Supporting Information

**Complete and limited substitution of rare-earth elements in apatite silicates La(9-*x*)Ln*x*(SiO4)6O1.5**

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Table S1.Rietveld refinement datafor La9-xLnx(SiO4)6OOH

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| *Ln* | *La* | *Nd* | *Eu* | *Eu* | *Gd* | *Gd* | *Tm* |
| Degree of substitution | *х = 0* | *х =* 9 | *х* = 6 | *х* = 9 | *х* = 6 | *х* = 9 | *x=*1.5 |
| Space group *P*63/*m* | | | | | | | |
| Structure type Apatite | | | | | | | |
| Cell parameters (Å): | | | | | | | |
| *a* | 9.7693(3) | 9.5904(9) | 9.5312(5) | 9.4594(6) | 9.4312(5) | 9.3594(6) | 9.6500(4) |
| *c* | 7.1864(3) | 7.0776(8) | 6.9912(4) | 6.9004(5) | 6.8912(4) | 6.8104(5) | 7.1088(5) |
| Radiation, λ1, λ2 (Å) Cu Kα , 1.54056, 1.54439 | | | | | | | |
| Angular (2θ) range 15.00 – 115.00 | | | | | | | |
| Number of measured reflections | 856 | 840 | 856 | 856 | 816 | 816 | 842 |
| Number of refinement parameters | 36 | 36 | 36 | 36 | 36 | 36 | 36 |
| Reliability factors (R·100) | | | | | | | |
| RB | 7.01 | 8.25 | 8.30 | 8.15 | 8.52 | 8.35 | 7.92 |
| RF | 4.49 | 5.71 | 4.79 | 4.56 | 4.89 | 4.73 | 4.56 |
| RP | 9.50 | 9.87 | 9.19 | 9.35 | 9.39 | 9.75 | 9.63 |
| RWP | 12.20 | 13.40 | 12.90 | 12.80 | 12.50 | 12.20 | 12.20 |
| χ2 | 1.08 | 1.05 | 1.10 | 1.28 | 1.22 | 1.15 | 1.18 |

Table S2.Atomic coordinates,isotropic displacement parameters (Biso) and site occupancies (G) for La9-xGdx(SiO4)6OOH

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom | Site | Parameter | La(9-x)Gdx(SiO4)6O(OH) | | |
| *х* = 0 | *х* = 6 | *х* = 9 |
| La1 | 4f | *x* | 2/3 | 2/3 | - |
| *y* | 1/3 | 1/3 | - |
| *z* | 0.0005(1) | 0.003(1) | - |
| *Biso, Å2* | 0.31(9) | 0.5(1) | - |
| *G* | 0.805(4) | 0.260(3) | - |
| Gd1 | 4f | *x* | - | 2/3 | 2/3 |
| *y* | - | 1/3 | 1/3 |
| *z* | - | 0.003(1) | 0.011(3) |
| *Biso, Å2* | - | 0.5(1) | 0.31(3) |
| *G* | - | 0.527(3) | 0.850(4) |
| La2 | 6h | *x* | 0.23027(3) | 0.233(4) | - |
| *y* | 0.98729(3) | 0.9887(7) | - |
| *z* | 1/4 | 1/4 | - |
| *Biso, Å2* | 0.09(6) | 0.5(1) | - |
| *G* | 0.963(4) | 0.327(3) | - |
| Gd2 | 6h | *x* | - | 0.233(4) | 0.232(1) |
| *y* | - | 0.9887(7) | 0.993(2) |
| *z* | - | 1/4 | 1/4 |
| *Biso, Å2* | - | 0.5(1) | 0.7(2) |
| *G* | - | 0.648(3) | 0.933(4) |
| Si | 6h | *x* | 0.402(2) | 0.403(4) | 0.401(5) |
| *y* | 0.372(2) | 0.378(2) | 0.381(6) |
| *z* | 1/4 | 1/4 | 1/4 |
| *Biso, Å2* | 1.1(3) | 1.4(3) | 1.1(9) |
| *G* | 1 | 1 | 1 |
| O1 | 6h | *x* | 0.324(3) | 0.319(2) | 0.325(9) |
| *y* | 0.486(4) | 0.484(6) | 0.486(8) |
| *z* | 1/4 | 1/4 | 1/4 |
| *Biso, Å2* | 1.9(4) | 1.4(9) | 1.3(9) |
| *G* | 1 | 1 | 1 |
| O2 | 6h | *x* | 0.587(3) | 0.597(3) | 0.615(9) |
| *y* | 0.468(3) | 0.476(2) | 0.479(7) |
| *z* | 1/4 | 1/4 | 1/4 |
| *Biso, Å2* | 1.9(4) | 1.4(9) | 1.3(9) |
| *G* | 1 | 1 | 1 |
| O3 | 12i | *x* | 0.351(2) | 0.340(3) | 0.326(4) |
| *y* | 0.250(2) | 0.248(2) | 0.242(4) |
| *z* | 0.069(2) | 0.064(3) | 0.061(5) |
| *Biso, Å2* | 1.9(4) | 1.4(9) | 1.3(9) |
| *G* | 1 | 1 | 1 |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| OН | 2a | *x* | 0 | 0 | 0 |
| *y* | 0 | 0 | 0 |
| *z* | 0.220(1) | 1/4 | 1/4 |
| *Biso, Å2* | 1.9(4) | 1.4(9) | 1.3(9) |
| *G* | 0.5 | 0.5 | 0.5 |
| O4 | 2a | *x* | 0 | 0 | 0 |
| *y* | 0 | 0 | 0 |
| *z* | 0.220(1) | 1/4 | 1/4 |
| *Biso, Å2* | 1.9(4) | 1.4(9) | 1.3(9) |
| *G* | 0.5 | 0.5 | 0.5 |

