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A new modification of slawsonite, $SrAl_2Si_2O_8$: Its structure and phase transition

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Paracelsian / Phase transition

Abstract. Slawsonite ($SrAl_2Si_2O_8$) from Sarusaka, Kochi Prefecture, Japan, is triclinic, space group $P\bar{1}$, with $a = 0.6145(1)$ nm, $b = 0.8987(2)$ nm, $c = 0.7456(3)$ nm, $\alpha = 90.01(3)°$, $\beta = 90.34(3)°$ and $\gamma = 89.98(3)°$, $Z = 4$ at $T = 298$ K. The cell dimensions are similar to the previous assignment to the monoclinic space group $P2_1/a$. The average structure was refined to $R = 0.049$ from 2695 reflections. A model is proposed for the real structure taking into account about 200 superstructure reflections. Thermal analysis revealed a phase transition to $P2_1/a$ at 593 K which is considered a new type of transition for the paracelsian-slawsonite group.

Introduction

The structure of the feldspars is characterized by the framework of chains of (Si, Al)$-O_4$ tetrahedra with the shape of a double crankshaft, which forms the eight-membered rings of tetrahedra. According to Smith and Rinaldi (1962), paracelsian can also be characterized by a similar configuration of four- and eight-membered rings of tetrahedra but its structure shows a different topology from that of feldspar. Slawsonite (Griffen, Ribbe, Gibbs, 1977) is isostructural to paracelsian (Smith, 1953; Bakakin, Below, 1961), a polymorph of $BaAl_2Si_2O_8$, danburite $CaB_2Si_2O_8$ (Dunbar, Machatschki, 1931; Johansson, 1959) and hurlbutite $CaBe_2P_2O_8$ (Bakakin, Below, 1959; Bakakin et al., 1959).

The crystal structure of slawsonite, precisely its calcian variety, was described by Griffen et al. (1977). The locality of their sample was from Wallowa County, Oregon, but no detailed mineralogical description has been performed. Only a partial replacement of Sr by Ca (ratio Ca : Sr = 13 : 87) is reported. For the present material, however, a complete mineralogical characterization (Matsubara, 1985; Kato, Matsubara, 1985) is available, which reveals that the composition is very close to the ideal formula $SrAl_2Si_2O_8$. Preliminary precession studies showed diffraction spots forbidden by the extinction rules of space group $P2_1/a$ assigned to Wallowa slawsonite. This observation together with the well characterized sample provoked a detailed structural investigation.

Experimental

The single crystal from Sarusaka, Kochi Prefecture, Japan (sample No. NSM-M2-23137), was removed from a prism forming a subparallel aggregate and contains minor amounts of celsian. The microprobe analysis gave an average value of SiO_2 36.63, Al_2O_3 31.30, SrO 29.99, BaO 1.53, K_2O 0.06, Total 99.51 wt%, yielding the empirical formula $(Sr_{0.95}Ba_{0.03})_{\Sigma 0.98}Al_{2.01}Si_{2.00}O_8$ calculated on the basis of a total of eight oxygen atoms. The present slawsonite was chemically homogeneous and the deviation of the chemical formula was within 0.02 on every measured point.

The precession photographs exposed for 72 hours using CuK_α radiation showed weak but sharp reflections indexed as (102), ($\bar{1}$02), (10$\bar{2}$) and ($\bar{1}$0$\bar{2}$) (Fig. 1). These indices are excluded by the space group $P2_1/a$. The examined crystal was then set on a four-circle goniometer and the diffraction data were collected using graphite monochromatized MoK_α radiation. A total of 3392 reflections was measured in a hemisphere of the reciprocal space and 180 reflections of ($h0l$) and eight reflections of ($0k0$) were selected from the three dimensional data. Among them 51 reflections of ($h0l$) with h = odd and two reflections of ($0k0$) with k = odd were recognized owing to their intensities stronger than 1σ. This fact indicates the absence of a-glide plane normal to [010] and of a twofold screw axis parallel to [010]. Therefore, the possible space groups are $P2/m$, Pm, $P2$, $P1$ and $P\bar{1}$, and the last one was preferred as stated later.

