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Supporting information for article:

Size effect of the guest cation on the AlO4 framework in aluminate sodalite-type oxides *M*8[Al12O24](SO4)2 (*M* = Sr and Ca) in the *I*43*m* phase

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Table S1 Volumetric thermal expansion coefficient α_V of (a) SAS and (b) CAS in each phase.

(a) SAS		(b) CAS	
Phase (temperature range)	α_V [10^{-5} K^{-1}]	Phase (temperature range)	α_V [10^{-5} K^{-1}]
Tetragonal ($300 < T < 520$ K)	1.8	Orthorhombic ($300 < T < 740$ K)	1.2
Cubic ($I\bar{4}3m$) ($520 < T < 960$ K)	3.0	Cubic ($I\bar{4}3m$) ($740 < T < 1100$ K)	2.9
Cubic ($Im\bar{3}m$) ($960 < T < 1100$ K)	5.0	-	-

Table S2 Structural parameters of SAS in the $Im\bar{3}m$ phase (1100 K) a = 9.483220(6) Å; wRp = 3.33%; R_F = 3.21%; R_B = 3.36%; goodness-of-fit = 1.54.

Atom	Site	Symmetry	g	x	y	z
Sr	8*c*	$\bar{3}m$	1	1/4	= x	= x
S	2*a*	$m\bar{3}m$	1	0	0	0
Al	12*d*	$\bar{4}2m$	1	1/4	1/2	0
O1	24*h*	*mm*2	1	0.15813(13)	= x	1/2
O2	16*f*	3*m*	1	0.0815(3)	= x	= x

Atom	U_{11} [Å^2]	U_{22} [Å^2]	U_{33} [Å^2]	U_{12} [Å^2]	U_{13} [Å^2]	U_{23} [Å^2]
Sr	0.1019(7)	= U_{11}	= U_{11}	0.0735(7)	= U_{12}	= U_{12}
S	0.1062(16)	= U_{11}	= U_{11}	0	0	0
Al	0.0236(10)	0.0208(5)	= U_{22}	0	0	0
O1	0.0293(8)	= U_{11}	0.0525(13)	0.0229(10)	0	= U_{12}
O2	0.401(6)	= U_{11}	= U_{11}	0.008(3)	= U_{12}	= U_{12}

Atom	C_{111} [10^{-3}]	C_{112} [10^{-3}]	C_{123} [10^{-3}]	D_{1111} [10^{-4}]	D_{1112} [10^{-4}]	D_{1122} [10^{-4}]	D_{1123} [10^{-4}]
Sr	0	0	0	−0.0025(7)	−0.0039(4)	−0.0034(4)	−0.0047(5)
O2	0.032(11)	0.026(13)	−0.121(19)	0.35(5)	0.211(7)	0.23(5)	0.29(2)

restriction of 8*c* site ($\bar{3}m$): $C_{ijk} = 0$ (i, j, k = 1, 2, 3), $D_{1111} = D_{2222} = D_{3333}$, $D_{1112} = D_{1113} = D_{1222} = D_{1333} = D_{2223} = D_{2333}$, $D_{1122} = D_{1133} = D_{2233}$, $D_{1123} = D_{1223} = D_{1233}$

restriction of 16*f* site (3*m*): $C_{111} = C_{222} = C_{333}$, $C_{112} = C_{113} = C_{122} = C_{133} = C_{223} = C_{233}$, $D_{1111} = D_{2222} = D_{3333}$, $D_{1112} = D_{1113} = D_{1222} = D_{1333} = D_{2223} = D_{2333}$, $D_{1122} = D_{1133} = D_{2233}$, $D_{1123} = D_{1223} = D_{1233}$

Table S3 Positions of maxima in the PDFs of the guest cations, O1 and O2 in the $I\bar{4}3m$ phase (850 K) of SAS and CAS. The maxima of O1 are the same as those listed in Table 2.

