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Structural data from X-ray powder diffraction for new high-temperature phases $(Y_{1-x}Ln_x)_2Si_2O_7$ with Ln = Ce, Pr, Nd

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Abstract

Extending the investigation on possible mixed phases with composition $(Y_{1-x}Ln_x)_2Si_2O_7$ formed at high temperature under oxidizing conditions in silicon nitride samples doped with Y_2O_3 and Ln_2O_3 as sintering aids, the compounds with Ln = Ce, Pr, Nd were successfully synthesized and structurally characterized by Rietveld whole powder pattern refinement. Some fluctuations in the x values were found as well, but all the compounds are monoclinic (space group $P2_1/c$), with lattice parameters close to those of the previously studied $(Y_{2/3}La_{1/3})_2Si_2O_7$. Further efforts with Sm (and Dy) failed in producing the expected G-form phase, indicating that the family does not extend beyond Nd: in these cases Ln ions partially substitute Y in its already known α- and δ-disilicates. Under the adopted experimental conditions (1 atm, ambient air), an explanation of the impossibility to obtain the phase in question containing lanthanides with $Z \geqslant 62$ was attempted on the basis of lattice strains introduced by foreign ions larger than Y.

Keywords: $(Y,Ln)_2$ Si_2O_7; X-ray methods; Phase composition; Grain boundary phase

1. Introduction

During previous studies of the oxidation resistance at high temperature in air of fully dense silicon nitride based materials densified with the addition of sintering aids (i.e Y_2O_3 and La_2O_3), a new mixed disilicate was found and completely characterized.[1] A synthesis of this new phase, out of a silicon nitride matrix, was successfully carried out as well in excess of SiO_2.

To improve the knowledge of such $(Y_{1-x}Ln_x)_2Si_2O_7$ possible class of compounds with high temperature G-form structure,[2,3] a systematic study with following light rare earths (Ln = Ce, Pr, Nd, Sm) was undertaken. Experiments were performed with Ln = Dy too, even if this element does not belong properly to the light group, due to the fact that its ionic radius is almost equal to that of Y^{3+}.

This paper describes the synthesis of these new mixed disilicates, the assessment of their stoichiometry and the relative structure determination. When the expected phase failed to form, the reasons for this finding were analyzed and tentatively explained.

2. Experimental

Several powder mixtures were prepared varying the molar content of the rare earth oxides involved (Y_2O_3, H.C. Starck - Germany; CeO_2, Merck- Germany; Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Dy_2O_3, Techsnabexport - Russia), the test temperature and the dwell time in view to obtain the highest amount and/or the best defined X-ray diffraction pattern of the expected new mixed disilicate. The prerequisite of the amorphous silica (SiO_2, Carlo Erba - Italy) in excess was kept constant for each prepared mixture.

Once the initial composition was designed, the oxide precursors were ultrasonically mixed in pure ethanol and dried. The blend was then softly pestled in agate mortar, pellettized (100 kg/cm^2), mounted on a platinum support, and finally placed in a laboratory kiln.

The as-treated pellet was finely ground in agate mortar and, on this powdered sample, the XRD analyses were conducted. Accurate XRD patterns were recorded over an angular range $10° < 2\theta < 60°$ on a Siemens mod. D500 (Ni filtered CuK_α, 25 mA 33 KV, step width 0.02°, sampling time 6 s). Table 1 summarizes the most significant attempts with starting composition, thermal cycle and crystalline phases identified.

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Parallel inspections were performed via SEM (Cambridge mod. S360) equipped with an EDX analyzer (eXL II Link Analytical Pentafet) in order to assess the composition associated to the new formed phases. For this need it was necessary to coat the selected powdered samples with a thin carbon film.

The experimental diffraction patterns were processed using the following software packages: DBWS-9411 for Rietveld refinement,[4] DMPLOT[5] and PowderCell 2.3[6] for the necessary graphic illustrations.

3. Results and discussion

Being the expected structure type of the possible $(Y_{1-x}Ln_x)_2Si_2O_7$ phases known from the early determined $(Y_{2/3}La_{1/3})_2Si_2O_7$,[1] a systematic search was carried out on mixtures thermally treated at different temperatures from 1400 to 1650°C.

By varying the starting compositions, as shown in Table 1, the G-form structure was clearly identified in some Ce-, Pr- and Nd-containing samples. In the first three Nd-containing samples, this form is not detectable due to the fact that, even if small quantities would have been present, the overlapping peaks of α- or δ-$Y_2Si_2O_7$ made the identification largely uncertain. Quantitative EDX analyses yielded for Ce a stoichiometry very similar to the La compound,[1] i.e $X \approx 1/3$, while for Pr $X \approx 1/2$ was found and for Nd $X \approx 2/5$, with no traces of other phases, excluding the unavoidable SiO_2 (α-cristobalite).

On the contrary the Sm-containing samples resisted to any effort: at temperatures 1400–1500°C only α-$Y_2Si_2O_7$, and δ-$Y_2Si_2O_7$ at temperatures 1550–1650°C were detected. A careful inspection of the XRD patterns revealed

