Supplementary Information for

Filling the gap between lansfordite and nesquehonite: $MgCO_3 \cdot 4H_2O$, a new magnesium carbonate hydrate

by
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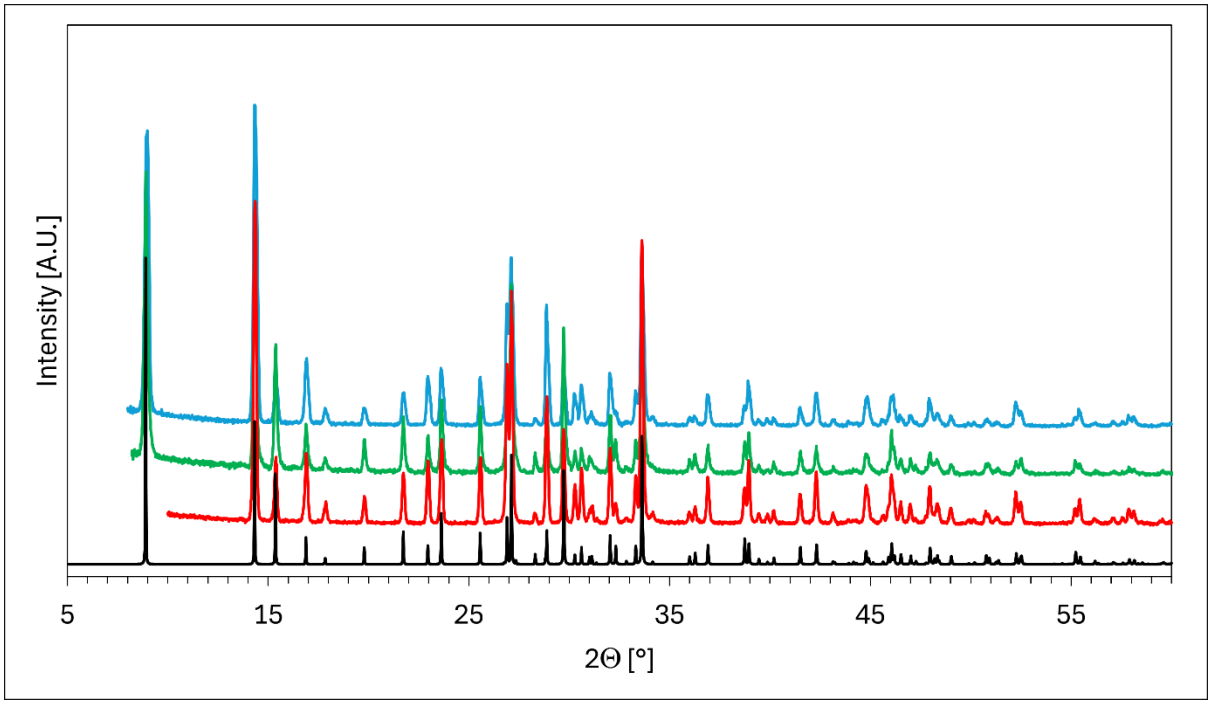
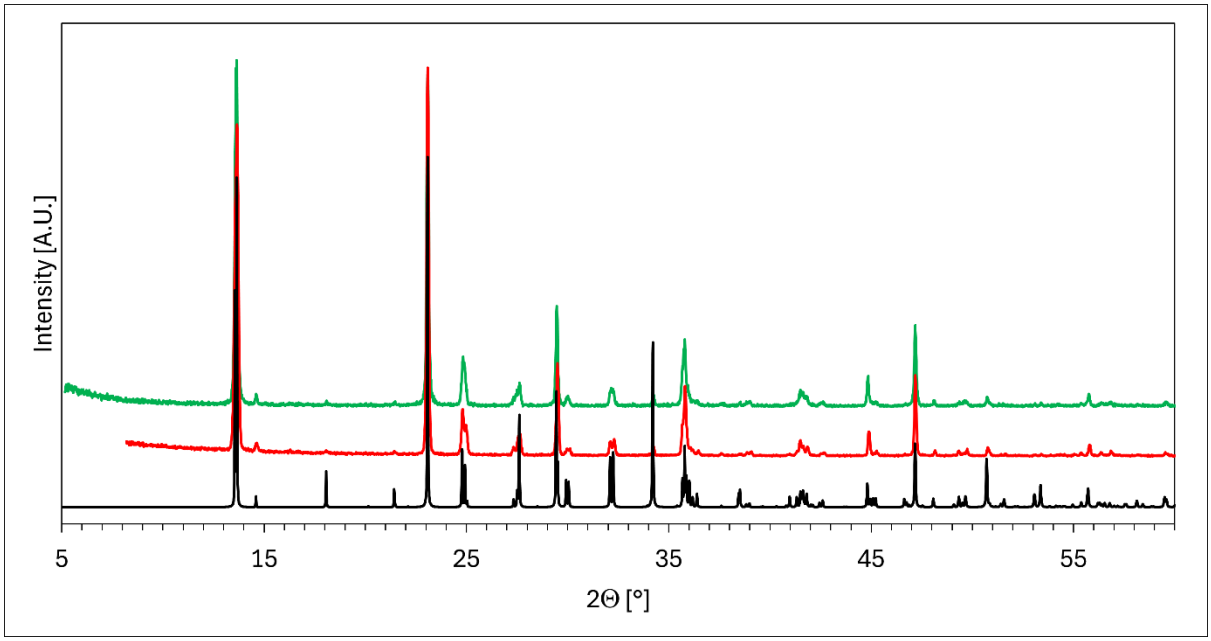
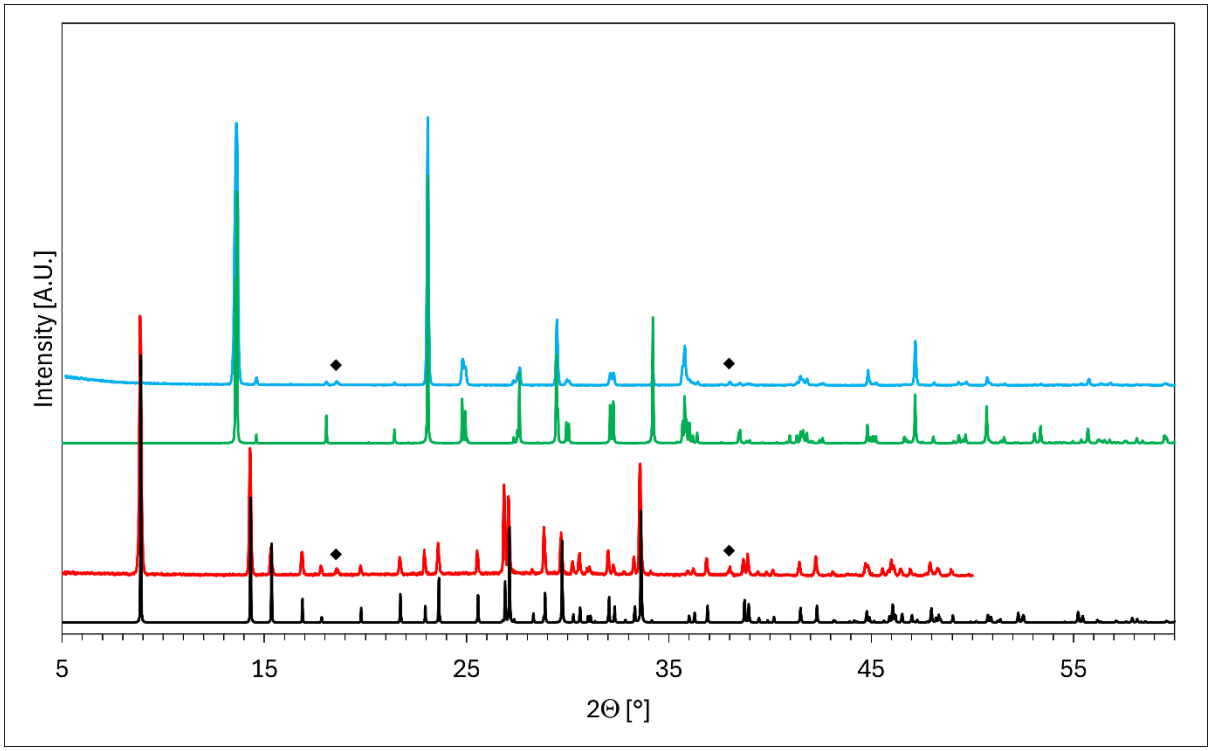