Assuming triclinic symmetry, the unit cell parameters were refined using 24 reflections: $a = 0.6145(1)$ nm, $b =$

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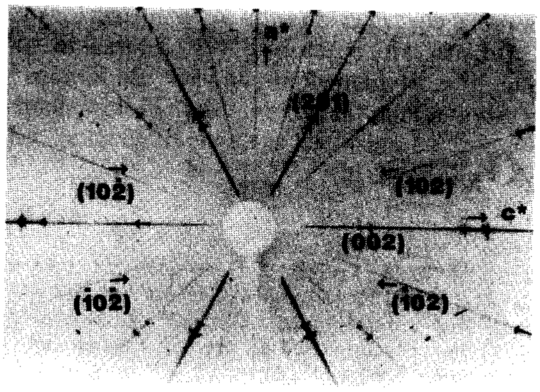

Fig. 1. A precession photograph of slawsonite from Sarusaka. Reflections from the real structure, which violate extinction rule of $P2_1/a$ symmetry, were indicated by arrows.

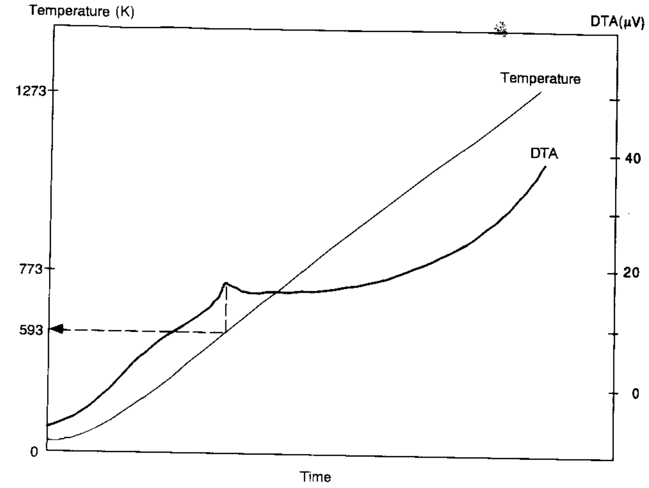

Fig. 2. DTA diagram in the temperature range of 298 K to 1273 K. A thinner line indicates temperature curve and a thicker one DTA curve. An exothermic peak was observed at 593 K.

0.8987(2) nm, $c = 0.7456(3)$ nm, $\alpha = 90.01(3)^\circ$, $\beta = 90.34(3)^\circ$ and $\gamma = 89.98(3)^\circ$, $Z = 4$. Within the limit of error, the lattice showed a monoclinic symmetry.

The selected crystal for collecting reflection data has a tabular form of about 0.10 × 0.12 × 0.06 mm in size. Integrated intensities were measured using a RIGAKU four-circle diffractometer with MoK_α radiation (0.07107 nm) and a graphite monochromator. The data were measured by $\omega - 2\theta$ scan in the 2θ range of 5°–120° and were converted to structure factors by applying Lorentz and polarization corrections and neither absorption correction ($\mu = 73.0\ \text{cm}^{-1}$ for MoK_α) nor extinction correction. Starting parameters for the refinement of the average structure were those of Griffen et al. (1977). After several cycles based on 2695 independent reflections the refinement converged to $R = 0.049$.

Differential thermal analysis (abbreviated to DTA) was carried out in the temperature range from 298 K to 1273 K (Fig. 2). 10 mg of the sample compared with standard Al_2O_3 was heated in Pt-crucibles. The temperature was raised at a rate of 10 K/min.

Table 1. Finally atomic coordinates and anisotropic temperature coefficients.

