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Order–Disorder in the α'-(Ca, Sr)$_2$SiO$_4$ Solid Solution: a Structural and Statistical-Thermodynamic Analysis

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Abstract

X-ray data were collected by single-crystal diffractometry (Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å) from the four compounds $Ca_{0\cdot5}Sr_{1\cdot5}SiO_4$, $CaSrSiO_4$, $Ca_{1\cdot5}Sr_{0\cdot5}SiO_4$ and $Ca_{1\cdot8}Sr_{0\cdot2}SiO_4$ [orthorhombic, space group *Pmnb* (non-standard setting of *Pnma*); crystal data range from $a = 5{\cdot}647\,(1)$, $b = 7{\cdot}037\,(1)$, $c = 9{\cdot}644\,(2)$ Å, $V = 383{\cdot}2$ Å^3, $M_r = 243{\cdot}552$, $D_x = 4{\cdot}221$ Mg m^{-3}, $Z = 4$, $\mu(\text{Mo } K\alpha) = 21{\cdot}2$ mm^{-1}, $F(000) = 452$ for $Ca_{0\cdot5}Sr_{1\cdot5}SiO_4$ to $a = 5{\cdot}5555\,(9)$, $b = 6{\cdot}8010\,(7)$, $c = 9{\cdot}317\,(2)$ Å, $V = 352{\cdot}0$ Å^3, $M_r = 181{\cdot}750$, $D_x = 3{\cdot}429$ Mg m^{-3}, $Z = 4$, $\mu(\text{Mo } K\alpha) = 6{\cdot}0$ mm^{-1}, $F(000) = 358{\cdot}4$ for $Ca_{1\cdot8}Sr_{0\cdot2}SiO_4$] synthesized by flux-growth crystallization. Least-squares refinements were based on the positionally disordered structure model of α'-Sr_2SiO_4, with atoms statistically distributed between mirror-related positions. Independent observations and final *R* values ranged from 826 to 1030 and from 0·030 to 0·052, respectively. An ordered model with most atoms on the (100) mirror plane (low-K_2SO_4 structure type) gave unsatisfactory results, particularly for the Ca-rich terms. The tilt of the SiO_4 group with respect to the (100) plane and its distortion from *m* symmetry increase with the Ca/Sr ratio, showing that positional

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disorder is favoured by a high Ca content. By refining occupancy factors, the cation substitutional order-disorder over two independent sites was determined, detecting a preference of Ca and Sr for the smaller and the larger site, respectively. Results were analysed on the basis of a 'simple equilibrium' statistical-thermodynamic model, relying on the assumption that energy differences between the sites are independent of composition and temperature. The theoretical function of order parameter *vs* composition was fitted to experimental data, and a best value of 0·060 eV ($1\ eV = 1{\cdot}602\times10^{-19}\ J$) for the Ca/Sr interchange energy between sites was obtained.

Introduction

Owing to their outstanding mineralogical and technological importance, alkaline-earth orthosilicates have been the object of several crystal-chemical studies. Recently, the crystal structures of the β and α' phases of Sr_2SiO_4 (Catti, Gazzoni & Ivaldi, 1983; Catti, Gazzoni, Ivaldi & Zanini, 1983) and the thermal and crystallographic aspects of the corresponding phase transition (Catti & Gazzoni, 1983) were explored, so that data on the polymorphism and structural features of all four end-members Mg_2SiO_4, Ca_2SiO_4, Sr_2SiO_4 and Ba_2SiO_4 are now available in the literature. Following this line of research, we have undertaken a full investigation of the binary system $Ca_ySr_{2-y}SiO_4$. Results on the phase-diagram determination are reported elsewhere (Catti, Gazzoni & Ivaldi, in preparation) and show that, at room temperature and pressure, the monoclinic β form is stable only within very narrow composition ranges close to the end-members Sr_2SiO_4 and Ca_2SiO_4 (in the latter case a small field of the olivine-like γ phase is observed as well), whereas the orthorhombic α' form is always found for intermediate chemical compositions; Ca/Sr solid solubility is complete throughout the whole range in both α' and β phases.

X-ray structural analyses at room temperature of $Ca_{0.5}Sr_{1.5}SiO_4$, $CaSrSiO_4$, $Ca_{1.5}Sr_{0.5}SiO_4$ and $Ca_{1.8}Sr_{0.2}SiO_4$, all belonging to the α' form, are presented here; these four compounds are labelled by the corresponding values of Ca mole fraction x_{Ca} = 0·25, 0·50, 0·75 and 0·90, where $x_{Ca} = n_{Ca}/(n_{Ca}+n_{Sr})$. By following the evolution of the α' structure against composition, possible crystal-chemical reasons for its unusual phase stability boundaries ($0{\cdot}03 \le x_{Ca} \le 0{\cdot}90$) might be found, *i.e.* why the less symmetrical β phase is favoured by a high proportion of either the larger or the smaller cation. The structure determination of α'-Sr_2SiO_4 (Catti, Gazzoni, Ivaldi & Zanini, 1983) has shown the presence of positional and orientational disorder of Sr atoms and SiO_4 groups, respectively, whereas the isotypic structures of Ba_2SiO_4 (Grosse & Tillmanns, 1974), low-temperature K_2SO_4 (McGinnety, 1972) and K_2BeF_4 (Mustafaev, Ilyukhin & Belov, 1965) are all ordered; thus it seems to be worthwhile exploring the influence of cation-size variation on this kind of order-disorder in the α' form. In this respect, of particular interest is the structure refinement of $Ca_{1.8}Sr_{0.2}SiO_4$, as it can simulate the crystal structure of α'-Ca_2SiO_4 which is stable only above 973 K and has not yet been fully analysed.

