



## Hydrogen storage technology based on sodium borohydride: Ulexite mineral as a starting material

**Mehmet Burcin Piskin\*, Ulku Banu Sarialioglu**

Yildiz Technical University, Department of Bioengineering, Istanbul 34210, Turkey,

\* mpiskin@yildiz.edu.tr



# OUTLINE . . .

☞ **Principle:** Hydrogen storage via sodium borohydride

☞ **Experimental:** Characterization of ulexite (XRD, FT-IR, DTA-TG)

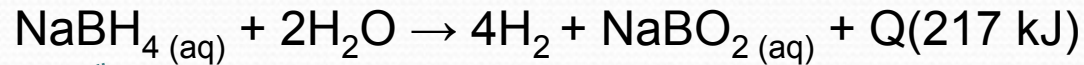
Production of  $\text{NaBH}_4$  from ulexite

☞ **Results and Discussion**

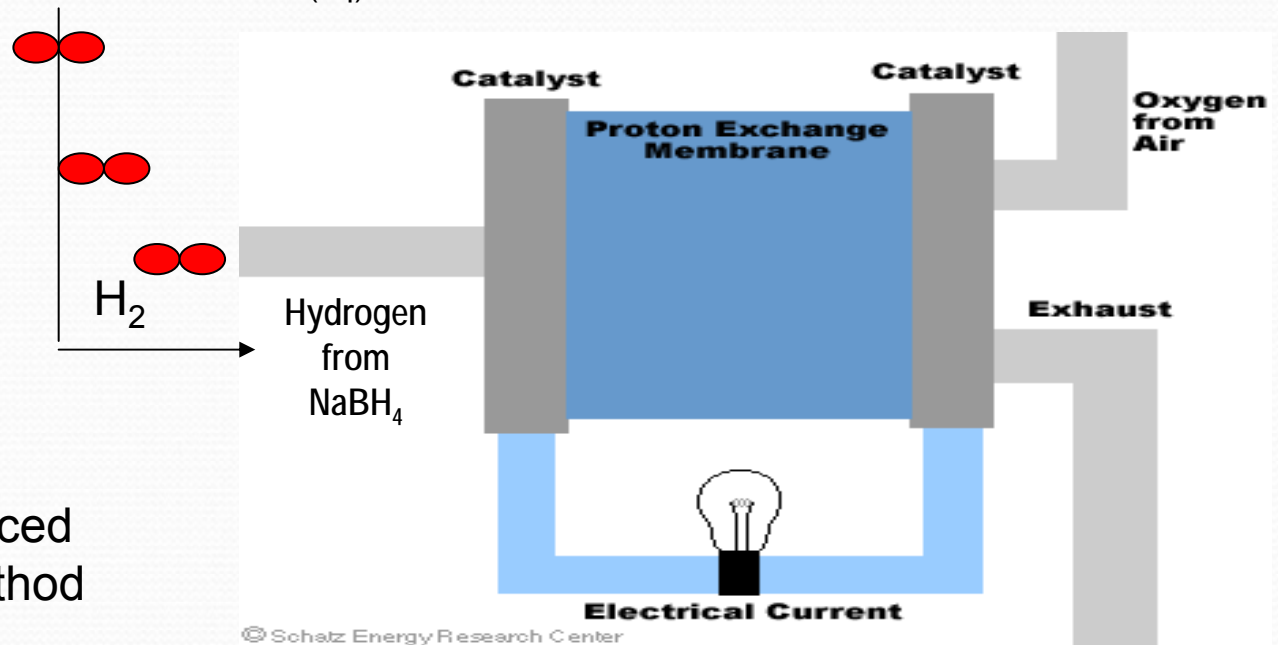
☞ **Conclusion**

# HYDROGEN STORAGE VIA SODIUM BOROHYDRIDE

Sodium borohydride (NaBH<sub>4</sub>) aqueous solution ⇨ liquid fuel ⇨ PEM fuel cells