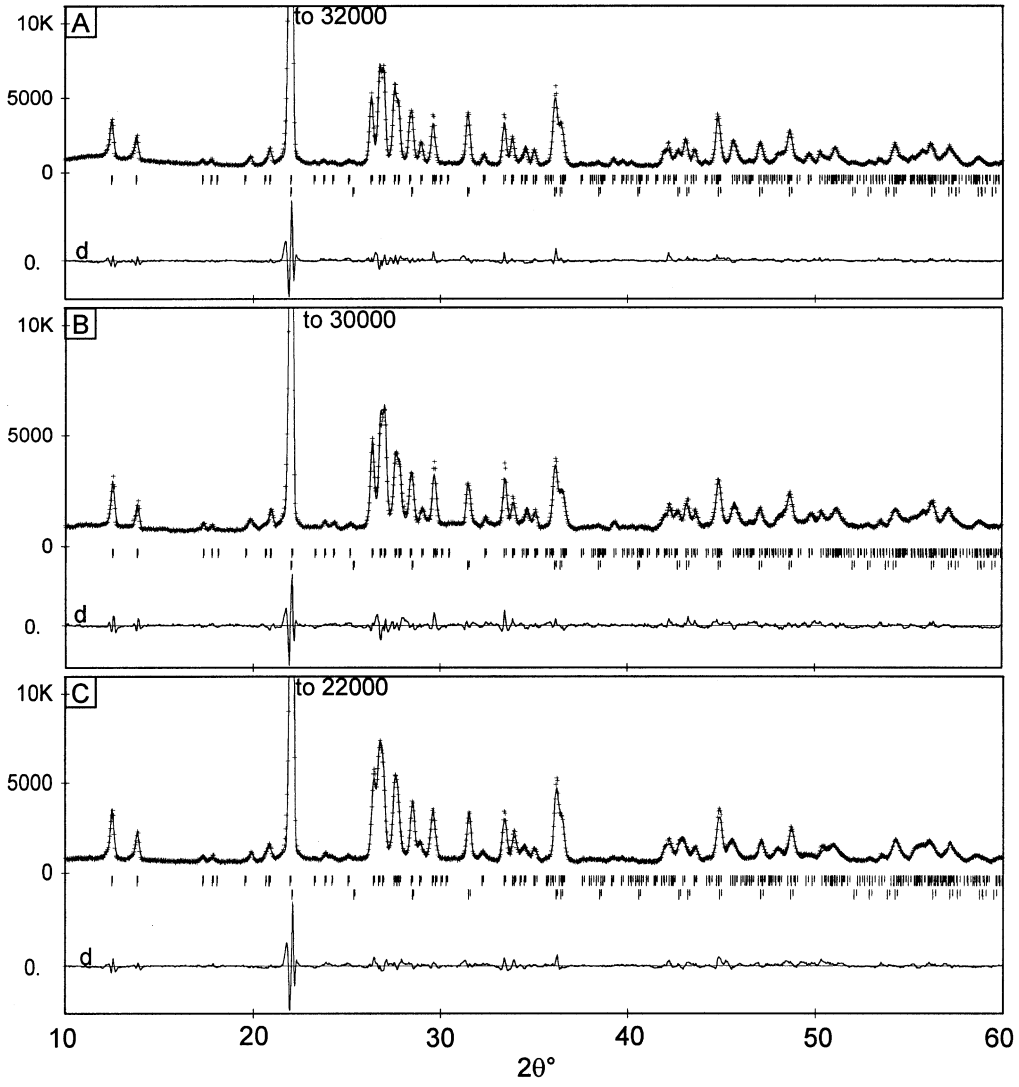

Fig. 1. Outputs of the whole-powder-X ray pattern fitting by Rietveld refinement [observed profile intensities (+) and calculated intensities (-)] for the selected compositions YCe3 (A), YPr5 (B), and YNd4 (C). The difference plot (d) between the observed and calculated intensities for each processed XRD patterns is shown. Short vertical bars represent the Bragg reflection positions of the expected new phase (upper) and α-cristobalite (lower)

that lattice parameters of the two Y-disilicates increased on the average by about 1% (α-form: $a=6.62$, $b=6.71$, $c=12.34$ Å, $\alpha=94$, $\beta=89$, $\gamma=93°$; δ-form: $a=13.81$, $b=5.02$, $c=8.30$ Å), indicating that Sm substituted partially for Y: instead of forming the expected phase, Sm prefers to occupy Y sites in both the well known disilicate polymorphs.[7]

While La, Ce, Pr and Nd elements have ionic radius r exceeding that of Y by more than 10% (corresponding to a volume increase $\geqslant 33\%$ in large cations fraction, representing 8–12% of the total cell volume), Sm is the first with r going below this limit: it seems that, when the linear strain induced by the substitution of Y by Ln element is lower that 10%, the lanthanide enters the Y-disilicate lattice (corresponding to the thermal treatment temperature) and does not give rise to G-form structure anymore.

A further experiment was performed with Dy, which exhibits a linear lattice strain, if compared to Y, of merely ~1%: such a element is the last showing a δ-type disilicate among the lanthanides: mainly δ-$(Y,Dy)_2Si_2O_7$ and traces of γ-$(Y,Dy)_2Si_2O_7$ were found with lattice parameters increased on the average by 0.1% ($a=13.70$, $b=5.01$ $c=8.18$ Å). Strong evidence can be deduced for the fact that $(Y_{1-x}Ln_x)_2Si_2O_7$ compounds with high temperature G-type structure are formed only with rare earth types characterized by a ionic radius sufficiently large.

The structural data for the isomorphous new compounds $(Y_{2/3}Ce_{1/3})_2Si_2O_7$, $(Y_{1/2}Pr_{1/2})_2Si_2O_7$ and $(Y_{3/5}Nd_{2/5})_2Si_2O_7$ are reported in Tables 2–5. The results of the whole-powder-pattern fitting are presented in Fig. 1a–c for the new formed high temperature Ln-Y disilicates, Ln = Ce(a), Pr(b), Nd(c). The comparison between observed and calculated intensities are shown in Tables 6–8 (excluded the reflections belonging to α-cristobalite). These outputs were obtained after Rietveld refinement by means of the DBWS-9411 program,[4] starting from structural parameters predetermined for $(Y_{2/3}La_{1/3})_2Si_2O_7$ (Table 5). The drawings in Fig. 2a–c, built with PowderCell 2.3[6] represent the projection of the monoclinic $(Y_{1-x}Ln_x)_2Si_2O_7$ structure with Ln = Ce (a), Pr (b), and Nd (c).

