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Thermal conversion of the hydrous aluminosilicate $\text{LiAlSiO}_3(\text{OH})_2$ into γ -eucryptite

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Abstract: $\text{LiAlSiO}_3(\text{OH})_2$ is a dense hydrous aluminosilicate which is formed from LiAlSiO_4 glass in hydrothermal environments at pressures around 5 GPa. The OH groups are part of the octahedral Al and Li coordination. We studied the dehydration behavior of $\text{LiAlSiO}_3(\text{OH})_2$ by a combination of TEM and multi-temperature PXRD experiments. Dehydration takes place in the temperature interval 350–400 °C. Above 700 °C $\text{LiAlSiO}_3(\text{OH})_2$ is converted via a transient and possibly still slightly hydrous phase into γ -eucryptite which is a metastable and rarely observed polymorph of LiAlSiO_4 . Its monoclinic structure is built from corner-sharing LiO_4 , AlO_4 and SiO_4 tetrahedra. The ordered framework of AlO_4 and SiO_4 tetrahedra is topologically equivalent to that of cristobalite.

Keywords: eucryptite; lithium aluminosilicate; oxyhydroxide; polymorphism; thermal expansion.

Dedicated to: Professor Richard Dronskowski of the Rwth Aachen on the occasion of his 60th birthday.

1 Introduction

Crystalline phases with LiAlSiO_4 composition include a zeolite, Li-ABW, as well as α - and β -eucryptite. They are all built from corner-sharing AlO_4 and SiO_4 tetrahedra (observing strict Si–Al ordering) with Li^+ ions being exclusively in a tetrahedral coordination. Most studied is hexagonal β -eucryptite which is formed when LiAlSiO_4 glass crystallizes in dry conditions. Its structure corresponds to that of stuffed β -quartz in which the open

channels are filled with Li^+ ions [1]. β -Eucryptite combines excellent ion mobility with a near zero coefficient of volume expansion and has been extensively studied for use as a solid electrolyte [2–5].

The orthorhombic zeolite Li-ABW ($\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$) is formed during hydrothermal treatment of glass or gels (made e.g. of LiOH , $\text{Al}(\text{OH})_3$ and SiO_2) with $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ composition at temperatures below 350 °C, whereas higher temperatures afford rhombohedral α -eucryptite [6, 7]. The zeolite framework contains channels that run along the crystallographic c direction and host a stoichiometric amount of water molecules (Figure 1a). Li ions coordinate to three framework O atoms (involving three different tetrahedra) and the water molecule. Li-ABW is a precursor for other (metastable) LiAlSiO_4 modifications upon thermal conversion. Water loss leads first to anhydrous Li-ABW (at around $T = 300$ °C) with narrowed, elongated, 8-ring channels in which Li^+ is four-coordinated by framework O atoms, and then (at around $T = 600$ °C) to monoclinic, cristobalite-like, γ - LiAlSiO_4 . Finally (at $T = 900$ – 1000 °C) β -eucryptite is obtained [8, 9].

Recently, another hydrous form of LiAlSiO_4 was reported, $\text{LiAlO}_3(\text{OH})_2$, which is a oxyhydroxide with the same composition as Li-ABW [10]. $\text{LiAlSiO}_3(\text{OH})_2$ was obtained from the crystallization of LiAlSiO_4 glass in a high-pressure hydrothermal environment. Its dense structure relates to pyroxenes and constitutes alternating layers of chains of corner-condensed SiO_4 tetrahedra and of edge-sharing AlO_6 and LiO_6 octahedra (Figure 1b). OH groups are part of the Al and Li coordination and extend into channels provided within the layers of chains of SiO_4 tetrahedra. Similar to the behavior of Li-ABW, the dehydration of $\text{LiAlSiO}_3(\text{OH})_2$ may yield new, metastable forms of LiAlSiO_4 . In this work we analyze the transformation of $\text{LiAlSiO}_3(\text{OH})_2$ upon dehydration.