Experimental

$Ca_{0.5}Sr_{1.5}SiO_4$, $CaSrSiO_4$, $Ca_{1.5}Sr_{0.5}SiO_4$ and $Ca_{1.8}Sr_{0.2}SiO_4$ were synthesized by the same method used for Sr_2SiO_4 (Catti, Gazzoni & Ivaldi, 1983), *i.e.* crystallization of molten salt solution in a flux of SrF_2 and CaF_2, starting from mixtures of $SrCO_3$, $CaCO_3$ and SiO_2 of appropriate compositions. Guinier powder photographs at room temperature showed the orthorhombic diffraction pattern typical of the single α' phase of Sr_2SiO_4 for all four compounds, proving that Ca–Sr solid solubility covers the whole range explored (*cf.* Catti, Gazzoni & Ivaldi, in preparation). A single crystal was selected for each compound and mounted on a four-circle automatic Syntex-Nicolet *R*3 diffractometer (Mo $K\alpha$ radiation, graphite monochromator); the unit-cell constants were determined by angular refinement of 25 reflexions (Table 1), and the space group *Pmnb* ($Z = 4$) was confirmed by systematic absences. Diffraction intensities were collected from *hkl* and $\bar{h}\bar{k}\bar{l}$ octants with a $\theta/2\theta$ scan and $\Delta\theta = 2{\cdot}4°$, except for $Ca_{1.5}Sr_{0.5}SiO_4$ where an ω scan with $\Delta\omega = 1{\cdot}6°$ was used. The scan speed was variable between 0·03 and 0·49° s^{-1}, with interpolation for intensities between 150 and 2500 counts s^{-1}; background time = $\frac{1}{2}$ scan time. An empirical correction for absorption, based on ψ scans of a few high-χ reflexions with variable 2θ (North, Phillips & Mathews, 1968), was applied; the transmission coefficient ranged from 0·7 to 1·0, except for $CaSrSiO_4$ (0·3 to 1·0). Centrosymmetrically related reflexions were averaged, and those with $I \le 2\sigma(I)$ were considered unobserved and removed (Table 1).

Structure refinements

For all four crystal structures, full-matrix least-squares refinements were attempted according to both the ordered (1) and the positionally disordered (2) models investigated for α'-Sr_2SiO_4 (Catti, Gazzoni, Ivaldi & Zanini, 1983), using the corresponding atomic coordinates as starting parameters. In model (1) the two alkaline-earth metal atoms, the Si and two O atoms lie on the (100) mirror plane, whereas in model (2) all atoms (except for Si) are split into two half-occupied mirror-related positions. The ordered refinements (with isotropic thermal factors) yielded the following *R* values for $Ca_{0.5}Sr_{1.5}SiO_4$,

Table 1. *Crystal data, results of data collection and final agreement indices of structure refinements (disordered model)*

	$Ca_{0\cdot 5}Sr_{1\cdot 5}SiO_4$	$CaSrSiO_4$	$Ca_{1\cdot 5}Sr_{0\cdot 5}SiO_4$	$Ca_{1\cdot 8}Sr_{0\cdot 2}SiO_4$
x_{Ca}	0·25	0·50	0·75	0·90
a (Å)	5·647 (1)	5·6049 (8)	5·570 (1)	5·5555 (9)
b (Å)	7·037 (1)	6·9623 (8)	6·865 (1)	6·8010 (7)
c (Å)	9·644 (2)	9·483 (1)	9·364 (2)	9·317 (2)
V (Å^3)	383·2	370·1	358·1	352·0
M_r	243·552	219·782	196·012	181·750
D_x (Mg m^{-3}) ($Z = 4$)	4·221	3·945	3·636	3·429
μ(Mo $K\alpha$) (mm^{-1})	21·2	15·7	9·7	6·0
$2\theta_{max}$ (°)	76	80	80	80
Reflexions measured	2176	2479	2412	2596
Independent reflexions	1108	1239	1188	1173
Independent observed reflexions	826	922	863	1030
R	0·050	0·052	0·049	0·030
F(000)	452	416	380	358·4
Crystal dimensions (mm)	0·30 × 0·12 × 0·10	0·35 × 0·15 × 0·12	0·32 × 0·10 × 0·10	0·33 × 0·13 × 0·11
Range of h, k, l	$0 \le h \le 9$	$0 \le h \le 10$	$0 \le h \le 10$	$0 \le h \le 10$
	$0 \le k \le 12$	$0 \le k \le 12$	$0 \le k \le 12$	$0 \le k \le 12$
	$0 \le l \le 16$	$0 \le l \le 17$	$0 \le l \le 16$	$0 \le l \le 16$
R_{int} from merging equivalent reflexions	0·030	0·024	0·032	0·020
$(\Delta/\sigma)_{max}$	0·47	0·07	0·27	0·01
$\Delta\rho_{max}$ (e Å^{-3})	2·7	2·7	3·0	2·3
$\Delta\rho_{min}$ (e Å^{-3})	−3·1	−2·3	−2·7	−2·1