*The data in Table S2 is given here for La9-xGdx(SiO4)6OOH as an example. Such data for other REapatite silicates may be obtained from the corresponding author* (prisedskyvadim@mail.ru).

Table S3. Cationic site occupancies (G) in La9-xLnx(SiO4)6OOH

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Lanthanide Ln | (La) | Nd | Eu | | Gd | | Tm |
| Substitution, *x* | *x* = 0 | *x* = 9 | *x =*6 | *x =* 9 | *x =* 6 | *x =* 9 | *x =* 1.5 |
| Cation(site) | Occupancy (G) | | | | | | |
| La(1) (4f) | 0.805(4) |  | 0.242(2) |  | 0.260(3) |  | 0.668(3) |
| Ln(1) (4f) |  | 0.807(4) | 0.542(2) | 0.815(4) | 0.527(3) | 0.850(4) | 0.142(3) |
| La(2) (6h) | 0.963(4) |  | 0.338(2) |  | 0.327(3) |  | 0,805(3) |
| Ln(2) (6h) |  | 0.962(4) | 0.638(2) | 0.956(4) | 0.648(3) | 0.933(4) | 0.155(3) |

Table S4. Selected interatomic distances in in La9-xLnx(SiO4)6OOH

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Bond | La | Nd | Eu | Eu | Gd | Gd | Tm |
| *x* = 0 | *x* = 9 | *x=*6 | *x =* 9 | *x =* 6 | *x =* 9 | *x =* 1.5 |
| Ln(1) – O(1)×3 | 2.48(3) | 2.46(6) | 2.42(3) | 2.45(5) | 2.46(1) | 2.44(6) | 2.46(4) |
| Ln(1) – O(2)×3 | 2.56(2) | 2.51(5) | 2.52(3) | 2.41(5) | 2.44(4) | 2.35(5) | 2.53(4) |
| Ln(1) – O(3)×3 | 2.80(2) | 2.83(3) | 2.84(3) | 2.83(4) | 2.85(5) | 2.89(4) | 2.83(4) |
| <Ln(1) – O(1, 2, 3)> | 2.61 | 2.60 | 2.59 | 2.56 | 2.58 | 2.56 | 2.61 |
| Ln(2) – O(1) | 2.75(4) | 2.96(6) | 2.67(4) | 2.88(7) | 2.71(6) | 2.73(8) | 2.81(5) |
| Ln(2) – O(2) | 2.54(3) | 2.44(4) | 2.41(3) | 2.35(7) | 2.43(5) | 2.36(8) | 2.47(3) |
| Ln(2) – O(3)×2 | 2.57(2) | 2.54(3) | 2.54(3) | 2.52(4) | 2.51(2) | 2.43(4) | 2.55(3) |
| Ln(2) – O(3)×2 | 2.49(2) | 2.36(4) | 2.37(2) | 2.27(3) | 2.35(3) | 2.28(4) | 2.41(3) |
| <Ln(2) – O(1, 2, 3)> | 2.57 | 2.53 | 2.48 | 2.47 | 2.48 | 2.45 | 2.53 |
| Ln(2) – OH,O(4) | 2.514(8) | 2.36(3) | 2.258(6) | 2.24(2) | 2.252(8) | 2.22(2) | 2.42(5) |
| Ln(2) – Ln(2) | 3.991(5) | 3.94(4) | 3.912(8) | 3.88(2) | 3.892(6) | 3.85(2) | 3.96(5) |
| Si – O(1) | 1.63(5) | 1.52(7) | 1.66(5) | 1.47(9) | 1.56(4) | 1.48(1) | 1.54(6) |
| Si – O(2) | 1.55(3) | 1.74(5) | 1.56(4) | 1.70(7) | 1.58(3) | 1.75(9) | 1.70(4) |
| Si – O(3)×2 | 1.66(2) | 1.70(4) | 1.62(3) | 1.68(4) | 1.64(2) | 1.72(5) | 1.68(4) |
| <Si – O> | 1.62 | 1.67 | 1.62 | 1.63 | 1.61 | 1.63 | 1.65 |