Project Outline – short and long description

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Project – short description	In the present study, the quasi-binary system $NaNH_2$ and $NaBH_4$ was investigated with respect to phase formation and structural, thermal and vibrational spectroscopical properties, as well its capability as complex hydrogen storage material. The phase analytical studies revealed the existence of the novel compound Na_2BNH_6 existed in two different modifications: the LT β- and the HT α-phase. Thermal analyses and p-XRD measurements revealed that the educts $NaNH_2$ and $NaBH_4$ react at 156 ºC and melt at 210 ºC for all reactant ratios. Between 210 – 300 ºC, no significant effects were detected both in DTA and TG. Above 300 ºC, a sudden decomposition takes place causing a mass loss between 6 – 7.7 wt. % % according to the reactant ratios (1:1, 2:1 and 3:1). The gaseous species formed during the decomposition process were followed by MS. The mass spectra obtained from 1:1, 2:1, and 3:1 mixtures of $NaNH_2$ and $NaBH_4$ in the range 600 ºC > T > 25 ºC prove that the main gaseous product evolved during the thermal decomposition is H_2. NH_3 was also detected but its concentration was quite small. These findings confirm that the mixture of the complex hydrides $NaNH_2$–$NaBH_4$ (molar ratio ≥ 1:1) are potential candidates for solid hydrogen storage materials.

Project – long description (max. 5 pages):

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Sodium Amide – Sodium Tetrahydridoborate System as a potential hydrogen storage material

In the present study, $NaNH_2$ – $NaBH_4$ binary complex metal hydride system was investigated with respect to its properties as hydrogen storage material. The educts were mixed in various ratios, but only one novel compound was detected having the chemical formula Na_2BNH_6. The compound exists in two modifications: HT α-Na_2BNH_6 and LT β-Na_2BNH_6 phase. Both two phases have the same chemical formula but crystallize in different types of structures. The cubic α- Na_2BNH_6 crystallizes in the K_3SO_4F-type of structure (Space group: $Pm\bar{3}m$; Z = 1) with lattice parameter of a = 4.7111(2) Å. β-Na_2BNH_6 is orthorhombic and crystallizes in the Ca_2PO_4Cl (Spodiosite)-type of structure (Space group: Pbcm; Z = 4) with lattice parameters a = 6.5384(2), b = 6.4960(1), c = 9.8512(2) Å.

The α - Na_2BNH_6 phase can be obtained by single heating of reactants in the molar ratios 1:1 to 1,6:1 ($NaNH_2$: $NaBH_4$) at 200 ºC, or heating the unreacted mixture over melting temperature for 1h in evacuated Pyrex ampoules. β-Na_2BNH_6 is accessible by annealing of reactants in the molar ratio over 1,6:1 ($NaNH_2$: $NaBH_4$) at 200 ºC for 24 h, or annealing the mixtures over melting temperature for 12 – 24 h. A phase transition was observed between two phases. β-Na_2BNH_6 is converted to α-Na_2BNH_6 at 99 ºC very quickly, however reverse transition occurs very slowly under the transition temperature.

According to thermal analyses (DTA/TG/MS), compound has a reaction temperature of 156 ºC and a melting temperature 210 ºC. By using Mass spectroscopy method gas evolution was investigated. The compound released its hydrogen content in the region 300 – 400 ºC and formed Na_3BN_2. Theoretical hydrogen capacity was calculated as 7.6 wt. % from the formula, and experimental results showed similar results. 6 – 9 wt. % mass losses were determined due to hydrogen release. Also trace amounts of NH_3 release was observed. Hydrogen

desorption occurred at molten state above melting temperature. An alternative synthesis route was discovered for the decomposition product, Na_3BN_2, by this study. Samples having the reactant ratio over 2:1 were decomposed at 380 ºC, which was the formation temperature of Na_3BN_2 in DSC measurement, and distinct peaks of Na_3BN_2 was clearly observed.

The vibrational spectra of the title compound Na_2BNH_6 have been measured and interpreted based on the C_{2v} and T_d symmetry of the relevant $[NH_2]^-$ and $[BH_4]^-$ groups. Both (N–H) and (B–H) frequencies exhibit small but significant shifts with respect to the neat binaries.

In conclusion, the binary system of $NaNH_2$ – $NaBH_4$ seems to be a promising material for hydrogen storage. Its hydrogen content satisfies the standards of DOE, however H_2 desorption temperature is still quite high for practical purposes. Catalyst effect on hydrogen storage properties must be examined for further studies. Also, thermal behaviors of H_2 desorption and formation of decomposition product, Na_3BN_2, must be investigated more accurately for the possible reversibility of the system. For $NaAlH_4$, Na_3AlH_4 and the $LiNH_2$–$LiBH_4$ system, the synthesis by using ball milling technique was reported to enhance both the reaction times and the hydrogenation/dehydrogenation processes. In this sense, the investigation of ball milling method on the phase formation and hydrogen uptake/release could be an important contribution for the improvement of hy hydrogen storage capacity of the $NaNH_2$–$NaBH_4$ system.