$CaSrSiO_4$, $Ca_{1\cdot 5}Sr_{0\cdot 5}SiO_4$, $Ca_{1\cdot 8}Sr_{0\cdot 2}SiO_4$, respectively: 0·10, 0·13, 0·19, 0·20; quite large thermal parameters for the O atoms were generally obtained. An attempt to refine anisotropic temperature factors was successful for the first compound only ($R =$ 0·062), while the thermal factors became non-positive-definite in the other three cases. On the other hand, the disordered model was refined isotropically to $R = 0{\cdot}050$, 0·052, 0·062, 0·060, respectively, for the four compounds, obtaining normal values of all thermal parameters. Refinements with anisotropic thermal factors for Si and O atoms could be performed for the first three compounds ($R = 0{\cdot}045$, 0·046, 0·049), and with thermal anisotropy for all atoms in the case of $Ca_{1\cdot 8}Sr_{0\cdot 2}SiO_4$ ($R = 0{\cdot}030$): however, very large e.s.d.'s of positional parameters were shown by $Ca_{0\cdot 5}Sr_{1\cdot 5}SiO_4$ and $CaSrSiO_4$. Therefore, taking also into account that the improvement of the R value in the passage to anisotropy was small with respect to the increase of number of parameters, the isotropic refinements were taken as final results for the two phases richer in Sr. As was discussed in the paper on α'-Sr_2SiO_4, an alternative model to positional disorder (split-atom positions with ordinary harmonic thermal factors) could be provided by single-site refinements with anharmonic temperature factors (Hutton & Nelmes, 1981). However, this kind of analysis requires a large number of very accurate high-order diffraction data, possibly measured at different temperature values (Mair, 1982), which could not be obtained in our case. Therefore experimental results were interpreted on the basis of a disordered harmonic model, although the possibility of anharmonic thermal motion should be kept in mind.

Since two independent sites St(1) and St(2) are available in the asymmetric unit for the alkaline-earth cations, the possible Ca/Sr substitutional order-disorder was accounted for by refining the occupation factor of Ca on St(1), with constraints on the overall site occupancies (fixed to 0·5) and chemical compositions. The refined occupation factors of Ca did not depend significantly on the choice of the ordered/disordered or isotropic/anisotropic models. Unit weights were used, since the average values of Δ^2 for groups of reflexions $vs|F_o|$ and sin θ were reasonably constant, except for a few very strong reflexions. Refinements were based on F magnitudes and performed with *RFINE*4 (Finger & Prince, 1975), with the scattering factors for neutral atoms (including corrections for anomalous scattering) in *International Tables for X-ray Crystallography* (1974); a quite low convergence rate was observed in all cases. The very strong 200 reflexion had to be removed from the data sets of $CaSrSiO_4$ and $Ca_{1\cdot 5}Sr_{0\cdot 5}SiO_4$ because it was strongly affected by secondary extinction. By comparison of the R values obtained for the ordered and the disordered models, the former was discarded, and the final positional and thermal parameters corresponding to disordered refinements are reported in Table 2 for the four compounds.* Interatomic distances and angles in the SiO_4 groups, and cation-oxygen bond lengths in the Ca/Sr coordination polyhedra are shown in Tables 3 and 4, respectively.

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* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39531 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates, isotropic temperature factors* (Å^2) *and occupancy factors for the disordered crystal structures of* Ca$_{0·5}$Sr$_{1·5}$SiO$_4$ (*isotropic refinement*), CaSrSiO$_4$ (*isotropic*), Ca$_{1·5}$Sr$_{0·5}$SiO$_4$ (*anisotropic except for cations*), Ca$_{1·8}$Sr$_{0·2}$SiO$_4$ (*full anisotropic*), *vertically in the above order*

E.s.d.'s are in parentheses. $B_{\rm eq} = \frac{1}{3}\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	B or $B_{\rm eq}^\dagger$	o.f. Ca	o.f. Sr
St(1)	0·2669 (4)	0·3390 (1)	0·57903 (9)	0·44 (2)	0·050 (5)	0·450
	0·2697 (2)	0·33677 (9)	0·57787 (7)	0·67 (1)	0·115 (4)	0·385
	0·2708 (3)	0·3355 (1)	0·57563 (8)	0·68 (2)	0·276 (4)	0·224
	0·2717 (6)	0·33564 (8)	0·57308 (6)	0·87 (3)†	0·410 (5)	0·090
St(2)	0·2686 (4)	−0·0030 (2)	0·3018 (1)	0·24 (2)	0·200	0·300
	0·2712 (3)	−0·0049 (1)	0·2997 (1)	0·56 (2)	0·385	0·115
	0·2734 (3)	−0·0068 (2)	0·2977 (1)	0·52 (2)	0·474	0·026
	0·2716 (7)	−0·00754 (8)	0·29688 (6)	0·74 (3)†	0·490	0·010
Si	0·25	0·7794 (3)	0·5843 (3)	0·45 (4)	1·0	
		0·7789 (2)	0·5844 (2)	0·79 (3)		
		0·7796 (2)	0·5851 (2)	0·80 (4)†		
		0·7811 (1)	0·58534 (8)	0·87 (2)†		
O(1)	0·300 (2)	1·006 (1)	0·5635 (8)	1·3 (2)	0·5	
	0·308 (1)	1·0056 (9)	0·5585 (6)	1·5 (1)		
	0·312 (1)	1·0056 (8)	0·5521 (5)	1·3 (2)†		
	0·3087 (5)	1·0077 (4)	0·5502 (3)	1·18 (5)†		
O(2)	0·206 (1)	0·670 (1)	0·4343 (7)	0·8 (1)	0·5	
	0·203 (1)	0·6653 (8)	0·4344 (6)	1·19 (9)		
	0·192 (1)	0·6613 (8)	0·4356 (5)	1·5 (2)†		
	0·1811 (6)	0·6598 (4)	0·4375 (3)	1·52 (6)†		
O(3)	0·490 (2)	0·687 (1)	0·652 (1)	1·0 (2)	0·5	
	0·485 (1)	0·688 (1)	0·6590 (9)	1·6 (1)		
	0·485 (2)	0·686 (1)	0·654 (1)	2·1 (2)†		
	0·4899 (7)	0·6870 (7)	0·6509 (4)	2·17 (9)†		
O(4)	0·021 (2)	0·732 (1)	0·683 (1)	0·9 (2)	0·5	
	0·018 (2)	0·740 (1)	0·6856 (8)	1·4 (1)		
	0·020 (2)	0·745 (1)	0·6928 (9)	1·4 (2)†		
	0·0246 (6)	0·7478 (5)	0·6987 (4)	1·25 (6)†		

