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**Supporting information for article:**

# Synthesis of new Ln4(Al2O6F2)O2 (Ln = Sm, Eu, Gd) phases with a cuspidine-related structure

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## Supporting information

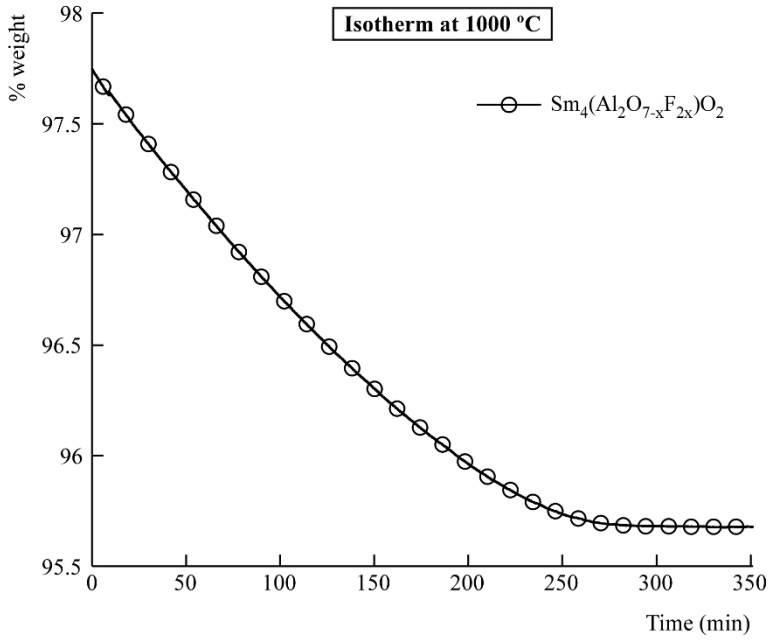


***Figure S1.*** Thermogravimetric analysis (TGA) isotherm of $Sm_4(Al_2O_6F_2)O_2$ phase at 1000 ºC. The isotherm starting point corresponds to the weight loss observed at 1000 ºC (time= 0 min).

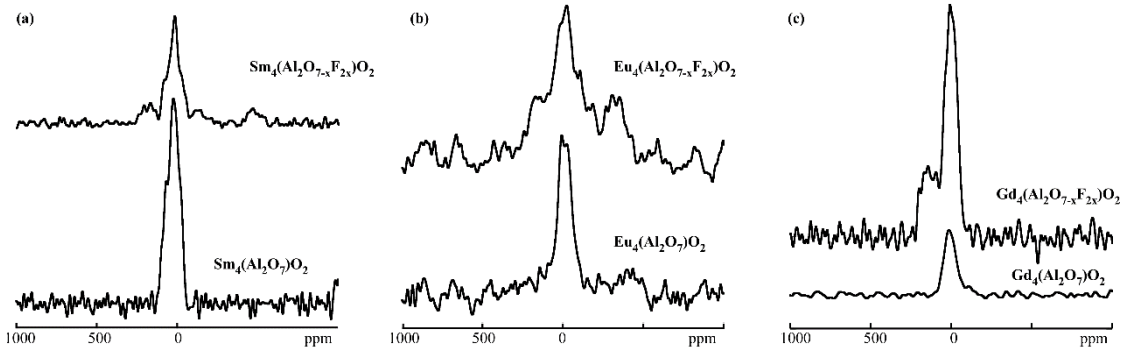


***Figure S2.*** $^{27}Al$ NMR spectra (a-c) of $Ln_4(Al_2O_7)O_2$ and $Ln_4(Al_2O_6F_2)O_2$ phases in which (a) Ln=Sm, (b) Ln=Eu and (c) Ln=Gd.

***Table S1.*** Refined cell parameters for $Sm_4(Al_2O_7\square)O_2$ and $Eu_4(Al_2O_7\square)O_2$ and their fluorinated derivatives in space group $P2_1/c$.

| ***Sample*** | ***a (Å)*** | ***b (Å)*** | ***c (Å)*** | ***β(º)*** |
|---|---|---|---|---|
| $Sm_4(Al_2O_7\square)O_2$ | 7.6356(5) | 10.7312(8) | 11.2307(8) | 109.23(1) |
| $Sm_4(Al_2O_6F_2)O_2$ | 7.6186(8) | 10.870(1) | 11.107(1) | 108.80(1) |
| $Eu_4(Al_2O_7\square)O_2$ | 7.5891(4) | 10.6833(6) | 11.2014(6) | 109.14(1) |
| $Eu_4(Al_2O_6F_2)O_2$ | 7.5885(7) | 10.839(1) | 11.077(1) | 108.78(1) |