2 Results and discussion

2.1 Thermal behavior of $\text{LiAlSiO}_3(\text{OH})_2$

As described in the Experimental Section, $\text{LiAlSiO}_3(\text{OH})_2$ is obtained as fine aggregated needles with lengths up to several μm . Earlier thermogravimetric (TG) investigations

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Figure 1: Crystal structures of hydrous forms of LiAlSiO_4 . (a) Orthorhombic zeolite Li-ABW ($\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$): the $\text{AlO}_4/\text{SiO}_4$ framework features channels that run along the c direction and host water molecules. Li ions are coordinated to three framework O atoms and the water molecule. (b) Monoclinic oxyhydroxide $\text{LiAlSi}_3(\text{OH})_2$ (related to pyroxene): SiO_4 tetrahedra and AlO_6 octahedra are arranged as chains that run along the a direction. Oxygen atoms that are part of hydroxyl are drawn as large red spheres. Li atoms are octahedrally coordinated. Large red spheres OH_2 or OH , small red spheres O, Li atoms/coordination polyhedra grey. SiO_4 tetrahedra yellow, Al coordination polyhedra blue.

showed that the dehydration of $\text{LiAlSi}_3(\text{OH})_2$ takes place in the temperature interval 350–500 °C, with the associated weight loss in very good agreement with the stoichiometric amount of water (12.5%). Above 550 °C there was no further weight change. During scanning electron microscopy studies of this material it was noticed that dehydration can also be induced in the electron beam and that the anhydrous product retained the needle-like crystal shape of $\text{LiAlSi}_3(\text{OH})_2$. We then studied the evolution of the dehydration on individual $\text{LiAlSi}_3(\text{OH})_2$ crystals in the transmission electron microscope (TEM, Figure 2d–f). Upon beam exposure the dimension of the needle-shaped crystals is reduced by about 10% and at the same time the edges become rounded. The process can also be followed with energy-dispersive X-ray (EDX) analysis and seems to be completed after 25–30 min. After beam irradiation the material appears to be amorphous.

Figure 3 shows the dehydration of $\text{LiAlSi}_3(\text{OH})_2$ as observed in a multi-temperature powder X-ray diffraction (PXRD) experiment. In good agreement with the TG analysis, the diffraction pattern of $\text{LiAlSi}_3(\text{OH})_2$ is maintained up to 300 °C. At 400 °C dehydration is apparent by a changed pattern (which still contains reflections from a minor fraction of $\text{LiAlSi}_3(\text{OH})_2$). At 500 °C a pure pattern of converted phase is seen, which is distinguished from the pattern of the precursor by the presence of a low angle reflection at $2\theta \approx 12^\circ$ ($d \approx 7.7$ Å) and two peaks in the 2θ range 27–29°. This new pattern then appears unchanged up to 700 °C. In the pattern at 800 °C clear changes can be noticed (e.g. the Bragg peak at high d is absent and in the 2θ range 27–29° there is a single peak), which manifest an

additional structural transition after dehydration. This pattern coincides with that of γ -eucryptite. Upon cooling there was no further structural change.

Attempts to index the PXRD pattern resulted in possible monoclinic and triclinic unit cells. However, attempts to solve the structure from the PXRD data or from continuous rotational electron diffraction (cRED) analysis were unsuccessful. Figure 2a–c compares TEM images of the original $\text{LiAlSi}_3(\text{OH})_2$ sample with that of the sample treated at 500 and 800 °C. While all of the samples exhibit needle-like morphology and a lack of uniform particle size distribution, the sharpness of the edges changes upon heating. Well-defined edges of the initial hydrous aluminosilicate crystals clearly become more rounded.

In Figure 4 the attenuated total reflection Fourier-transform infrared (ATR-FTIR, or simply IR hereafter) spectra of original $\text{LiAlSi}_3(\text{OH})_2$ are compared with that of the samples treated at 500 and 800 °C. Generally, IR spectra of lithium aluminosilicates are characterized by the bands of the framework of tetrahedra. There are two distinct regions where T(Si, Al)–O stretches and Si–O–Al inter-tetrahedral bending modes appear (i.e. bending of T–O–T angles), respectively. For LiAlSiO_4 glass these regions have broad bands with absorption maxima at 936 and 695 cm^{-1} . In the crystalline materials α - and β -eucryptite these modes are resolved into more or less narrow bands. Clearly, the IR spectrum of the 800 °C product (i.e. γ -eucryptite) follows this pattern. $\text{LiAlSi}_3(\text{OH})_2$ is a structurally different material and its IR spectrum was described earlier [10]. There are distinct O–H stretches from structural hydroxy groups in the spectral region 2900–3800 cm^{-1} . Further, the T–O–T

Figure 2: TEM bright field images of $\text{LiAlSi}_3(\text{OH})_2$ sample before (a) and after heat treatment at 500 °C (b) and 800 °C (c). Shrinkage of a $\text{LiAlSi}_3(\text{OH})_2$ crystal upon dehydration (e–f) as observed in TEM investigation after respectively 0, 275 and 1434 s of continuous beam exposure. The inset shows a selected area diffraction pattern of the amorphized particle after the investigation.

