

New series of bimetallic borohydrides base on $\text{La}(\text{BH}_4)_3$

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Eco-Store Project

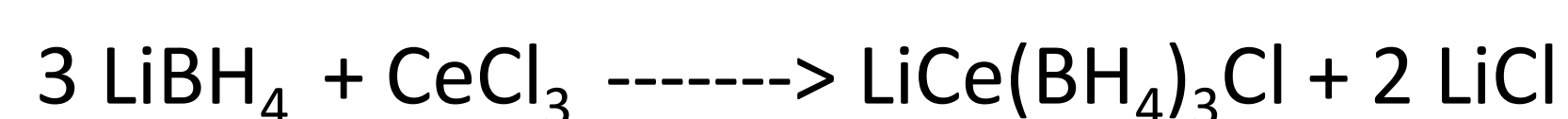
Joint research program for

1. Direct storage of electricity in batteries.
2. Storage of hydrogen.

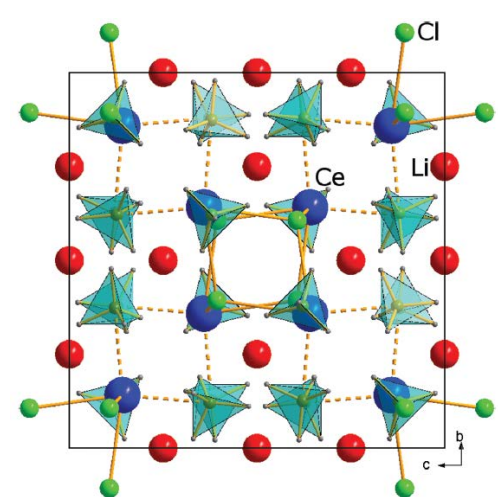
12 early stage researchers (ESR)
3 experienced researchers (ER)
9 Universities and institutes
3 companies – 2 associate partners

Introduction

The first method that was introduced for preparing $\text{La}(\text{BH}_4)_3/\text{Ce}(\text{BH}_4)_3$ was based on ball milling (BM) of the LaCl_3 and LiBH_4 . However, later researches revealed that ball milling of these compounds would lead to this reaction:



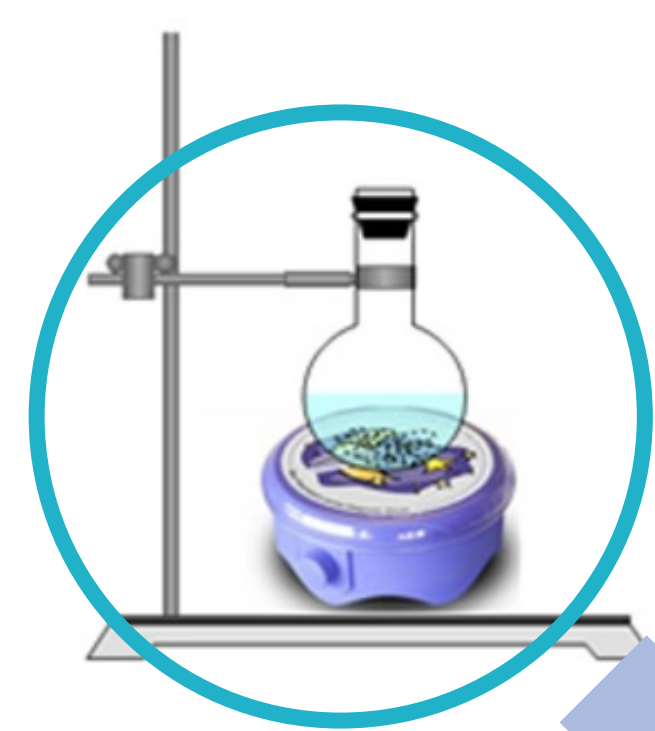
It was found that Li is occupying 2/3 of wyckoff sites in $\text{LiCe}(\text{BH}_4)_3\text{Cl}$ compound and it showed a high ion conductivity of $1.03 \times 10^{-4} \text{ S cm}^{-1}$ at RT [1,2].



