

## Chemical Synthesis of Iron Borate, Fe<sub>3</sub>B<sub>6</sub>O<sub>16</sub>

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**ABSTRACT:** As part of a study on the Fe<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> phase diagram, the compound Fe<sub>3</sub>B<sub>6</sub>O<sub>16</sub> has been synthesized through a chemical route involving chelation with citric acid. The precursor was prepared by dissolving ferrous nitrate and boric acid in an aqueous medium and then drying the solution in the presence of citric acid. The conversion of the precursor into a resin and its subsequent transformation into the borate compound was studied as a function of temperature by X-ray diffraction methods. The compound Fe<sub>3</sub>B<sub>6</sub>O<sub>16</sub> was found to form as a phase-pure material at temperatures as low as 700 °C. Lattice parameters were determined by quantitative evaluation of the relevant X-ray data. Results of the present study on iron borates suggest that phase equilibria in the iron oxide-boric oxide system might be modified with respect to melting relations and solid solubilities.

**ÖZET:** Fe<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> faz diyagramı üzerinde yürütülmekte olan bir araştırmanın parçası olarak Fe<sub>3</sub>B<sub>6</sub>O<sub>16</sub> bileşiği jelleştirme yöntemi kullanılarak sentezlenmiştir. Bileşik, demir nitrat ve borik asidin sulu ortamda çözülmesi ve sitrik asit ilavesinden sonra elde edilen çözeltinin kurutulması sonucunda hazırlanmıştır. Reçine haline dönüşüm ve reçineden demir borat bileşiğinin meydana gelmesi, sıcaklığın bir fonksiyonu olarak X-ışınlan kırınımı yöntemi kullanılarak çalışılmıştır. Fe<sub>3</sub>B<sub>6</sub>O<sub>16</sub> bileşiğinin, 700 °C civarındaki düşük sıcaklıklarda saf faz olarak oluştuğu belirlenmiştir. Kristal kafesinin parametreleri, X-ışınlan verilerinin ölçülerek değerlendirilmesi ile elde edilmiştir. Bu çalışmanın sonuçları, demir oksit-bor oksit sistemindeki faz dengelerinin, erime ve katı çözünürlük ilişkileri açısından tekrar gözden geçirilmesi gerektiğini göstermektedir.

### 1. INTRODUCTION

Recently, iron borates, *VeJUOs* and FeB<sub>3</sub>O<sub>8</sub> were investigated as candidate anode materials for next-generation lithium secondary batteries (Rowell et al., 2001, Ivanova et al., 2002, Okada et al., 2003). Previously, these compounds have been the object of considerable interest both from the practical and the theoretical view point, because they have unusual magneto-optical properties. Production of these borates are rather difficult, because they are unstable above 900 °C, so diffusion rate is low and synthesis through oxide mix route takes at least several days. In this research, a chemical route involving chelation with citric acid was used and

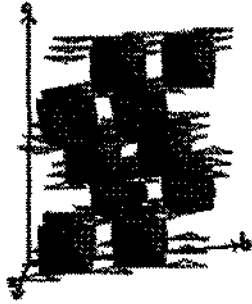
compound formation was completed in one hour at 700°C for Fe<sub>3</sub>B<sub>6</sub>O<sub>16</sub>.

Iron borate, Fe<sub>3</sub>B<sub>6</sub>O<sub>16</sub> is a compound of the binary system Fe<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>. Fe<sub>3</sub>B<sub>6</sub>O<sub>16</sub> has the same crystal structure with nobergite mineral, Mg<sub>3</sub>Si<sub>4</sub>(OH)<sub>2</sub>. Fe atoms are surrounded by 6 oxygen atoms forming distorted octahedra. Boron is exclusively tetrahedrally coordinated by oxygen (Diehl et. al., 1975). The other compound of the same binary is FeB<sub>3</sub>O<sub>8</sub> which has the calcite structure. The crystal structures of iron borates as determined by Rowell et al, 2003 are given in Figure 1.

Fe<sub>3</sub>B<sub>6</sub>O<sub>16</sub> is a weak ferromagnet. The structure consist of a sublattice of Fe ions made up of alternating layers normal to the c axis with

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ferromagnetic ordering inside the layers and antiferromagnetic ordering between the layers (Hirano et. al., 1974).



a) FeBO<sub>3</sub>



b) Fe<sub>3</sub>BO<sub>6</sub>

Figure 1. (a) Polyhedral structures of FeBO<sub>3</sub> space group R-3c: a=4.624 Å, c=14.47 Å (JPDS No: 21-423) and (b) Fe<sub>3</sub>BO<sub>6</sub> space group Pnma: a=10.048 Å, b=8.531 Å, c=4.466 Å (JPDS No:70-880). The dark octahedra are Fe(III), light polyhedra are boron (Roswell et. al., 2001).

In previous studies, phase relations in the system Fe<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> were investigated in air up to 900 °C (Diehl et. al. 1976, Joubert et. al., 1968, Makram et. al., 1972). In the present study, the phases and the phase boundaries of this phase diagram were checked with some compositions at selected temperatures. Results indicated that phase equilibria in the iron oxide-boric oxide system should be modified with respect to melting relations and solubilities of phases in solid state.