Material	Atom	Symmetry	*x*	*y*	*z*
SAS	Sr	3*m*	0.220(1)	= *x*	0.235(1)
	O1	*m*	0.15715(10)	= *x*	0.48364(18)
	O2	3*m*	0.078(1)	= *x*	= *x*
CAS	Ca	3*m*	0.212(1)	= *x*	= *x*
	O1	*m*	0.15379(11)	= *x*	0.44811(11)
	O2	3*m*	0.130(1)	0.046(1)	= y

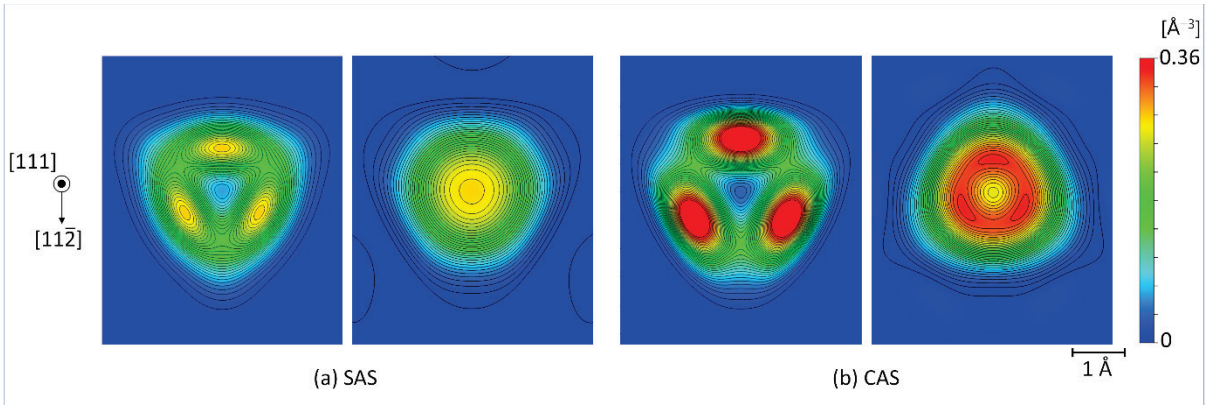

Figure S1 Two-dimensional maps of PDF of O2 atom in the $I\bar{4}3m$ phase (850 K). Datasets D1 and D2 were used. (a) SAS. (b) CAS. The left- and right-hand figures show the maps derived from the 3-site model and the Gram-Charlier method, respectively.