In this work the goal is to first synthesize pure $\text{La}(\text{BH}_4)_3$ and then mix it with other metal halides to form bimetallic compounds base on $\text{La}(\text{BH}_4)_3$. Using this method, the formation of metal halides as by products would be eliminated.

Formation of $\text{La}(\text{BH}_4)_3$

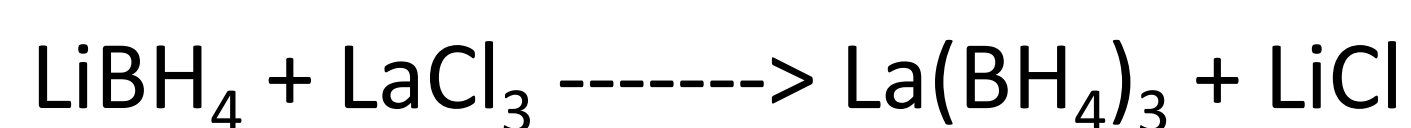
Step 1 Synthesizing $\text{La}(\text{BH}_4)_3$



$\text{La}(\text{BH}_4)_3$ - LiCl



In the first step, LaCl_3 is mixed with LiBH_4 in toluene to form $\text{La}(\text{BH}_4)_3$ base on this reaction:



Then toluene is extracted and DMS is added to dissolve the $\text{La}(\text{BH}_4)_3$. At the end LiCl is filtered and pure $\text{La}(\text{BH}_4)_3$ is obtained by removing the DMS.