The reliability index R_{WP} is quite good (Table 5), even if not as satisfactory as in the case of La: from Tables 2–4 it can be noted again the tendency of Y to occupy preferentially positions (2) leaving the major part of substituting Ln in position (1). In the case of Pr, the sharing is complete, with Y and Pr occupying in equal proportions position (2) and (1), respectively.

SEM micrographs from some as-treated powder mixtures and corresponding EDX spectra are presented in Fig. 3.

The apparent deviation of Pr-based compound cell volume from the expected monotonic decrease, coming from the well known "lanthanide contraction", is easily understood taking into account the fact that larger Pr ions substitute Y in an anomalously high proportion.

The reason why more Ln enters in the compound $(Y_{1-x}Ln_x)_2Si_2O_7$ when Ln = Pr, Nd is not easy to understand. It seems that a sort of volume compensating mechanism is activated which prevents the cell volume from becoming too small (allow for the fact that all the cell volumes of the new mixed phases lie within a poor 1.5%).

Theoretical calculations based on the volumes of the different ions involved in the formula units treated as cubes of edge $2r$ yielding a complete space filling, properly

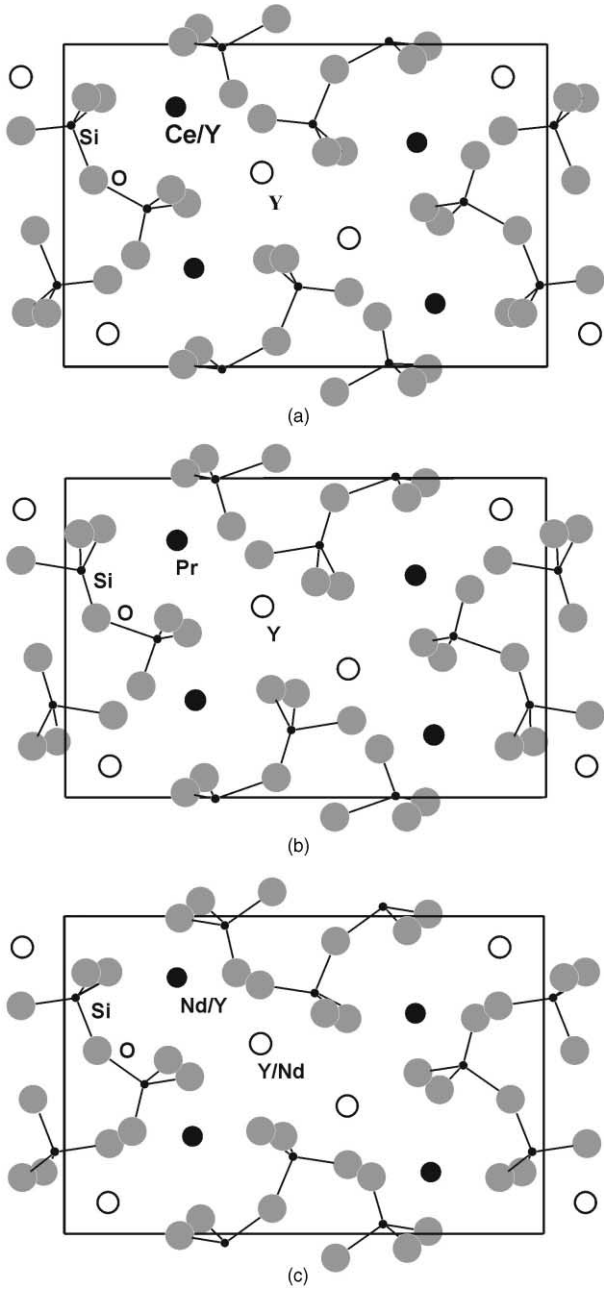

Fig. 2. Projection of the monoclinic structure (space group $P2_1/c$) seen along [100] at $(10\bar{1})$ of $(Y_{2/3}Ce_{1/3})_2Si_2O_7$ (a), $(Y_{1/2}Pr_{1/2})_2Si_2O_7$ (b), and $(Y_{3/5}Nd_{2/5})_2Si_2O_7$ (c).