Atom	x	y	z
Sr	0.89134(7)	0.41194(7)	0.25050(7)
T_{1o}	0.2307(2)	0.9251(2)	0.9313(2)
T_{1m}	0.2393(2)	0.9196(2)	0.5605(2)
T_{2o}	0.0603(2)	0.2000(2)	0.9439(2)
T_{2m}	0.0559(2)	0.1941(2)	0.5707(2)
O_{1o}	0.1904(4)	0.0919(5)	0.0089(5)
O_{1m}	0.1895(4)	0.0739(5)	0.4947(5)
O_{2o}	0.1196(4)	0.3657(5)	0.9469(5)
O_{2m}	0.1262(5)	0.3689(5)	0.5541(5)
O_{3o}	0.9224(4)	0.1915(5)	0.0677(5)
O_{3m}	0.8985(4)	0.1911(5)	0.4409(5)
O_4	0.0104(5)	0.1547(5)	0.7668(5)
O_5	0.3110(4)	0.9231(5)	0.7413(5)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sr	0.00316(6)	0.00210(5)	0.00279(6)	0.00006(6)	−0.00067(5)	−0.00019(6)
T_{1o}	0.0015(2)	0.0012(2)	0.0014(2)	0.0000(2)	−0.0005(2)	0.0000(2)
T_{1m}	0.0014(2)	0.0010(2)	0.0014(2)	0.0001(2)	−0.0005(1)	−0.0002(2)
T_{2m}	0.0013(2)	0.0009(2)	0.0013(2)	−0.0001(1)	−0.0005(1)	0.0000(1)
T_{2o}	0.0013(2)	0.0011(2)	0.0016(2)	0.0000(2)	−0.0007(2)	0.0001(2)
O_{1o}	0.0021(5)	0.0016(5)	0.0036(5)	0.0011(4)	−0.0010(4)	−0.0004(5)
O_{1m}	0.0019(5)	0.0015(5)	0.0030(5)	0.0003(4)	−0.0004(4)	0.0000(4)
O_{2o}	0.0018(5)	0.0010(5)	0.0022(5)	−0.0007(4)	−0.0015(4)	0.0004(4)
O_{2m}	0.0017(5)	0.0016(5)	0.0025(6)	−0.0004(4)	0.0004(4)	0.0004(4)
O_{3o}	0.0015(5)	0.0023(5)	0.0017(5)	0.0003(4)	−0.0004(4)	0.0000(4)
O_{3m}	0.0009(5)	0.0023(5)	0.0021(6)	−0.0007(4)	−0.0007(4)	0.0007(4)
O_4	0.0035(5)	0.0025(5)	0.0014(5)	−0.0007(4)	−0.0005(4)	−0.0002(4)
O_5	0.0019(5)	0.0037(5)	0.0017(5)	−0.0006(4)	−0.0012(4)	0.0005(5)

Results

Average and real structure

Final atomic coordinates and anisotropic temperature coefficients of the average structure are given in Table 1.[1] The selected bond distances and angles are summarized in Table 2. The figures match those reported by Griffen et al. (1977) within an error of 3σ.

The weak intensities of extra reflections indicate the real structure to be derivable from the average one by slight structural changes. If the real structure has a space group $P2/m$, Pm, or $P2$, it requires significant structural changes from the average one, because the positions of atoms in the average structure are due to $P2_1/a$ symmetry. Therefore, the space group $P\bar{1}$ is provisionally employed for the real structure.

At the initial stage, two-dimensional Fourier synthesis was carried out and then the structure was refined by least squares methods using two dimensional diffraction data. Because of fewer reflections, only positional parameters were obtained in the course of least squares refinement. After several cycles of refinement the structure converged to an $R = 0.051$ for 229 observed reflections, while 77 extra reflections due to the real structure showed an $R = 0.242$. When the three-dimensional refinement was carried out, the result converged to an average structure because the number of extra reflections was small and their intensities were generally weak. The converged x- and z-parameters are listed in Table 3.

Table 2. Selected bond lengths.

M-cation site			
$Sr-O_{1o}$	0.2691(4) nm		
$Sr-O_{1m}$	0.2729(4) nm		
$Sr-O_{2o}$	0.2659(4) nm		
$Sr-O_{2m}$	0.2629(4) nm		
$Sr-O_{3o}$	0.2585(4) nm		
$Sr-O_{3m}$	0.2611(4) nm		
$Sr-O_5$	0.2654(3) nm		
MEAN	0.2651 nm		
Tetrahedral sites			
$T_{1o}-O_{1o}$	0.1732(5) nm	$T_{1m}-O_{1m}$	0.1609(4) nm
$T_{1o}-O_{2o}$	0.1763(4) nm	$T_{1m}-O_{2m}$	0.1608(4) nm
$T_{1o}-O_{3o}$	0.1749(4) nm	$T_{1m}-O_{3m}$	0.1609(4) nm
$T_{1o}-O_5$	0.1744(4) nm	$T_{1m}-O_5$	0.1637(4) nm
MEAN	0.1747 nm	MEAN	0.1616 nm
$T_{2o}-O_{1o}$	0.1631(4) nm	$T_{2m}-O_{1m}$	0.1760(4) nm
$T_{2o}-O_{2o}$	0.1641(4) nm	$T_{2m}-O_{2m}$	0.1761(4) nm
$T_{2o}-O_{3o}$	0.1612(4) nm	$T_{2m}-O_{3m}$	0.1769(4) nm
$T_{2o}-O_4$	0.1600(4) nm	$T_{2m}-O_4$	0.1728(4) nm
MEAN	0.1621 nm	MEAN	0.1754 nm

Table 3. Two-dimensional atomic coordinates of real structure of slawsonite.

