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Iron Doped Biomaterial Calcium Borate: Synthesis and Characterization

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***Abstract*—**Colemanite is the most common borate mineral, and the main source of the boron required by plants, human, and earth. Transition metals exhibit optical and physical properties such as; non-linear optical character, structural diversity, thermal stability, long cycle life and luminescent radiation. The doping of colemanite with a transition metal, bring it very interesting and attractive properties which make them applicable in industry. Iron doped calcium borate was synthesized by conventional solid state method at 1200 °C for 12 h with a systematic pathway. X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy/energy dispersive analyze (SEM/EDS) were used to characterize structural and morphological properties. Also, thermal properties were recorded by thermogravimetric-differential thermal analysis (TG/DTA).

***Keywords*—**Colemanite, conventional synthesis, powder x-ray diffraction, borates.

I. Introduction

COLEMANITE, represented by $Ca_2B_6O_{11}.5H_2O$ simple chemical formula, contains 27.28% CaO, 50.81% B_2O_3 and 21.91% H_2O. Colemanite is crystallized in monoclinic crystal system with unit cell parameters a=8.743 Å, b=11.264 Å, c=6.102 Å, and space group P21/a [1], [2].

The "d" values of highest three intensive peaks are at 3.13, 3.85, 5.64 Å, respectively with ICDD card number 33-267 [3]. The colemanite appears colorless, white and transparent/ translucent with the density of 2.42 g/cm^3. The chains are extended in "a" direction in the crystal structure which formed layers of trimer borate compounds by ionic bonding with Ca ions horizontally. The layers are connected with hydrogen bonds owing to hydroxyl groups and water molecules in the chains. One $BO_2(OH)$ triangle and two $BO_2(OH)_2$ tetrahedral groups compose of ring form with $(B_3O_3(OH_5)^{2-}$ formula by sharing corners. Colemanite (Fig. 1) is different boron mineral by having perfect cleavage, harder structure and crystal form [4].

The DTA studies show that the water decomposition of colemanite occurs at 400 °C. The lattice changing with second endothermic reaction resulting of the formation of new crystals (forming of new lattice) are shown by the support of gradual exothermic peaks in DTA graphic. The first melting point is 960 °C; nevertheless, main melting point is about 1100 °C. However, the melt has a small amount of stable crystalline phase, the crystalline phase turns into melt utterly via to continue heating [5]-[8]. Colemanite has been intensively used to be a source to obtain borate compounds due to abundancy, chemically inertness, and structure containing both Ca and B atoms.

Many metal borate compounds are known as non-linear optical and laser-host material [9]. The researches about these compounds made possibility to produce laser beams with the wavelengths and power features which had not been obtained before [10]-[17].

The atomic structure of each element has a settlement layout which is specific for it; that is, the electrons in the atoms existed in a certain energy levels which has stable orbits. The electrons which are stable at their orbits get excited to upper energy level with excitement, and they come back to same energy level by leaving energy. This is the main working principle of laser [14]-[18].

Borate compounds including alkaline, alkaline earth and transition metals have some features like catalytic activity, unique magnetic behavior and high recycling in Li-ion battery [19]. Besides, the borate compounds which include rare earth metal have common usage areas which are named as phosphors [17].

The advanced side of this experimental research is obtaining of iron doped calcium borate by conventional solid state route, investigation of all structural properties for instance "d" values, crystal system, unit cell structure and unit cell parameters; moreover, colemanite is used both calcium and boron source.

Fig. 1 The crystal structure of colemanite

II. Experimental Details

The starting materials were supplied by Riedel and Sigma companies as analytical grade. Colemanite and iron(III) oxide were weighed in three amounts of 1:1, 2:1 and 1:2. After grinding of starting materials, the samples are treated to three different temperatures 700 °C, 800 °C and 900 °C. Alls samples were characterized by X-ray powder diffraction (XRD) pattern using Panalytical X'Pert Pro Diffractometer

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and Cu K_α radiation (λ=1.54056 Å, 40 mA, 50 kV). Structural properties were determined with High Score + Program and Rietveld Refinement Method.

