Characterization of the Magnesium Borates Hydrothermally Synthesized from $Na_2B_4O_7.5H_2O$, $MgCl_2$ and H_3BO_3 at the Boiling Point

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Abstract

There are more than 230 boron minerals which contain different amounts of boron oxide (B_2O_3) percentages. Magnesium borates are one of the boron mineral groups that have important properties of high elasticity coefficient, resistance to corrosion and high heat resistance. In this study, magnesium borate production is studied by hydrothermal synthesis method from a sodium borate mineral of tincalconite ($Na_2B_4O_7.5H_2O$) at 100^oC while stoichiometric mole ratio Mg/B is 1:8 determined from pre-experiments. The other raw materials are used as dehydrated magnesium chloride ($MgCl_2$) and boric acid (H_3BO_3). Four different reaction times studied which are 30, 60, 120, 240 minutes. For the characterization analysis Philips PANanalytical X-Ray Diffraction (XRD) and Perkin Elmer Spectrum One Fourier Transform Infrared Spectroscopy (FT-IR) are used. From the results of the experiments magnesium borates are synthesized at the form of "Admontite" [$MgO(B_2O_3)_3.7(H_2O)$], "Aksaite" [$Mg(B_6O_7(OH)_6).2H_2O$] and "Magnesium Boron Hydrate" [$MgB_{12}O_{19}.5(H_2O)$].

Key words: Magnesium borate, sodium borate, hydrothermal synthesis, tincalconite, boric acid

1. Introduction

Boron minerals are important chemical compounds which can be used for more than 500 industrial applications such as glass (fiber glass, borosilicate glass), ceramic (enameling, porcelain), nuclear industry (control rods) etc. Boron minerals can be classified as calcium borates, magnesium borates and sodium borates.

Magnesium borates with their superior properties arouse attention of many researchers. These types of borate minerals show high corrosion and temperature endurance. Magnesium borates are also wear resistant minerals and have excellent mechanical properties. Therefore, they are used in ceramic industry, detergent industry, super-conducting materials production, as a compound in neutron and gamma radiation shielding materials. Magnesium borates as raw materials in the alkali-free glassfibre industry can reduce fluorite discharging to avoid air pollution [1]. Magnesium borate is also used for removing radioactive wastes which due to its boric acid content [2].

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Although they are significant additives for many fields magnesium borate minerals cannot be found widespread. When compared with other boron minerals, magnesium borates are less refinely produced in Turkey and production of magnesium borates takes place at the region of Liao-dong peninsula, where it is adjacent to North Korea part of China by metallurgical methods or transformation of double salt of sea water [3].

There are two major ways to produce magnesium borate minerals; hydrothermal and thermal methods. In hydrothermal method boron and magnesium sources are dissolved in an aqueous medium and reaction starts by the aid of temperature. In thermal method the boron and magnesium sources are reacted with each other at a high temperature furnace in an air atmosphere.

In literature hydrothermal synthesis of magnesium borates was studied by many researchers but reactions were took place at high temperatures (>100^{o}C) and the reaction times were long (>2 hours). Some of synthesized magnesium borates in literature were $MgBO_2(OH)$, $2MgO.B_2O_3.H_2O$, $Mg_7B_4O_{13}.2H_2O$, $MgB_6O_{10}\cdot 7H_2O$, $MgB_4O_7.9H_2O$ [4-8].

In this study, on the purpose of investigation the effect of reaction time on magnesium borate production, synthesizes are carried out with four different reaction time (30, 60, 120, 240 minutes). The characterization studies are done by XRD, FT-IR.

2. Materials and Method

2.1. Preparation of the Raw Materials

In this study tincalconite ($Na_2B_4O_7.5H_2O$), dehydrated magnesium chloride ($MgCl_2$) and boric acid are raw materials for magnesium borate synthesis. Tincalconite and boric acid are supplied from Boron Management Plant in Bandırma, Turkey. Boric acid is grinded with agate mortar before usage. Dehydrated magnesium chloride is supplied from Merck Chemicals.