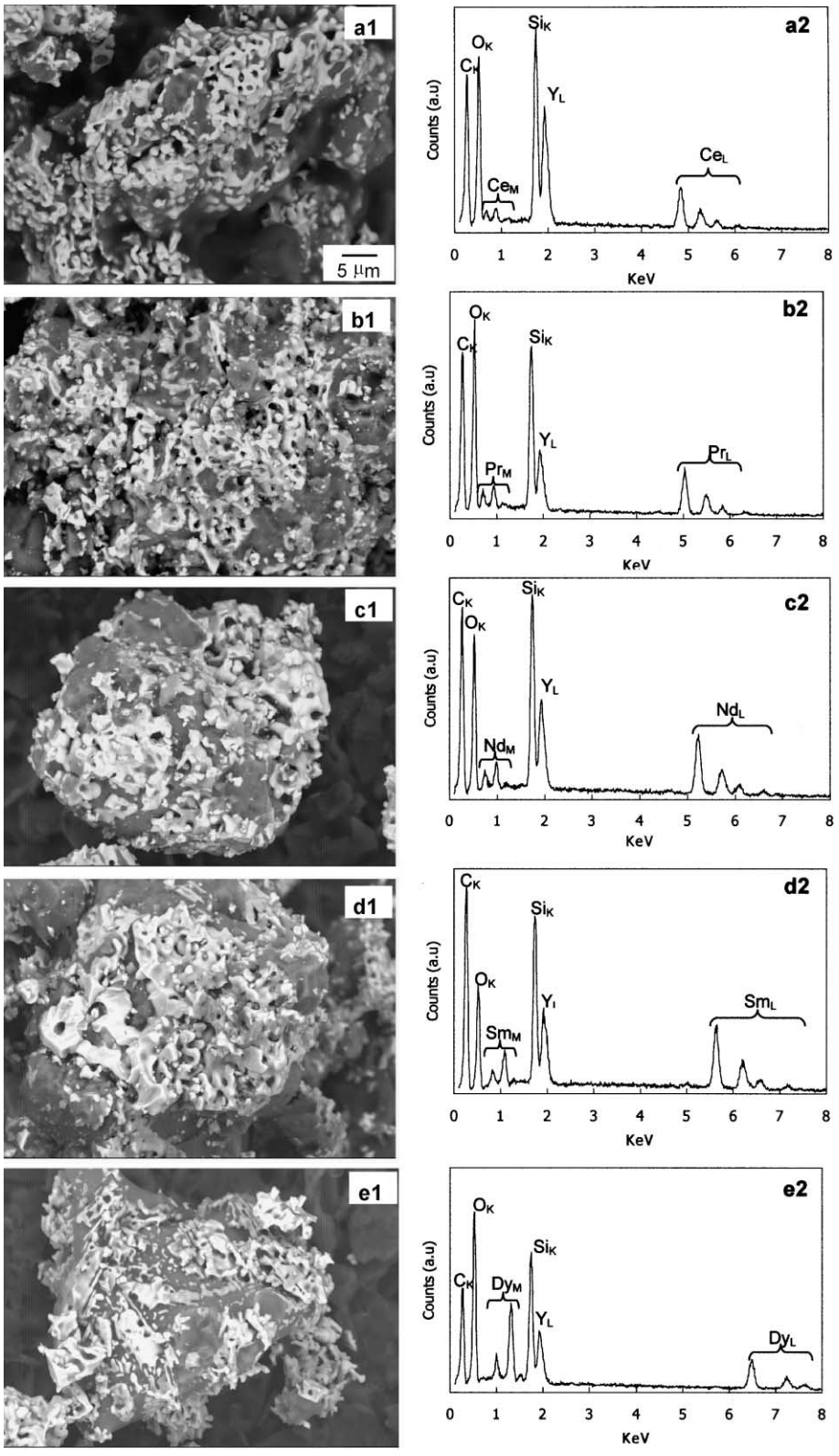

Fig. 3. BSE–SEM micrographs (left column) from the as treated mixtures YCe2 (a1), YPr6 (b1), YNd5 (c1), YSm4 (d1), and YDy1 (e1). The EDX spectra (right column) were collected on the bright features (placed upon the grey α-cristobalite particles) of the corresponding micrograph.

Table 1
Summary of the most significant attempts: the complement to 100% (wt. or mol) for each composition consists of amorphous silica

Mixture	Composition				Thermal treatment		Crystalline phases			Notes
	Y		Ln		Temperature (°C)	dwell (h)	NSP[c]	α-cristobalite		
	wt.%	mol%	wt.%	mol%						
YPr1	6	2	24	2	1450	2	Y[d]	Y	Y_2SiO_5*[a]	
YPr2	15	5.3	15	1.2	1500	2	Y	Y	δ-$Y_2Si_2O_7$	
YPr3	6	2	24	2	1500	2	Y	Y	–	
YPr4	10	1.6	20	3.6	1500	2	Y	Y	–	
YPr5	6	2	24	2	1550	2	Y	Y	–	**[b]
YPr6	10	1.6	20	3.6	1550	2	Y	Y	–	
YPr7	15	5.3	15	1.2	1600	2	–	Y	δ-$Y_2Si_2O_7$	Fused
YCe1	14.1	5	20.3	9.2	1450	2	Y	Y	Y_2SiO_5*, CeO_2	
YCe2	15	6.6	15	5.0	1500	2	Y	Y	–	
YCe3	15	6.6	15	5.0	1550	2	Y	Y	–	**
YCe4	14.1	5	20.3	9.2	1550	2	Y	Y	–	
YCe5	15	6.6	15	5.0	1600	2	–	Y	δ-$Y_2Si_2O_7$	Fused
YNd1	15	5.2	15	3.5	1450	2	–	Y	α-$Y_2Si_2O_7$	
YNd2	15	5.2	15	3.5	1500	2	–	Y	α-$Y_2Si_2O_7$	
YNd3	15	5.2	15	3.5	1550	2	–	Y	δ-$Y_2Si_2O_7$	
YNd4	14	5.1	21	5.2	1550	2	Y	Y	–	**
YNd5	18	4.2	12	4.2	1600	2	Y	Y	δ-$Y_2Si_2O_7$	
YNd6	14	5.1	21	5.2	1600	2	Y	Y	–	
YSm1	10	3.5	20	4.5	1400	2	–	Y	α-$Y_2Si_2O_7$	
YSm2	15	5.2	15	3.4	1450	2	–	Y	α-$Y_2Si_2O_7$	
YSm3	15	5.2	15	3.4	1500	2	–	Y	α-$(Y,Sm)_2Si_2O_7$	
YSm4	15	5.2	15	3.4	1550	2	–	Y	δ-$(Y,Sm)_2Si_2O_7$, Sm_2O_3/$Sm_2Si_2O_7$*	
YSm5	14	5.1	21	5.2	1550	2	–	Y	δ-$(Y,Sm)_2Si_2O_7$, Sm_2O_3/$Sm_2Si_2O_7$*	
YSm6	10	3.5	20	4.5	1600	2	–	Y	δ-$(Y,Sm)_2Si_2O_7$, Sm_2O_3/$Sm_2Si_2O_7$*	
YSm7	10	3.5	20	4.5	1650	2	–	Y	δ-$(Y,Sm)_2Si_2O_7$, Sm_2O_3/$Sm_2Si_2O_7$*	
YDy1	18.7	5	11.3	5	1600	2	–	Y	δ-$(Y,Dy)_2Si_2O_7$, γ-$(Y,Dy)_2Si_2O_7$*	

[a] * Traces.
[b] ** Pattern processed for Rietveld refinement.
[c] NSP: new synthesized phase.
[d] Y: yes.