Step 2 Synthesizing bimetallic borohydrides base on $\text{La}(\text{BH}_4)_3$

$\text{La}(\text{BH}_4)_3$ MX

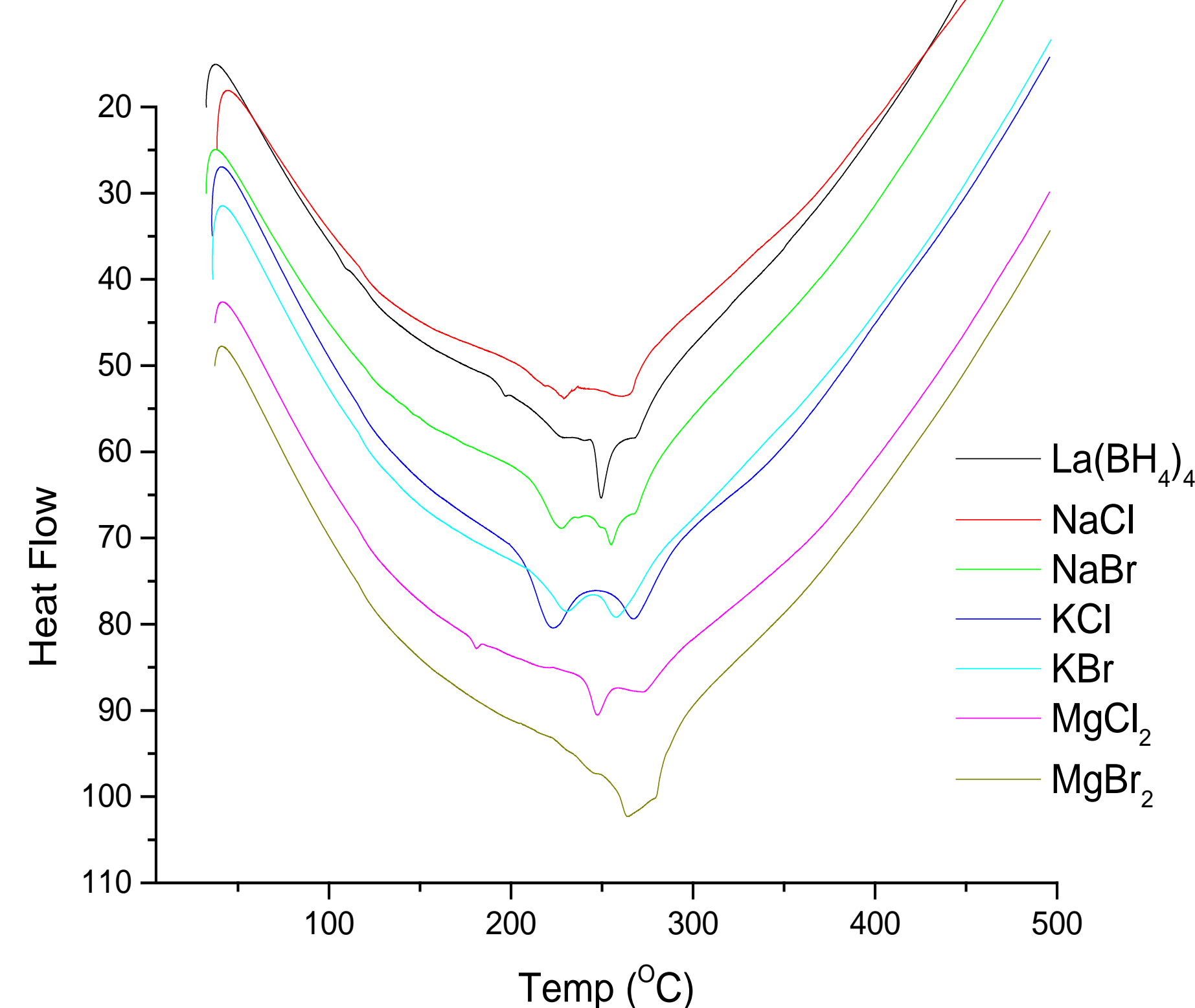


In this step, pure $\text{La}(\text{BH}_4)_3$ is ball milled with other metal halides to form $\text{MLa}(\text{BH}_4)_3\text{X}$ compounds. The samples are annealed at 150 °C for 5 hours for completing the reaction.

