

Crystal Structures of the High-Temperature Forms of $\text{Ln}_2\text{Si}_2\text{O}_7$ (Ln = La, Ce, Pr, Nd, Sm) Revisited

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The crystal structures of the high-temperature forms of light lanthanide pyrosilicates (disilicates), i.e., $(\text{La-to-Sm})_2\text{Si}_2\text{O}_7$, have been studied with powder X-ray diffraction on the quenched samples. These compounds have monoclinic structures with the space group $P2_1/n$ rather than orthorhombic structures. In the research of the last two decades, the smallness of the monoclinic angles (90.1° – 91°) has possibly obscured the revelation of the true structural nature of these compounds. New XRD patterns are suggested for the studied lanthanide pyrosilicates exhibiting the monoclinic characteristics of the unit cells.

I. Introduction

THE crystal structures of the high-temperature polymorphs of the synthetic pyrosilicates ($\text{Ln}_2\text{Si}_2\text{O}_7$) of light lanthanides, where Ln was La, Ce, Nd, Sm and Eu, were first fully investigated by Smolin and Shepelev in a single-crystal study.¹ From this study, the above five pyrosilicate phases were claimed to be orthorhombic with the space group $P2_12_12_1$. The range of cell dimensions of these phases were reported¹ as $a = 5.410$ – 5.374 Å (La–Eu), $b = 13.17$ – 12.82 Å (La–Eu), and $c = 8.76$ – 8.65 Å (La–Eu) in accord with the lanthanide contraction. Later Felsche and Hirsiger² confirmed the existence of the orthorhombic structure in their powder X-ray diffraction patterns for the light lanthanides (La to Sm) but suggested the possible space groups $Pna2_1$ or $Pnma$ with the extinction rules $0kl: k + l = 2n$ and $h0l: h = 2n$, assuming the presence of a close structural similarity with orthorhombic α - $\text{Sr}_2\text{P}_2\text{O}_7$.³ Shortly after this publication, Felsche⁴ suggested a change in the space group to $P2_1/n$ of the monoclinic class after observing some $h0l$ reflections with $h \neq 2n$ present in the patterns of light lanthanide pyrosilicates, assuming the structure resembled more that of α - $\text{Ca}_2\text{P}_2\text{O}_7$.⁵ Although α - $\text{Ca}_2\text{P}_2\text{O}_7$ is monoclinic with $\beta = 90.3^\circ$ and $a = 12.66$ Å, $b = 8.542$ Å, and $c = 5.315$ Å, Felsche⁴ was apparently not able to detect an angle different than 90.0° in the cells and preferred to call the high-temperature structure “pseudo-orthorhombic” with a monoclinic space group. The observed range of cell dimensions of those pseudo-orthorhombic phases were given by Felsche⁴ as $a = 5.409$ – 5.383 Å (La–Sm), $b = 13.201$ – 12.855 Å (La–Sm), and $c = 8.794$ – 8.564 Å (La–Sm) and were in good agreement with those of the work of Smolin and Shepelev.¹

The present authors were the first to observe a monoclinic angle ($\beta = 90.13^\circ$) in one of the high-temperature polymorphs

of the light lanthanide pyrosilicates, i.e., $\text{Ce}_2\text{Si}_2\text{O}_7$, in a recent study⁶ of the phase relations in the system Al_2O_3 – $\text{Ce}_2\text{Si}_2\text{O}_7$. Do the other light lanthanide pyrosilicates (of La, Pr, Nd, and Sm) exhibit a structural similarity, as $\text{Ce}_2\text{Si}_2\text{O}_7$ does, to α - $\text{Ca}_2\text{P}_2\text{O}_7$, and do they have such small monoclinic angles? This paper reports the results of our investigative efforts that have focused mainly on these questions.

II. Experimental Methods

Mixtures of $\text{Ln}_2\text{Si}_2\text{O}_7$ stoichiometry (Ln = La, Pr, Nd, and Sm) were prepared by mixing solid oxides, La_2O_3 , Pr_6O_{11} , Nd_2O_3 , and Sm_2O_3 (99.95 wt% pure, Molycorp, White Plains, NY) and fumed SiO_2 (99.98 wt% pure, Sigma Chemical, St. Louis, MO) under ethyl alcohol in an agate mortar for about 1 h. The oxides were heated in air at 800°C for 12 h just prior to weighing. For each composition, approximately 1.5-g samples of the mixtures were weighed and uniaxially pressed into 1.27-cm-diameter pellets in a tungsten carbide-lined steel die at about 70 MPa. These pellets were then cold isostatically pressed at 210 MPa.