NaBH<sub>4</sub> should be produced by simple and easily method





# EXPERIMENTAL PROCEDURE



1

## Characterization of ulexite

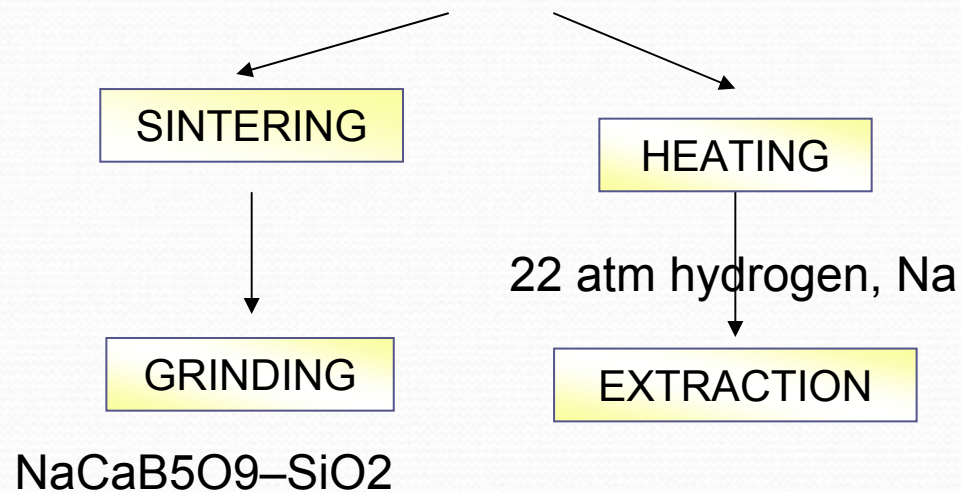
**XRD:** Crystalline structure

**FT-IR:** Chemical structure

**DTA-TG:** Thermal properties

2

## Production of $\text{NaBH}_4$ from ulexite



# ULEXITE MINERAL

Empirical formula	$B_5CaH_{26}NaO_{27}$
ICSD name	Sodium calcium borate hydroxide hydrate
Composition	%
$B_2O_3$	42.97
$Na_2O$	7.65
$CaO$	13.83
$H_2O$	35.55
Hardness	2.5 Mohs
Specific gravity	1.955 g/cm <sup>3</sup>
Colour and transparency	White, colorless, silky, transparent



The largest world reserves of borates occur in an L-shaped area in western Turkey. Especially, ulexite reserves are found at different borate deposits in the Marmara Region, Central Anatolia Region, and Aegean Region. The deposits have average ore grades of 29%  $B_2O_3$  for the ulexite and appear to have been formed from a larger basin.