Table 3. *Bond lengths* (Å) *and angles* (°) *in the* SiO$_4$ *groups of four structures, with e.s.d.'s in parentheses*

$x_{\rm Ca}$	0·25	0·50	0·75	0·90
Si-O(1)	1·632 (7)	1·630 (6)	1·619 (6)	1·609 (3)
Si-O(2)	1·657 (7)	1·649 (6)	1·650 (5)	1·651 (3)
Si-O(3)	1·64 (1)	1·624 (6)	1·59 (1)	1·600 (4)
Si-O(4)	1·64 (1)	1·639 (9)	1·65 (1)	1·654 (3)
Average	1·642	1·636	1·627	1·629
O(1)-Si-O(2)	111·9 (4)	111·5 (3)	110·6(2)	110·9 (1)
O(1)-Si-O(3)	107·1 (5)	106·3 (3)	106·8 (3)	107·0 (2)
O(1)-Si-O(4)	114·0 (4)	114·0 (3)	114·9 (3)	114·5 (2)
O(2)-Si-O(3)	106·7 (4)	108·6 (3)	107·8 (3)	108·2 (2)
O(2)-Si-O(4)	107·1 (4)	107·4 (3)	107·2 (3)	106·8 (2)
O(3)-Si-O(4)	109·9 (4)	108·9 (3)	109·4 (3)	109·4 (2)
Average	109·5	109·5	109·5	109·5

Only Si-O and (Ca/Sr)-O bonds belonging to one of the two mirror-related orientations of the disordered structure are reported, excluding possible bonds between atoms of different orientation states.

Table 4. *Bond lengths* (Å) *in the coordination polyhedra surrounding the* (Ca,Sr) *cation sites, with e.s.d.'s in parentheses*

For symmetry code see text.

$x_{\rm Ca}$	0·25	0·50	0·75	0·90
St(1)-O(1$^{\rm i}$)	2·356 (7)	2·323 (6)	2·287 (6)	2·250 (3)
St(1)-O(2)	2·737 (7)	2·687 (6)	2·630 (5)	2·590 (3)
St(1)-O(2,2$^{\rm iii}$)	2·674 (6)	2·652 (6)	2·580 (6)	2·518 (5)
St(1)-O(2,2$^{\rm ii}$)	2·980 (6)	2·958 (6)	2·994 (6)	3·042 (5)
St(1)-O(3)	2·842 (8)	2·833 (7)	2·784 (8)	2·776 (5)
St(1)-O(4)	3·253 (8)	3·304 (8)	3·325 (8)	3·333 (4)
St(1)-O(3,2$^{\rm ii}$)	2·62 (1)	2·639 (7)	2·549 (1)	2·476 (4)
St(1)-O(4,2$^{\rm iii}$)	3·05 (1)	3·021 (8)	3·041 (9)	3·073 (4)
St(1)-O(3,4$^{\rm v}$)	3·16 (1)	3·056 (7)	3·081 (9)	3·122 (4)
St(1)-O(4,4$^{\rm v}$)	2·70 (1)	2·627 (8)	2·539 (9)	2·482 (4)
Average	2·837	2·810	2·781	2·766
St(2)-O(1$^{\rm i}$)	2·531 (8)	2·464 (6)	2·393 (5)	2·371 (3)
St(2)-O(2$^{\rm i}$)	2·656 (7)	2·655 (6)	2·658 (5)	2·662 (3)
St(2)-O(2,4$^{\rm i}$)	2·586 (7)	2·521 (6)	2·478 (5)	2·477 (3)
St(2)-O(1,2$^{\rm ii}$)	2·76 (1)	2·715 (6)	2·704 (5)	2·733 (3)
St(2)-O(3,2$^{\rm ii}$)	2·646 (8)	2·625 (7)	2·620 (8)	2·597 (5)
St(2)-O(4,2$^{\rm iii}$)	2·517 (8)	2·459 (8)	2·431 (8)	2·415 (3)
St(2)-O(3,3$^{\rm vi}$)	2·498 (9)	2·445 (7)	2·430 (9)	2·406 (4)
St(2)-O(4,3$^{\rm viii}$)	2·437 (9)	2·401 (8)	2·351 (8)	2·341 (4)
Average	2·579	2·536	2·508	2·500
St(2)-O(1,2$^{\rm iii}$)	3·41 (1)	3·513 (6)	3·551 (6)	3·525 (3)