The pellets were equilibrated at 1560°C in a MoSi_2 quench furnace with a vertical 120-cm-long alumina reaction tube. The inert atmosphere in the sealed furnace tube was maintained by a moderate flow of prepurified argon + 10% H_2 gas. The pellets were contained in envelopes made from thin foils of Mo and suspended with Mo wires in the hot zone. The temperatures in the hot zone were controlled to within $\pm 6^\circ\text{C}$ by using B-type monitoring thermocouples calibrated against the melting points of Au (1064°C) and Pd (1554°C). After the first 6 h of heating at 1560°C , with a heating rate of $3^\circ\text{C}/\text{min}$ from ambient to T_{max} , the samples were quenched by dropping into a stirred, ice-deionized water bath (covered with a thin layer of low vapor pressure diffusion pump oil), crushed, ground, repelletized, and reheated at 1560°C for an additional 15 h, followed by quenching and phase analysis for the compound formation. The densities of the equilibrated samples were measured with the Archimedes technique, using deionized water as suspension medium.

For structure analyses, the ground (to a mean particle size of about 6 μm) quenched samples were examined using XRD in the 5° – 85° 2θ range using a powder diffractometer (XDS 2000, Scintag, Santa Clara, CA) with a step scanning (step = 0.02° , preset = 10 s, $\text{CuK}\alpha$ radiation) of 0.1° $2\theta/\text{min}$. Silicon (NBS640a) was used as an external standard. The cell reduction, symmetry determination, refinement, indexing, and the least-squares analyses of the powder XRD data were performed by using the routines Appleman and Evans,⁷ TREOR,⁸ NIST-Lattice,^{9,10} and DBWS-9006PC (Rietveld analysis).¹¹

III. Results and Discussion

All of the high-temperature polymorphs of light lanthanide pyrosilicates investigated in this work, i.e., $\text{La}_2\text{Si}_2\text{O}_7$, $\text{Pr}_2\text{Si}_2\text{O}_7$, $\text{Nd}_2\text{Si}_2\text{O}_7$, and $\text{Sm}_2\text{Si}_2\text{O}_7$, did exhibit the monoclinic crystal

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structures with the space group $P2_1/n$ and the extinction rules $h0l: h + 1 \neq 2n$ and $0k0: k \neq 2n$. The monoclinic angles, β , observed were in the range 90.12° – 91.06° . The cell parameters and densities of the compounds are listed in Table I. The new XRD patterns for the above four phases are given in Tables IIa through II.d.⁷

For the orthorhombic symmetry to be found in the patterns of light lanthanide pyrosilicates, conforming to the previously suggested² space groups $Pnma$ (centric) or $Pna2_1$, the two reflection conditions $0kl: k + l = 2n$ and $h0l: h = 2n$ must be obeyed. However, as later realized by Felsche,⁴ $h0l$ reflections with $h \neq 2n$ could be found in the XRD data of the pyrosilicates, depending on the resolving power. $0kl$ reflections with $k + l \neq 2n$ are also seen in the patterns. These two observations alone suffice to lower the symmetry to that of a monoclinic structure with a possible space group $P2_1/n$.

In our XRD patterns of $(\text{La-Sm})_2\text{Si}_2\text{O}_7$, $0k0$ reflections with $k = 2n$ were observed with strong intensities along with the strong $h00$ (where $h = 2n$) reflections. These reflections show that the strong orthorhombic character is still present in the structure. It should be remembered that the same character was also noted by Calvo⁵ in a similar $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$ cell. This very well might be one of the reasons why the previous researchers on the pyrosilicates felt hesitant to dismiss the orthorhombic cell.

This is not a new polymorphic transformation to be observed in the light lanthanide pyrosilicates. It is just a question of the resolving power of the equipment, quality of the data collected, and the indexing procedures utilized. Felsche, in his later article⁴ on this matter, was able to intuitively feel the peak splitting present (to 021 and 301) in the strongest peak of the "pseudo-orthorhombic" $\text{Nd}_2\text{Si}_2\text{O}_7$ and assigned both indexes to the same reflection after finding the space group $P2_1/n$. On the other hand, the strongest peak of $\text{Nd}_2\text{Si}_2\text{O}_7$ (like the other light pyrosilicates) could be resolved to three separate reflections, -301 , 021 , and 301 . Figure 1 shows the result of our profile fitting study by using Pearson VII curves (Peakfit 3.0, Jandel Scientific, Corte Madera, CA) in this range for this compound.