## XRD

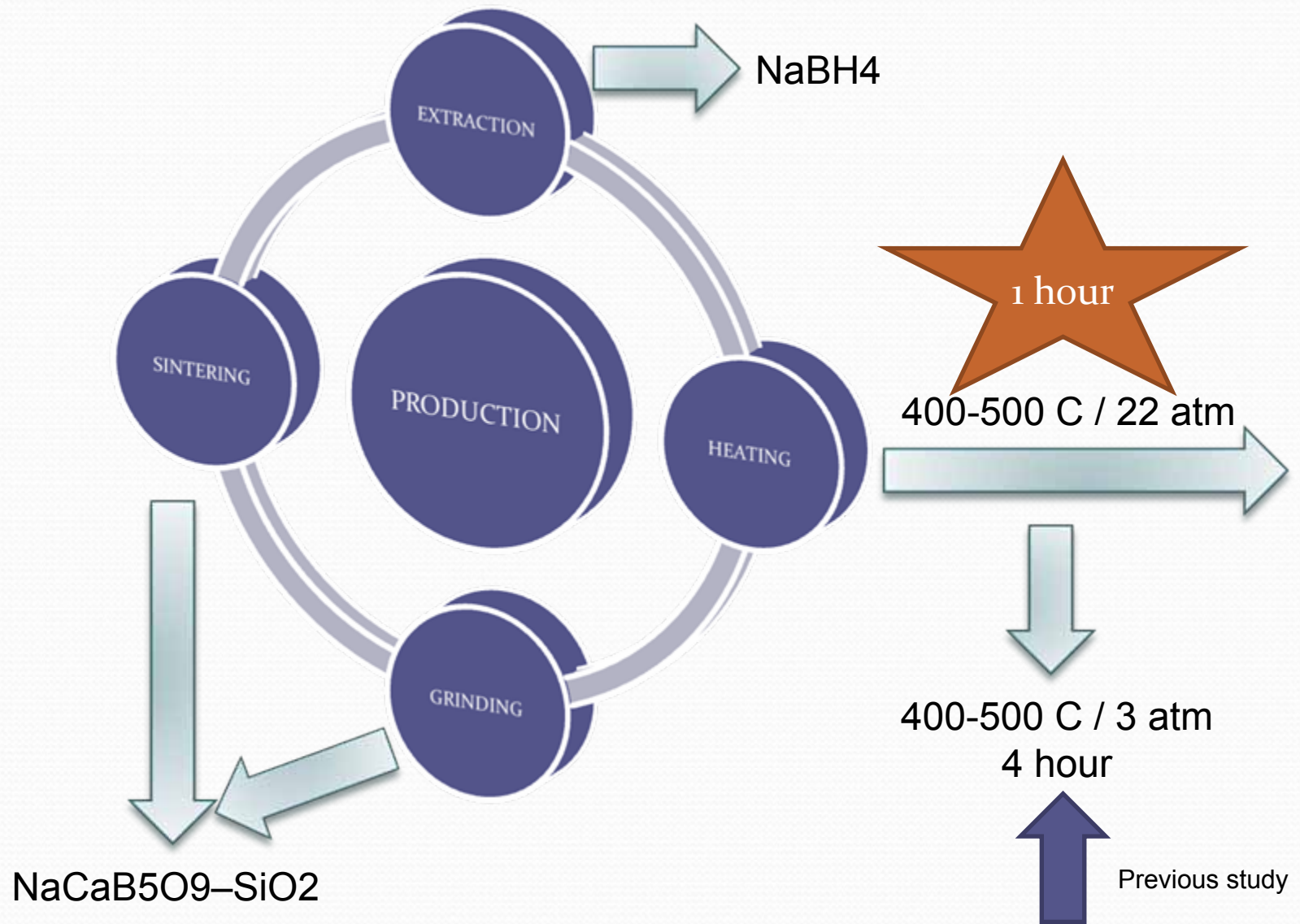
- XRD analysis was used to determine the crystalline structure of  $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$
- The analysis was carried out in a range of diffraction angles from  $0^\circ$  to  $50^\circ$  (45 kV and 40 mA)
- Data were collected on a Philips Panalytical X'Pert-Pro diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda=1.54178 \text{ \AA}$ )

## FT-IR

- To characterize chemical bonds in the ulexite structure, the technique of ATR/FT-IR spectroscopy (Perkin Elmer Spectrum One) was used. Before the analysis, the crystal area was cleaned and the background corrected, the solid material was placed over the small crystal area on a Universal diamond ATR top-plate. The FT-IR spectrum was obtained after force was applied to the sample, pushing it onto the diamond surface. The IR spectrum was recorded in the spectral range of  $4000$  to  $650 \text{ cm}^{-1}$  at a resolution of  $8 \text{ cm}^{-1}$


## DTA-TG

- Thermal decomposition of  $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$  was conducted with a Perkin Elmer Diamond DTA/TG instrument. Analysis was carried out under  $\text{N}_2$  atmosphere at a constant flow rate of  $100 \text{ ml/min}$  in the temperature range of  $30$ – $900 \text{ }^\circ\text{C}$ , with a heating rate of  $10 \text{ }^\circ\text{C/min}$ . TG\DTA instrument which was calibrated by means of the melting points of indium ( $T_m=156.6 \text{ }^\circ\text{C}$ ) and tin ( $T_m=231.9 \text{ }^\circ\text{C}$ ) under the same conditions with the sample. Samples were ground in agate mortar and stored under inert atmosphere before the analyses.