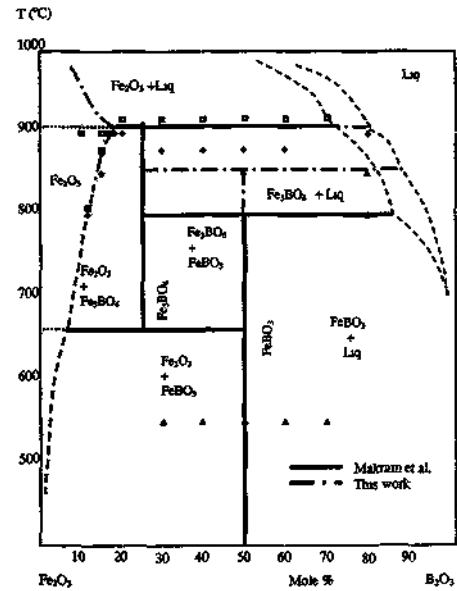


Figure 2. Phase diagram of the binary system Fe<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> conducted by Makram et al. and modified by this study. \*, 0, and A indicates experimental points Fe<sub>2</sub>O<sub>3</sub> identified only, Fe<sub>3</sub>BO<sub>6</sub> identified, and FeBO<sub>3</sub> identified respectively.

## 2. EXPERIMENTAL WORK

In the chemical synthesis of Fe<sub>3</sub>BO<sub>6</sub>, BDH ferrous nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and Merck boric acid (H<sub>3</sub>BO<sub>3</sub>) were used as starting materials. Iron nitrate and boric acid were dissolved in distilled water. To this solution citric acid, (HOOCCH<sub>2</sub>CH(OH)COOH) was added and the resulting solution was dried by evaporation at 100 °C in 24 hours. Within the next 24 hours, further drying was carried out in a muffle furnace where the temperature was increased gradually to 350 °C. The resulting powder precursor was calcined for one hour at temperatures 600, 700, 800, and 900 °C. The phases in the calcined product were identified by SEM analysis of fracture surfaces in a JEOL 6400 unit and by X-ray diffraction techniques using Rigaku D-MAX/B powder diffractometer with monochromatic Fe-K $\alpha$  radiation. Silicon was used

as the external Standard to find correct peak positions.

The X-ray diffraction patterns of the powder samples produced by the chemical chelation route are presented in Figure 3. Results show that  $\text{Fe}_3\text{BO}_6$  crystallized as a phase-pure material at calcination temperatures as low as 700 °C in 1 hour. Lattice parameters of the  $\text{Fe}_3\text{BO}_6$  were calculated from the sample sintered at 800 °C for one hour. The calculations were carried out by using the software embedded in the Rigaku unit. The values of the  $\text{Fe}_3\text{BO}_6$  lattice parameters a, b, and c were calculated as  $10.049 \pm 0.005$ ,  $8.538 \pm 0.005$ , and  $4.472 \pm 0.002$  respectively. These parameters were found to be in close concordance with those listed in JPDSONo:70-880.

SEM photographs of the samples produced by citrate chelation route and calcined at different temperatures can be seen in Figure 4. Irregular shape of the powder particles is due to chelation technique. Powders could be reduced to desired size and round shape by ball milling.

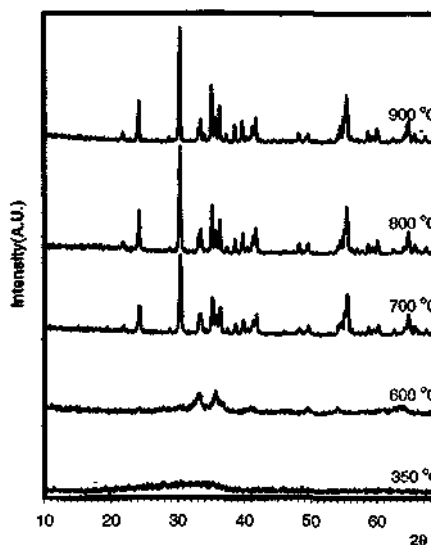


Figure 3. X-ray diffraction patterns of  $\text{Fe}_3\text{BO}_6$  powders produced by citrate route calcined at different temperatures for one hour.

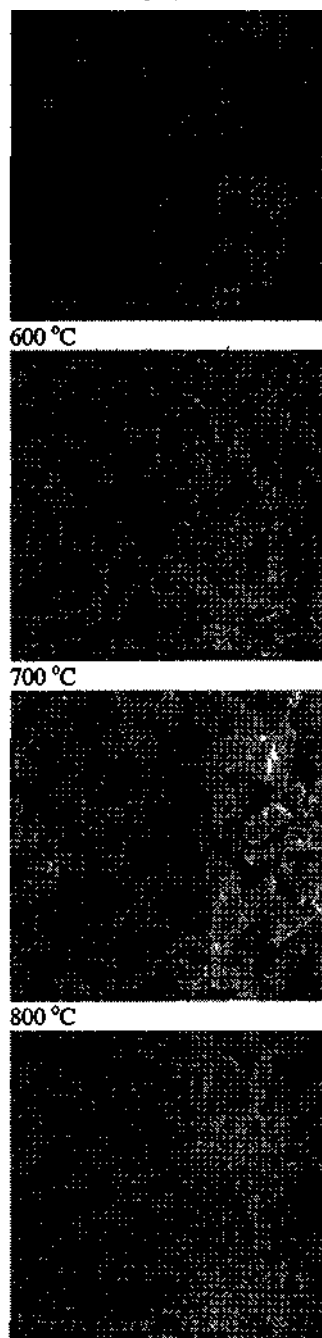


Figure 4. Electron microscope photographs of  $\text{Fe}_3\text{BO}_6$  powders calcined at 600, 700, 800, 900 °C.