The cell volumes and the calculated densities of the monoclinic light (La-Sm) lanthanide pyrosilicates are plotted in Fig. 2 against the atomic number. A monotonic decrease trend in cell volumes depicting the lanthanide contraction was observed. The same decrease was seen when the cell parameters were plotted against the atomic number.

The structure of the light lanthanide pyrosilicates projected onto the xy plane is shown in Fig. 3. A significant similarity to the structure of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$ published by Calvo⁵ must be noted. The numbers adjacent to the atoms represent the z coordinates in the unit cell. The tentative positional parameters of the cell determined by Rietveld analysis¹¹ (with $R_w = 17.2\%$) on the $\text{Ce}_2\text{Si}_2\text{O}_7$ powder sample are given in Table III with the e.s.d.'s in parentheses adjacent to the decimal they belong. These atomic positions did not change noticeably throughout the light lanthanide series of pyrosilicates in our powdered sample Rietveld analyses. We believe that the more accurate determination

of the atomic parameters awaits the preparation of good-quality single crystals of pyrosilicates.

IV. Conclusions

The monoclinic nature of the high-temperature polymorphs of $\text{La}_2\text{Si}_2\text{O}_7$, $\text{Pr}_2\text{Si}_2\text{O}_7$, $\text{Nd}_2\text{Si}_2\text{O}_7$, and $\text{Sm}_2\text{Si}_2\text{O}_7$, has been revealed. Together with the recently studied⁶ $\text{Ce}_2\text{Si}_2\text{O}_7$, it was made clear that all of the light lanthanide pyrosilicates do have similar monoclinic unit cells as opposed to the previously

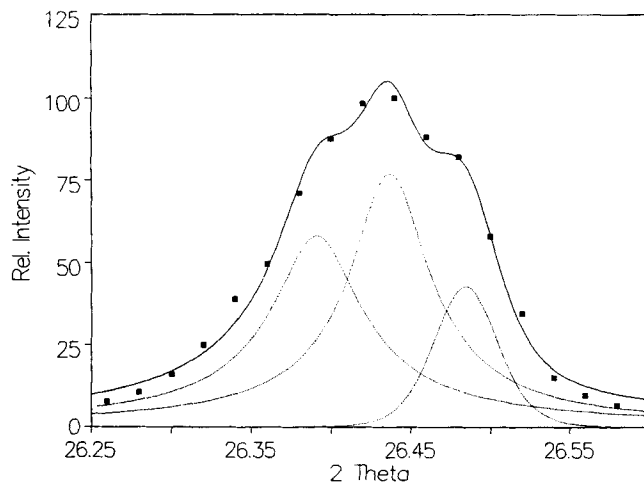


Fig. 1. Sample of the profile fitting study carried out on the whole of the XRD pattern of $\text{Nd}_2\text{Si}_2\text{O}_7$. -301 , 021 , and 301 peaks are depicted at the 2θ values of 26.391° , 26.437° , and 26.485° , respectively.

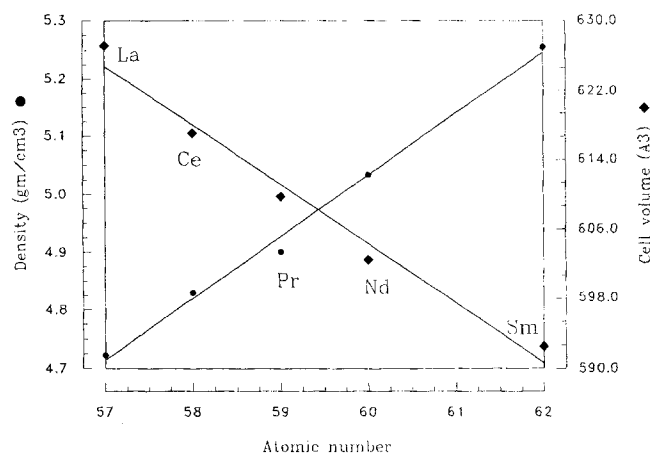


Fig. 2. Cell volumes and calculated densities versus atomic number of the high- T forms of light lanthanide pyrosilicates.

