Synthesis and Characterization of a New Ternary Imide

- $\text{Li}_2\text{Ca}(\text{NH})_2$

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Supporting Information

Theoretical investigations on $\text{Li}_2\text{Ca}(\text{NH})_2$ were performed using first-principle calculations based on the density functional theory (DFT) and the pseudopotential-planewave method.^{1S} The projector augmented wave potentials^{2S} were used to describe the electron-ion interaction, and the generalized gradient approximation (GGA) due to Perdew, Burke and Ernzerhof (PBE)^{3S} was used for exchange-correlation functional. A plane-wave cutoff corresponding to an energy of 320 eV was used in our calculations. For a unit cell containing one formula unit of $\text{Li}_2\text{Ca}(\text{NH})_2$, a k-point mesh of $8 \times 8 \times 4$ was used.

It is assumed that H atoms should be restricted somewhere in the system host consisting of N, Ca and Li atoms, and therefore H atoms have little effect on the system host. Lattice constants are derived from the XRD experimental values ($a=b=3.5664\text{\AA}$ and $c=5.9540\text{\AA}$, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$). The N, Ca and Li are in the same positions as those suggested by our Rietveld refinement results. Li1(0.3333, 0.6667, 0.8841), Li2(0.6667, 0.3333, 0.11591), Ca(0,0,0.5), N1(0.3333, 0.6667, 0.2565), and

N2(0.6667,0.3333,0.7435) are included in a conventional cell. The initial site of each H is randomly selected around each N. Only the H atom coordinates are relaxed. The relaxed H atom coordinates are essentially the same as those special sites represented by 2d, 6i sites of the space group P-3m1, as shown in the Table 1S. Total energies of structures with H atoms located in different sites are listed in Table 2S. It can be seen in Table 1S that the N-H vector orients towards the middle point or center of adjacent lithium sites or adjacent Ca sites. When each H occupies one of Site-III sites around each N, the $\text{Li}_2\text{Ca}(\text{NH})_2$ structure has the lowest total energy, in which the N-H vector orients towards the middle point of two adjacent lithium sites (Li-Li distance 3.566 Å). The Site-III sites correspond to 6i equivalent sites of the space group P-3m1. Unfortunately, H atoms can not fully occupy equivalent positions of 6i sites according to the composition of $\text{Li}_2\text{Ca}(\text{NH})_2$. In general, the H atom in lithium imide is delocalized over several equivalent sites around each N^{4S}. Similarly, it is likely that each H in $\text{Li}_2\text{Ca}(\text{NH})_2$ is delocalized over the 6i equivalent sites around each N to satisfy the crystallographic symmetry.

References for Supporting Information

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Table 1S. Stable H sites in the system host consist of N, Ca and Li atoms

The relaxed H atom coordinates		Equivalent sites in S.G P-3m1
Near N1 atom	Near N2 atom	N-H vector orientation
I) (0.3333,0.6667,0.4307)	(0.6667,0.3333,0.5693)	2d, the center of triangle adjacent Ca sites (Ca-Ca distance 3.566 Å)
II) (0.3333,0.6667,0.0909)	(0.6667,0.3333,0.9091)	2d, the center of triangle adjacent Li sites (Li-Li distance 3.566 Å)
III) (0.1838,0.8162,0.1723)	(0.8162,0.1838,0.8277)	6i, the middle point of two adjacent Li sites (Li-Li distance 3.566 Å),
(0.6324,0.8162,0.1723)	(0.3676,0.1838,0.8277)	
(0.1838,0.3676,0.1723)	(0.8162,0.6324,0.8277)	
IV) (0.4278,0.5722,0.1179)	(0.5722,0.4278,0.8821)	6i, the middle point of two adjacent Li sites (Li-Li distance 2.479Å),
(0.1444,0.5722,0.1179)	(0.8556,0.4278,0.8821)	
(0.4278,0.8556,0.1179)	(0.5722,0.1444,0.8821)	
V) (0.4875,0.5125,0.3243)	(0.5125,0.4875,0.6757)	6i, the middle point of two adjacent Ca sites (Ca-Ca distance 3.566 Å)
(0.0250,0.5125,0.3243)	(0.9750,0.4875,0.6757)	
(0.4875,0.9750,0.3243)	(0.5125,0.0250,0.6757)	

Table 2S. Total energies from DFT calculations for the system host with H atoms at various sites

The relaxed H atom coordinates		Symmetry	Total Energy (eV)
H1 atom near N1 atom	H2 atom near N2 atom		
Site I	Site I	C _{2h}	-32.486
Site II	Site II	C _{2h}	-30.897
Site III	Site III	C1	-33.094
Site IV	Site IV	C1	-31.868
Site V	Site V	C1	-32.577
Site I	Site II	C _{1h}	-31.734
Site III	Site V	C1	-32.841