XRD patterns

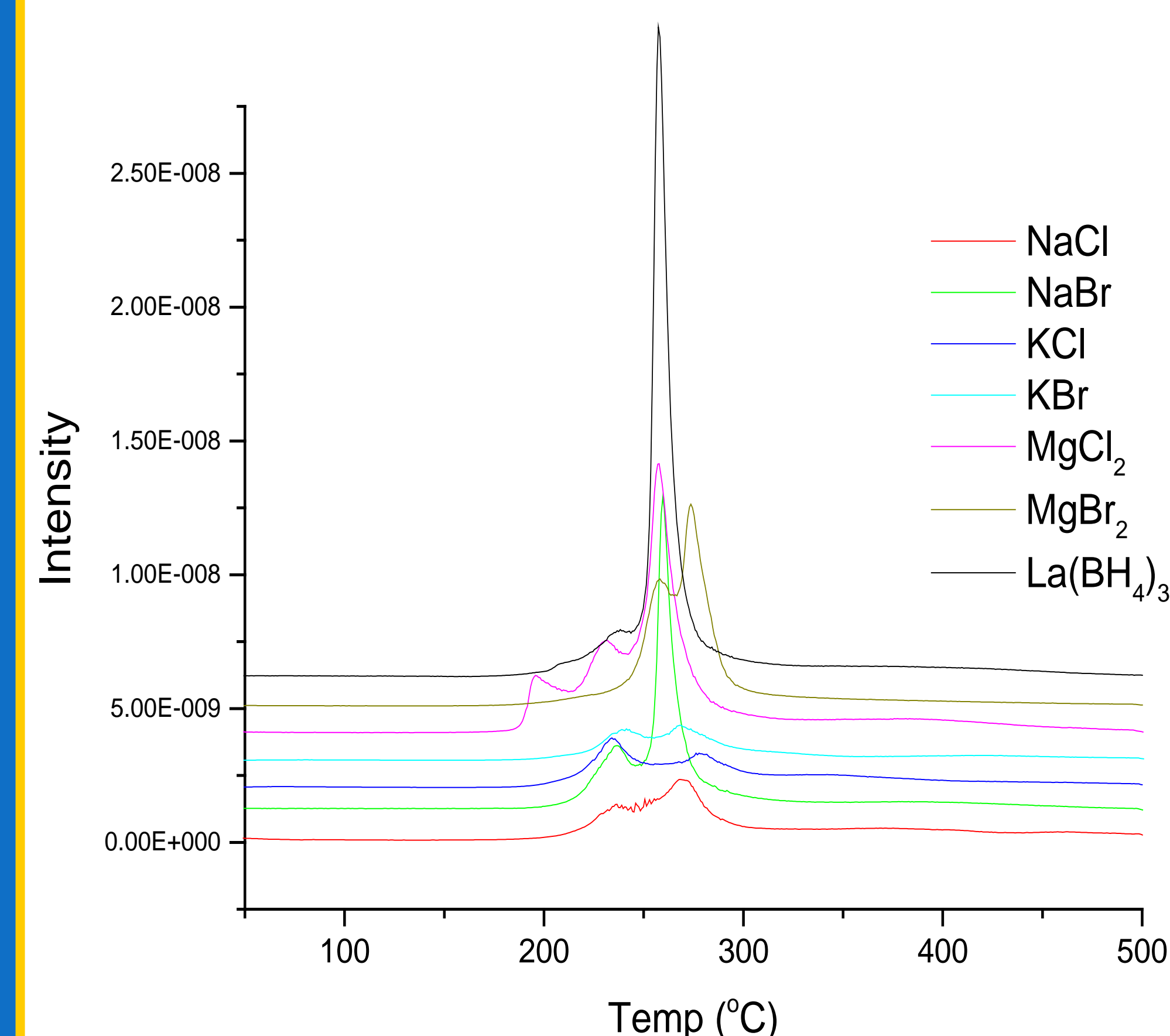
XRD patterns show new peaks in addition to reactants' peaks when $\text{La}(\text{BH}_4)_3$ was mixed with NaCl, NaBr, KCl, KBr and MgBr_2 .

DSC Peaks



The DSC curves show endothermic peaks at different temperatures and with different intensities. This suggest the formation of new compounds.

Hydrogen Release



The hydrogen release peaks of the samples were different from $\text{La}(\text{BH}_4)_3$ compound which suggests that new compounds are formed.

Conclusion

XRD patterns, DSC peaks and hydrogen release peaks of the different samples, suggest that $\text{La}(\text{BH}_4)_3$ is reacted with alkali metal halides and these new compounds have been formed:

$\text{LaLi}(\text{BH}_4)_3\text{Br}$
 $\text{LaNa}(\text{BH}_4)_3\text{Cl}$
 $\text{LaNa}(\text{BH}_4)_3\text{Br}$
 $\text{LaK}(\text{BH}_4)_3\text{Cl}$
 $\text{LaK}(\text{BH}_4)_3\text{Br}$

And

$\text{LaMg}(\text{BH}_4)_3\text{Br}_2$

Acknowledgement

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References

- [1] M.B. Ley, D.B. Ravnsbæk, Y. Filinchuk, Y. Lee, $\text{LiCe}(\text{BH}_4)_3\text{Cl}$, a New Lithium-Ion Conductor and Hydrogen Storage Material with Isolated Tetranuclear Anionic Clusters, Chem. Mater. 24 (2012) 1654–1663.
- [2] M.B. Ley, S. Boulineau, Y. Filinchuk, T.R. Jensen, New Li Ion Conductors and Solid State Hydrogen Storage Materials: $\text{LiM}(\text{BH}_4)_3\text{Cl}$, M = La, Gd, J. Phys. Chem. C. 116 (2012) 21267–21276.