

New guideline for designing hydrogen storage complex hydrides

Complex hydrides have potentials to store high hydrogen gravimetric and volumetric densities. In this project we have investigated crystal structures of complex hydrides for better understanding of the hydrogen storage properties at atomic level, and firstly proposed a crystal structural indicator for the hydrides. The indicator suggests a suitable crystal structure model and a criterion for the formation of the hydrides with specific anions.

Complex hydrides, which are composed of metal cations such as Li^+ and a homoleptic hydride complex such as $[\text{AlH}_4]^-$, have attractive material properties, such as the ability to be used in hydrogen storage, fast ionic conductivity, superconductivity and so on.

In particular, studies for developing of hydrogen storage materials on complex hydrides with high hydrogen gravimetric and volumetric densities have been intensively investigated since discovery of reversible hydrogen uptake and release reactions on Ti-enhanced NaAlH_4 .^{1, 2, 3} To date, we have found a linear relationship between the electronegativity of metal cations and thermodynamic stability related to hydrogen desorption temperature in complex hydrides.⁴ The correlation has been widely acknowledged as a guideline for designing hydrogen storage complex hydrides. The results are expected to be true in isomorphous complex hydrides.

In addition to the correlation, it is challenging to understand the relationships between the material properties and the crystal structures with complicated atomic arrangements due to flexibility of the chemical bonds formed by hydrogen,⁵ which are often difficult to determine. For instance, H^- and homoleptic hydride complexes such as pentagonal-bipyramidal $[\text{CrH}_7]^{6-}$ often coexist in complex hydrides.⁶

On the other hand, perovskite-type compounds have been acknowledged to be summarized by Goldschmidt tolerance factor, which has been frequently used to understand materials properties viewed from crystal structure in fundamental and applied studies, including material designs. Though the Goldschmidt tolerance factor has been used to study hydrides, it cannot be applied to materials that do not have perovskite-type structures. Thus different approaches are required to be able to study other hydride crystal structures. The availability of an appropriate approach could allow our understanding of the material properties associated with the presence of hydrogen in materials to be improved.

In this project, we focused on experimental and theoretical studies on crystal structures of complex hydrides.⁵⁻¹⁰ From this project, we have successfully constructed an indicator (Fig. 1) for the crystal structures of Al-based complex hydrides, which are composed of metal cations and $[\text{AlH}_4]^-$ (tetra-alanates) or $[\text{AlH}_6]^{3-}$ (hexa-alanates).¹⁰

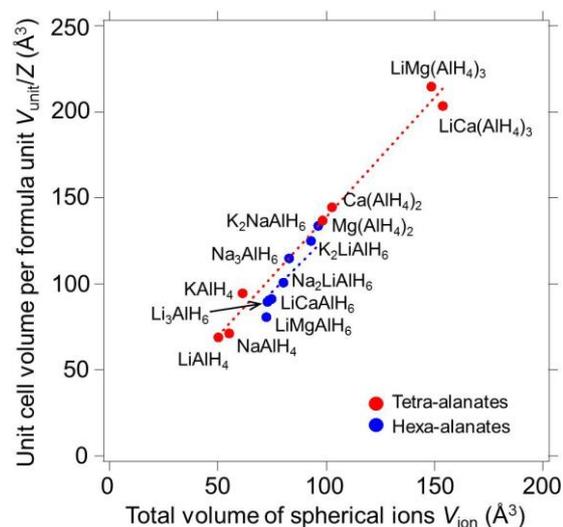


Fig. 1 Plots of V_{unit}/Z as a function of V_{ion} . Red and blue circles and dotted lines are plots and IFF for tetra-alanates and hexa-alanates, respectively.

The indicator is summarized by two types of volume: the unit cell volume (V_{unit}) normalized by the number of formula units (Z), V_{unit}/Z , and the total volume of the spherical ion, V_{ion} , of constituting the hydrides. These volumes allow the ionic filling fraction (IFF) of the hydrides to be determined. Interestingly, related hydrides with arbitrarily arranged ionic components including other complex hydrides can be also summarized by the same method. Then, the IFF followed a linear trend dependent on the type of hydride, and it could be used as a criterion for the formation of the hydrides with specific anions. The linearity of the IFF means that the initial crystal structure model, with a suitable unit cell and chemical formula, can be predicted. Based on the

indicator, we could determine the new crystal structures of the mixed metal cation complex hydrides $\text{LiCa}(\text{AlH}_4)_3$ and LiCaAlH_6 (Fig. 2).¹⁰ In addition, we also suggest that the use of the indicator can be extended to other ionic compounds, including halides and oxides, for which we identify similar trends to those found for the hydrides. Our approach could therefore be suggested to be universally adaptable for not only hydrides but also other ionic compounds. The indicator is expected to be a key to find a relationship between material properties and crystal structures. Then, it could be a new guideline for designing hydrogen storage complex hydrides as well as a correlation between the electronegativity of metal cations and thermodynamic stability.

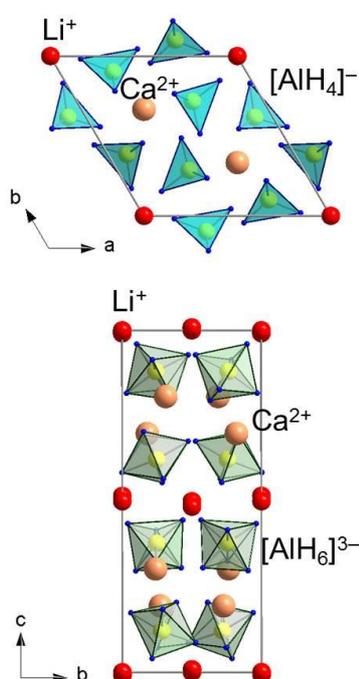


Fig. 2 Crystal structures of (top) $\text{LiCa}(\text{AlH}_4)_3$ and (bottom) LiCaAlH_6 . In the crystal structure, Li, Ca and H atoms, $[\text{AlH}_4]^-$ and $[\text{AlH}_6]^{3-}$ are displayed as red, green, yellow and blue circles and cyan and green tetrahedra, respectively.

References

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