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The samples for phase equilibration studies of the system FejOs-BiC<sup>^</sup> were prepared as mentioned before. Equilibration runs were conducted in a muffle furnace maintained at desired constant temperatures. The temperature of the furnace where the samples placed was measured with an external thermocouple. The variation in fixed equilibration temperatures was within + 3 °C. Each sample was equilibrated for 4 days to ensure equilibrium at elevated temperatures. At the end of the runs, the samples were air-quenched. The phases identified in the quenched samples are listed in Table 1. These results were used to modify the phase diagram of the system as shown in Figure 2.

Table 1. Results of the phase equilibration runs.

Composition mole * B10İ in F003-B2O3	Temp °C	Equilibration Time Days	Phases Identified After Air-quenching
10	750	4	<b>Fe<sub>2</sub>O<sub>3</sub></b>
10	900	4	<b>Fe<sub>2</sub>O<sub>3</sub></b>
12	800	4	<b>Fe<sub>2</sub>O<sub>3</sub>+Fe<sub>3</sub>B0<sub>6</sub></b>
12	810	4	<b>Fe<sub>2</sub>O<sub>3</sub></b>
15	750	4	<b>Fe<sub>2</sub>O<sub>3</sub>+Fe<sub>3</sub>B0<sub>6</sub></b>
15	850	4	<b>Fe<sub>2</sub>O<sub>3</sub>+Fe<sub>3</sub>B0<sub>6</sub></b>
15	870	4	<b>Fe<sub>2</sub>O<sub>3</sub>+Fe<sub>1</sub>B0<sub>n</sub></b>
15	875	4	<b>Fe<sub>2</sub>O<sub>3</sub></b>
15	880	4	<b>Fe<sub>2</sub>O<sub>3</sub></b>
17	900	4	<b>FejOj</b>
18	900	4	<b>Fe<sub>2</sub>O<sub>3</sub> + Fe<sub>3</sub>B0<sub>n</sub></b>
20	900	4	<b>FejBO« + FeiO,</b>
20	920	4	<b>Fe<sub>2</sub>O<sub>3</sub></b>
30	550	20	<b>FeB0<sub>3</sub> + Fe A</b>
30	875	4	<b>FejBO«</b>
30	920	4	<b>Fe<sub>2</sub>O<sub>3</sub></b>
40	550	20	<b>FeB0<sub>3</sub> + Fe, 0,</b>
40	875	4	<b>FejBO«</b>
40	920	4	<b>Fe A</b>
50	850	4	<b>FeB0<sub>3</sub></b>
50	875	4	<b>FejBO«</b>
50	920	4	<b>Fe<sub>2</sub>O<sub>3</sub></b>
60	550	20	<b>FeB0<sub>3</sub></b>
60	875	4	<b>FejBO«</b>
60	920	4	<b>Fe<sub>2</sub>O<sub>3</sub></b>
70	550	20	<b>FeB0<sub>3</sub></b>
70	875	4	<b>FejBO«</b>
70	920	4	<b>Fe<sub>2</sub>O<sub>3</sub></b>
80	750	4	<b>FeB0<sub>3</sub></b>
80	800	4	<b>FeB0<sub>3</sub></b>
80	850	4	<b>FeBO,</b>
80	900	4	<b>FejBO«</b>

PS- The phase written in bolt letters indicates higher relative proportion.

### 3. CONCLUSION

The compound Fe3B06 has been synthesized successfully through a chemical route involving chelation with citric acid. The lattice parameters of calculated from XRD data for Fe<sub>3</sub>B0<sub>6</sub> were found to be in good agreement with the lattice parameters listed in JPDS card.

The equilibration experiments indicated that existing Fe203-B<sub>2</sub>O<sub>3</sub> phase diagram should be modified with respect to melting relations. In addition, the peritectic reaction involving FeB0<sub>3</sub> shifted to higher temperatures. A considerable solid solubility of B<sub>2</sub>O<sub>3</sub> in Fe<sub>2</sub>O<sub>3</sub> was detected. Sub-solidus phase relations on the Fe<sub>2</sub>O<sub>3</sub> rich side of the phase diagram indicated that a new invariant reaction could be present at low temperatures. This invariant reaction must be associated with the phase transition of Y-<sup>^</sup>a-Fe<sub>2</sub>O<sub>3</sub> at about 400 °C (Hsiang et. al., 2003).

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