***Table S2.*** Refined positional parameters for $Sm_4(Al_2O_7□)O_2$ and their fluorinated derivative in space group $P2_1/c$.

| ***$Sm_4(Al_2O_7□)O_2$*** | | | | ***$Sm_4(Al_2O_6F_2)O_2$*** | | | |
|---|---|---|---|---|---|---|---|
| **Atom** | **x** | **y** | **z** | **Atom** | **x** | **y** | **z** |
| Sm1 | 0.531(2) | 0.0998(8) | 0.7887(7) | Sm1 | 0.5304(7) | 0.0876(5) | 0.7899(4) |
| Sm2 | 0.022(2) | 0.0888(8) | 0.8103(7) | Sm2 | 0.0270(7) | 0.0759(4) | 0.8243(4) |
| Sm3 | 0.335(2) | 0.124(1) | 0.4221(9) | Sm3 | 0.3326(9) | 0.1310(5) | 0.4140(4) |
| Sm4 | 0.834(2) | 0.122(1) | 0.423(1) | Sm4 | 0.8389(7) | 0.1324(5) | 0.4284(4) |
| Al1 | 0.201(8) | 0.176(5) | 0.122(5) | Al1 | 0.199(1) | 0.1837(7) | 0.1338(8) |
| Al2 | 0.682(7) | 0.183(5) | 0.121(5) | Al2 | 0.682(1) | 0.1832(8) | 0.1212(7) |
| O1 | 0.79(1) | 0.248(7) | 0.751(8) | O1 | 0.790(1) | 0.2381(8) | 0.7523(8) |
| O2 | 0.25(1) | 0.225(7) | 0.764(8) | O2 | 0.244(1) | 0.2095(7) | 0.7676(9) |
| O3 | 0.19(1) | 0.017(1) | 0.156(7) | O3 | 0.194(1) | 0.0166(8) | 0.156(2) |
| O4 | 0.07(1) | 0.233(8) | 0.976(7) | O4 | 0.085(3) | 0.230(2) | 0.979(1) |
| O5 | 0.41(1) | 0.224(5) | 0.107(6) | F1 | 0.414(1) | 0.2237(9) | 0.1070(8) |
| O6 | 0.64(1) | 0.231(9) | 0.970(7) | O6 | 0.639(5) | 0.222(2) | 0.967(1) |
| O7 | 0.682(9) | 0.01(1) | 0.160(6) | O7 | 0.682(2) | 0.0124(9) | 0.160(2) |
| O8 | 0.08(1) | -0.008(9) | 0.379(8) | O8 | 0.072(1) | -0.0044(8) | 0.4088(7) |
| O9 | 0.54(2) | 0.02(1) | 0.389(8) | O9 | 0.536(1) | 0.0217(8) | 0.4004(8) |
| - | - | - | - | F2 | 0.052(1) | 0.7711(9) | 0.3416(8) |

***Table S3.*** Refined positional parameters for $Eu_4(Al_2O_7□)O_2$ and their fluorinated derivative in space group $P2_1/c$.