Figure 3: Dehydration of $\text{LiAlSi}_3(\text{OH})_2$ as observed in PXRD investigations (Cu $K\alpha$ radiation).

bending bands at around 700 cm^{-1} are very weak because of the small proportion of corner-condensed TO_4 tetrahedra in the structure. The IR spectrum of the product immediately after dehydration (i.e. the 500 °C treated sample) shows sharp bands in the $400\text{--}1250\text{ cm}^{-1}$ region, characteristic for a well crystallized product. Their rather large number indicates a larger unit cell and/or low space group symmetry of the structure. Bands at around 700 cm^{-1} manifest the presence of a framework with corner-connected tetrahedra (and thus the absence of AlO_6 octahedra). There are also weak but significant bands in the range $2800\text{--}3000\text{ cm}^{-1}$ (which are at wavenumbers too low for O–H stretches unless they reflect a very strong hydrogen bond environment [11]) and in the range $1200\text{--}1600\text{ cm}^{-1}$ (that could relate to O–H bending). At this point, there is no further information about the structure of the initial dehydration product. As mentioned above, all attempts to solve the structure – either from PXRD or electron diffraction data – failed.

We note a striking (but coincidental) relationship with the thermal behavior of Li-ABW, which is summarized in

Figure 4: ATR-FTIR spectra of $\text{LiAlSiO}_3(\text{OH})_2$ before and after heat treatment at 500 and 800 °C.

Scheme 1. The Li-ABW dehydration has been described in detail by Norby [8]. Complete water loss occurs at around 300 °C upon which the zeolite structure collapses. Rehydration is possible to a limited extent. The powder pattern of anhydrous Li-ABW was indexed with an orthorhombic cell, and it was assumed that the structure has narrowed elongated, 8-ring channels in which 4-coordinated Li ions are situated. Based on this model, a transformation path was then proposed for the transition to γ -eucryptite. Yet, the structure model of anhydrous Li-ABW did not conform to the intensities of the PXRD data. Although the dehydration temperature and occurrence of an intermediate phase is strikingly similar for $\text{LiAlSiO}_3(\text{OH})_2$, it can be safely assumed that its transition follows a different route, through nucleation and growth of the new phase, since the coordination of Al and Li changes from octahedral to tetrahedral. As a matter of fact, we initially envisioned that the octahedral coordination for Al may be maintained in a metastable intermediate phase. However, this is at least not realized in the product obtained at 500 °C because the IR spectrum clearly shows the presence of a framework of tetrahedral units.

Scheme 1: Comparison of the thermal behavior of $\text{LiAlSiO}_3(\text{OH})_2$ and Li-ABW.

2.2 Analysis of γ -eucryptite

The γ -eucryptite structure has rarely been observed. Its presence was first recognized in rapidly cooled melts of $\text{LiAl}_{0.5}\text{Ga}_{0.5}\text{SiO}_4$ [12] and then seen in the crystallization of glasses in the systems LiAlSiO_4 - LiGaGeO_4 , LiAlSiO_4 - LiGaGeO_4 , LiAlGeO_4 [13], and LiAlSiO_4 - NaAlSiO_4 [14]. It was further observed as a byproduct in the thermal conversion of Li-LTA (i.e. Linde type A zeolite in which Na ions were exchanged by Li) [15]. The thermal decomposition of Li-ABW established γ -eucryptite unambiguously as a polymorph of LiAlSiO_4 . Its metastable nature with respect to the ground state, rhombohedral α - LiAlSiO_4 , has been shown from DFT calculations of the equation of states [16]. The dehydration of $\text{LiAlSiO}_3(\text{OH})_2$ provides another way to access pure γ -eucryptite.

Using PXRD and powder neutron diffraction data of pure γ -eucryptite samples Norby could determine its structure as a “stuffed” cristobalite [8]. We performed a Rietveld refinement of the PXRD pattern of our product obtained at 800 °C (Figure 5) and could confirm Norby’s model (cf. Tables 1–3). The structure is shown in Figure 6, together with (tetragonal) cristobalite. The topology of the tetrahedra (i.e. the arrangement of tetrahedral nodes) with the six-ring motif is identical for cristobalite and γ -eucryptite. The rings are largely skewed in γ -eucryptite in order to establish the coordination of the Li ions. When adding tetrahedra, further deviations are seen regarding their orientation.