2.2. Hydrothermal Synthesis

The mole ratio of reactants are determined as 1 mole tincalconite to 1 mole magnesium chloride and 4 moles boric acid from pre-experiments. The selected reaction temperature is 100^{o}C. After synthesis pure alcohol solution is used for removing the excess amount of unreacted boric acid from product.

2.3. Characterization Analysis

Both raw materials and produced magnesium borates are subjected to X-Ray Diffraction (XRD) analysis with Philips PANanalytical in the 2θ range from 10° to 60°. X-rays are produced from Cu-Kα tube at the parameters of 45kV and 40mA. Also, Perkin Elmer Spectrum One Fourier

Transform Infrared Spectroscopy (FT-IR) is used for identification analysis. In this method Universal ATR sampling accessory – Diamond / ZnSe is used and measurement range is selected as 1800–650 cm^{-1}, scan number is 4 and resolution set as 4 cm^{-1}[8].

3. Results

3.1. Raw Materials Characterization Results

XRD patterns and results of tincalconite, dehydrated magnesium chloride and boric acid are shown in Figure 1 and Table 1.

Table 1. XRD Results of Raw Materials

Pdf #	Mineral name	Mineral formula
01-074-0521	Magnesium Chloride	$MgCl_2$
01-072-1517	Magnesium Chloride	$MgCl_2$
00-053-0260	Magnesium Chloride Hydrate	$MgCl_2.H_2O$
00-011-0328	Magnesium Chloride Hydroxide	Mg(OH)Cl
01-073-2158	Sassolite	H_3BO_3
01-079-1529	Tincalconite	$Na_2B_4O_7.5H_2O$

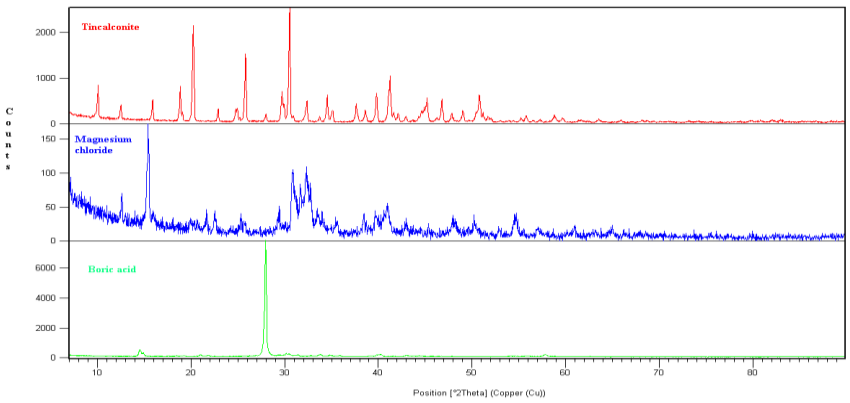

Figure 1. XRD Spectrums of Raw Materials

FT-IR spectrums of raw materials are shown in Figure 2.

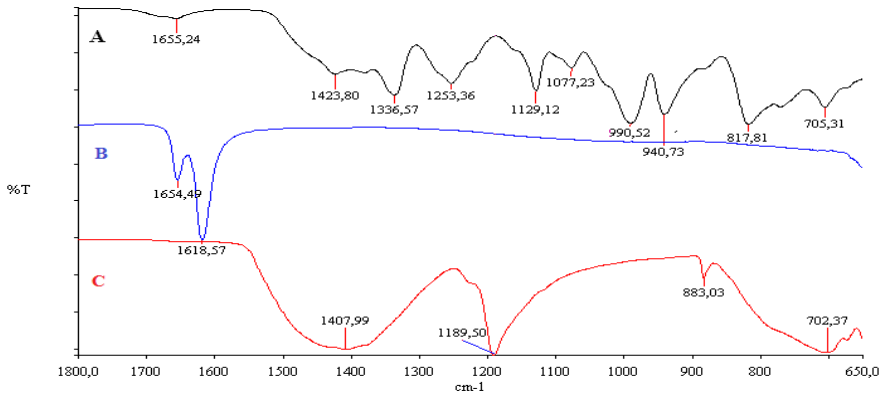

Figure 2. FT-IR Spectrums of Raw Materials (A: Tincalconite, B: Magnesium chloride, C: Boric acid)