| ***$Eu_4(Al_2O_7□)O_2$*** | | | | ***$Eu_4(Al_2O_6F_2)O_2$*** | | | |
|---|---|---|---|---|---|---|---|
| **Atom** | **x** | **y** | **z** | **Atom** | **x** | **y** | **z** |
| Eu1 | 0.5268(7) | 0.0994(5) | 0.7892(4) | Eu1 | 0.5336(7) | 0.0850(5) | 0.7979(4) |
| Eu2 | 0.0256(7) | 0.0929(4) | 0.8089(4) | Eu2 | 0.0252(7) | 0.0759(4) | 0.8236(4) |
| Eu3 | 0.3343(8) | 0.1233(5) | 0.4228(4) | Eu3 | 0.3323(8) | 0.1313(5) | 0.4146(5) |
| Eu4 | 0.8349(7) | 0.1221(5) | 0.4224(5) | Eu4 | 0.8367(7) | 0.1303(4) | 0.4242(4) |
| Al1 | 0.192(1) | 0.1818(8) | 0.1171(7) | Al1 | 0.194(1) | 0.2046(7) | 0.1270(7) |
| Al2 | 0.690(1) | 0.1776(7) | 0.1351(7) | Al2 | 0.690(1) | 0.1776(7) | 0.1351(7) |
| O1 | 0.790(1) | 0.2482(8) | 0.7508(8) | O1 | 0.784(3) | 0.230(1) | 0.7590(9) |
| O2 | 0.246(1) | 0.2252(8) | 0.7644(8) | O2 | 0.246(1) | 0.2028(7) | 0.7727(9) |
| O3 | 0.194(2) | 0.017(1) | 0.156(4) | O3 | 0.191(2) | 0.0357(9) | 0.136(3) |
| O4 | 0.071(3) | 0.233(2) | 0.9759(9) | O4 | 0.073(3) | 0.228(2) | 0.976(1) |
| O5 | 0.414(1) | 0.224(2) | 0.107(2) | F1 | 0.414(2) | 0.224(3) | 0.107(2) |
| O6 | 0.644(3) | 0.231(2) | 0.9704(8) | O6 | 0.662(3) | 0.214(1) | 0.9808(8) |
| O7 | 0.682(2) | 0.012(1) | 0.160(3) | O7 | 0.682(2) | 0.0124(8) | 0.160(2) |
| O8 | 0.075(1) | -0.0082(9) | 0.3790(7) | O8 | 0.074(1) | -0.0051(8) | 0.3783(7) |
| O9 | 0.537(1) | 0.0222(8) | 0.3890(8) | O9 | 0.532(1) | 0.0201(8) | 0.3961(8) |
| - | - | - | - | F2 | 0.051(1) | 0.7606(9) | 0.3570(8) |

**Table S4.** Selected bond distances (diagonal) (Å) and angles (º) for $Sm_4(Al_2O_7)O_2$ from the full structural refinement.

| **Sm(1)** | O(1) | O(2) | O(3) | O(5) | O(6) | O(7) | O(9) |
|---|---|---|---|---|---|---|---|
| O(9) | 99.61(1) | 105.88(1) | 81.47(1) | 79.64(1) | 171.69(2) | 86.64(1) | **2.298(1)** |
| O(7) | 173.75(2) | 68.82(1) | 107.91(2) | 118.84(2) | 100.82(1) | **2.243(1)** | |
| O(6) | 72.96(1) | 80.46(1) | 92.66(1) | 99.65(2) | **2.394(1)** | | |
| O(5) | 62.68(1) | 58.89(1) | 127.88(2) | **2.710(1)** | | | |
| O(3) | 73.44(1) | 171.46(2) | **2.344(1)** | | | | |
| O(2) | 108.94(2) | **2.494(1)** | | | | | |
| O(1) | **2.680(1)** | | | | | | |

| **Sm(2)** | O(1) | O(2) | O(3) | O(4) | O(7) | O(8) |
|---|---|---|---|---|---|---|
| O(8) | 91.67(1) | 93.91(1) | 85.91(1) | 160.75(2) | 87.51(2) | **2.186(1)** |
| O(7) | 158.04(2) | 67.11(1) | 118.55(2) | 106.70(1) | **2.428(1)** | |
| O(4) | 70.26(1) | 80.30(1) | 98.05(1) | **2.351(1)** | | |
| O(3) | 83.24(1) | 174.31(2) | **2.137(1)** | | | |
| O(2) | 91.08(1) | **2.430(1)** | | | | |
| O(1) | **2.395(1)** | | | | | |

| **Sm(3)** | O(2) | O(4) | O(5) | O(6) | O(8) | O(9) | O(9)´ |
|---|---|---|---|---|---|---|---|
| O(9)´ | 172.77(2) | 105.49(2) | 78.16(1) | 96.65(1) | 82.47(1) | 73.56(1) | **2.556(1)** |
| O(9) | 106.53(2) | 177.45(2) | 120.23(2) | 71.42(1) | 106.42(2) | **2.020(1)** | |
| O(8) | 104.25(2) | 75.69(1) | 120.67(2) | 177.83(2) | **2.355(1)** | | |
| O(6) | 76.72(1) | 106.47(2) | 60.94(1) | **2.731(1)** | | | |
| O(5) | 95.89(2) | 57.22(1) | **2.556(1)** | | | | |
| O(4) | 74.10(1) | **2.755(1)** | | | | | |
| O(2) | **2.332(1)** | | | | | | |