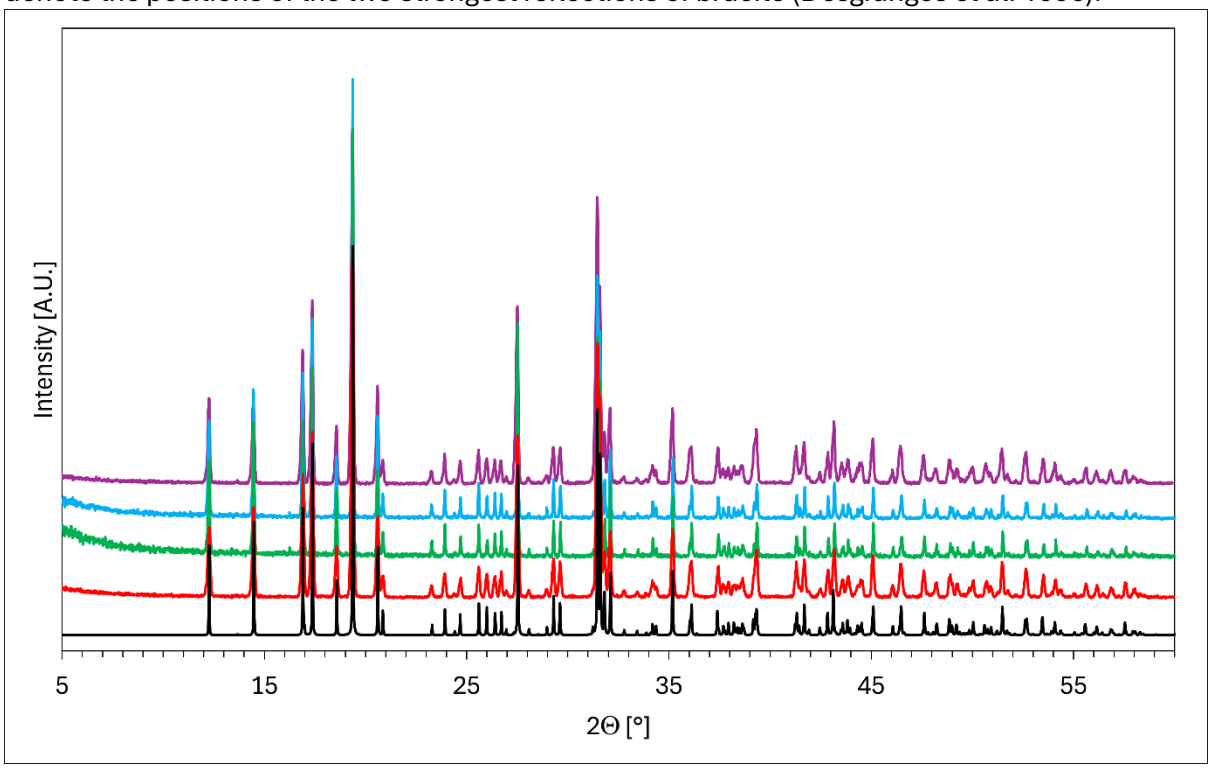
SI Fig. 1 X-ray powder diffractograms (Cu$K\alpha$1 radiation) of $MgCO_3 \cdot 6H_2O$ (Rincke et al. 2020; black, bottom), the product of synthesis #6 (red, second from bottom), the product of synthesis #7 (green, third from bottom), and the product of synthesis #8 after 28 days (blue, top).



