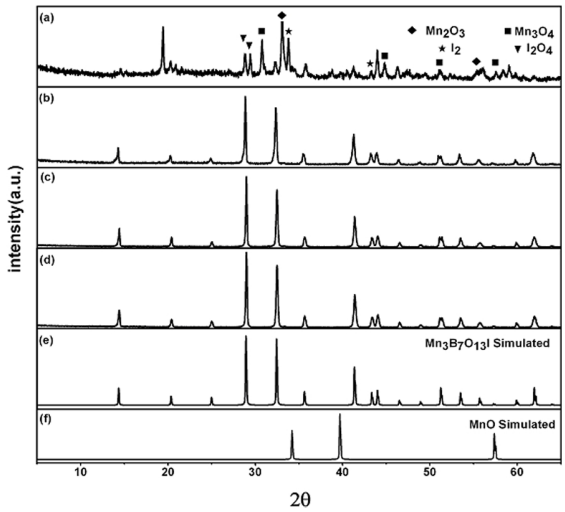


Fig. S5 X-ray powder diffaction patterns of the products of reactions of MnO at different temperatures for 1 days. (a): 12, 600°C; (b): 13, 650°C; (c): 14, 700°C; (d): 15, 750°C. Reaction 13–15 generates single phased $Mn_3B_7O_{13}I$ and no starting MnO has been observed. 12 only products are the mixture of $Mn_2O_3$, $Mn_3O_4$, $I_2$ and $I_2O_4$.

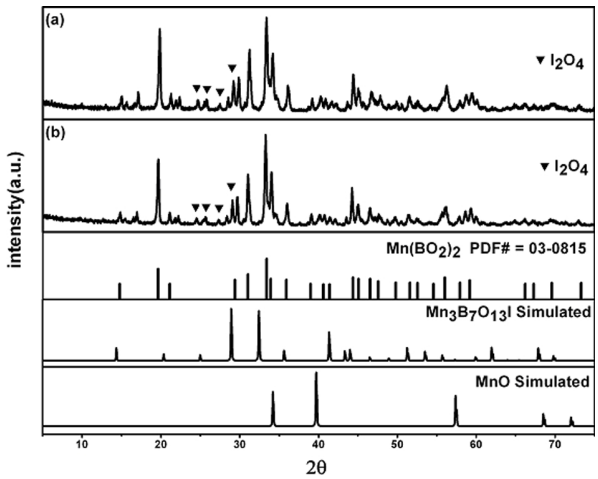


Fig. S6 X-ray powder diffraction patterns of the products of reactions of MnO without B loaded: (a): **16**, 450°C, 3d; (b): **17**, 600°C, 3d. The products are 80% of $Mn(BO_2)_2$ together with 20% of $I_2O_4$. No targeting $Mn_3B_7O_{13}I$ has been observed.

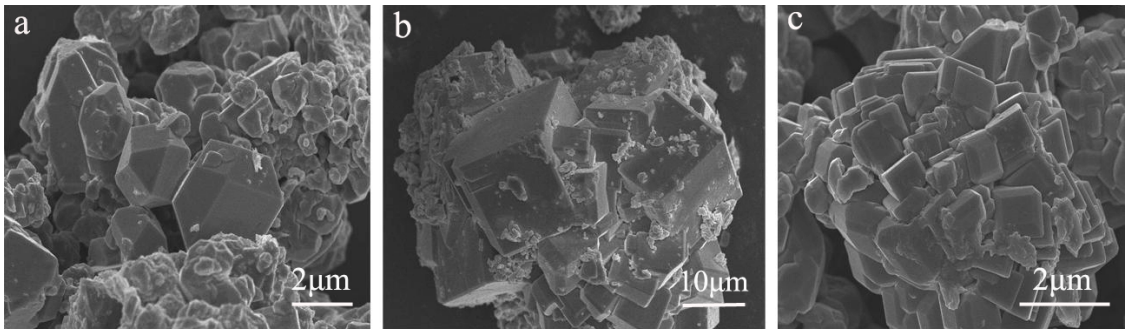


Fig. S7. SEM images of $Mn_3B_7O_{13}I$ from the reactions: (a) **1**, 450 °C, 3d; (b) **10**, 500 °C, 3d; (c) **11**, 600 °C, 3d.

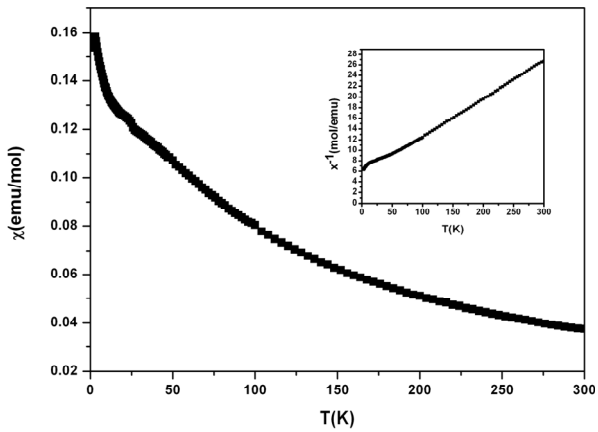


Fig. S8. Magnetic susceptibility of $Mn_3B_7O_{13}I$ obtained by reaction **1** plotted against temperature between 2 K and 300K. Inset: Inverse magnetic susceptibility dependence of the temperature.

Table S1. The yields relative to the metal oxide loaded of reactions producing pure phased $M_3B_7O_{13}I$ after washing by distilled water and ethanol that are listed in Table 1.

| **reaction** | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| yield | 82.45% | 76.63% | 82.35% | 76.04% | 76.55% |
| **reaction** | **6** | **7** | **8** | | |
| yield | 73.08 | 76.43% | 81.73% | | |
| **reaction** | **10** | **11** | **13** | **14** | **15** |
| yield | 75.53% | 70.7% | 87.12% | 95.21% | 77.8% |