

## Supplementary Information

**Table S1.** Crystallographic data for selected crystals of the series  $\text{Ca}_{1-x}\text{Na}_x\text{FFeAs}$ . (Na contents are adopted from EDX analyses.)

| $x$ in $\text{Ca}_{1-x}\text{Na}_x\text{FFeAs}$                                    |                                            | 0                                                | 0.03          | 0.08          | 0.14          |
|------------------------------------------------------------------------------------|--------------------------------------------|--------------------------------------------------|---------------|---------------|---------------|
| Crystal system                                                                     |                                            | tetragonal                                       |               |               |               |
| Space group                                                                        |                                            | $P4/nmm$ (No. 129)                               |               |               |               |
| Lattice parameters                                                                 | $a/\text{pm}$                              | 387.57(9)                                        | 387.57(2)     | 387.65(2)     | 387.68(3)     |
|                                                                                    | $c/\text{pm}$                              | 858.4(2)                                         | 859.48(5)     | 859.89(6)     | 859.87(9)     |
|                                                                                    | $c/a$                                      | 2.215                                            | 2.218         | 2.218         | 2.218         |
| Formula units per unit cell $Z$                                                    |                                            | 2                                                |               |               |               |
| Molar volume $V_m/\text{cm}^3\cdot\text{mol}^{-1}$                                 |                                            | 38.83                                            | 38.87         | 38.91         | 38.91         |
| Calculated density $D_x/\text{g}\cdot\text{cm}^{-3}$                               |                                            | 4.89                                             | 4.87          | 4.84          | 4.82          |
| Diffractometer                                                                     |                                            | Nonius KappaCCD (Bruker AXS, Karlsruhe, Germany) |               |               |               |
| Radiation                                                                          |                                            | Mo- $K\alpha$ ( $\lambda = 71.07$ pm)            |               |               |               |
| $hkl$ range                                                                        | $\pm h_{\max}, \pm k_{\max}, \pm l_{\max}$ | 5, 5, 11                                         | 5, 5, 12      | 6, 6, 13      | 5, 5, 11      |
|                                                                                    | $2\theta_{\max}/^\circ$                    | 58.80                                            | 60.66         | 71.20         | 56.27         |
|                                                                                    | $F(000)$                                   | 176                                              | 176           | 176           | 176           |
| Absorption correction                                                              |                                            | numerical (Program <i>HABITUS</i> [1])           |               |               |               |
| Absorption coefficient $\mu/\text{mm}^{-1}$                                        |                                            | 20.24                                            | 20.22         | 20.20         | 20.20         |
| Extinction coefficient $g$                                                         |                                            | –                                                | 0.0239        | 0.0226        | –             |
| Collected reflections                                                              |                                            | 1589                                             | 2278          | 3232          | 1622          |
| Unique reflections                                                                 |                                            | 118                                              | 145           | 211           | 118           |
| Reflexions with $ F_o  \geq 4\sigma(F_o)$                                          |                                            | 99                                               | 142           | 202           | 109           |
| Refined parameters                                                                 |                                            | 11                                               | 12            | 12            | 11            |
| $R_{\text{int}}, R_\sigma$                                                         |                                            | 0.083, 0.028                                     | 0.060, 0.018  | 0.068, 0.021  | 0.104, 0.039  |
| Solution and refinement                                                            |                                            | Program package <i>SHELX-97</i> [2,3]            |               |               |               |
| Scattering factors                                                                 |                                            | <i>International Tables</i> , Vol. C [4]         |               |               |               |
| $R_1, R_1$ with $ F_o  \geq 4\sigma(F_o)$                                          |                                            | 0.076, 0.062                                     | 0.018, 0.018  | 0.022, 0.021  | 0.026, 0.024  |
| $wR_2, \text{GooF}$                                                                |                                            | 0.157, 1.178                                     | 0.044, 1.168  | 0.053, 1.166  | 0.058, 1.165  |
| Residual electron density<br>$\rho_{\max}, \rho_{\min}/10^{-6}\cdot\text{pm}^{-3}$ |                                            | 2.03, $-1.73$                                    | 0.59, $-0.68$ | 1.30, $-0.87$ | 0.97, $-0.49$ |