Positional disorder

In the study of α'-Sr$_2$SiO$_4$ at 383 K evidence was given of a statistical distribution of atoms betwen (100) mirror-related positions, probably coexisting with a very small amount of ordered structure (Catti, Gazzoni, Ivaldi & Zanini, 1983). This result shows that α'-Sr$_2$SiO$_4$ is not really isostructural with Ba$_2$SiO$_4$ and low-K$_2$SO$_4$, as such compounds have the completely ordered configuration only. By examining the R values of the refinements of α'-Sr$_2$SiO$_4$ and of the four Ca$_y$Sr$_{2-y}$SiO$_4$ compounds for both the ordered and the disordered model, the former appears to be less and less reliable as the $x_{\rm Ca}$ mole fraction increases. For the compound closest to the Ca end-member, $Ca_{1\cdot8}Sr_{0\cdot2}SiO_4$, not only is model (1) to be rejected completely, but also model (2) can be refined fully anisotropically reaching a very low R value.

The results of the least-squares refinement are confirmed by analysing the geometric parameters which control deviations of the disordered configuration from the ordered one. Model (2) is a statistical average with symmetry *Pmnb* of two $P2_1/n$ asymmetrical configurations related by the (100) mirror plane, which are called 'orientation states' according to the terminology used for ferroic crystals (Aizu, 1970). Its deviation from model (1) can be measured by the atomic path connecting the orientation states (I) and (II) to each other. The corresponding atomic displacements are: ΔSt(1) = St(1) − St(1,5),* ΔSt(2) = St(2) − St(2,5), ΔO(1) = O(1) − O(1,5), ΔO(2) = O(2) − O(2,5), ΔO(3) = O(3) − O(4,5). Let then the (I)$\leftrightarrows$(II) transformation be supposed to occur by a mechanism of correlated atomic motion, *i.e.* a semi-rigid rotation of the SiO_4 tetrahedron, as proposed for Sr_2SiO_4 (Catti & Gazzoni, 1983); a sketch of the two asymmetrical and of the symmetrical configuration of the tetrahedron is shown in Fig. 1. The amount of rigid-body rotation can be expressed by the angle, χ, between the O(1)-Si-O(2) and the (100) planes, and the internal deformation of the tetrahedron with respect to the m symmetry is measured by the difference between the Si-O(3) and Si-O(4) bond lengths and by the two differences between the ∠O(1)-Si-O(3), ∠O(1)-Si-O(4) and ∠O(2)-Si-O(3), ∠O(2)-Si-O(4) bond angles (Table 3). The atomic shifts, Δ, and the rotation angles, χ, of the SiO_4 group are given in Table 5 for all five structures considered. All these geometric parameters are zero for the ordered structure, and deviate from zero by as much as the disordered configuration departs from the ordered one.

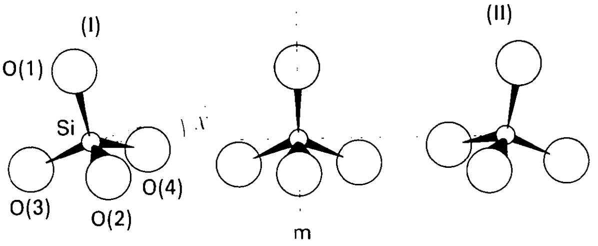

Fig. 1. Orientation states (I) and (II) of the disordered model and intermediate ordered configuration of the SiO_4 tetrahedron in α'-$(Ca,Sr)_2SiO_4$, viewed along [00$\bar{1}$].

Table 5. *Atomic shifts Δ(Å) relating the orientation states* (I) *and* (II) *in the disordered structures of the four* α'-$(Ca,Sr)_2SiO_4$ *compounds and in* α'-Sr_2SiO_4 ($x_{Ca} = 0$)

χ is the angle (°) between the O(1)-Si-O(2) and (100) planes.

x_{Ca}	0	0·25	0·50	0·75	0·90
ΔSt(1)	0·172	0·191	0·221	0·232	0·241
ΔSt(2)	0·185	0·210	0·238	0·261	0·240
ΔO(1)	0·477	0·565	0·650	0·691	0·652
ΔO(2)	0·489	0·497	0·527	0·646	0·766
ΔO(3)	0·449	0·440	0·442	0·545	0·613
χ	10·20	11·30	12·72	14·43	15·38

Only the internal angular distortion of the tetrahedron appears to be practically constant, whereas all other parameters increase with x_{Ca}. This seems to be consistent with the results of the least-squares refinements, which show an increasing stabilization of the disordered model as the Ca end-member is approached. The observed features of positional disorder can be understood on simple crystal-chemical grounds. As x_{Ca} increases the 'average' cation becomes smaller, so that the coordination numbers of cation sites tend to decrease (*cf.* the discussion in *Coordination polyhedra*); this process is favoured by the asymmetrical configuration of the disordered model, since each cation can easily move closer to some O atoms and farther from others, if mirror constraints are removed.