3.2. Product Characterization Results

XRD patterns and results of synthesized magnesium borate minerals are shown in Figure 2 and Table 2. With regard to XRD results of experiments, it is seen that "01-076-0540" pdf numbered Admontite occurs at all reaction times. At reaction time of 30 minutes Admontite is formed majorly and also "01-083-2390" pdf numbered Magnesium Boron Hydrate and "01-071-2409" Aksaite are formed. 60 minutes after the reaction Magnesium Boron Hydrate and Aksaite minerals are change to Admontite. At the reaction time of 120 minutes the occurred forms of magnesium borate are Admontite and Aksaite. At 240 minutes of reaction time Aksaite formation is disappeared and turned to Admontite and Magnesium Boron Hydrate.

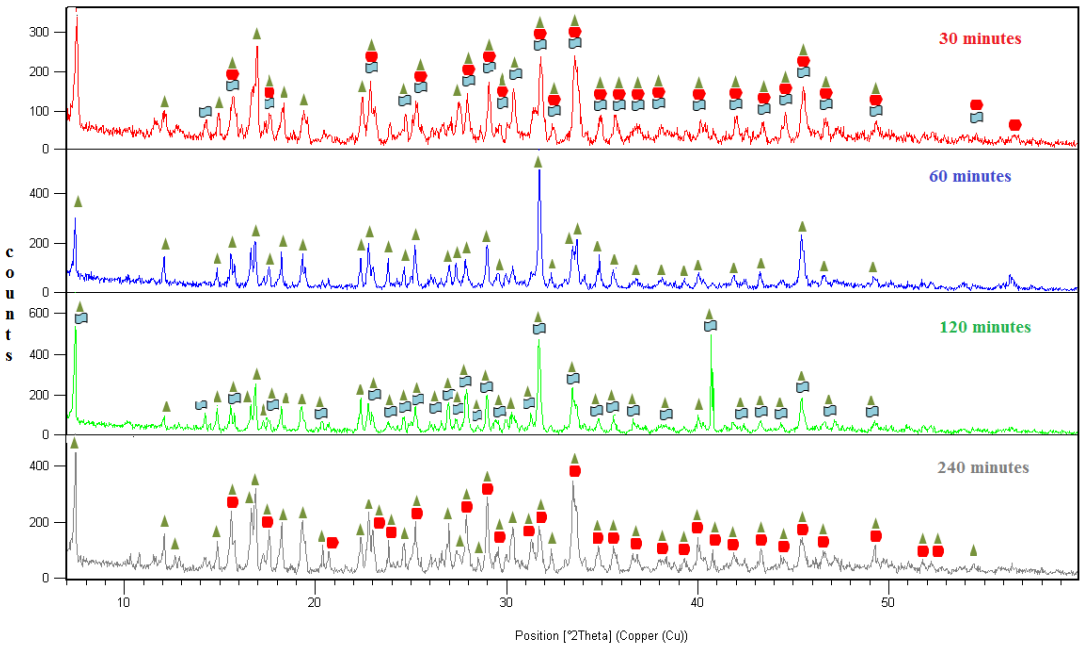

Figure 3. XRD Spectrums of Magnesium Borates for Different Reaction Times

: Admontite : Aksaite : Magnesium boron hydrate

Table 2. XRD Results of the Synthesized Magnesium Borates

Reaction time (minutes)	Pdf #	Mineral name	Mineral formula	Score
30	01-076-0540 01-083-2390 01-071-2409	Admontite Magnesium Boron Hydrate Aksaite	$MgO(B_2O_3)_3.7H_2O$ $MgB_{12}O_{19}.5(H_2O)$ $Mg(B_6O_7(OH)_6).2H_2O$	54 20 13
60	01-076-0540	Admontite	$MgO(B_2O_3)_3.7H_2O$	56
120	01-076-0540 01-071-2409	Admontite Aksaite	$MgO(B_2O_3)_3.7H_2O$ $Mg(B_6O_7(OH)_6).2H_2O$	56 14
240	01-076-0540 01-083-2390	Admontite Magnesium Boron Hydrate	$MgO(B_2O_3)_3.7H_2O$ $MgB_{12}O_{19}.5(H_2O)$	67 17

FT-IR spectrums of synthesized magnesium borate compounds are shown in Figure 4.