Table 2
Structural data of the new phase $(Y_{2/3}Ce_{1/3})_2\ Si_2O_7$[a]

Atom	X	Y	Z	Occupancy
Y(1)	0.5172	0.8055	0.7689	0.335
Ce(1)				0.665
Y(2)	0.8295	0.6008	0.5890	1
Si(1)	0.730	0.253	0.014	1
Si(2)	0.910	0.510	0.171	1
O(1)	0.806	0.421	0.059	1
O(2)	0.999	0.164	0.045	1
O(3)	0.574	0.168	0.078	1
O(4)	0.560	0.268	0.910	1
O(5)	0.798	0.493	0.253	1
O(6)	0.231	0.451	0.221	1
O(7)	0.034	0.655	0.150	1

[a] $B_{OV} = 0.4$.

Table 3
Structural data of the new phase $(Y_{1/2}Pr_{1/2})_2Si_2O_7$[a]

Atom	X	Y	Z	Occupancy
Pr(1)	0.5161	0.8044	0.7688	1
Y(2)	0.8371	0.5988	0.5876	1
Si(1)	0.753	0.289	0.028	1
Si(2)	0.928	0.505	0.186	1
O(1)	0.801	0.438	0.059	1
O(2)	0.009	0.174	0.025	1
O(3)	0.597	0.161	0.072	1
O(4)	0.540	0.258	0.903	1
O(5)	0.790	0.484	0.249	1
O(6)	0.288	0.439	0.215	1
O(7)	0.019	0.650	0.159	1

[a] $B_{OV} = 1.5$.

Table 4
Structural data of the new phase $(Y_{3/5}Nd_{2/5})_2Si_2O_7$[a]

Atom	X	Y	Z	Occupancy
Y(1)	0.5234	0.8056	0.7662	0.5
Nd(1)				0.5
Y(2)	0.8346	0.5984	0.5889	0.7
Nd(2)				0.3
Si(1)	0.745	0.258	0.021	1
Si(2)	0.920	0.530	0.164	1
O(1)	0.811	0.422	0.066	1
O(2)	0.018	0.194	0.046	1
O(3)	0.577	0.176	0.090	1
O(4)	0.542	0.282	0.908	1
O(5)	0.854	0.507	0.260	1
O(6)	0.297	0.453	0.216	1
O(7)	0.043	0.678	0.142	1

[a] $B_{OV} = 0.7$.

account for unit cell volumes found in the given stoichiometry: the monotonic reduction in O^{2-} radius with decreasing trivalent cations size observed in lanthanides pyrosilicates has to be held in due consideration, being oxygen responsible of about 90% of cell volume occupation.

The overall thermal factor B_{OV} significantly higher for Pr compound (Table 3) has likely to be attributed to the lower stability of Pr oxides.

The best fit implies not neglibible displacements of some oxygen atoms from the geometrically regular tetrahedral positions, leading to a typical distorted arrangement linked to the non-equilibrium conditions of nucleation and growth. On the other hand the spatial positions of the heavy ions in the real lattice remain remarkably constant, and those of Si undergo only minor changes (Tables 2–4). In general, the partial substitution of Y to Ln ions, doesn't introduce substantial modification in the G-form structure as described in Refs [2] and [3] (accounting for the choice in Ref. [3] of a description by $P2_1/n$ space group with β very close to 90°), apart from the enhanced tetrahedra distortion. An estimate of SiO_4 tetrahedra distortion, based both on the discrepancy of Si–O average bond distances as compared to the theoretical value (1.65 Å) and on the half maximum spread of the same distance, gave 11% for La, 8% for Ce, 15% for Pr and 6% for Nd compounds, respectively. Once more Pr, besides the peculiar Ln-rich stoichiometry, involves the most perturbed structure.

While Y-La compound is white, Y-Ce appears very pale yellow, Y-Pr very pale green and Y-Nd very pale purple coloured: of course the colours are faded by the contemporary presence of large fraction of white SiO_2 (α-cristobalite).

4. Conclusions

Extending the study of the class of compounds $(Y_{1-X}Ln_X)_2Si_2O_7$ with high temperature G-form structure, whose first member was that with Ln = La and X = 1/3, three new phases were synthesized (with Ln = Ce, Pr, Nd and X = 1/3, 1/2, 2/5 respectively) in excess of silica, and structurally characterized by whole powder X-ray pattern Rietveld refinement. All the new phases are monoclinic, space group $P2_1/c$[14], with cell parameters as follows (Z = 4 for everyone): $(Y_{2/3}Ce_{1/3})_2Si_2O_7$, $a = 5.365(1)$Å, $b = 8.509(1)$Å, $c = 13.804(1)$Å, $\beta = 111.45(1)°$, $\rho_{XRD} = 4.305$ g/cm^3; $(Y_{1/2}Pr_{1/2})_2Si_2O_7$, $a = 5.370(1)$Å, $b = 8.542(2)$Å, $c = 13.838(2)$Å, $\beta = 111.76(2)°$, $\rho_{XRD} = 4.485$ g/cm^3; $(Y_{3/5}Nd_{2/5})_2Si_2O_7$, $a = 5.362(1)$Å, $b = 8.496(1)$Å, $c = 13.782(1)$Å, $\beta = 111.46(1)°$; $\rho_{XRD} = 4.435$ g/cm^3.

In these cases too the atomic coordinates showed that substitution of Ln for Y cations preferentially occurs in half of the possible lattice positions: only Nd presents replacement in both of them. Si-O tetrahedra are slightly distorted in Ce and Nd compounds, while Pr compound is characterized by a deformation even larger than that previously found for La.