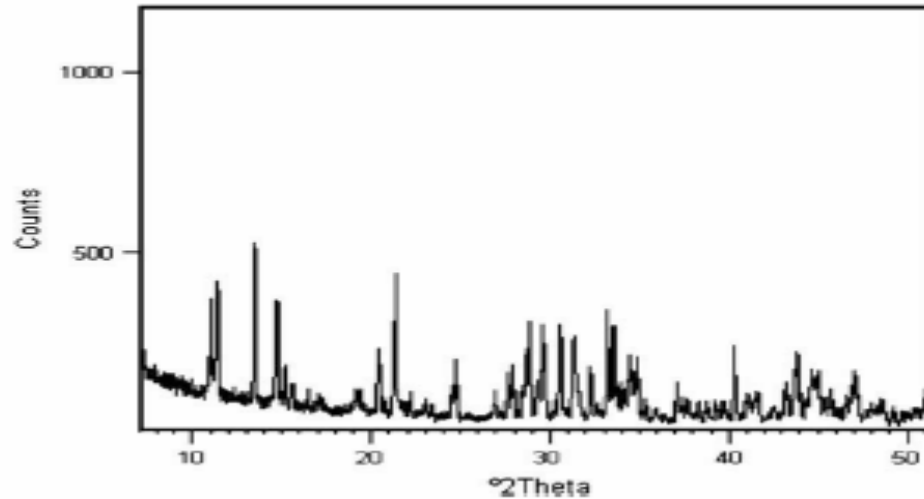


# **RESULT & DISCUSSION**



# **CHARACTERIZATION OF ULEXITE**

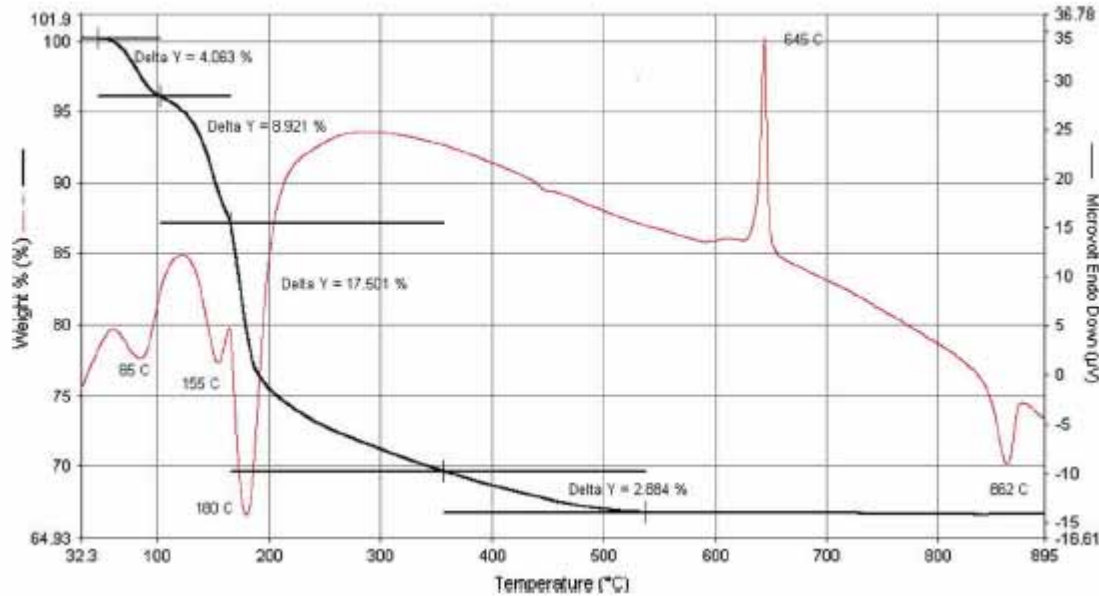
## XRD Pattern



In the sample, the peak representative of (0 1 0) diffraction peak, corresponding to 12.35719 Å peak at 7.1538°, had the maximum (100%) intensity.