Coordination polyhedra

Within the SiO_4 group (Table 3), O-Si-O bond angles are not affected substantially by changes of the Ca/Sr ratio, but the Si-O(3) and Si-O(4) bond lengths decrease and increase, respectively, as x_{Ca} becomes larger. This effect is related to a dependence of positional disorder on composition, as discussed previously. Considering the behaviour of cation-oxygen distances in the coordination polyhedra surrounding sites St(1) and St(2) as a function of Ca/Sr ratio (Table 4), the average St-O lengths in both polyhedra decrease with an increase of Ca content. However, individual bond lengths behave differently: the shortest ones decrease strongly, but the longest ones remain more or less constant. This is due to the tendency of the smaller Ca^{2+} cation to have a lower coordination number, which causes the St-O contacts to split into a group of shorter and a group of longer distances as x_{Ca} increases. For St(1), four long contacts do not change appreciably, whereas all others and particularly St(1)-O($4,4^{v}$) shorten with an increase of the Ca/Sr ratio; thus in $Ca_{1\cdot8}Sr_{0\cdot2}SiO_4$ a first coordination sphere with CN = 6 can be distinguished clearly from a second sphere including the four O atoms left. This phenomenon is less sharp in the St(2) polyhedron, where the coordination number is always 8 [the contact with O($1,2^{iii}$) is much longer than the others

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* A second figure in parentheses, ranging from 2 to 8, denotes atoms in the positions $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}-x, y, z$; $\frac{1}{2}+x, \bar{y}, \bar{z}$; $x, \frac{1}{2}+y, \frac{1}{2}-z$; $\bar{x}, \frac{1}{2}-y, \frac{1}{2}+z$. Roman numeral superscripts represent the following translations: (i) $-\mathbf{b}$; (ii) $\mathbf{a}+\mathbf{b}+\mathbf{c}$; (iii) $\mathbf{b}+\mathbf{c}$; (iv) $-\mathbf{a}+\mathbf{b}+\mathbf{c}$; (v) $-\mathbf{b}+\mathbf{c}$; (vi) $-\mathbf{a}-\mathbf{c}$; (vii) $\mathbf{a}-\mathbf{c}$; (viii) $-\mathbf{c}$.

also in α'-Sr$_2$SiO$_4$], and all bond distances are spread within a much narrower range. The largest shortening for an increase of x_{Ca} is shown by the St(2)-O(1^i) bond, while the two longest bonds St(2)-O(2^i) and St(2)-O($3,2^{ii}$) shorten very little. These results are summarized in Fig. 2, where distributions of cation-oxygen bond lengths are shown for different compositions.

Substitutional order–disorder

The X-ray analysis has shown a partial ordering of Ca and Sr atoms on the St(1) and St(2) sites: the former is richer in Sr and the latter in Ca with respect to the overall chemical composition of each phase. The direction of ordering is in accord with the average St(1)-O distance being longer than St(2)-O in the end-members, so that St(1) prefers the larger and St(2) the smaller cation. These results can be interpreted on the basis of a statistical-thermodynamic model of solid solutions. The α'-(Ca,Sr)$_2$SiO$_4$ system is characterized by two features: (i) a complete Ca,Sr solid solubility at room temperature over the whole compositional range, (ii) the St(1) and St(2) sites have coordination environments of quite different sizes, and their difference is approximately constant as the composition changes. Thus the model of 'simple equilibrium' can be applied to this solid solution, according to the assumption that the energy difference of the two sites is independent of the degree of disorder and of temperature, so that complete disorder would be attained at infinite temperature only (the disordering process is non-convergent). Such a model was used to analyse the distribution equilibrium of cations in spinels (Navrotsky & Kleppa, 1967) and in orthopyroxenes (Navrotsky, 1971).

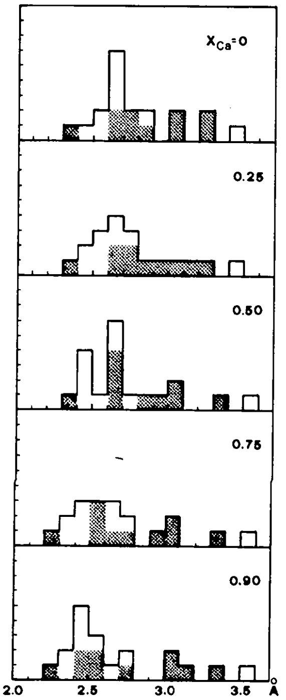

Fig. 2. Histograms of (Ca,Sr)-O bond lengths for α'-Sr$_2$SiO$_4$ (Catti, Gazzoni, Ivaldi & Zanini, 1983) and for the four α'-(Ca,Sr)$_2$SiO$_4$ compounds (this work); shaded areas represent contributions from the St(1) site only.