**Table S2.** Atomic coordinates and equivalent isotropic displacement parameters for selected crystals of the series  $\text{Ca}_{1-x}\text{Na}_x\text{FFeAs}$ .

| Atom    | Site | $x/a$ | $y/b$ | $z/c$     | $U_{\text{eq}}^{(a)}/\text{pm}^2$ |
|---------|------|-------|-------|-----------|-----------------------------------|
| CaFFeAs |      |       |       |           |                                   |
| Ca      | 2c   | $1/4$ | $1/4$ | 0.1514(6) | 265(13)                           |
| F       | 2a   | $3/4$ | $1/4$ | 0         | 263(35)                           |
| Fe      | 2b   | $3/4$ | $1/4$ | $1/2$     | 251(11)                           |
| As      | 2c   | $1/4$ | $1/4$ | 0.6645(3) | 251(9)                            |

**Table S2. Cont.**

| Atom                                           | Site | $x/a$ | $y/b$ | $z/c$       | $U_{eq}^{(a)}/\text{pm}^2$ |
|------------------------------------------------|------|-------|-------|-------------|----------------------------|
| <b>Ca<sub>0.97</sub>Na<sub>0.03</sub>FFeAs</b> |      |       |       |             |                            |
| Ca/Na <sup>(b)</sup>                           | 2c   | $1/4$ | $1/4$ | 0.15111(12) | 84(3)                      |
| F                                              | 2a   | $3/4$ | $1/4$ | 0           | 90(6)                      |
| Fe                                             | 2b   | $3/4$ | $1/4$ | $1/2$       | 74(2)                      |
| As                                             | 2c   | $1/4$ | $1/4$ | 0.66461(5)  | 75(2)                      |
| <b>Ca<sub>0.92</sub>Na<sub>0.08</sub>FFeAs</b> |      |       |       |             |                            |
| Ca/Na <sup>(c)</sup>                           | 2c   | $1/4$ | $1/4$ | 0.15072(10) | 92(2)                      |
| F                                              | 2a   | $3/4$ | $1/4$ | 0           | 115(5)                     |
| Fe                                             | 2b   | $3/4$ | $1/4$ | $1/2$       | 88(2)                      |
| As                                             | 2c   | $1/4$ | $1/4$ | 0.66444(4)  | 90(2)                      |
| <b>Ca<sub>0.86</sub>Na<sub>0.14</sub>FFeAs</b> |      |       |       |             |                            |
| Ca/Na <sup>(d)</sup>                           | 2c   | $1/4$ | $1/4$ | 0.1513(2)   | 94(4)                      |
| F                                              | 2a   | $3/4$ | $1/4$ | 0           | 136(11)                    |
| Fe                                             | 2b   | $3/4$ | $1/4$ | $1/2$       | 105(4)                     |
| As                                             | 2c   | $1/4$ | $1/4$ | 0.66440(10) | 112(3)                     |

<sup>(a)</sup>  $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$ ; <sup>(b)</sup> Site occupation (from EDX): 97% Ca, 3% Na; <sup>(c)</sup> Site occupation (from EDX): 92% Ca, 8% Na; <sup>(d)</sup> Site occupation (from EDX): 86% Ca, 14% Na.

**Table S3.** Anisotropic displacement parameters ( $U_{ij}^{(a)}$  in  $\text{pm}^2$ ) for selected crystals of the series  $\text{Ca}_{1-x}\text{Na}_x\text{FFeAs}$ . ( $U_{12} = U_{13} = U_{23} = 0$  for all atoms.)