This identified the  $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$  in the anorthic crystal system with P-1 space group and, space group number of 2.  $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$  has a unit cell structure of a, b, c = 8.8160 Å, 12.8700 Å, 6.6780 Å, according to references (PDF number: 01-083-2421).

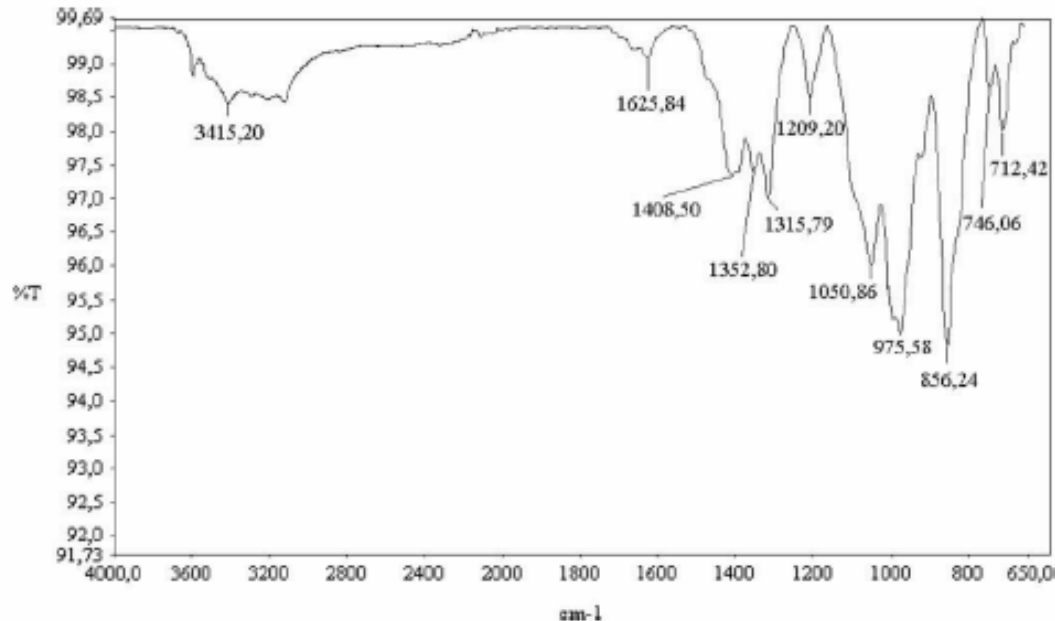
## DTA-TG Curves



The first three steps showed weight loss of 4.063%, 8.921% and 17.501%, respectively, observed in the temperature ranges of 70–280 °C, attributed to removal of the crystal water. Weight loss of 2.884% corresponded to the release of OH<sup>-</sup> groups in the temperature range of 350–527 °C.

It is concluded that  $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$  releases 8 moles of water in the temperature range of 70–527 °C, and it is converted to the  $\text{NaCaB}_5\text{O}_9$  form. After further heating, one exothermic peak occurred at 645 °C corresponding to the recrystallization of amorphous  $\text{NaCaB}_5\text{O}_9$  to  $\text{CaB}_2\text{O}_4$ . Residual  $\text{NaB}_3\text{O}_5$  is melted at 862 °C and transformed to the amorphous structure through an endothermic reaction.