Attempts to obtain the high temperature G-form phase with Ln = Sm, Dy failed, probably because the lanthanides more easily substituted Y in α- and/or δ-disilicates lattice when the produced strain is sufficiently small. If the ratio $r(Ln)/r(Y)$, at least for lanthanides with cation radius larger than that of Y, deviates from unit by less than 10%, it looks energetically more favoured for Ln to replace Y in Y-disilicates instead of a general rearrangement to form the new phase. Clear

Table 5
Structural parameters (a, b, c, β, V, Z), density (ρ_{XRD}), and reliability index (R_{WP}) for the Rietveld refinement of the high temperature new formed phases

Compound	Lattice parameter				Cell volume	Z[a]	ρ_{XRD}	R_{WP}	Ref.
	a(Å)	b(Å)	c(Å)	β(°)	(Å^3)		(g/cm^3)	(%)	
$(Y_{2/3}La_{1/3})_2Si_2O_7$	5.375(1)	8.569(1)	13.863(1)	111.79(1)	592.9	4	4.250	6.6	[1]
$(Y_{2/3}Ce_{1/3})_2Si_2O_7$	5.365(1)	8.509(1)	13.804(1)	111.45(1)	586.5	4	4.305	8.6	TW[b]
$(Y_{1/2}Pr_{1/2})_2Si_2O_7$	5.370(1)	8.542(2)	13.838(2)	111.76(2)	589.6	4	4.485	8.6	TW
$(Y_{3/5}Nd_{2/5})_2Si_2O_7$	5.362(1)	8.496(1)	13.782(1)	111.46(1)	584.3	4	4.435	7.3	TW

[a] Z: formula units per cell.
[b] TW: this work.

Table 6
X-ray diffraction data of the new phase $(Y_{2/3}Ce_{1/3})_2Si_2O_7$ ($I_{OBS} \geqslant 5$)

h	k	l	d (Å)	I calc	I obs	h	k	l	d (Å)	I calc	I obs
0	1	1	7.094	454	396	1	3	−5	1.9655	16	19
0	0	2	6.424	265	224	1	4	0	1.9571	28	31
0	1	2	5.127	54	43	1	1	5	1.9523	22	34
1	0	0	4.993	56	52	1	4	−2	1.9517	6	
1	0	−2	4.907	17	11	2	3	−2	1.9486	7	9
0	2	0	4.255	129	128	2	3	−1	1.9317	18	19
1	1	−2	4.251	16		1	1	−7	1.9211	20	21
0	2	1	4.039	106	130	0	2	6	1.9127	10	12
0	1	3	3.825	36	28	0	4	3	1.9052	5	6
1	1	1	3.743	24	49	0	3	5	1.9043	15	18
1	1	−3	3.670	14	32	1	4	1	1.8947	151	149
0	2	2	3.547	9	29	1	4	−3	1.8851	155	149
1	0	2	3.388	738	774	2	3	0	1.8741	29	30
1	2	−1	3.333	1000	1000	2	2	2	1.8715	153	157
1	0	−4	3.307	941	943	2	3	−4	1.8555	94	92
1	2	0	3.238	783	800	2	2	−6	1.8351	164	196
1	2	−2	3.214	523	625	2	1	3	1.8345	27	
0	0	4	3.212	82		1	2	5	1.8143	180	194
1	1	2	3.147	240	251	1	3	4	1.8050	40	44
1	1	−4	3.082	238	251	1	4	2	1.8015	39	43
0	2	3	3.018	439	488	0	1	7	1.7942	45	47
0	1	4	3.005	77	80	2	1	−7	1.7918	6	6
1	2	1	2.977	5	5	1	2	−7	1.7891	152	189
1	2	−3	2.940	16	19	1	4	−4	1.7891	31	
0	3	1	2.770	114	114	2	3	1	1.7858	35	99
2	0	−2	2.682	494	482	1	3	−6	1.7843	62	
1	2	2	2.650	55	306	3	0	−2	1.7767	26	27
1	1	3	2.648	254		0	4	4	1.7736	58	57
1	2	−4	2.611	46	43	2	3	−5	1.7618	31	25
1	1	−5	2.596	108	181	1	0	6	1.7498	21	20
0	3	2	2.595	103		3	1	−2	1.7392	8	6
0	2	4	2.563	146	136	3	1	−4	1.7280	6	6
2	1	−2	2.558	13	13	1	0	−8	1.7236	13	13
2	1	−1	2.520	10	8	1	1	6	1.7140	76	89
1	3	−1	2.507	8	8	2	0	4	1.6938	23	25
2	1	−3	2.497	16	48	1	4	3	1.6908	63	66
2	0	0	2.497	31		1	1	−8	1.6893	72	75
1	3	0	2.466	176	179	0	5	1	1.6871	21	23
0	1	5	2.460	97	96	3	1	−5	1.6779	6	108
1	3	−2	2.456	121	115	1	4	−5	1.6771	113	
2	1	0	2.396	31	22	3	0	0	1.6645	101	95
0	3	3	2.365	25	16	2	1	4	1.6612	23	21
2	1	−4	2.357	16	10	2	4	−1	1.6560	77	71
1	3	1	2.345	25	21	2	0	−8	1.6535	30	28
1	0	4	2.340	6	6	2	4	−3	1.6495	48	46
1	2	3	2.331	7	5	3	2	−3	1.6482	164	155
1	0	−6	2.295	72	75	3	2	−2	1.6395	86	204
2	2	−2	2.269	57	61	0	4	5	1.6386	105	
2	2	−1	2.242	38	43	1	3	5	1.6377	10	
2	1	−5	2.173	13	6	3	0	−6	1.6355	117	121
2	2	0	2.153	171	176	3	2	−4	1.6301	50	49
1	3	−4	2.153	13		2	1	−8	1.6232	44	44
0	0	6	2.141	175	210	1	3	−7	1.6191	21	66
0	3	4	2.126	7	59	1	2	6	1.6183	43	
2	2	−4	2.125	52		1	5	−2	1.6078	23	22
0	4	1	2.099	337	354	3	1	−6	1.6061	30	29
2	0	2	2.084	6	6	1	2	−8	1.5975	14	12
0	1	6	2.077	182	200	1	5	1	1.5755	64	54
1	2	4	2.050	44	45	1	4	4	1.5740	13	19
2	0	−6	2.034	6	7	2	2	4	1.5737	9	
2	1	2	2.024	74	526	1	5	−3	1.5700	51	43
2	2	1	2.022	404		2	4	1	1.5612	11	12
1	2	−6	2.020	37	85	1	4	−6	1.5603	8	
0	4	2	2.019	40		3	1	1	1.5523	28	20
2	2	−5	1.9876	309	353	2	4	−5	1.5451	6	5
1	3	3	1.9876	43		2	2	−8	1.5412	8	38
2	1	−6	1.9783	97	122	0	3	7	1.5409	31	
1	4	−1	1.9774	22							