Atom	x	z
Sr	0.8923(4)	0.2539(5)
T_{1o}	0.226(1)	0.930(1)
T_{1m}	0.237(1)	0.559(1)
T_{2o}	0.060(2)	0.942(2)
T_{2m}	0.057(1)	0.567(1)
O_{1o}	0.199(3)	0.010(4)
O_{1m}	0.186(3)	0.496(3)
O_{2o}	0.123(4)	0.953(4)
O_{2m}	0.126(4)	0.575(4)
O_{3o}	0.924(5)	0.068(6)
O_{3m}	0.894(4)	0.450(5)
O_4	0.008(3)	0.766(3)
O_5	0.312(3)	0.742(3)
Sr_z	0.6095(4)	0.7531(5)
T_{1oz}	0.266(1)	0.067(1)
T_{1mz}	0.259(1)	0.439(1)
T_{2oz}	0.439(2)	0.056(3)
T_{2mz}	0.443(1)	0.428(1)
O_{1oz}	0.315(3)	0.987(4)
O_{1mz}	0.308(3)	0.504(4)
O_{2oz}	0.381(3)	0.059(4)
O_{2mz}	0.371(3)	0.457(5)
O_{3oz}	0.577(5)	0.938(7)
O_{3mz}	0.598(3)	0.567(4)
O_{4z}	0.488(3)	0.237(4)
O_{5z}	0.188(2)	0.254(4)

Phase transition

In the present DTA, study a weak exothermic peak was observed at 593 K. A sample was repeatedly heated and cooled in the temperature range between 523 K and 673 K and the exothermic peak was observed only once in the course of increasing temperature on the first run. Then the slawsonite specimen was heated in a Pt-crucible at 623 K for one hour and cooled in air. The heated specimen was subjected to a precession study. On the photographs exposed for 96 hours, reflections of (102), $(\bar{1}02)$, $(10\bar{2})$ and $(\bar{1}0\bar{2})$ disappeared (Fig. 3). Then, an in situ observation of the transition was carried out on the precession camera equipped with an infrared furnace, where the temperature was controlled within ±5 K. The diffraction pattern was recorded on the imaging plate (abbreviated to IP), which is characterized by its high sensitivity and wide dynamic range for X-ray detection. The IP is, therefore, adequate for the present in situ observation. The diffraction photographs with IP were taken every 30 K from 533 K to 623 K, where the exposure time was one hour. The digital data of the diffraction image were converted to the readable one for a Macintosh computer. Then, the diffraction profiles were approximated with a Gaussian curve. Fig. 4 shows the diffraction profiles of (202) and (102) fitted by the Gaussian approximation at room temperature, 593 K and 623 K. In Fig. 4 it can be seen that the reflection of (102) became diffuse and weak at 593 K and disappeared at 623 K. This fact confirms that a phase transition from $P\bar{1}$ phase to $P2_1/a$ phase took place as already indicated by the exothermic peak in the DTA curve.

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[1] Additional material to this paper can be ordered referring to the no. CSD 58539, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. The list of F_o/F_c-data is available from the author up to one year after the publication has appeared.

Fig. 3. A precession photograph of slawsonite heated at 623 K for one hour. Reflections of (102), ($\bar{1}$02), (10$\bar{2}$) and ($\bar{1}$0$\bar{2}$), which were indicated in Fig. 1, disappeared.

Discussion

The refined real structure was not the final one, because a close agreement between the observed and calculated structure factors was not obtained for the weak reflections due to the real structure. However, the tendency of the intensity distributions was similar in the observed and calculated ones. Furthermore no high intensities were calculated for the observed real-structure reflections which were weak. Small discrepancies in some T–O bond lengths still remain but the bond lengths were calculated with the *y*-coordinates of the average structure.