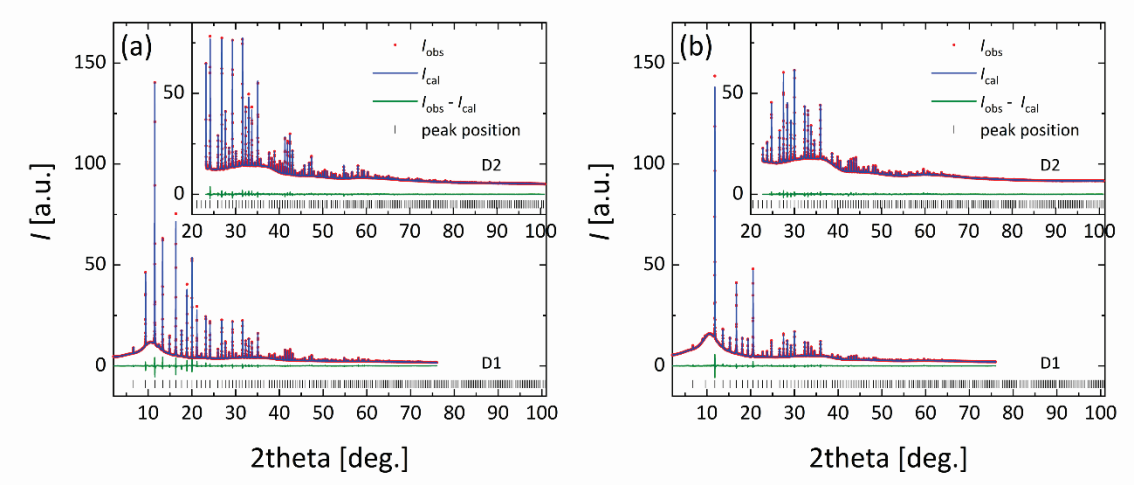

Figure S2 Rietveld profile fitting results of (a) SAS and (b) CAS in the $I\bar{4}3m$ phase (850 K). Insets represent fitting results of high-angular D2 data (d > 0.5 Å).

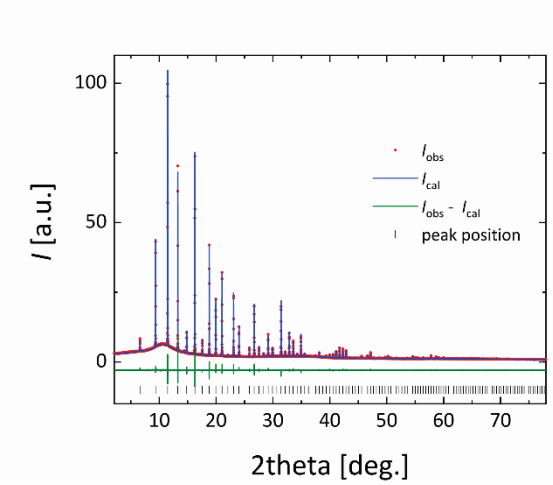

Figure S3 Rietveld profile fitting results of SAS in the $Im\bar{3}m$ phase (1100 K). The structural parameters and R-factors are summarized in Table S2.

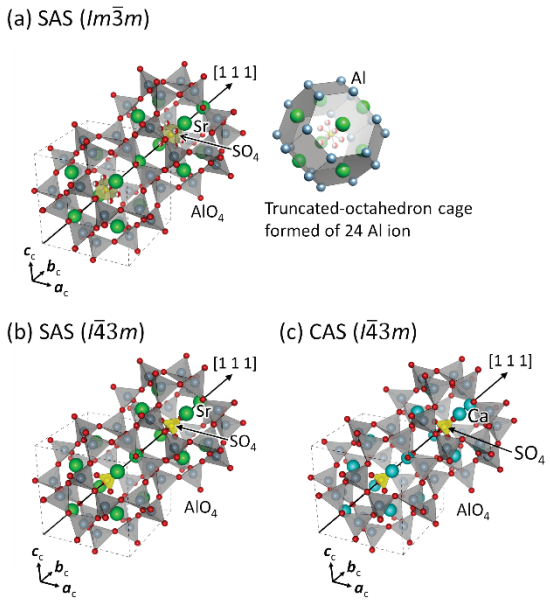

Figure S4 Crystal structure models of SAS and CAS. (a) SAS in the $Im\bar{3}m$. A truncated octahedron-shaped cage comprising Al atoms is shown. Eight Sr atoms were located at the centers of the eight hexagonal surfaces. SO_4 ions were present in the cages. The four O atoms of SO_4 occupy the eight sites by symmetry restriction. (b) SAS in the $I\bar{4}3m$ phase (c) CAS in the $I\bar{4}3m$ phase.

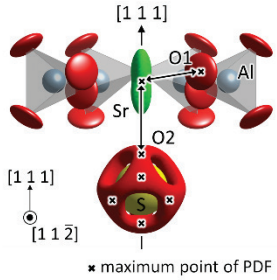

Figure S5 ORTEP-like view of PDF (isosurface of 0.17 $Å^{-3}$) of SAS in the $Im\bar{3}m$ phase (1100 K). The cross mark represents the maximum point in the PDF of each atom. O2 had eight maximum points in the PDF in the <1 1 1> direction.