*O(9)´: -x, -y, -z

| **Sm(4)** | O(1) | O(4) | O(6) | O(8) | O(8)´ | O(9) |
|---|---|---|---|---|---|---|
| O(9) | 105.27(1) | 162.08(2) | 73.27(1) | 115.77(2) | 83.70(2) | **2.424(1)** |
| O(8)´ | 170.41(2) | 97.96(1) | 98.13(1) | 83.73(1) | **2.433(1)** | |
| O(8) | 95.11(1) | 82.12(1) | 170.95(2) | **2.483(1)** | | |
| O(6) | 81.58(1) | 88.85(1) | **2.320(1)** | | | |
| O(4) | 72.46(1) | **2.310(1)** | | | | |
| O(1) | **2.311(1)** | | | | | |

*O(8)´: -x, -y, -z

| **Al(1)** | O(2) | O(3) | O(4) | O(5) |
|---|---|---|---|---|
| O(5) | 90.24(1) | 113.40(2) | 93.60(2) | **1.768(1)** |
| O(4) | 120.11(2) | 120.09(2) | **1.729(1)** | |
| O(3) | 112.48(2) | **1.755(1)** | | |
| O(2) | **1.851(1)** | | | |

| **Al(2)** | O(1) | O(5) | O(6) | O(7) |
|---|---|---|---|---|
| O(7) | 105.98(2) | 98.65(2) | 120.76(2) | **1.884(1)** |
| O(6) | 129.49(3) | 91.24(1) | **1.701(1)** | |
| O(5) | 100.15(2) | **2.041(1)** | | |
| O(1) | **1.596(1)** | | | |

**Table S5.** Bond-valence for $Sm_4(Al_2O_7)O_2$ phase calculated from the Rietveld refinement.

| | Sm(1) | Sm(2) | Sm(3) | Sm(4) | Al(1) | Al(2) | |
|---|---|---|---|---|---|---|---|
| O(1) | 0.20(1) | 0.44(1) | | 0.55(1) | | 1.07(1) | 2.25(1) |
| O(2) | 0.33(1) | 0.40(1) | 0.52(1) | | 0.54(1) | | 1.78(1) |
| O(3) | 0.50(1) | 0.88(1) | | | 0.69(1) | | 2.07(1) |
| O(4) | | 0.49(1) | 0.16(1) | 0.55(1) | 0.75(1) | | 1.95(1) |
| O(5) | 0.19(1) | | 0.28(1) | | 0.67(1) | 0.32(1) | 1.46(1) |
| O(6) | 0.44(1) | | 0.18(1) | 0.53(1) | | 0.80(1) | 1.95(1) |
| O(7) | 0.66(1) | 0.40(1) | | | | 0.49(1) | 1.55(1) |
| O(8) | | 0.77(1) | 0.49(1) | 0.34(1) | | | |
| O(8)´ | | | | 0.39(1) | | | 1.99(1) |
| O(9) | 0.57(1) | | 1.20(1) | 0.40(1) | | | |
| O(9)´ | | | 0.28(1) | | | | 2.45(1) |
| | 2.88(1) | 3.37(1) | 3.11(1) | 2.77(1) | 2.65(1) | 2.68(1) | Valence |

*O(8)´: -x, -y, -z; O(9)´: -x, -y, -z

**Table S6.** Selected bond distances (diagonal) (Å) and angles (º) for $Sm_4(Al_2O_6F_2)O_2$ from the full structural refinement.

| **Sm(1)** | O(1) | O(2) | O(3) | F(1) | O(6) | O(7) | O(9) |
|---|---|---|---|---|---|---|---|
| O(9) | 97.13(1) | 104.63(1) | 84.16(2) | 77.98(1) | 168.41(2) | 90.78(1) | **2.334(1)** |
| O(7) | 171.48(2) | 65.77(1) | 112.49(2) | 117.53(2) | 100.74(1) | **2.166(1)** | |
| O(6) | 71.30(1) | 79.30(1) | 92.52(1) | 95.34(2) | **2.380(1)** | | |
| F(1) | 61.53(1) | 58.78(1) | 126.67(2) | **2.821(1)** | | | |
| O(3) | 71.67(1) | 170.91(2) | **2.286(1)** | | | | |
| O(2) | 108.88(2) | **2.496(1)** | | | | | |
| O(1) | **2.701(1)** | | | | | | |

| **Sm(2)** | O(1) | O(2) | O(3) | O(4) | O(7) | O(8) | F(2) |
|---|---|---|---|---|---|---|---|
| F(2) | 44.14(1) | 54.02(1) | 114.32(1) | 90.63(2) | 109.36(2) | 61.25(1) | **2.410(1)** |
| O(8) | 86.80(1) | 85.51(1) | 88.60(1) | 151.87(2) | 84.98(2) | **2.573(1)** | |
| O(7) | 152.01(2) | 64.06(1) | 125.46(2) | 106.61(1) | **2.369(1)** | | |
| O(4) | 70.89(1) | 77.30(1) | 103.98(1) | **2.339(1)** | | | |
| O(3) | 80.94(1) | 168.33(2) | **2.035(1)** | | | | |
| O(2) | 88.67(1) | **2.431(1)** | | | | | |
| O(1) | **2.465(1)** | | | | | | |