Table 7
Diffraction data of the new phase $(Y_{1/2}Pr_{1/2})_2Si_2O_7$ ($I_{OBS} \geqslant 5$)

h	k	l	d (Å)	I calc	I obs	h	k	l	d (Å)	I calc	I obs
0	1	1	7.114	455	391	1	4	−2	1.9590	8	9
0	0	2	6.426	244	217	1	1	5	1.9496	33	39
0	1	2	5.135	62	63	2	3	−1	1.9350	6	7
1	0	0	4.987	37	48	1	1	−7	1.9259	24	26
1	0	−2	4.922	19	14	0	2	6	1.9147	5	7
1	1	0	4.307	20	11	0	4	3	1.9112	9	11
0	2	0	4.271	88	94	0	3	5	1.9080	12	15
1	1	−2	4.264	39		1	4	1	1.8997	96	110
0	2	1	4.053	43	53	1	4	−3	1.8923	109	126
0	1	3	3.829	34	20	2	3	0	1.8759	33	43
1	1	1	3.739	40	67	2	2	2	1.8695	105	118
1	1	−3	3.684	27	41	2	3	−4	1.8618	90	99
0	2	2	3.557	18	39	2	2	−6	1.8418	72	115
1	0	2	3.380	811	843	2	1	3	1.8306	47	70
1	2	−1	3.342	1000	1000	1	2	5	1.8131	136	191
1	0	−4	3.319	899	892	1	3	4	1.8057	52	99
1	2	0	3.244	659	683	1	4	2	1.8053	24	
1	2	−2	3.226	484	496	2	1	−7	1.7983	13	15
0	0	4	3.213	100	109	1	4	−4	1.7958	34	184
1	1	2	3.143	198	212	0	1	7	1.7950	22	
1	1	−4	3.093	180	188	1	2	−7	1.7940	114	
0	2	3	3.025	514	525	1	3	−6	1.7900	57	65
0	1	4	3.007	70	69	2	3	1	1.7864	40	48
0	3	1	2.780	72	100	0	4	4	1.7785	36	48
2	0	−2	2.685	505	488	3	0	−2	1.7771	6	8
1	2	2	2.650	68	67	2	3	−5	1.7682	33	33
1	1	3	2.644	233	243	1	0	6	1.7473	27	18
1	2	−4	2.621	31	30	3	1	−4	1.7314	10	8
1	1	−5	2.604	90	178	1	0	−8	1.7274	10	7
0	3	2	2.603	103		1	1	6	1.7118	60	72
0	2	4	2.568	109	110	3	1	−1	1.6979	6	6
2	1	−2	2.561	31	30	0	5	1	1.6935	34	166
1	3	−1	2.515	6	7	1	4	3	1.6935	78	
2	1	−3	2.503	27	30	1	1	−8	1.6931	51	
2	0	0	2.494	33	35	2	0	4	1.6898	23	22
1	3	0	2.473	133	134	1	4	−5	1.6831	114	105
1	3	−2	2.465	131	125	2	3	2	1.6792	11	10
0	1	5	2.461	131	133	3	0	0	1.6625	69	73
2	0	−4	2.461	9		2	4	−1	1.6597	64	115
2	1	0	2.394	23	23	2	0	−8	1.6593	51	
0	3	3	2.371	27	25	2	1	4	1.6577	30	29
2	1	−4	2.365	11	10	2	4	−3	1.6548	45	43
1	3	1	2.349	19	16	3	2	−3	1.6506	154	150
1	2	−5	2.303	9	49	0	4	5	1.6426	62	66
1	0	−6	2.302	43		3	2	−2	1.6408	76	191
2	2	−2	2.273	27	41	3	0	−6	1.6405	100	
2	2	−1	2.244	16	24	1	3	5	1.6379	4	5
2	1	−5	2.181	15	5	3	2	−4	1.6336	42	46
1	3	−4	2.161	9	6	3	1	0	1.6318	6	7
2	2	0	2.153	141	135	2	1	−8	1.6288	27	29
0	0	6	2.142	154	173	1	3	−7	1.6238	24	26
2	2	−4	2.132	52	51	2	4	0	1.6220	6	6
0	3	4	2.131	17	17	1	2	6	1.6172	40	45
0	4	1	2.107	285	283	1	5	−2	1.6139	8	9
2	0	2	2.079	5	189	2	4	−4	1.6129	5	5
0	1	6	2.078	168		3	1	−6	1.6111	16	16
1	2	4	2.049	28	25	1	2	−8	1.6014	13	13
0	4	2	2.027	47	95	1	5	1	1.5802	61	47
1	2	−6	2.026	49		1	5	−3	1.5760	54	59
2	2	1	2.021	365	443	1	4	4	1.5760	6	
2	1	2	2.020	40		2	2	4	1.5713	7	6
2	2	−5	1.9948	257	269	2	4	−5	1.5509	7	31
1	3	3	1.9891	25	24	3	1	1	1.5499	21	
2	1	−6	1.9855	77	106	3	2	0	1.5492	6	
1	4	−1	1.9843	26		2	2	−8	1.5467	7	7
1	3	−5	1.9723	9	12	2	3	−7	1.5451	5	5
1	4	0	1.9631	23	25	0	3	7	1.5430	33	36