By introducing the site mole fractions $x_{Ca(1)}$, $x_{Ca(2)}$, $x_{Sr(1)}$, $x_{Sr(2)}$, and taking into account the balance relationships $x_{Ca(1)}+x_{Sr(1)}=1$, $x_{Ca(2)}+x_{Sr(2)}=1$, $x_{Ca(1)}+x_{Ca(2)}=2x_{Ca}$, $x_{Sr(1)}+x_{Sr(2)}=2x_{Sr}$, $x_{Ca}+x_{Sr}=1$, it turns out that, for a given overall composition x_{Ca}, just one site mole fraction out of four [for example, $x_{Ca(1)}$] is required to determine the compositions of both sites. Alternatively, an order parameter s can be usefully defined as follows: $s\equiv[x_{Ca}-x_{Ca(1)}]/x_{Ca}$ for $x_{Ca}\le\frac{1}{2}$, and $s\equiv[x_{Ca}-x_{Ca(1)}]/(1-x_{Ca})$ for $x_{Ca}\ge\frac{1}{2}$. Since Ca prefers the smaller site St(2), the relations $x_{Ca(1)}\le x_{Ca}$ and $s\ge 0$ always hold. For complete disorder, the overall composition is equal to those of both sites, so that $x_{Ca(1)}=x_{Ca}$ and $s=0$; in the case of complete order, for $x_{Ca}\le\frac{1}{2}$ all Ca goes into St(2) and $x_{Ca(1)}=0$, $s=1$, while for $x_{Ca}>\frac{1}{2}$ calcium fills St(2) and also occupies a fraction of St(1) equal to $x_{Ca(1)}=2x_{Ca}-1$, so that $s=1$. Thus the order parameter grows from 0 to 1 as the substitutional order increases.

The thermodynamic equilibrium relative to the following process is to be considered:

$$\mathrm{Ca(1)+Sr(2)} \rightleftarrows \mathrm{Ca(2)+Sr(1)}. \qquad (1)$$

For a given distribution of cations between the two sites, the mixing entropy per mole is, according to standard statistical mechanics,

$$S=-\mathcal{N}k[x_{Ca(1)}\log x_{Ca(1)}+x_{Sr(1)}\log x_{Sr(1)} + x_{Ca(2)}\log x_{Ca(2)}+x_{Sr(2)}\log x_{Sr(2)}]; \qquad (2)$$

$\mathcal{N}$ is the Avogadro number and k the Boltzmann constant. Let then $w_{Ca(1)}$, $w_{Ca(2)}$, $w_{Sr(1)}$, $w_{Sr(2)}$ be the interaction energies of a Ca atom with the environments of St(1) and St(2), and of an Sr atom with the same environments; the energy per mole is:

$$E=\mathcal{N}[x_{Ca(1)}w_{Ca(1)}+x_{Sr(1)}w_{Sr(1)} + x_{Ca(2)}w_{Ca(2)}+x_{Sr(2)}w_{Sr(2)}]. \qquad (3)$$

By expressing *all* site mole fractions as functions of the order parameter s and of the composition parameter x_{Ca}, and using the relation $F=E-TS$, the change of Helmholtz free energy $\Delta F=F(s)-F(0)$ between an initial state of complete disorder and a final state of partial disorder can be calculated. From the condition of thermodynamic equilibrium $\partial(\Delta F)/\partial s=0$, the following final equilibrium equation is derived:

$$\frac{(1+s)[1-(1-s)x_{Ca}]}{(1-s)[1-(1+s)x_{Ca}]}=\exp\left(\frac{W}{kT}\right) \quad (x_{Ca}\le\tfrac{1}{2}). \qquad (4)$$

For $x_{Ca} > \frac{1}{2}$, the corresponding equation is obtained by substituting x_{Ca} by $1 - x_{Ca}$ in (4). The quantity $W \equiv w_{Ca(1)} + w_{Sr(2)} - w_{Ca(2)} - w_{Sr(1)}$ represents the energy required to interchange the site positions of a pair of Ca and Sr atoms from the favoured Ca(2) + Sr(1) to the unfavoured Ca(1) + Sr(2) configuration.

By solving equation (4) with respect to s, the equilibrium relationship of variation of the order parameter as a function of composition and temperature is found:

$$s(x_{Ca}, T) = \frac{1}{x_{Ca}}\left\{\left[\frac{1}{2} + \frac{1}{\exp(W/kT) - 1}\right] - \left[\left(\frac{1}{2} + \frac{1}{\exp(W/kT) - 1}\right)^2 - x_{Ca}(1 - x_{Ca})\right]^{1/2}\right\}$$
$$(x_{Ca} \le \tfrac{1}{2}); \qquad (5)$$

for $x_{Ca} > \frac{1}{2}$, x_{Ca} is replaced by $1 - x_{Ca}$. Thus the function is symmetrical with respect to $x_{Ca} = \frac{1}{2}$, *i.e.* $s(1 - x_{Ca}, T) = s(x_{Ca}, T)$. Alternatively, the expression of the equilibrium site composition can be obtained:

$$x_{Ca(1)} = x_{Ca} + \left[\left(\frac{1}{2} + \frac{1}{\exp(W/kT) - 1}\right)^2 - x_{Ca}(1 - x_{Ca})\right]^{1/2} - \left[\frac{1}{2} + \frac{1}{\exp(W/kT) - 1}\right]. \qquad (6)$$

The above simple theory is based on two assumptions: (i) cations interact with O atoms of the site coordination environments, but not with one another; (ii) interaction energies, and the quantity W, remain constant as x_{Ca}, T and s change.

