Supplementary Information

Table S1. Crystallographic data for selected crystals of the series $Ca_{1-x}Na_xFFeAs$. (Na contents are adopted from EDX analyses.)

***x* in $Ca_{1-x}Na_xFFeAs$**	**0**	**0.03**	**0.08**	**0.14**
Crystal system	tetragonal			
Space group	*P*4/*nmm* (No. 129)			
Lattice parameters *a*/pm	387.57(9)	387.57(2)	387.65(2)	387.68(3)
Lattice parameters *c*/pm	858.4(2)	859.48(5)	859.89(6)	859.87(9)
Lattice parameters *c*/*a*	2.215	2.218	2.218	2.218
Formula units per unit cell *Z*	2			
Molar volume V_m/cm^3·mol^{-1}	38.83	38.87	38.91	38.91
Calculated density D_x/g·cm^{-3}	4.89	4.87	4.84	4.82
Diffractometer	Nonius KappaCCD (Bruker AXS, Karlsruhe, Germany)			
Radiation	Mo-*Kα* (λ = 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
$2\theta_{max}$/°	58.80	60.66	71.20	56.27
F(000)	176	176	176	176
Absorption correction	numerical (Program *HABITUS* [1])			
Absorption coefficient μ/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 $\lvert F_o\rvert \geq 4\sigma(F_o)$	99	142	202	109
Refined parameters	11	12	12	11
R_{int}, R_σ	0.083, 0.028	0.060, 0.018	0.068, 0.021	0.104, 0.039
Solution and refinement	Program package *SHELX-97* [2,3]			
Scattering factors	*International Tables, Vol. C* [4]			
R_1, R_1 with $\lvert F_o\rvert \geq 4\sigma(F_o)$	0.076, 0.062	0.018, 0.018	0.022, 0.021	0.026, 0.024
wR_2, *GooF*	0.157, 1.178	0.044, 1.168	0.053, 1.166	0.058, 1.165
Residual electron density ρ_{max}, ρ_{min}/10^{-6}·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 $Ca_{1-x}Na_xFFeAs$.

Atom	**Site**	***x*/*a***	***y*/*b***	***z*/*c***	$U_{eq}^{(a)}$/**pm^2**
		CaFFeAs			
Ca	2*c*	$^1/_4$	$^1/_4$	0.1514(6)	265(13)
F	2*a*	$^3/_4$	$^1/_4$	0	263(35)
Fe	2*b*	$^3/_4$	$^1/_4$	$^1/_2$	251(11)
As	2*c*	$^1/_4$	$^1/_4$	0.6645(3)	251(9)

Table 2S. *Cont.*

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[(a)]/pm^2
		$Ca_{0.97}Na_{0.03}FFeAs$			
Ca/Na[(b)]	2*c*	$^1/_4$	$^1/_4$	0.15111(12)	84(3)
F	2*a*	$^3/_4$	$^1/_4$	0	90(6)
Fe	2*b*	$^3/_4$	$^1/_4$	$^1/_2$	74(2)
As	2*c*	$^1/_4$	$^1/_4$	0.66461(5)	75(2)
		$Ca_{0.92}Na_{0.08}FFeAs$			
Ca/Na[(c)]	2*c*	$^1/_4$	$^1/_4$	0.15072(10)	92(2)
F	2*a*	$^3/_4$	$^1/_4$	0	115(5)
Fe	2*b*	$^3/_4$	$^1/_4$	$^1/_2$	88(2)
As	2*c*	$^1/_4$	$^1/_4$	0.66444(4)	90(2)
		$Ca_{0.86}Na_{0.14}FFeAs$			
Ca/Na[(d)]	2*c*	$^1/_4$	$^1/_4$	0.1513(2)	94(4)
F	2*a*	$^3/_4$	$^1/_4$	0	136(11)
Fe	2*b*	$^3/_4$	$^1/_4$	$^1/_2$	105(4)
As	2*c*	$^1/_4$	$^1/_4$	0.66440(10)	112(3)

[(a)] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$; [(b)] Site occupation (from EDX): 97% Ca, 3% Na; [(c)] Site occupation (from EDX): 92% Ca, 8% Na; [(d)] Site occupation (from EDX): 86% Ca, 14% Na.

Table S3. Anisotropic displacement parameters (U_{ij}[(a)] in pm^2) for selected crystals of the series $Ca_{1-x}Na_xFFeAs$. ($U_{12} = U_{13} = U_{23} = 0$ for all atoms.)

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

[(a)] 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 $Ca_{1-x}Na_xFFeAs$.

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×)
		$Ca_{0.97}Na_{0.03}FFeAs$			
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×)
		$Ca_{0.92}Na_{0.08}FFeAs$			
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×)
		$Ca_{0.86}Na_{0.14}FFeAs$			
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×)
		$Ca_{0.97}Na_{0.03}FFeAs$			
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–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×)
		$Ca_{0.92}Na_{0.08}FFeAs$			
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–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×)
		$Ca_{0.86}Na_{0.14}FFeAs$			
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–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

1. Herrendorf, W.; Bärnighausen, H. *HABITUS: Program for the Optimization of the Crystal Shape for Numerical Absorption Correction*; Universities of Gießen and Karlsruhe: Gießen, Karlsruhe, Germany, 1996.
2. Sheldrick, G.M. *SHELX-97: Program Package for the Determination of Crystal Structures by Single Crystal X-ray and Neutron Diffraction*; University of Göttingen: Göttingen, Germany, 1997.
3. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr.* **2008**, *A64*, 112–122.
4. Prince, E. *International Tables for Crystallography,* 3rd ed.; Kluwer Academic Publishers: Dordrecht, Netherlands, 2004; Volume C3.