FTIR spectra were recorded between 4000 and 600 cm^{-1} using Perkin Elmer Spectrum 100 FTIR Spectrometer. TG/DTA was carried out by Perkin Elmer Diamond TG/DTA. Morphological property and ratio of the elements of the sample were analyzed by ZEISS Supra 40 VP.

III. Results and Discussion

The XRD patterns of the three systems in three temperatures are given in Fig. 2. When we compare the patterns to Inorganic Crystal Structure Database (ICSD), all samples were corresponded to double phase Fe_2O_3 (ICSD=016-1285)/CaB_2O_4 (ICSD=002-2060) compounds (Table I) except one sample. The Fe_2O_3-$Ca_2B_6O_{11}\cdot 5H_2O$ system with 2:1 molar ratio at 900 °C is displayed (Table II) as pure CaB_2O_4 (ICSD=002-2060) doped with Fe^{3+} ion (Fig. 3). The absence of impurities confirms the success of doping process of calcium borate. In Table II, the calculated and observed XRD data of iron doped calcium borate can be seen with estimated "hkl" values. The unit cell structure is shown in Fig. 4 which indicates atomic positions. The unit cell parameters (Table III) are calculated by Rietveld Refinement Method using XRD data.

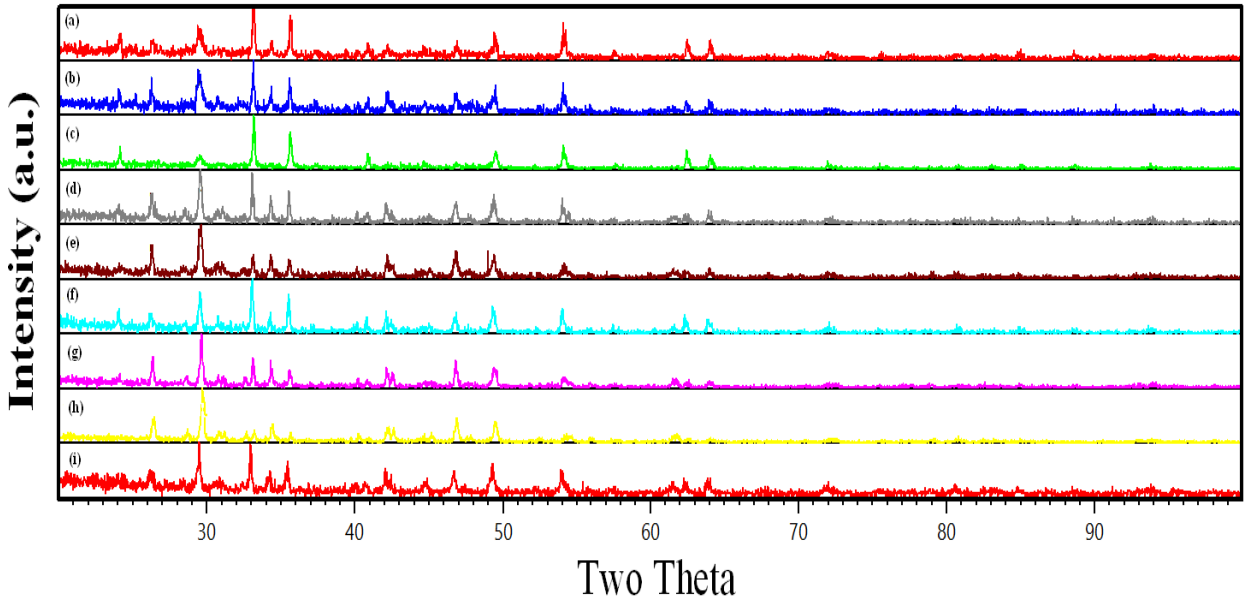

Fig. 2 The XRD patterns of Fe_2O_3-CaO-B_2O_3 systems

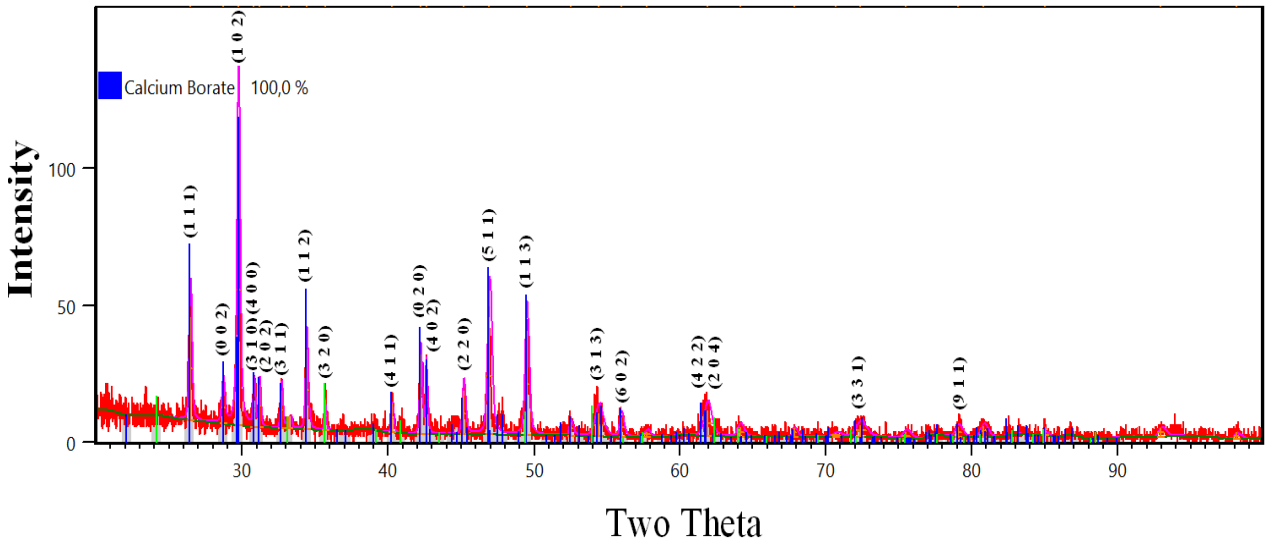

Fig. 3 The XRD pattern of iron doped CaB_2O_4

TABLE I
MOLECULAR COMPOSITIONS OF Fe_2O_3–CAO-B_2O_3 SYSTEMS

Fe_2O_3–CaO-B_2O_3 systems	Synthesis temperature	Phases percentages	
		Fe_2O_3 (ICSD=016-1285)	CaB_2O_4 (ICSD=002-2060)
(a) 1 Fe_2O_3 + 1 $Ca_2B_6O_{11}$·5H_2O	700 °C	36.8	62.3
(b) 2 Fe_2O_3 + 1 $Ca_2B_6O_{11}$·5H_2O	700 °C	20.9	79.1
(c) 1 Fe_2O_3 + 2 $Ca_2B_6O_{11}$·5H_2O	700 °C	74.1	25.9
(d) 1 Fe_2O_3 + 1 $Ca_2B_6O_{11}$·5H_2O	800 °C	16.8	83.2
(e) 2 Fe_2O_3 + 1 $Ca_2B_6O_{11}$·5H_2O	800 °C	11.3	88.7
(f) 1 Fe_2O_3 + 2 $Ca_2B_6O_{11}$·5H_2O	800 °C	34.7	65.3
(g) 1 Fe_2O_3 + 1 $Ca_2B_6O_{11}$·5H_2O	900 °C	13.5	86.5
(h) 2 Fe_2O_3 + 1 $Ca_2B_6O_{11}$·5H_2O	900 °C	0.0	100.0
(I) 1 Fe_2O_3 + 2 $Ca_2B_6O_{11}$·5H_2O	900 °C	23.3	76.7