Our data are the four occupation factors of Ca on St(1) corresponding to $x_{Ca} = 0·25$, 0·50, 0·75, 0·90 (Table 2). By dividing them by the 0·5 site multiplicity due to positional disorder, the experimental values of $x_{Ca(1)}$, and of the order parameter s are obtained. Considering the interchange energy W as an empirical parameter to be fitted to the data, the four W values obtained from (4) are averaged, yielding $\bar{W} = 0·060$ eV. This value is then put into (5) and (6), to calculate back the order parameter and the site occupancy as functions of composition. The results are given in Table 6. The goodness of fit can be evaluated by examining the deviations of the individual values of W from $\bar{W}$, and by comparing experimental and calculated values of $x_{Ca(1)}$ and s. The overall agreement appears to be satisfactory, except perhaps for results corresponding to $x_{Ca} = 0·25$ which, besides, are not fully consistent with the symmetry $s(1 - x_{Ca}) = s(x_{Ca})$ required by the model used. However, to a first approximation the simple equilibrium theory seems to be adequate to interpret substitutional order-disorder in Ca/Sr orthosilicates, as is shown by the graph of the calculated $x_{Ca(1)}(x_{Ca})$ function compared to the experimental points (Fig. 3). To achieve a better fit, a more complicated model should be assumed so as to take into account a small dependence of the site energy on composition and/or order parameter,, as in the Bragg & Williams (1934) analysis. Moreover, site energies for St(1) and St(2) could be calculated straightforwardly on the basis of structural data for different compositions, provided that a suitable interatomic potential is used. On the other hand, more structure refinements possibly at several temperature values would be required to test such complex theories.

Table 6. *Experimental (X-ray analysis) and calculated [equations* (5), (6)] *values of the* Ca *mole fraction on* St(1), $x_{Ca(1)}$, *and of the order parameter, s, for the four* α'-(Ca,Sr)$_2$SiO$_4$ *compounds.*

Calculated values are based on the average (0·060 eV) site interchange energy W derived from equation (4).

x_{Ca}	0·25	0·50	0·75	0·90
$x_{Ca(1)}$(exp.)	0·10	0·23	0·55	0·82
s(exp.)	0·60	0·54	0·80	0·80
W (eV)	0·046	0·062	0·070	0·061
$x_{Ca(1)}$(calc.)	0·07	0·24	0·57	0·82
s(calc.)	0·73	0·53	0·73	0·79

α'/β phase relationships

In the (Ca,Sr)$_2$SiO$_4$ system, the β phase shows two stability fields for $0 \le x_{Ca} \le 0·03$ and for $0·90 < x_{Ca} < 0·96$ (at larger x_{Ca} values the γ form is observed), limiting the α' range (Catti, Gazzoni & Ivaldi, in preparation). Thus the latter phase would seem to be stabilized with respect to β by the mixing entropy related to Ca/Sr solid solubility, rather than by a size effect of either cation, showing that positional and

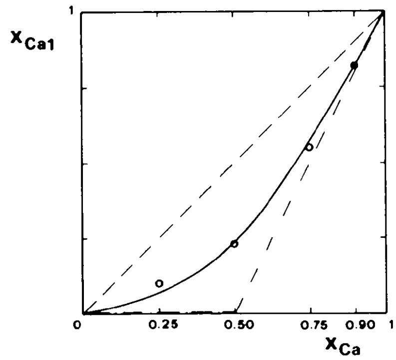

Fig. 3. Graph of $x_{Ca(1)}$ [mole fraction of Ca in St(1)] against the overall Ca mole fraction x_{Ca}, calculated according to equation (6). Circles are experimental values from occupancy refinements. Dashed and dashed-dotted lines represent complete substitutional disorder and complete order, respectively.

substitutional disorder are likely to be intimately coupled phenomena in the α' structure.

Crystals of the β form are polysynthetically twinned about (100) and the structure of each β twin orientation state is very similar to that of the corresponding orientation state of the disordered α' form, apart from the small monoclinic distortion of the β lattice; the α' modification can therefore be considered as a limiting case of the β form, when macroscopic twin domains decrease their size to dimensions of a few unit cells, and the monoclinic cell transforms to orthorhombic so that both orientation states can be fitted into a unique lattice (Catti & Gazzoni, 1983). Thus as the orientation difference between the two α' states increases as the Ca content grows (*cf. Positional disorder*), a critical composition close to pure Ca$_2$SiO$_4$ is reached when the two orientation states can no longer coexist on a microscopic scale and have to split into twin domains of the β phase. No simple structural explanation of this kind, however, can be devised for the α'/β phase boundary on the opposite (Sr-rich) side of the state diagram; in this case, only the above argument that positional disorder is stabilized somehow by substitutional disorder seems to be proposable.

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Determination of the Structure Factors of Cu and Cu$_3$Au by the Intersecting Kikuchi-Line Method

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Abstract

The intersecting Kikuchi-line method combined with the convergent-beam method was applied to Cu and Cu$_3$Au alloy in order to determine the structure factors of low-order reflections. Splittings of Kikuchi lines for higher-order reflections at intersections were observed so clearly using a high-voltage electron microscope that the separations could be measured. From the measured separations, the structure factors of low-order reflections were obtained by means of many-beam calculations based on the dynamical electron diffraction theory. The structure factors of Cu determined for reflections 111 and 200 are in good agreement with those determined by the critical-voltage method and X-ray diffraction. For Cu$_3$Au alloy, structure factors of both fundamental and superlattice reflections were determined. It is demonstrated that the intersecting Kikuchi-line method is useful for the estimation of the degree of order in a

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