In the monoclinic γ -eucryptite structure (space group Pc) the Li ions are distributed over two positions, Li1 and Li2. Li1 attains a rather regular tetrahedral coordination by

Figure 5: (a) Overnight PXRD pattern and Rietveld refinement of γ -eucryptite with the 40–90° 2θ range being 12.5 times magnified. (b) Zoom in on the 34–38° 2θ range. Arrows denote the reflection at 35.5°, which could not be reasonably described with the existing model, and an unindexed low-intensity peak at 37.8°.

Table 1: Crystal data and structure refinement results for γ -eucryptite LiAlSiO_4 from PXRD data with DFT-optimized data in brackets.

Empirical formula	LiAlSiO_4
Formula weight, g mol^{-1}	126.01
Temperature, K	295
Crystal system	Monoclinic
Space group	Pc (No. 7)
Z	4
a , Å	8.2733(7) [8.1839]
b , Å	5.0477(4) [5.1471]
c , Å	8.2773(6) [8.2645]
β , deg	107.339(4)° [106.252°]
Volume, Å ³	329.97(5) [334.21]
R_p , R_{wp} , R_{exp}	3.79, 5.18, 3.04
χ^2	2.90

O atoms belonging to four different Al/SiO_4 tetrahedra. In contrast, Li_2 is coordinated to an edge of a SiO_4 tetrahedron and its O environment appears rather distorted. Norby could establish the Li positions from neutron diffraction data. For us it was not possible to perform a reliable refinement of the Li atom positions from in-house PXRD data, and eventually these were constraint to correspond to those of the DFT optimized structure (which is discussed subsequently). Also, we note that the Rietveld refinement was not perfect (cf. Figure 5). While the overall fit produced low R values, the peak at 35.5° could not be reasonably described with the existing model. Further, a number of low-intensity peaks were not indexed, which hints to the possibility of either triclinic symmetry or the presence of an unidentified impurity. In order to explore a possible lower (triclinic) symmetry for γ - LiAlSiO_4 we subjected model

Table 2: Fractional atomic coordinates and isotropic equivalent displacement parameters for γ -eucryptite LiAlSiO_4 ^a from PXRD data. DFT-optimized fractional atomic coordinates are given in brackets.

Atom	Wyckoff position	x	y	z	U_{iso} (Å ²)
Si1	2a	1/2	0.3243(3) [0.3284]	1/4	0.0513(4)
Si2	2a	0.9993(1) [0.9946]	0.1787(2) [0.1705]	0.6081(1) [0.5836]	0.0513(4)
Al1	2a	0.6333(1) [0.6222]	0.1866(4) [0.1763]	0.6346(3) [0.6244]	0.0513(4)
Al2	2a	0.1310(5) [0.1208]	0.6851(4) [0.6684]	0.4848(7) [0.4628]	0.0513(4)
O1	2a	0.4661(1) [0.4722]	0.1980(2) [0.2224]	0.4356(5) [0.4279]	0.0429(7)
O2	2a	0.2843(3) [0.3079]	0.2788(2) [0.2941]	0.1351(5) [0.1251]	0.0429(7)
O3	2a	0.6162(3) [0.6342]	0.1390(2) [0.155]	0.1678(4) [0.1778]	0.0429(7)
O4	2a	0.5539(3) [0.5776]	0.6500(2) [0.6243]	0.2622(8) [0.2799]	0.0429(7)
O5	2a	0.0402(1) [0.0687]	0.3780(2) [0.3338]	0.4655(5) [0.4475]	0.0429(7)
O6	2a	0.1213(1) [0.1326]	0.2475(6) [0.1918]	0.8013(3) [0.7717]	0.0429(7)
O7	2a	0.8033(3) [0.8134]	0.2986(3) [0.2956]	0.5913(2) [0.5911]	0.0429(7)
O8	2a	0.9681(1) [0.9688]	0.1340(2) [0.139]	0.0375(3) [0.0293]	0.0429(7)
Li1	2a	0.7558	0.3326	0.0243	0.0501(9)
Li2	2a	0.2284	0.1553	0.3311	0.0501(9)

^aSpace group Pc , $Z = 4$, $T = 295$ K, estimated standard deviations in parentheses. The Li atomic coordinates were constraint to the DFT-relaxed structure.

Table 3: Interatomic distances ($<3.0 \text{ \AA}$) for γ -eucryptite LiAlSiO_4 ^a from PXRD data. Estimated standard deviations are given in parentheses. DFT-optimized interatomic distances are given in brackets.

