

# Oral Contributions

## [MS33-02] Bonding and Phase Change in Ammonia borane and Lithium Amidoborane under High Pressure

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Ammonia borane and its derivatives have been considered as highly potential candidates for materials of hydrogen energy. These molecular crystals have weak intermolecular interactions, and therefore show a range of changes in atomic bonding upon compression. Pressure introduces abundant phase transformations in these materials. At ambient temperature, in-situ Raman spectroscopy indicates ammonia borane experiences four significant changes in bonding characteristics, two of which are confirmed to be first order transition by x-ray diffractions, upon compression up to 13 GPa. The first pressure-induced phase transition shows a positive Clapeyron slope above room temperature. Upon cooling, ammonia borane shows a structural phase transition at 225K. The Clapeyron slope for this low-temperature phase transition is determined by in-situ Raman spectroscopy to be positive as well. These results indicate that the high pressure / low temperature phases of ammonia borane have lower enthalpies than the ambient condition phase. Lithium amidoborane show only two major characteristic changes in its Raman spectra at room temperature and high pressures up to 19 GPa. But x-ray diffraction does not show very clear structural changes within 15 GPa. While Raman spectroscopy of ammonia borane evidences the existence of dihydrogen bonding, i.e. redshift of N-H vibration mode with pressure, all vibration modes of lithium amidoborane show blueshift upon compression indicating absence of such dihydrogen bonding in this derivative of ammonia borane. Therefore,

the dehydrogenation mechanisms in these parent and derivative phases are significantly different from each other. One of the major barriers for rehydrogenation from decomposed ammonia borane is its high exothermic enthalpy during the reaction. Decrease in the enthalpy of the reactant before decomposition may help to reduce the barrier, and therefore make the reaction easier to proceed and to reverse as well. Lithium amidoborane has lower exothermic enthalpy during decomposition. Consequently, its thermolysis is easier than ammonia borane (lower temperature and faster rate). One can expect that rehydrogenation to lithium amidoborane or to high-pressure phase of ammonia borane from the corresponding decomposed materials may be easier with regard to the case of pristine ammonia borane.