⁷For Table II, order ACSD-218 from Data Depository Service, American Ceramic Society, 735 Ceramic Place, Westerville, OH 43081-8720. The previously published pattern for $\text{Ce}_2\text{Si}_2\text{O}_7$ is available as ACSD-212.

Table I. Structural Parameters and Densities of the High- T Light Lanthanide Pyrosilicates

Compound	Lattice parameters (\AA)	β	Cell volume (\AA^3)	Z^*	ρ , XRD (g/cm^3)	ρ , mes (g/cm^3)	Ref.
$\text{La}_2\text{Si}_2\text{O}_7$	$a = 13.1914, b = 8.7935, c = 5.4104$	92.06°	627.19	4	4.723	4.69	TS ⁷
$\text{Ce}_2\text{Si}_2\text{O}_7$	$a = 13.0803, b = 8.7270, c = 5.4054$	90.13°	617.03	4	4.830	4.78	6, 12
$\text{Pr}_2\text{Si}_2\text{O}_7$	$a = 13.0149, b = 8.6717, c = 5.4033$	90.51°	609.76	4	4.901	4.87	TS
$\text{Nd}_2\text{Si}_2\text{O}_7$	$a = 12.9461, b = 8.6326, c = 5.3908$	90.12°	602.47	4	5.034	5.00	TS
$\text{Sm}_2\text{Si}_2\text{O}_7$	$a = 12.8553, b = 8.5603, c = 5.3849$	91.47°	592.50	4	5.256	5.23	TS

* Z = Formula units per cell. ⁷TS = this study.

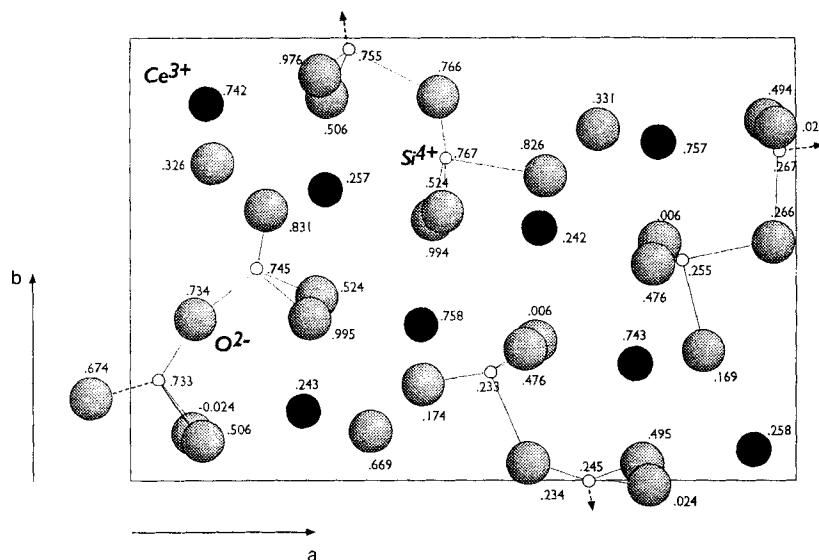


Fig. 3. Tentative unit cell contents of the high- T forms of light lanthanide pyrosilicates projected onto the xy plane.

Table III. Positional Parameters of the Structure of High-Temperature Form of $Ce_2Si_2O_7$

Atom	x	y	z
Ce (1)	0.767(1)	0.803(1)	0.757(4)
Ce (2)	0.589(1)	0.609(2)	0.242(4)
Si (1)	0.0337(1)	0.242(1)	0.733(2)
Si (2)	0.180(1)	0.488(2)	0.745(5)
O (1)	0.0663(6)	0.4133(8)	0.734(2)
O (2)	0.247(1)	0.463(2)	0.524(3)
O (3)	0.062(1)	0.155(2)	-0.024(3)
O (4)	0.237(1)	0.415(2)	0.995(3)
O (5)	0.077(1)	0.138(2)	0.506(3)
O (6)	0.172(1)	0.659(2)	0.831(2)
O (7)	-0.093(1)	0.235(2)	0.674(3)

assumed orthorhombic structure. It was shown that this structure strongly resembled that of α - $Ca_2P_2O_7$, and the monoclinic angles were found to be extremely small, in the range 90.12° – 91° , as also was the case with calcium pyrophosphate. New XRD patterns have been suggested for these phases. The cell parameters displayed a monotonic decrease with increasing atomic number in a manner expected for the lanthanide contraction.

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