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Si1:	O1	1.761(4)	Si2:	O5	1.661(3)
		[1.642]			[1.650]
	O2	1.769(2)		O6	1.654(2)
		[1.631]			[1.650]
	O3	1.629(3)		O7	1.697(3)
		[1.651]			[1.634]
	O4	1.699(2)		O8	1.676(2)
		[1.642]			[1.652]
Al1:	O1	1.809(3)	Al2:	O2	1.500(5)
		[1.757]			[1.741]
	O3	1.679(2)		O5	1.709(3)
		[1.757]			[1.770]
	O4	1.625(6)		O6	1.535(7)
		[1.761]			[1.762]
	O7	1.651(3)		O8	1.786(5)
		[1.773]			[1.793]
Li1:	O3	2.125(3)	Li2:	O1	1.910(1)
		[2.035]			[1.961]
	O4	2.312(5)		O2	1.919(4)
		[2.146]			[2.110]
	O7	1.949(2)		O5	2.441(3)
		[2.011]			[2.045]
	O8	1.997(1)		O6	2.202(3)
		[1.998]			[1.957]
				O8	2.727(2)
					[2.789]

^aSpace group Pc , $Z = 4$, $T = 295 \text{ K}$.

structures with $P1$ symmetry to DFT optimization. In the optimized structure the monoclinic symmetry was restored with unit cell parameters and Al, Si, and O atom position parameters being in good agreement with the results of the Rietveld refinement (Tables 1–3). The Li–O distances in the DFT optimized structure are in a narrow range around $2.0 \text{ \AA}$.

Lastly, we evaluated the temperature dependence of the volume and lattice parameters for $\text{LiAlSiO}_3(\text{OH})_2$ and γ -eucryptite, obtained respectively upon heating and cooling in multi-temperature PXRD measurements (Figure 7). The volumetric thermal expansion coefficients are 36×10^{-6} and $47 \times 10^{-6} \text{ K}^{-1}$, respectively, which is similar to Li-ABW in the same temperature range ($43 \times 10^{-6} \text{ K}^{-1}$) [9], and thus in sharp contrast to the zero thermal expansion behavior of β -eucryptite. The expansion of both $\text{LiAlSiO}_3(\text{OH})_2$ and γ -eucryptite is anisotropic, affecting primarily the a , b axes and a , c axes, respectively, whereas the axis parallel to the framework channels stays virtually unchanged (c axis for $\text{LiAlSiO}_3(\text{OH})_2$ and b axis for γ -eucryptite).

3 Conclusions

From hydrous $\text{LiAlSiO}_3(\text{OH})_2$ an intermediate dehydrated phase is obtained at $T = 350\text{--}400^\circ \text{C}$ which is subsequently converted into the rare LiAlSiO_4 polymorph γ -eucryptite above $T = 700^\circ \text{C}$. The structure of the intermediate phase could not be solved from X-ray and electron diffraction data.

Figure 6: Comparison of the crystal structure of tetragonal cristobalite (a) and monoclinic γ -eucryptite (b). The upper row depicts the framework of T atoms (which has been artificially decorated for cristobalite), the lower row depicts the polyhedral representation. (c) Is the same as (b) but with Li atoms included (grey spheres/tetrahedra). The structure of γ -eucryptite is based on the DFT-optimized model (cf. Tables 1 and 2).

Figure 7: Volume (a) and lattice parameters of $\text{LiAlSi}_3(\text{OH})_2$ (b) and γ -eucryptite (c) as a function of temperature. The lattice parameters were refined from the multi-temperature PXRD data obtained on heating and cooling, respectively. Both phases show little to none thermal expansion in the axis parallel to the channels, while in-plane dimensions change significantly.

From IR spectroscopy data it is inferred that this phase possesses a low symmetry and/or a large unit cell and constitutes a framework of corner-connected TO_4 tetrahedra. The change of Al and Li coordination from octahedral in hydrous $\text{LiAlSi}_3(\text{OH})_2$ to tetrahedral upon dehydration strongly suggests a phase transition via nucleation and growth, which is in contrast to the topotactic Li-ABW to γ -eucryptite transformation. The structure refinement of γ -eucryptite and the DFT structure optimization confirmed a monoclinic cristobalite-like motif with six-membered rings of TO_4 tetrahedra, with the rings being largely skewed to accommodate the lithium atoms in LiO_4 tetrahedra. Using multi-temperature PXRD data, the volumetric thermal expansion coefficients for both $\text{LiAlSi}_3(\text{OH})_2$ and γ -eucryptite have been calculated to be 36×10^{-6} and $47 \times 10^{-6} \text{ K}^{-1}$ in the 25–800 °C temperature range, respectively, with the axis parallel to the channels of the framework staying virtually unchanged.