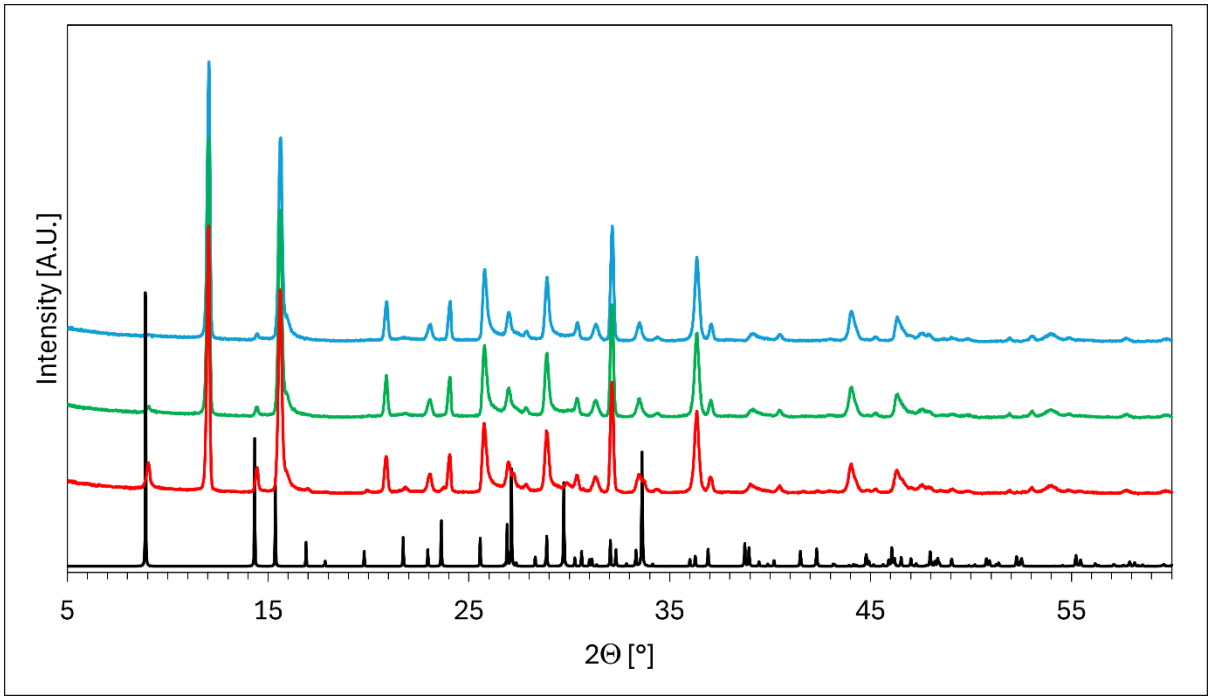
SI Fig. 2 X-ray powder diffractograms (Cu$K\alpha$1 radiation) of nesquehonite ($MgCO_3 \cdot 3H_2O$; Giester et al. 2000; black, bottom), the product of synthesis #9 (red, second from bottom), the product of synthesis #10 (green, top).