The compositional similarity between Wallowa and Sarusaka slawsonites requires a direct comparison. The substitution of Ca for Sr in the former up to 13 : 87 serves to stabilize the $P2_1/a$ structure even under room temperature conditions. At present, $P\bar{1}$ phase is neither found in calcian slawsonite nor paracelsian. There are no essential differences of the crystal structures in the present slawsonite, paracelsian and calcic slawsonite. However, the sizes of the seven-coordinated polyhedra of cation-oxygen (M–O) are different, though the forms of th are almost identical. These facts can be explained by occupations of the cations with different ionic radii. T average M–O bond lengths are 0.2651 nm, 0.2185 n and 0.2630 nm in the present slawsonite, paracelsian a calcian slawsonite, respectively and the effective io radii of Sr^{2+}, Ba^{2+} and Ca^{2+} in seven-coordinat polyhedra are 0.129 nm, 0.147 nm and 0.115 nm, resp tively (Shannon, Prewitt, 1969; Whittaker, Munt 1970). If the average atomic radii are taken into account, both phases with smaller ($Sr_{0.87}Ca_{0.13}$) and larger (Ba) average atomic radii than Sr are expected to have $P2_1/a$ structure. It is thus very likely that the ionic radius of cations to be placed in the cationic site of the $P2_1/a$ structure is most significantly responsible for the appearance of transition, or generation of the low temperature modification with the $P\bar{1}$ structure, since no low temperature modification of calcian slawsonite and of paracelsian is known. The high temperature modification of nearly pure slawsonite is supposed to have a rather large range of cationic solid solubility due to the capability of smaller to larger cations to be accommodated in the $P2_1/a$ structure while the range of solid solubility of $P\bar{1}$ slawsonite will be considerably narrower than that of the high temperature modification.

Both of Wallowa and Sarusaka slawsonite structures indicate essentially similar Si–O and Al–O distances, proving the complete ordering of Si and Al atoms in the four-membered ring. The average T–O distances are 0.1747 nm, 0.1754 nm, 0.1616 nm and 0.1621 nm in the present slawsonite and 0.1748 nm, 0.1748 nm, 0.1623 nm and 0.1624 nm in the calcian slawsonite. In the anorthite with perfect Al/Si ordering, Al–O and Si–O distances are 0.1743 nm–0.1757 nm and 0.1613 nm–0.1618 nm, respectively, according to the results by Kalus (1978).

The $P\bar{1}$ structure produced at 593 K was derived from the $P2_1/a$ structure after slight atomic displacements and phase transition from the $P\bar{1}$ structure to the $P2_1/a$ one

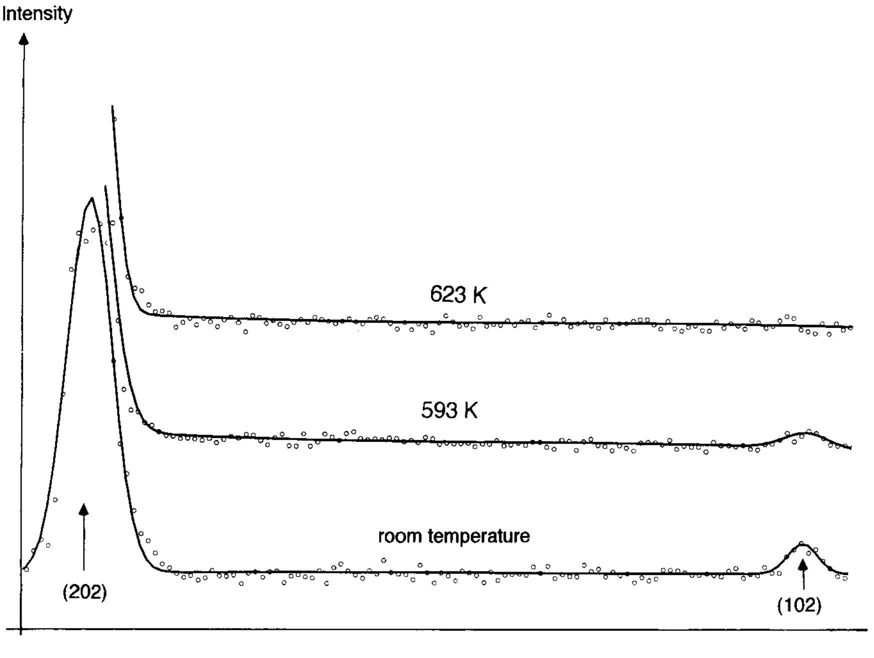

Fig. 4. Diffraction profiles of (202) and (102) recorded on Imaging Plate through in situ observation at room temperature, 593 K and 623 K. The small circles indicate raw intensity data and the thick lines indicate the profiles fitted by Gaussian curve. The (102) reflection becomes diffuse at 593 K and disappeared at 623 K.

takes place irreversibly. The phase transition found in the present slawsonite presents an example of a new type of transition found in the paracelsian-slawsonite series.

The newly realized transition temperature does not seem to conflict with the geological circumstances. That is, slawsonite occurs as narrow veins cutting metagabbro, which is composed of aggregates of clinopyroxene, grossular and minor chlorite (Kato, Matsubara, 1985). The formation of slawsonite was subsequent to that of chlorite in the metagabbro, where its lower temperature formation is very reasonable.

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