| **Sm(3)** | O(2) | O(4) | F(1) | O(6) | O(8) | O(9) | O(9)´ |
|---|---|---|---|---|---|---|---|
| O(9)´ | 171.17(2) | 105.68(1) | 78.57(1) | 96.75(1) | 74.73(1) | 64.41(1) | **2.584(1)** |
| O(9) | 116.64(2) | 169.26(2) | 116.28(1) | 74.52(1) | 106.52(2) | **1.997(1)** | |
| O(8) | 112.32(1) | 73.21(1) | 111.31(2) | 169.38(2) | **2.460(2)** | | |
| O(6) | 75.61(1) | 103.73(2) | 59.99(1) | **2.728(1)** | | | |
| F(1) | 93.59(2) | 55.46(1) | **2.573(1)** | | | | |
| O(4) | 72.47(1) | **2.693(1)** | | | | | |
| O(2) | **2.323(1)** | | | | | | |

*O(9)´: -x, -y, -z

| **Sm(4)** | O(1) | O(4) | O(6) | O(8) | O(8)´ | O(9) | F(2) |
|---|---|---|---|---|---|---|---|
| F(2) | 119.10(2) | 61.94(1) | 64.63(1) | 109.01(1) | 62.58(1) | 107.38(2) | **2.636(1)** |
| O(9) | 106.86(1) | 165.68(2) | 73.71(1) | 111.61(2) | 80.21(1) | **2.531(1)** | |
| O(8)´ | 170.88(2) | 101.22(1) | 108.84(1) | 68.75(1) | **2.208(1)** | | |
| O(8) | 102.85(1) | 81.85(1) | 173.14(2) | **2.3758(2)** | | | |
| O(6) | 79.08(1) | 92.50(1) | **2.329(1)** | | | | |
| O(4) | 73.41(1) | **2.323(1)** | | | | | |
| O(1) | **2.341(1)** | | | | | | |

*O(8)´: -x, -y, -z

| **Al(1)** | O(2) | O(3) | O(4) | F(1) | F(2) |
|---|---|---|---|---|---|
| F(2) | 64.77(1) | 110.64(2) | 79.81(1) | 140.84(2) | **2.227(1)** |
| F(1) | 92.17(1) | 108.41(1) | 87.60(2) | **1.814(1)** | |
| O(4) | 121.70(2) | 113.36(2) | **1.728(1)** | | |
| O(3) | 121.68(2) | **1.835(1)** | | | |
| O(2) | **1.829(1)** | | | | |

| **Al(2)** | O(1) | F(1) | O(6) | O(7) | F(2) |
|---|---|---|---|---|---|
| F(2) | 55.51(1) | 140.64(2) | 86.86(2) | 117.04(2) | **2.159(1)** |
| O(7) | 109.78(2) | 99.00(1) | 117.50(2) | **1.907(1)** | |
| O(6) | 129.56(2) | 90.24(1) | **1.688(1)** | | |
| F(1) | 99.12(2) | **2.040(1)** | | | |
| O(1) | **1.660(1)** | | | | |

**Table S7.** Bond-valence for $Sm_4(Al_2O_6F_2)O_2$ phase calculated from Rietveld refinement.

| | Sm(1) | Sm(2) | Sm(3) | Sm(4) | Al(1) | Al(2) | |
|---|---|---|---|---|---|---|---|
| O(1) | 0.19(1) | 0.36(1) | | 0.50(1) | | 0.90(1) | 1.96(1) |
| O(2) | 0.33(1) | 0.40(1) | 0.53(1) | | 0.57(1) | | 1.82(1) |
| O(3) | 0.59(1) | 1.15(1) | | | 0.56(1) | | 2.30(1) |
| O(4) | | 0.51(1) | 0.20(1) | 0.53(1) | 0.75(1) | | 1.98(1) |
| F(1) | 0.11(1) | | 0.21(1) | | 0.48(1) | 0.26(1) | 1.06(1) |
| O(6) | 0.45(1) | | 0.18(1) | 0.52(1) | | 0.83(1) | 1.98(1) |
| O(7) | 0.81(1) | 0.47(1) | | | | 0.46(1) | 1.74(1) |
| O(8) | | 0.27(1) | 0.37(1) | 0.46(1) | | | |
| O(8)´ | | | | 0.72(1) | | | 1.82(1) |
| O(9) | 0.51(1) | | 1.28(1) | 0.30(1) | | | |
| O(9)´ | | | 0.26(1) | | | | 2.36(1) |
| F(2) | | 0.31(1) | | 0.18(1) | 0.16(1) | 0.19(1) | 0.83(1) |
| | 3.00(1) | 3.46(1) | 3.01(1) | 3.22(1) | 2.52(1) | 2.64(1) | Valence |