4 Experimental methods

4.1 Synthesis

Phase-pure $\text{LiAlSi}_3(\text{OH})_2$ was obtained when treating mixtures of LiAlSiO_4 glass and water with a molar ratio 1:1–1:2 at 5 GPa and 400–600 °C for 8 h in a multi-anvil high pressure device. Mixtures were confined in Au–Pd alloy capsules which were sealed by laser welding to prevent water loss. The recovered capsule was pinched open, verified to still contain free H_2O , and the water then removed by evaporation at ~50 °C in a drying oven. For details on the preparation of the LiAlSiO_4 glass precursor and its crystallization in hydrothermal environments at gigapascal pressures see Ref. [10].

4.2 Powder X-ray diffraction (PXRD) analysis

Multi-temperature PXRD studies were performed on a Panalytical X'Pert PRO instrument operating with $\text{CuK}\alpha$ radiation and in θ - 2θ

diffraction geometry using the XRK 900 chamber from Anton Paar. The powder sample was mounted on a gold sample holder. Measurements were performed in air atmosphere from room temperature up to 500 or 800 °C and back. The data was collected in the 2θ range of 10–50° with steps of 100 °C between individual measurements. Each measurement had 5 min equilibration time, 45 min acquisition time and 5 K min^{-1} heating or cooling rate between the steps. Measurements for Rietveld refinement were recorded on a Panalytical X'Pert Alpha1 diffractometer operated with $\text{CuK}\alpha_1$ radiation. The sample was mounted on a zero-background Si wafer and measured at room temperature in Bragg-Brentano geometry in a 2θ range of 10–110° with 0.013° step size. Powder patterns were indexed using the programs DICVOL06 [17] and McMAILL [18]. Structure solution and Rietveld refinement were performed using the FOX [19] and FULLPROF [20] software packages, respectively. The following parameters were refined: background, zero shift or sample displacement, unit cell parameters, peak profile and asymmetry, and anisotropic peak broadening using spherical harmonics whenever necessary [21]. Pseudo-Voigt or Thompson-Cox-Hastings Pseudo-Voigt functions were used for the peak shape refinement.

CCDC 2104036 contains the supplementary crystallographic data of monoclinic γ -eucryptite, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.3 Transmission electron microscopy (TEM) investigations

Transmission electron microscopy (TEM) morphological observations and *in-situ* decomposition studies were performed on a JEOL 2100F instrument operating at 200 kV accelerating voltage. A 100 μm condenser aperture and spot size three were used in order to slow down the beam induced decomposition. Morphological observations were made through conventional bright-field (BF) imaging. The *in-situ* study comprised time series of a combination of BF imaging and energy dispersive X-ray (EDX) measurements. All measurements were performed on powder samples deposited onto a copper micro-grid coated with holey carbon. Electron diffraction investigations intended for obtaining structural information by applying the continuous rotation electron diffraction (cRED) technique [22–24] were performed on a JEOL 2100 LaB₆ microscope operating at 200 kV. In order to reduce the electron beam damage, a 70 μm condenser aperture was used and spot

size 3. To further reduce the potential beam damage during data acquisition, the sample was cooled to approximately -170°C in a cryo TEM sample holder. The cRED data were collected using the Timepix Quad, a high-speed hybrid detection camera.

4.4 Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were acquired on a Varian 610-IR FTIR spectrometer in the $400\text{--}4000\text{ cm}^{-1}$ wavenumber range (32 scans, resolution 4 cm^{-1}) using a Specac Goldengate micro-ATR accessory equipped with KRS-5 lenses and a diamond ATR element. Spectra were normalized in a range from 0 to 1.

4.5 DFT calculations

DFT total energy calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [25, 26] in the framework of the projector augmented wave method (PAW) [27] within generalized gradient approximation (GGA), and employing the Perdew-Burke-Ernzerhof (PBE) parametrization of the exchange-correlation functional [28, 29]. The cutoff energy for the plane wave basis set was 600 eV. Structural relaxations employed a $2 \times 2 \times 2$ Γ -centered $\mathbf{k}$ -point grid, and Brillouin zone integration was done with the tetrahedron method [30]. Forces on all atoms were converged to at least $0.01\text{ eV \AA}^{-1}$.

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