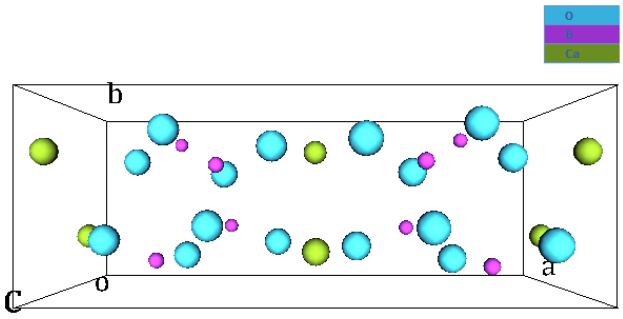

Fig. 4 Unit cell structure of iron doped CaB_2O_4

In Fig. 5, the FTIR spectrum of the sample was given. The wave numbers at 1480, 1275, 803, 706, and 633 cm^{-1} are corresponded to various vibrations of BO_3 and BO_4 groups [18]-[23]. Fig. 6 is SEM micrograph of iron doped CaB_2O_4. The homogeneous distribution of the sample is seen in the figure. The average particle size of the sample was measured in 2-5 μm.

TABLE II
OBSERVED AND CALCULATED XRD DATA OF IRON DOPED CALCIUM BORATE

$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	h k l
3.3721	3.3720	1 1 1
3.1094	3.1094	0 0 2
3.0032	3.0033	1 0 2
2.8989	2.8985	4 0 0
2.8667	2.8677	3 1 0
2.7409	2.7401	2 0 2
2.6052	2.6042	3 1 1
2.4589	2.4580	1 1 2
2.4234	2.4227	3 2 0
2.2379	2.2388	4 1 1
2.1397	2.1390	0 2 0
2.1211	2.1203	4 0 2
2.0075	2.0068	2 2 0
1.9356	1.9372	5 1 1
1.8423	1.8418	1 1 3
1.6814	1.6801	3 1 3
1.6408	1.6413	6 0 2
1.5061	1.5059	4 2 2
1.5009	1.5017	2 0 4
1.3087	1.3080	3 3 1
1.2117	1.2100	9 1 1

TABLE III
UNIT CELL PARAMETERS OF IRON DOPED CALCIUM BORATE

Crystal system	Unit cell parameters		
	a (Å)	b (Å)	c (Å)
Orthorhombic	11.5953	4.2783	6.2195

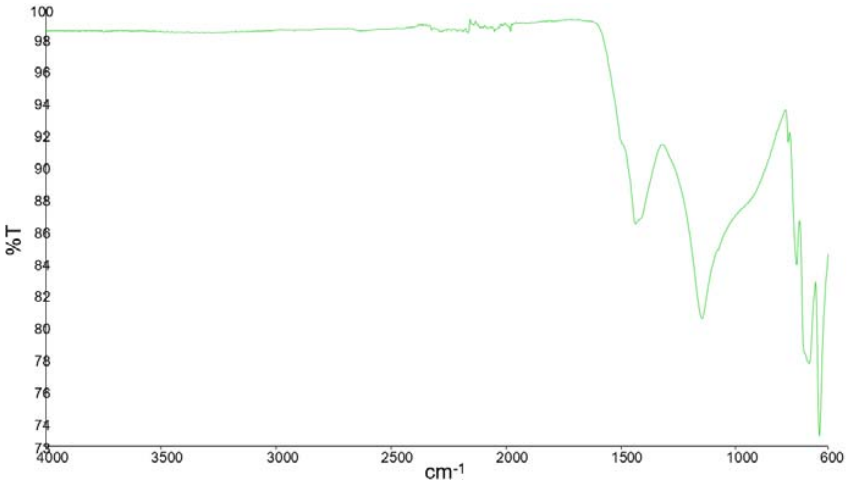

Fig. 5 The Infrared spectrum of iron doped CaB_2O_4

The result of EDX analyze as mass percentages of composition of iron doped calcium borate is given in Table IV. The results in the table are in a good accordance with the molar composition of calcium borate 1:2:4.