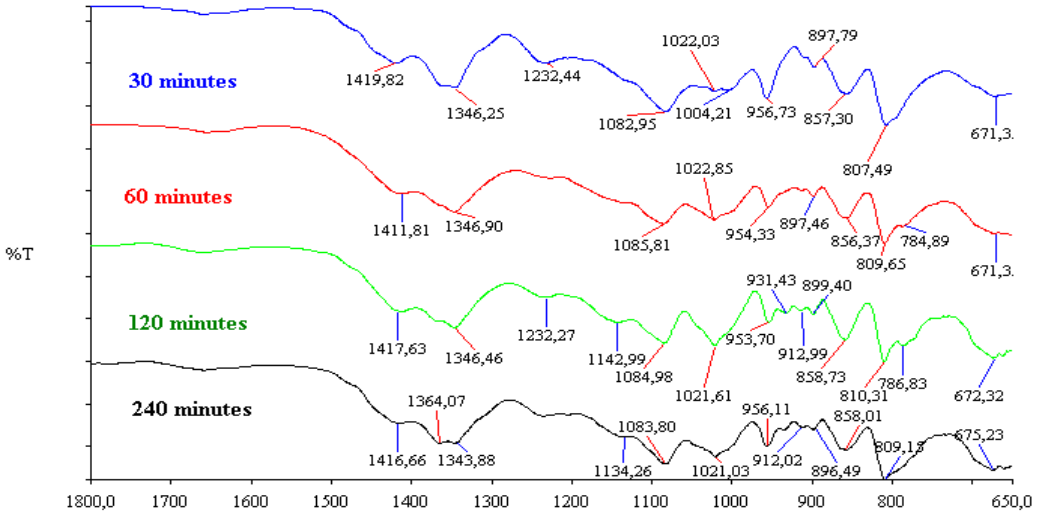

Figure 4. FT-IR Patterns of Magnesium Borates

According to the FT-IR spectrums for various reaction times, there are some minor differences between peaks. The peaks with 1419,82 and 1343,88 cm^{-1} might be the asymmetric stretching of tri-coordinate boron ($B_{(3)}$–O). The peaks with band values between 1232,44 and 912,02 cm^{-1}, might be the asymmetric stretching of tri-coordinate boron ($B_{(4)}$–O). Symmetric stretching of $B_{(3)}$–O can be seen between 899,40 and 784,89 cm^{-1}. The peaks formed around 672,32 might be the out-of-plane OH^{-1} bending band and bending of $B_{(3)}$–O in the structure.

4. Discussion

Magnesium borates are considerable minerals due to their thermal and mechanical properties. Magnesium borates, as source of magnesium and boron, are widely used instead of refined borates or metallic borates. Furthermore, they are used for removing the pesticides from earth, production of superconductive magnesium diboride, as lubricating additive in oil, for metal surfaces as insulating coat material, in heat sensitive colored ink compositions, anticorrosive additive for dyes, in contact lens washing solutions and wood protection as fire retardant [10].

In this study, hydrothermal production of magnesium borate is analyzed for different reaction periods. Starting from tincalconite, dehydrated magnesium borate and boric acid as raw materials at 100^{o}C, liquid state synthesis of magnesium borate is occurred. It can be seen from XRD results that for all reaction times, the major produced magnesium borate mineral is Admontite. The XRD scores of Admontite are gradually increase by increasing reaction times.

Conclusions

A new route for the synthesis of magnesium borate minerals is reported, using tincalconite, boric acid and $MgCl_2$ as Boron and Magnesium sources via hydrothermal method. In order to investigate the effect of reaction time on synthesized minerals, different reaction times are studied. Admontite, Aksaite and Magnesium Borate Hydrate are produced with different XRD scores at different reaction times. Also the new procedure of magnesium borate synthesis that searched in this study provides more crystalline minerals than previous studies.

In future researches, the reaction temperature will be decreased under 100^{o}C and the ways of pure magnesium borate production with the same raw materials will be investigated.

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