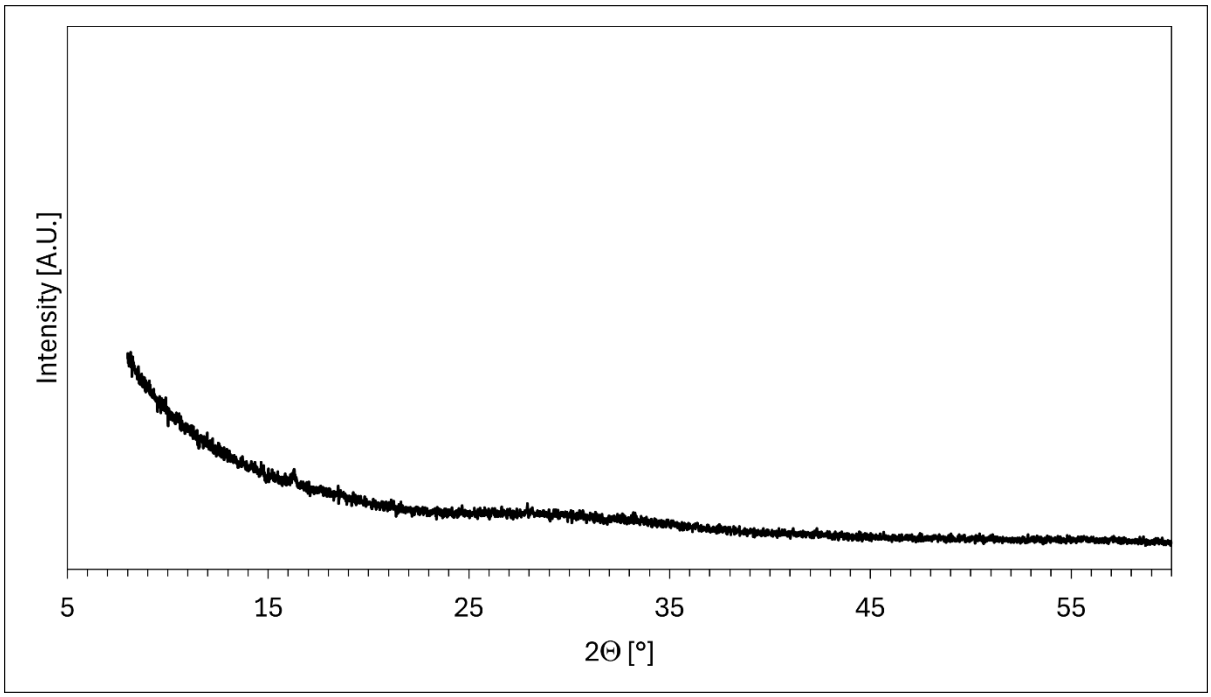
SI Fig. 3 X-ray powder diffractograms (Cu$K\alpha$1 radiation) of $MgCO_3 \cdot 6H_2O$ (Rincke et al. 2020; black, bottom), the product of synthesis #12 (red, second from bottom), nesquehonite (Giester et al. 2000; green, third from bottom), and the product of synthesis #13 (blue, top). Diamonds denote the positions of the two strongest reflections of brucite (Desgranges et al. 1996).



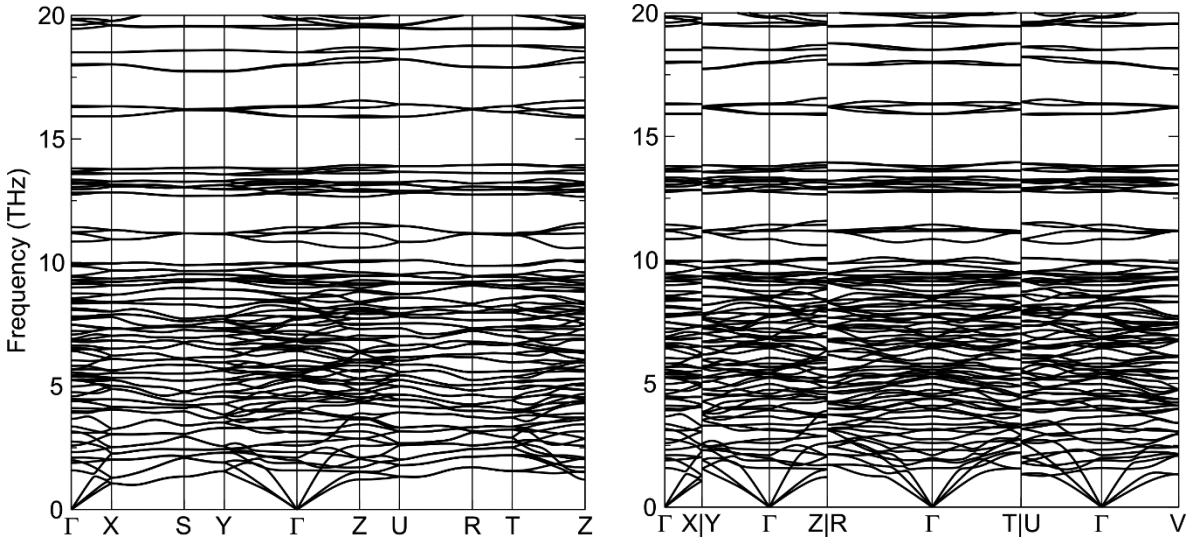
SI Fig. 4 X-ray powder diffractograms (Cu$K\alpha$1 radiation) of lansfordite (Liu et al. 1990; black, bottom), the product of synthesis #14 (red, second from bottom), #15 (green, third from bottom), #16 (blue, fourth from bottom), #17 (violett, top), noticeable intensity at approx. 16.2 °2Θ originates from the sample holder.