The result of thermal analyze of iron doped CaB_2O_4 is given in Fig. 7. There is no significant mass loss until 1000 ºC. After this temperature, a sharp mass loss starts. This mass loss which started at 1000 ºC displays that the compound is quite stable in the range of 400-1000 ºC.

TABLE IV
EDX RESULTS OF IRON DOPED CALCIUM BORATE

Element	Mass percentages
B	16.89
O	51.14

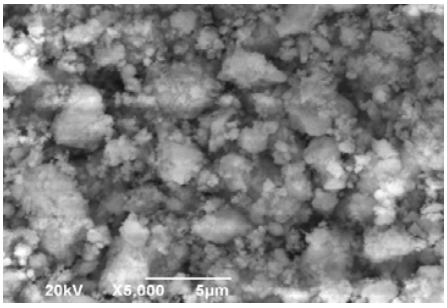

Fig. 6 SEM micrograph of iron doped CaB_2O_4

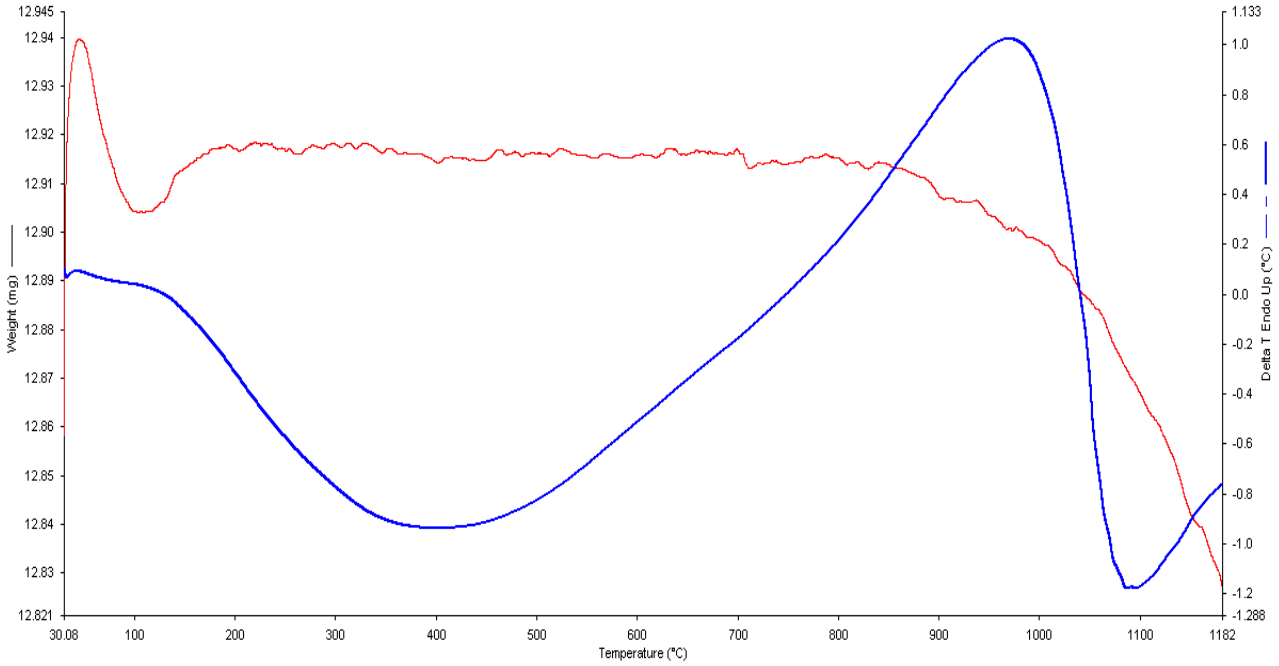

Fig. 7 TGA diagram of iron doped CaB_2O_4

IV. CONCLUSION

As a conclusion, iron doped calcium borate is synthesized via conventional solid state technique using iron (III) oxide and colemanite (both calcium and boron source) with 2:1 molar ratio at 900 °C by intermediate grindings. The XRD data and unit cell parameters are calculated via Rietveld Refinement Method, and infrared spectrum was measured to support functional groups.

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