*O(8)´: -x, -y, -z; O(9)´: -x, -y, -z

**Table S8.** Selected bond distances (diagonal) (Å) and angles (º) for $Eu_4(Al_2O_7)O_2$ from the full structural refinement.

| **Eu(1)** | O(1) | O(2) | O(3) | O(5) | O(6) | O(7) | O(9) |
|---|---|---|---|---|---|---|---|
| O(9) | 98.72(1) | 106.45(1) | 81.02(1) | 79.35(1) | 170.20(1) | 87.23(1) | **2.296(1)** |
| O(7) | 174.02(1) | 69.77(1) | 107.99(1) | 119.80(1) | 101.55(1) | **2.203(1)** | |
| O(6) | 72.48(1) | 80.94(1) | 92.03(1) | 99.65(1) | **2.388(1)** | | |
| O(5) | 62.26(1) | 59.06(1) | 126.77(1) | **2.706(1)** | | | |
| O(3) | 72.71(1) | 171.86(1) | **2.353(1)** | | | | |
| O(2) | 108.68(1) | **2.458(1)** | | | | | |
| O(1) | **2.693(1)** | | | | | | |

| **Eu(2)** | O(1) | O(2) | O(3) | O(4) | O(7) | O(8) |
|---|---|---|---|---|---|---|
| O(8) | 91.83(1) | 95.28(1) | 84.56(1) | 162.12(1) | 87.64(1) | **2.186(1)** |
| O(7) | 160.65(1) | 68.18(1) | 116.61(1) | 107.28(1) | **2.407(1)** | |
| O(4) | 70.80(1) | 81.71(1) | 96.96(1) | **2.331(1)** | | |
| O(3) | 82.55(1) | 175.18(1) | **2.178(1)** | | | |
| O(2) | 92.64(1) | **2.363(1)** | | | | |
| O(1) | **2.370(1)** | | | | | |

| **Eu(3)** | O(2) | O(4) | O(5) | O(6) | O(8) | O(9) | O(9)´ |
|---|---|---|---|---|---|---|---|
| O(9)´ | 172.65(1) | 105.80(1) | 78.21(1) | 96.60(1) | 82.80(1) | 73.68(1) | **2.542(1)** |
| O(9) | 106.04(1) | 177.41(1) | 120.16(1) | 71.30(1) | 106.35(1) | **2.015(1)** | |
| O(8) | 104.17(1) | 76.02(1) | 121.15(1) | 177.64(1) | **2.336(1)** | | |
| O(6) | 76.53(1) | 106.34(1) | 60.83(1) | **2.723(1)** | | | |
| O(5) | 95.95(1) | 57.32(1) | **2.545(1)** | | | | |
| O(4) | 74.14(1) | **2.734(1)** | | | | | |
| O(2) | **2.332(1)** | | | | | | |

*O(9)´: -x, -y, -z

| **Eu(4)** | O(1) | O(4) | O(6) | O(8) | O(8)´ | O(9) |
|---|---|---|---|---|---|---|
| O(9) | 105.12(1) | 161.81(1) | 73.20(1) | 115.73(1) | 83.63(1) | **2.415(1)** |
| O(8)´ | 170.52(1) | 97.90(1) | 97.88(1) | 83.84(1) | **2.429(1)** | |
| O(8) | 95.33(1) | 82.42(1) | 171.07(1) | **2.464(1)** | | |
| O(6) | 81.52(1) | 88.66(1) | **2.314(1)** | | | |
| O(4) | 72.65(1) | **2.296(1)** | | | | |
| O(1) | **2.302(1)** | | | | | |