SI Fig. 5 Comparison of the X-ray powder diffractograms (Cu$K\alpha$1 radiation) of $MgCO_3 \cdot 6H_2O$ (Rincke et al. 2020; black, bottom) and its transformation product in air within an open container at 20 °C (transformation type *iiia*) after one (red, second from bottom), three (green, third from bottom), and six weeks (blue, top), respectively.



SI Fig. 6 X-ray powder diffractogram (Cu$K\alpha$1 radiation) of the transformation product in air within an open container at 120 °C (transformation type *iiib*).



SI Fig. 7 Detailed presentation of the range 0-20 THz of the phonon dispersion curves (Fig. 11) of magnesium carbonate hexahydrate (left) and DFT-calculated structure of magnesium carbonate tetrahydrate (right). The phonon dispersion curves were obtained by the finite differences method with MTPs passively trained over AIMD trajectories as the force constant engine.

CIF file from DFT simulations (B3LYP functional)

```
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_cell_angle_beta   89.9778752705
_cell_angle_gamma  89.9662250000
_cell_volume      564.7562232548

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_symmetry_Int_Tables_number 1
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_space_group_symop_operation_xyz
1 x,y,z

loop_
_atom_type_symbol
H
C
O
Mg

loop_
_atom_site_label
_atom_site_type_symbol
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_atom_site_Wyckoff_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
H1  H   1 a  0.6819840000  0.0223980000 -0.0645450000  1.0000000000 Dx,Dy,Dz
H2  H   1 a  0.2288390000  0.1806240000  0.7929500000  1.0000000000 Dx,Dy,Dz
H3  H   1 a  0.7289860000  0.3193290000  0.7071780000  1.0000000000 Dx,Dy,Dz
H4  H   1 a  0.1816930000  0.4776440000  0.5645930000  1.0000000000 Dx,Dy,Dz
H5  H   1 a  0.3180350000 -0.0224430000  0.0646300000  1.0000000000 Dx,Dy,Dz
H6  H   1 a  0.7712830000  0.8194280000  0.2070000000  1.0000000000 Dx,Dy,Dz
H7  H   1 a  0.2711320000  0.6806190000  0.2928630000  1.0000000000 Dx,Dy,Dz
H8  H   1 a  0.8182460000  0.5223650000  0.4353360000  1.0000000000 Dx,Dy,Dz
H9  H   1 a  0.8151070000  0.1524990000 -0.0037600000  1.0000000000 Dx,Dy,Dz
H10 H   1 a  0.1549910000  0.3554890000  0.8262130000  1.0000000000 Dx,Dy,Dz
H11 H   1 a  0.6543180000  0.1449660000  0.6736270000  1.0000000000 Dx,Dy,Dz
H12 H   1 a  0.3147050000  0.3474840000  0.5037210000  1.0000000000 Dx,Dy,Dz
H13 H   1 a  0.1849010000  0.8475330000  0.0037930000  1.0000000000 Dx,Dy,Dz
```