Table 8
Diffraction data of the new phase $(Y_{3/5}Nd_{2/5})Si_2O_7$ ($I_{OBS} \geqslant 5$)

h	k	l	d (Å)	I calc	I obs	h	k	l	d (Å)	I calc	I obs
0	1	1	7.083	396	352	2	1	−6	1.9760	59	102
0	0	2	6.413	218	199	1	4	−1	1.9746	35	
0	1	2	5.119	76	86	1	3	−5	1.9625	9	12
1	0	0	4.990	29	41	1	4	0	1.9543	14	20
1	0	−2	4.903	27	21	1	1	5	1.9495	12	37
1	1	−1	4.533	4	7	1	4	−2	1.9489	11	
1	1	0	4.303	34	36	2	3	−2	1.9466	4	6
0	2	0	4.248	145	140	2	3	−1	1.9298	28	32
1	1	−2	4.246	22		2	3	−3	1.9194	4	5
0	2	1	4.033	114	130	1	1	−7	1.9180	4	5
1	1	1	3.739	51	57	0	2	6	1.9096	11	12
1	1	−3	3.666	40	58	0	3	5	1.9013	7	7
0	2	2	3.542	13	29	1	4	1	1.8921	149	138
1	0	2	3.384	794	802	1	4	−3	1.8823	161	149
1	2	−1	3.329	947	956	2	3	0	1.8722	49	51
1	0	−4	3.303	1000	1000	2	2	2	1.8696	129	134
1	2	0	3.235	614	632	2	3	−4	1.8534	86	85
1	2	−2	3.210	487	555	2	2	−6	1.8328	149	205
0	0	4	3.207	35		2	1	3	1.8326	36	
1	1	2	3.144	234	252	1	2	5	1.8117	174	207
1	1	−4	3.078	155	156	1	3	4	1.8024	42	43
0	2	3	3.013	482	511	1	4	2	1.7990	28	30
0	1	4	3.000	49	47	0	1	7	1.7912	46	49
0	3	1	2.765	64	76	2	1	−7	1.7895	5	5
2	0	−2	2.680	514	547	1	4	−4	1.7864	19	192
1	2	2	2.647	59	273	1	2	−7	1.7863	171	
1	1	3	2.644	191		2	3	1	1.7839	41	41
1	2	−4	2.607	26	29	1	3	−6	1.7815	36	36
1	1	−5	2.592	68	195	3	0	−2	1.7758	9	9
0	3	2	2.591	141		0	4	4	1.7708	49	44
0	2	4	2.559	141	141	2	3	−5	1.7597	13	6
2	1	−2	2.556	33	32	1	0	6	1.7474	13	5
2	1	−1	2.518	6	9	3	1	−2	1.7382	14	8
2	1	−3	2.495	39	86	1	0	−8	1.7208	12	6
2	0	0	2.495	42		1	1	6	1.7114	48	55
1	3	0	2.463	193	194	2	0	4	1.6919	24	25
0	1	5	2.456	81	79	1	4	3	1.6883	67	69
1	3	−2	2.452	138	133	1	1	−8	1.6865	54	56
2	0	−4	2.451	5	5	0	5	1	1.6845	23	24
2	1	0	2.394	17	21	3	1	−5	1.6766	5	5
0	3	3	2.361	20	21	1	4	−5	1.6746	109	96
2	1	−4	2.355	31	27	3	0	0	1.6634	84	84
1	3	1	2.342	13	15	2	1	4	1.6594	30	30
1	0	−6	2.292	71	75	2	4	−1	1.6541	67	64
2	2	−2	2.267	16	17	2	0	−8	1.6513	55	51
1	1	4	2.253	5	6	2	4	−3	1.6475	36	164
2	2	−1	2.240	21	23	3	2	−3	1.6470	141	
2	1	1	2.217	6	6	3	2	−2	1.6384	86	88
1	1	−6	2.213	15	15	0	4	5	1.6360	95	115
2	2	0	2.151	137	143	1	3	5	1.6353	14	
1	3	−4	2.150	6		3	0	−6	1.6342	136	144
0	0	6	2.138	191	220	3	1	0	1.6324	12	12
2	2	−4	2.123	42	68	3	2	−4	1.6289	43	43
0	3	4	2.123	23		2	1	−8	1.6210	26	25
0	4	1	2.095	280	318	2	4	0	1.6174	6	85
2	0	2	2.082	5	6	1	3	−7	1.6166	20	
0	1	6	2.073	153	170	1	2	6	1.6159	59	
1	2	4	2.047	35	21	1	5	−2	1.6055	10	22
2	0	−6	2.032	13	14	2	4	−4	1.6052	2	
2	1	2	2.022	57	472	3	1	−6	1.6048	9	
2	2	1	2.020	365		1	2	−8	1.5949	24	17
1	2	−6	2.017	37	66	1	5	1	1.5733	47	32
0	4	2	2.016	25		1	5	−3	1.5676	45	30
2	2	−5	1.9854	268	328	3	1	1	1.5511	35	10
1	3	3	1.9848	44		2	4	−5	1.5432	8	5

evidence of this phenomenon was supplied by SEM investigations and XRD determination of the modified lattice parameters.

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