## FT-IR Spectrum



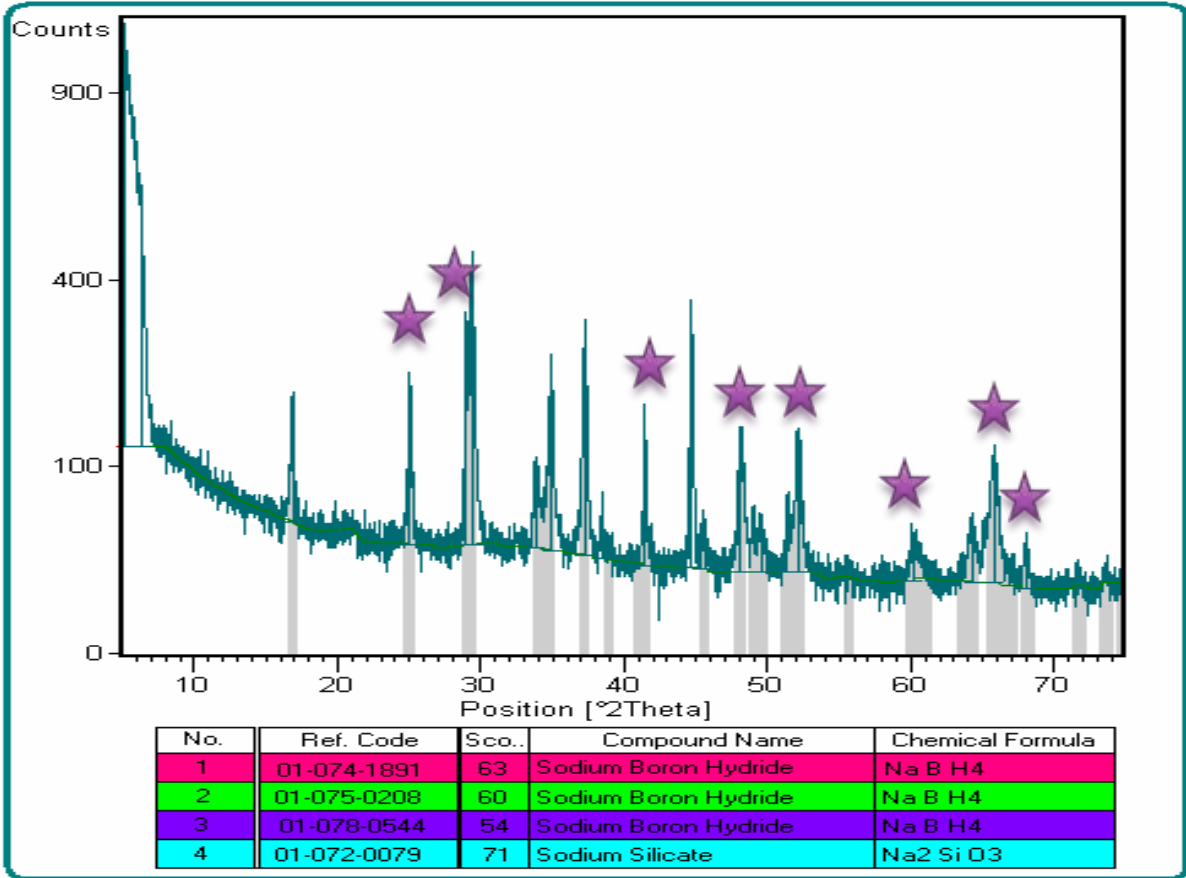
The FT-IR spectra of the ulexite mineral showed the following infrared absorption bands, as depicted in Figure 5. The bands at  $3415.49\text{ cm}^{-1}$  represent the stretching mode of O-H. The band at  $1625.84\text{ cm}^{-1}$  is assigned to free  $\text{H}_2\text{O}$  band. The band at  $1408.50\text{ cm}^{-1}$  is assigned to the asymmetric stretching mode of B-O in  $\text{BO}_3$ .

The bands at  $1352.80$ ,  $1315.79$ , and  $1209.20\text{ cm}^{-1}$  are assigned to the in-plane bending band of  $(\text{OH})^{-1}$ . The bands at  $1050.86$ ,  $975.58$ , and  $856.24\text{ cm}^{-1}$  are assigned to the asymmetric stretching of B-O in  $\text{BO}_4$ . The bands at  $746.06$  and  $712.42\text{ cm}^{-1}$  are assigned to the out-of-plane bending of  $(\text{OH})^{-1}$  and symmetric stretching band of B-O in  $\text{BO}_4$ .