| Atom                                           | $U_{11} = U_{22}$ | $U_{33}$ |
|------------------------------------------------|-------------------|----------|
| <b>CaFFeAs</b>                                 |                   |          |
| Ca                                             | 241(19)           | 315(24)  |
| F                                              | 218(55)           | 352(67)  |
| Fe                                             | 195(14)           | 365(18)  |
| As                                             | 212(11)           | 329(15)  |
| <b>Ca<sub>0.97</sub>Na<sub>0.03</sub>FFeAs</b> |                   |          |
| Ca/Na                                          | 73(3)             | 106(5)   |
| F                                              | 74(8)             | 123(13)  |
| Fe                                             | 62(3)             | 99(4)    |
| As                                             | 69(2)             | 87(3)    |
| <b>Ca<sub>0.92</sub>Na<sub>0.08</sub>FFeAs</b> |                   |          |
| Ca/Na                                          | 82(2)             | 114(4)   |
| F                                              | 104(7)            | 137(11)  |
| Fe                                             | 77(2)             | 110(3)   |
| As                                             | 85(2)             | 99(2)    |
| <b>Ca<sub>0.86</sub>Na<sub>0.14</sub>FFeAs</b> |                   |          |
| Ca/Na                                          | 77(6)             | 127(9)   |
| F                                              | 146(17)           | 116(24)  |
| Fe                                             | 84(5)             | 148(7)   |
| As                                             | 97(4)             | 141(5)   |

<sup>(a)</sup> given in the expression  $\exp[-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2b^*c^*klU_{23} + 2a^*c^*hlU_{13} + 2a^*b^*hkU_{12})]$ .

**Table S4.** Interatomic distances and angles for selected crystals of the series  $\text{Ca}_{1-x}\text{Na}_x\text{FFeAs}$ .

| Distance                                    | d/pm       | Multiplicity | Distance            | d/pm       | Multiplicity |
|---------------------------------------------|------------|--------------|---------------------|------------|--------------|
| CaFFeAs                                     |            |              |                     |            |              |
| Ca–F                                        | 233.4(3)   | (4 ×)        | Fe–Fe               | 274.05(7)  | (4 ×)        |
| Ca–As                                       | 316.4(3)   | (4 ×)        | Fe–As               | 239.76(16) | (4 ×)        |
| Ca <sub>0.97</sub> Na <sub>0.03</sub> FFeAs |            |              |                     |            |              |
| Ca/Na–F                                     | 233.28(6)  | (4 ×)        | Fe–Fe               | 274.05(1)  | (4 ×)        |
| Ca/Na–As                                    | 316.53(6)  | (4 ×)        | Fe–As               | 239.94(3)  | (4 ×)        |
| Ca <sub>0.92</sub> Na <sub>0.08</sub> FFeAs |            |              |                     |            |              |
| Ca/Na–F                                     | 233.16(5)  | (4 ×)        | Fe–Fe               | 274.11(1)  | (4 ×)        |
| Ca/Na–As                                    | 316.86(5)  | (4 ×)        | Fe–As               | 239.92(2)  | (4 ×)        |
| Ca <sub>0.86</sub> Na <sub>0.14</sub> FFeAs |            |              |                     |            |              |
| Ca/Na–F                                     | 233.46(11) | (4 ×)        | Fe–Fe               | 274.13(3)  | (4 ×)        |
| Ca/Na–As                                    | 316.63(11) | (4 ×)        | Fe–As               | 239.91(6)  | (4 ×)        |
| Angle                                       | ∠/ °       | Multiplicity | Angle               | ∠/ °       | Multiplicity |
| CaFFeAs                                     |            |              |                     |            |              |
| F–Ca–F'                                     | 71.92(10)  | (4 ×)        | As–Fe–As'           | 107.85(10) | (2 ×)        |
|                                             | 112.3(2)   | (2 ×)        |                     | 110.29(5)  | (4 ×)        |
| F–Ca–As                                     | 76.68(4)   | (8 ×)        | Ca–As–Ca'           | 75.55(8)   | (4 ×)        |
|                                             | 141.90(2)  | (8 ×)        |                     | 120.06(18) | (2 ×)        |
| As–Ca–As'                                   | 75.55(8)   | (4 ×)        | Ca–As–Fe            | 78.41(7)   | (8 ×)        |
|                                             | 120.06(18) | (2 ×)        |                     | 142.12(3)  | (8 ×)        |
| Ca–F–Ca'                                    | 108.08(10) | (4 ×)        | Fe–As–Fe'           | 69.71(5)   | (4 ×)        |
|                                             | 112.3(2)   | (2 ×)        |                     | 107.85(10) | (2 ×)        |
| Ca <sub>0.97</sub> Na <sub>0.03</sub> FFeAs |            |              |                     |            |              |
| F–Ca/Na–F'                                  | 71.94(2)   | (4 ×)        | As–Fe–As'           | 107.73(2)  | (2 ×)        |
|                                             | 112.34(4)  | (2 ×)        |                     | 110.35(1)  | (4 ×)        |
| F–Ca/Na–As                                  | 76.70(1)   | (8 ×)        | Ca/Na–As–<br>Ca/Na' | 75.50(2)   | (4 ×)        |
|                                             | 141.92(1)  | (8 ×)        |                     | 119.95(4)  | (2 ×)        |
| As–Ca/Na–As'                                | 75.50(2)   | (4 ×)        | Ca/Na–As–Fe         | 78.50(1)   | (8 ×)        |
|                                             | 119.95(4)  | (2 ×)        |                     | 142.14(1)  | (8 ×)        |
| Ca/Na–F–Ca/Na'                              | 108.06(2)  | (4 ×)        | Fe–As–Fe'           | 69.65(1)   | (4 ×)        |
|                                             | 112.34(4)  | (2 ×)        |                     | 107.74(2)  | (2 ×)        |
| Ca <sub>0.92</sub> Na <sub>0.08</sub> FFeAs |            |              |                     |            |              |
| F–Ca/Na–F'                                  | 72.00(2)   | (4 ×)        | As–Fe–As'           | 107.78(1)  | (2 ×)        |
|                                             | 112.46(3)  | (2 ×)        |                     | 110.32(1)  | (4 ×)        |
| F–Ca/Na–As                                  | 76.72(1)   | (8 ×)        | Ca/Na–As–<br>Ca/Na' | 75.43(1)   | (4 ×)        |
|                                             | 141.94(1)  | (8 ×)        |                     | 119.78(3)  | (2 ×)        |
| As–Ca/Na–As'                                | 75.43(1)   | (4 ×)        | Ca/Na–As–Fe         | 78.55(1)   | (8 ×)        |
|                                             | 119.78(3)  | (2 ×)        |                     | 142.17(1)  | (8 ×)        |
| Ca/Na–F–Ca/Na'                              | 108.00(2)  | (4 ×)        | Fe–As–Fe'           | 69.68(1)   | (4 ×)        |
|                                             | 112.46(3)  | (2 ×)        |                     | 107.78(1)  | (2 ×)        |