*O(8)´: -x, -y, -z

| **Al(1)** | O(2) | O(3) | O(4) | O(5) |
|---|---|---|---|---|
| O(5) | 89.18(1) | 108.95(1) | 95.56(1) | **1.784(1)** |
| O(4) | 124.73(1) | 120.91(1) | **1.640(1)** | |
| O(3) | 108.96(1) | **1.816(1)** | | |
| O(2) | **1.854(1)** | | | |

| **Al(2)** | O(1) | O(5) | O(6) | O(7) |
|---|---|---|---|---|
| O(7) | 114.79(1) | 99.92(1) | 117.13(1) | **1.791(1)** |
| O(6) | 125.27(1) | 85.60(1) | **1.851(1)** | |
| O(5) | 101.63(1) | **2.074(1)** | | |
| O(1) | **1.496(1)** | | | |

**Table S9.** Bond-valence for $Eu_4(Al_2O_7)O_2$ phase calculated from Rietveld refinement.

| | Eu(1) | Eu(2) | Eu(3) | Eu(4) | Al(1) | Al(2) | |
|---|---|---|---|---|---|---|---|
| O(1) | 0.19(1) | 0.45(1) | | 0.54(1) | | 1.40(1) | 2.58(1) |
| O(2) | 0.35(1) | 0.46(1) | 0.50(1) | | 0.53(1) | | 1.84(1) |
| O(3) | 0.47(1) | 0.76(1) | | | 0.59(1) | | 1.81(1) |
| O(4) | | 0.50(1) | 0.17(1) | 0.55(1) | 0.95(1) | | 2.16(1) |
| O(5) | 0.18(1) | | 0.28(1) | | 0.64(1) | 0.29(1) | 1.40(1) |
| O(6) | 0.43(1) | | 0.17(1) | 0.52(1) | | 0.54(1) | 1.66(1) |
| O(7) | 0.70(1) | 0.41(1) | | | | 0.63(1) | 1.74(1) |
| O(8) | | 0.74(1) | 0.49(1) | 0.35(1) | | | |
| O(8)´ | | | | 0.38(1) | | | 1.96(1) |
| O(9) | 0.55(1) | | 1.17(1) | 0.40(1) | | | |
| O(9)´ | | | 0.28(1) | | | | 2.40(1) |
| | 2.88(1) | 3.31(1) | 3.07(1) | 2.74(1) | 2.71(1) | 2.86(1) | Valence |

*O(8)´: -x, -y, -z; O(9)´: -x, -y, -z

**Table S10.** Selected bond distances (diagonal) (Å) and angles (º) for $Eu_4(Al_2O_6F_2)O_2$ from the full structural refinement.

| **Eu(1)** | O(1) | O(2) | O(3) | F(1) | O(6) | O(7) | O(9) |
|---|---|---|---|---|---|---|---|
| O(9) | 95.26(1) | 103.27(1) | 85.37(1) | 75.73(1) | 165.69(2) | 90.45(1) | **2.340(1)** |
| O(7) | 172.52(2) | 64.17(1) | 108.96(2) | 115.78(1) | 103.82(1) | **2.121(1)** | |
| O(6) | 70.61(1) | 84.24(1) | 88.96(1) | 98.46(2) | **2.394(1)** | | |
| F(1) | 61.32(1) | 59.28(1) | 131.06(2) | **2.891(1)** | | | |
| O(3) | 76.39(1) | 168.63(2) | **2.376(1)** | | | | |
| O(2) | 109.66(2) | **2.468(1)** | | | | | |
| O(1) | **2.609(1)** | | | | | | |

| **Eu(2)** | O(1) | O(2) | O(3) | O(4) | O(7) | O(8) | F(2) |
|---|---|---|---|---|---|---|---|
| F(2) | 48.58(1) | 54.42(1) | 122.57(2) | 91.14(2) | 107.67(1) | 63.05(1) | **2.595(1)** |
| O(8) | 87.84(1) | 89.84(1) | 88.91(1) | 153.52(2) | 86.71(1) | **2.252(1)** | |
| O(7) | 154.81(2) | 62.41(1) | 120.28(2) | 108.09(1) | **2.370(1)** | | |
| O(4) | 69.34(1) | 78.56(1) | 101.44(1) | **2.309(1)** | | | |
| O(3) | 84.16(1) | 176.95(2) | **2.194(1)** | | | | |
| O(2) | 93.02(1) | **2.369(1)** | | | | | |
| O(1) | **2.408(1)** | | | | | | |

| **Eu(3)** | O(2) | O(4) | F(1) | O(6) | O(8) | O(9) | O(9)´ |
|---|---|---|---|---|---|---|---|
| O(9)´ | 168.50(2) | 106.22(1) | 77.84(1) | 94.36(1) | 80.52(1) | 65.48(1) | **2.600(1)** |
| O(9) | 116.97(2) | 171.55(2) | 117.84(1) | 75.78(1) | 102.58(1) | **1.997(1)** | |
| O(8) | 108.98(1) | 76.69(1) | 119.22(2) | 174.82(2) | **2.384(1)** | | |
| O(6) | 76.02(1) | 104.18(1) | 58.40(1) | **2.907(1)** | | | |
| F(1) | 91.60(2) | 56.83(1) | **2.558(1)** | | | | |
| O(4) | 70.83(1) | **2.740(1)** | | | | | |
| O(2) | **2.340(1)** | | | | | | |