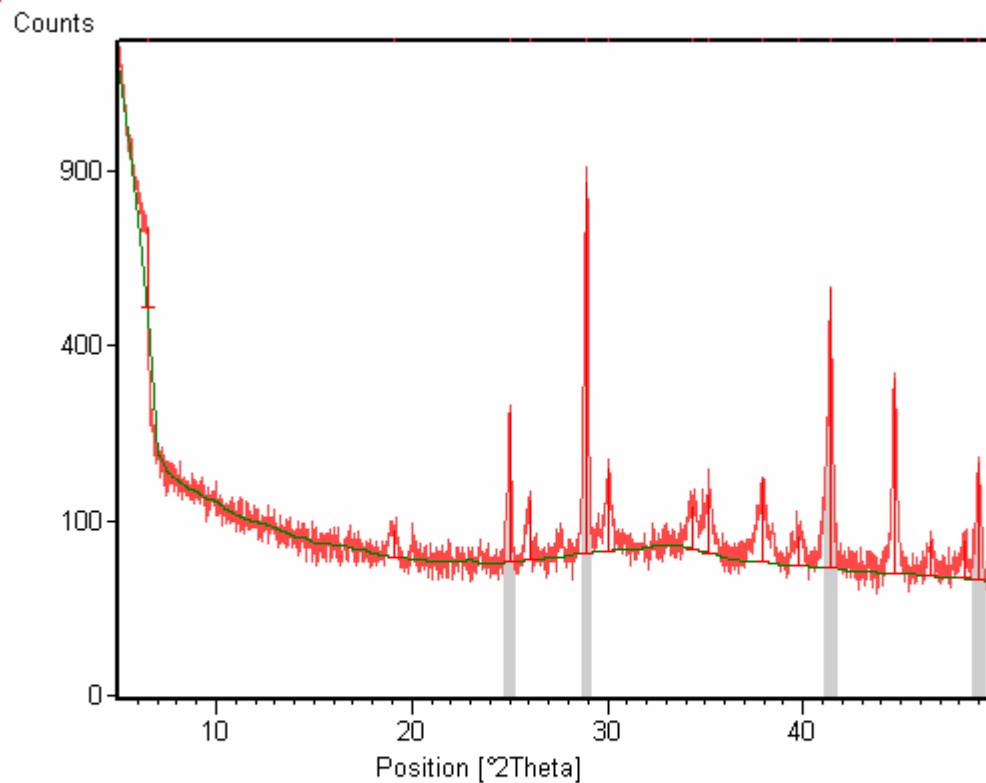
# **CHARACTERIZATION OF PRODUCT**

- Reaction Product-  
NaBH<sub>4</sub> by product



★ NaBH<sub>4</sub>

- Main Product-  
 $\text{NaBH}_4$



No.	Visib..	Ref. Code	Scor..	Compound Name	Chemical Formula
1	<input checked="" type="checkbox"/>	01-075-0208	70	Sodium Boron Hydride	Na B H4
2	<input checked="" type="checkbox"/>	01-074-1891	72	Sodium Boron Hydride	Na B H4

## CONCLUSION

The NaBH<sub>4</sub> production process consists of four steps such as characterization of the ulexite mineral (NaCaB<sub>5</sub>O<sub>9</sub>·8H<sub>2</sub>O) by XRD, DTA–TG, and FT-IR/ATR analysis techniques, preparation of ulexite–borosilicate glass (NaCaB<sub>5</sub>O<sub>9</sub>–SiO<sub>2</sub>), synthesis of NaBH<sub>4</sub>, and separation of NaBH<sub>4</sub> from the reaction mixture.

NaBH<sub>4</sub> can be produced by heating ulexite–borosilicate glass with metallic sodium between the temperature ranges of 400–500 C under 22-atm. hydrogen pressure, for 1 hour

It is suggested that ULEXITE can be used as a starting material with sintering together with silica and then heated in the presence of metallic sodium under hydrogen pressure.



**THANK YOU FOR YOUR  
ATTENTION...**