Table S4. *Cont.*

| Distance                                    | d/pm      | Multiplicity | Distance            | d/pm      | Multiplicity |
|---------------------------------------------|-----------|--------------|---------------------|-----------|--------------|
| Ca <sub>0.86</sub> Na <sub>0.14</sub> FFeAs |           |              |                     |           |              |
| F–Ca/Na–F'                                  | 71.90(4)  | (4 ×)        | As–Fe–As'           | 107.80(4) | (2 ×)        |
|                                             | 112.26(8) | (2 ×)        |                     | 110.32(2) | (4 ×)        |
| F–Ca/Na–As                                  | 76.74(1)  | (8 ×)        | Ca/Na–As–<br>Ca/Na' | 75.50(3)  | (4 ×)        |
|                                             | 141.93(1) | (8 ×)        |                     | 119.94(6) | (2 ×)        |
| As–Ca/Na–As'                                | 75.50(3)  | (4 ×)        | Ca/Na–As–Fe         | 78.48(3)  | (8 ×)        |
|                                             | 119.94(6) | (2 ×)        |                     | 142.14(1) | (8 ×)        |
| Ca/Na–F–Ca/Na'                              | 108.10(4) | (4 ×)        | Fe–As–Fe'           | 69.68(2)  | (4 ×)        |
|                                             | 112.26(8) | (2 ×)        |                     | 107.80(4) | (2 ×)        |

## References

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