*O(9)´: -x, -y, -z

| **Eu(4)** | O(1) | O(4) | O(6) | O(8) | O(8)´ | O(9) | F(2) |
|---|---|---|---|---|---|---|---|
| F(2) | 111.34(2) | 57.37(1) | 57.69(1) | 114.67(1) | 60.54(1) | 110.15(2) | **2.582(1)** |
| O(9) | 107.18(1) | 163.41(2) | 78.58(1) | 112.80(2) | 80.16(1) | **2.532(1)** | |
| O(8)´ | 171.06(2) | 100.06(1) | 100.13(1) | 81.23(1) | **2.477(1)** | | |
| O(8) | 100.09(1) | 83.47(1) | 168.55(2) | **2.499(1)** | | | |
| O(6) | 76.83(1) | 85.09(1) | **2.353(1)** | | | | |
| O(4) | 71.42(1) | **2.289(1)** | | | | | |
| O(1) | **2.309(1)** | | | | | | |

*O(8)´: -x, -y, -z

| **Al(1)** | O(2) | O(3) | O(4) | F(1) | F(2) |
|---|---|---|---|---|---|
| **F(2)** | 72.54(1) | 105.53(1) | 79.40(1) | 155.66(2) | **2.012(1)** |
| **F(1)** | 95.88(1) | 98.80(1) | 95.34(2) | **1.771(1)** | |
| **O(4)** | 134.42(2) | 101.52(2) | **1.644(1)** | | |
| **O(3)** | 120.05(2) | **1.834(1)** | | | |
| **O(2)** | **1.833(1)** | | | | |
| **Al(2)** | O(1) | F(1) | O(6) | O(7) | F(2) |
| F(2) | 64.44(1) | 140.72(2) | 76.12(1) | 119.07(2) | **2.137(1)** |
| O(7) | 119.59(2) | 100.21(1) | 112.52(2) | **1.816(1)** | |
| O(6) | 124.96(2) | 90.00(1) | **1.698(1)** | | |
| F(1) | 96.99(2) | **2.078(1)** | | | |
| O(1) | **1.664(1)** | | | | |

**Table S11.** Bond-valence for $Eu_4(Al_2O_6F_2)O_2$ phase calculated from Rietveld refinement.

| | Eu(1) | Eu(2) | Eu(3) | Eu(4) | Al(1) | Al(2) | |
|---|---|---|---|---|---|---|---|
| O(1) | 0.24(1) | 0.41(1) | | 0.53(1) | | 0.89(1) | 2.06(1) |
| O(2) | 0.34(1) | 0.45(1) | 0.49(1) | | 0.56(1) | | 1.84(1) |
| O(3) | 0.44(1) | 0.72(1) | | | 0.56(1) | | 1.79(1) |
| O(4) | | 0.53(1) | 0.16(1) | 0.56(1) | 0.94(1) | | 2.19(1) |
| F(1) | 0.08(1) | | 0.20(1) | | 0.54(1) | 0.24(1) | 1.06(1) |
| O(6) | 0.42(1) | | 0.10(1) | 0.47(1) | | 0.81(1) | 1.81(1) |
| O(7) | 0.88(1) | 0.45(1) | | | | 0.59(1) | 1.99(1) |
| O(8) | | 0.62(1) | 0.43(1) | 0.32(1) | | | |
| O(8)´ | | | | 0.34(1) | | | 1.70(1) |
| O(9) | 0.49(1) | | 1.23(1) | 0.29(1) | | | |
| O(9)´ | | | 0.24(1) | | | | 2.25(1) |
| F(2) | | 0.18(1) | | 0.19(1) | 0.28(1) | 0.20(1) | 0.85(1) |
| | 2.89(1) | 3.36(1) | 2.86(1) | 2.69(1) | 2.89(1) | 2.72(1) | Valence |

*O(8)´: -x, -y, -z; O(9)´: -x, -y, -z