H14 H 1 a 0.8450760000 0.6445090000 0.1737950000 1.0000000000 Dx,Dy,Dz
H15 H 1 a 0.3454880000 0.8551410000 0.3262860000 1.0000000000 Dx,Dy,Dz
H16 H 1 a 0.6852310000 0.6524210000 0.4963000000 1.0000000000 Dx,Dy,Dz
H17 H 1 a 0.7987350000 0.5121910000 0.8057640000 1.0000000000 Dx,Dy,Dz
H18 H 1 a 0.1901320000 0.2080670000 0.0957510000 1.0000000000 Dx,Dy,Dz
H19 H 1 a 0.6897840000 0.2919430000 0.4041530000 1.0000000000 Dx,Dy,Dz
H20 H 1 a 0.2983520000 -0.0120460000 0.6942570000 1.0000000000 Dx,Dy,Dz
H21 H 1 a 0.2013700000 0.4878160000 0.1942370000 1.0000000000 Dx,Dy,Dz
H22 H 1 a 0.8098970000 0.7919370000 -0.0957440000 1.0000000000 Dx,Dy,Dz
H23 H 1 a 0.3102270000 0.7081160000 0.5958210000 1.0000000000 Dx,Dy,Dz
H24 H 1 a 0.7014970000 0.0120410000 0.3056630000 1.0000000000 Dx,Dy,Dz
H25 H 1 a 0.5954510000 0.5690780000 0.7236100000 1.0000000000 Dx,Dy,Dz
H26 H 1 a 0.4017080000 0.1488810000 0.1724960000 1.0000000000 Dx,Dy,Dz
H27 H 1 a -0.0985130000 0.3508820000 0.3274390000 1.0000000000 Dx,Dy,Dz
H28 H 1 a 0.0950870000 -0.0689720000 0.7764300000 1.0000000000 Dx,Dy,Dz
H29 H 1 a 0.4045860000 0.4308270000 0.2764120000 1.0000000000 Dx,Dy,Dz
H30 H 1 a 0.5983450000 0.8510930000 0.8275090000 1.0000000000 Dx,Dy,Dz
H31 H 1 a 0.0985580000 0.6491120000 0.6725310000 1.0000000000 Dx,Dy,Dz
H32 H 1 a -0.0950710000 0.0689850000 0.2236080000 1.0000000000 Dx,Dy,Dz
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C2 C 1 a 0.1407740000 0.6238690000 0.8907080000 1.0000000000 Dx,Dy,Dz
C3 C 1 a 0.6407760000 0.8762620000 0.6093620000 1.0000000000 Dx,Dy,Dz
C4 C 1 a 0.3591800000 0.1237440000 0.3906540000 1.0000000000 Dx,Dy,Dz
O1 O 1 a 0.6946490000 0.4450790000 0.0480440000 1.0000000000 Dx,Dy,Dz
O2 O 1 a 0.3053810000 0.5548950000 -0.0480200000 1.0000000000 Dx,Dy,Dz
O3 O 1 a 0.8054500000 -0.0548790000 0.5481160000 1.0000000000 Dx,Dy,Dz
O4 O 1 a 0.1944780000 0.0549080000 0.4518830000 1.0000000000 Dx,Dy,Dz
O5 O 1 a 0.7071890000 0.1445450000 -0.0648390000 1.0000000000 Dx,Dy,Dz
O6 O 1 a 0.2521580000 0.2535830000 0.8485350000 1.0000000000 Dx,Dy,Dz
O7 O 1 a 0.7513330000 0.2468700000 0.6511510000 1.0000000000 Dx,Dy,Dz
O8 O 1 a 0.2065660000 0.3554940000 0.5647060000 1.0000000000 Dx,Dy,Dz
O9 O 1 a 0.2928650000 0.8554330000 0.0648470000 1.0000000000 Dx,Dy,Dz
O10 O 1 a 0.7478650000 0.7463840000 0.1514810000 1.0000000000 Dx,Dy,Dz
O11 O 1 a 0.2484680000 0.7532500000 0.3487480000 1.0000000000 Dx,Dy,Dz
O12 O 1 a 0.7934110000 0.6444790000 0.4353290000 1.0000000000 Dx,Dy,Dz
O13 O 1 a 0.6512780000 0.4753230000 0.7889710000 1.0000000000 Dx,Dy,Dz
O14 O 1 a 0.3470910000 0.1832000000 0.0903800000 1.0000000000 Dx,Dy,Dz
O15 O 1 a 0.8467290000 0.3167150000 0.4095310000 1.0000000000 Dx,Dy,Dz
O16 O 1 a 0.1508880000 0.0248800000 0.7111420000 1.0000000000 Dx,Dy,Dz
O17 O 1 a 0.3488050000 0.5246600000 0.2110920000 1.0000000000 Dx,Dy,Dz
O18 O 1 a 0.6529300000 0.8167690000 -0.0903720000 1.0000000000 Dx,Dy,Dz
O19 O 1 a 0.1532780000 0.6833350000 0.5904300000 1.0000000000 Dx,Dy,Dz
O20 O 1 a 0.8490200000 -0.0248690000 0.2888570000 1.0000000000 Dx,Dy,Dz
O21 O 1 a -0.0526340000 0.4515630000 0.1834350000 1.0000000000 Dx,Dy,Dz
O22 O 1 a 0.0645250000 0.7697340000 -0.0982840000 1.0000000000 Dx,Dy,Dz
O23 O 1 a 0.5647000000 0.7304010000 0.5983920000 1.0000000000 Dx,Dy,Dz
O24 O 1 a 0.4473970000 0.0482470000 0.3165180000 1.0000000000 Dx,Dy,Dz
O25 O 1 a 0.0527230000 0.5484570000 0.8165500000 1.0000000000 Dx,Dy,Dz
O26 O 1 a -0.0644760000 0.2302480000 0.0983030000 1.0000000000 Dx,Dy,Dz
O27 O 1 a 0.4353220000 0.2695700000 0.4016540000 1.0000000000 Dx,Dy,Dz
O28 O 1 a 0.5525080000 -0.0482240000 0.6834690000 1.0000000000 Dx,Dy,Dz

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Mg1 Mg   1 a  0.4920030000  0.3353300000 -0.0604790000  1.0000000000 Dx,Dy,Dz
Mg2 Mg   1 a -0.0083770000  0.1647540000  0.5604450000  1.0000000000 Dx,Dy,Dz
Mg3 Mg   1 a  0.5080310000  0.6646450000  0.0604870000  1.0000000000 Dx,Dy,Dz
Mg4 Mg   1 a  0.0082640000  0.8352600000  0.4395590000  1.0000000000 Dx,Dy,Dz

# end of cif
```

CIF file after Findsym and LeBail fit

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_cell_length_b    6.4465000000
_cell_length_c    8.1015000000
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_cell_angle_beta   112.9970000000
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_cell_volume      598.2700000000

_symmetry_space_group_name_H-M "P 1 21/a 1"
_symmetry_Int_Tables_number 14
_space_group.reference_setting '014:-P 2ybc'
_space_group.transform_Pp_abc -a-c,b,a;0,0,0

loop_
_space_group_symop_id
_space_group_symop_operation_xyz
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2 -x+1/2,y+1/2,-z
3 -x,-y,-z
4 x+1/2,-y+1/2,z

loop_
_atom_type_symbol
H
C
O
Mg

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
H1  H   4 e -0.0646050000  0.6818475000 -0.0422200000  1.0000000000 Dx,Dy,Dz
H2  H   4 e  0.7929075000  0.2288550000 -0.0264725000  1.0000000000 Dx,Dy,Dz
H3  H   4 e -0.0037425000  0.8149200000  0.1487300000  1.0000000000 Dx,Dy,Dz
H4  H   4 e  0.8262675000  0.1546850000  0.1815600000  1.0000000000 Dx,Dy,Dz
H5  H   4 e  0.8057300000  0.7985525000  0.3178475000  1.0000000000 Dx,Dy,Dz
H6  H   4 e  0.0957900000  0.1899450000  0.3038675000  1.0000000000 Dx,Dy,Dz
H7  H   4 e  0.7235950000  0.5952550000  0.2926450000  1.0000000000 Dx,Dy,Dz
H8  H   4 e  0.1725200000  0.4015725000  0.3215250000  1.0000000000 Dx,Dy,Dz
C1  C   4 e  0.1093250000  0.8592300000  0.4855175000  1.0000000000 Dx,Dy,Dz
```

O1 O 4 e 0.0480750000 0.6945750000 0.4931725000 1.0000000000 Dx,Dy,Dz
O2 O 4 e -0.0647675000 0.7068700000 0.0797600000 1.0000000000 Dx,Dy,Dz
O3 O 4 e 0.8486650000 0.2517875000 0.1020575000 1.0000000000 Dx,Dy,Dz
O4 O 4 e 0.7889000000 0.6510875000 0.2641275000 1.0000000000 Dx,Dy,Dz
O5 O 4 e 0.0904125000 0.3469025000 0.2736725000 1.0000000000 Dx,Dy,Dz
O6 O 4 e 0.1834600000 -0.0526150000 0.6351200000 1.0000000000 Dx,Dy,Dz
O7 O 4 e -0.0983300000 0.0645975000 0.6713325000 1.0000000000 Dx,Dy,Dz
Mg1 Mg 4 e -0.0604650000 0.4918325000 0.2748350000 1.0000000000 Dx,Dy,Dz

end of cif