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Synthesis and crystal structures of $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$

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Abstract

New compounds $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ were prepared by heating mixtures of $CaCO_3$, Y_2O_3 and GeO_2 at 1200 °C. $CaY_2Ge_3O_{10}$ is stable at 1300 °C, while $CaY_2Ge_4O_{12}$ decomposes into a melt and $CaY_2Ge_3O_{10}$ at approximately 1250 °C. We obtained single crystals of $CaY_2Ge_3O_{10}$ by cooling a sample with an initial composition of Ca:Y:Ge = 1:2:8 from 1300 °C with a rate of −6 °C/h. The crystal structure of $CaY_2Ge_3O_{10}$ was determined by single crystal X-ray diffraction. $CaY_2Ge_3O_{10}$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 6.0906(8)$, $b = 6.8329(8)$, $c = 18.752(2)$ Å and $\beta = 109.140(3)^\circ$, $Z = 4$, and $R_1 = 0.029$ for $I > 2\sigma(I)$. In the structure of $CaY_2Ge_3O_{10}$, Ca and Y atoms are situated disorderly in three 7-fold coordination sites between isolated germanate groups of triple GeO_4 tetrahedra, Ge_3O_{10}. The structural formula of $CaY_2Ge_3O_{10}$ is expressed as $(Ca_{0.45}Y_{0.55})(Ca_{0.46}Y_{0.54})(Ca_{0.09}Y_{0.91})Ge_3O_{10}$. The crystal structure of $CaY_2Ge_4O_{12}$ was analyzed by the Rietveld method for the X-ray powder diffraction pattern. $CaY_2Ge_4O_{12}$ is isotypic with $SrNa_2P_4O_{12}$, crystallizing in the orthorhombic space group $P4/nbm$, $a = 9.99282(6)$, $c = 5.06701(4)$ Å, $Z = 2$, $R_{wp} = 0.092$, $R_p = 0.067$. $CaY_2Ge_4O_{12}$ contains four-membered GeO_4-tetrahedra rings, Ge_4O_{12}. Eight-fold coordinated square-anitiprism sites and 6-fold octahedral sites between the layers of the Ge_4O_{12} rings are occupied by Y atom and Ca/Y atoms, respectively The structural formula is $Y(Ca_{0.5}Y_{0.5})_2Ge_4O_{12}$.

Keywords: Calcium yttrium germanates; Crystal structure; X-ray diffraction; Germanate group

1. Introduction

Many reports of the compounds in $CaO–SiO_2$ system have been published because it is a basic and important system for inorganic materials. In $CaO–Y_2O_3–SiO_2$ system, two new quaternary compounds $Ca_3Y_2Si_6O_{18}$ [1,2] and $Ca_3Y_2Si_3O_{12}$ [3] were found in addition to the previously known compounds of $Ca_2Y_8Si_6O_{26}$ (apatite-type) and $Ca_2Y_2Si_2O_9$ (cuspidine-type). $Ca_3Y_2Si_6O_{18}$ comprises three-membered silicate rings of Si_3O_9, and Ca and Y atoms are between the layers of the Si_3O_9 rings. $Ca_3Y_2Si_3O_{12}$ crystallizes not in the garnet-type structure but in the structure isotypic with $Ca_5(PO_4)_2SiO_4$ (silico-carnotite). It was also found that $Ca_2Y_2Si_2O_9$ has an order–disorder phase transition at a temperature between 1400 and 1600 °C [4,5]. In $CaO–Y_2O_3–GeO_2$ system, $Ca_3Y_2Ge_3O_{12}$ having the garnet-type structure was first reported by Isaacs [6], and the structure was studied in detail by Lévy and Barbier [7]. The luminescence properties of Nd-, Eu-, or Tb-doped $Ca_3Y_2Ge_3O_{12}$ were investigated [8–10].

Because of the resemblance of Ge^{IV} to Si^{IV}, the Ge analogues of the major types of silicates have been prepared. Thus, we expected that some new quaternary oxides might exist in $CaO–Y_2O_3–GeO_2$ system. We explored compounds in this system and synthesized two new germanates $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$. The present paper reports the preparation and the crystal structures of the compounds.

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2. Experimental

Starting materials of $CaCO_3$ (99.99%), Y_2O_3 (99.99%), and GeO_2 (99.99%) powders were weighed with a predetermined molar ratio, and mixed with an agate mortar. The mixture was pressed into a pellet and placed on a platinum plate. The pellet was heated from room temperature to 1200 °C with a heating rate of 250 °C/h in air. After heating at these temperatures for 20 h, the samples were cooled to room temperature in a furnace. Differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) were carried out (Shimadzu TMA-50) for $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ powders on a Pt pan with a heating and cooling rate of 10 or 20 °C/mim. The as-prepared samples and the samples after DTA–TGA were powdered and examined by X-ray diffraction using Cu*Kα* radiation with a pyrolitic graphite monochromator and a powder diffractometer (Rigaku RINT2500).

Single crystals of $CaY_2Ge_3O_{10}$ were prepared by heating a sample pellet with the initial composition of Ca:Y:Ge = 1:2:8 at 1300 °C for 30 h in air, and then was cooled to 1000 °C with a cooling rate of 6 °C/h. The outer part of the sample and the Pt plate around it were covered with transparent colorless platelet single crystals of $CaY_2Ge_3O_{10}$. The Ca:Y:Ge molar ratio 0.96:1.95:3.08, that was close to the ideal ratio of $CaY_2Ge_3O_{10}$, was analyzed for a platelet crystal using a scanning electron microscope (Hitachi X-650S) equipped with an energy dispersive X-ray (EDX) analyzer (Horiba EMAX-700).

Diffraction data of $CaY_2Ge_3O_{10}$ were collected on a single-crystal X-ray diffractometer with a two-dimensional CCD detector and graphite-monochromatized Mo*Kα* radiation (Bruker SMART System). The SMART software [11] was used for data acquisition and SAINT [11] for data extraction and reduction. The unit cells were refined during the integration with the program SAINT. Face-indexed analytical absorption correction was applied to the collected diffraction intensity data of $CaY_2Ge_3O_{10}$ with the program XPREP [12]. Structural models were obtained by a direct method with the program SIR97 [13]. Refinement was carried out using SHELXL97 [14]. The complete data collection parameters, details of the structure solution and refinement results are given in Table 1.

The crystal structure of $CaY_2Ge_4O_{12}$ was analyzed by the Rietveld method of the X-ray powder diffraction pattern using a program RIETAN 2000 [15]. The intensity data were collected with a 2θ-width 0.02° in the 2θ range from 10° to 140°. The initial crystal structure model used for the Rietveld analysis was from the structure of $SrNa_2P_4O_{12}$ [16].

Table 1
Crystal data and structure refinement for $CaY_2Ge_3O_{10}$

Chemical formula	$CaY_2Ge_3O_{10}$
Formula weight (g/mol)	595.67
Temperature (°C)	20(2)
Crystal system, space group	Monoclinic $P2_1/c$
Unit cell dimensions	
a (Å)	6.9060(8)
b (Å)	6.8329(8)
c (Å)	18.752(2)
β (deg)	109.140(3)
Volume (Å^3)	836.0(2)
Z, Calculated density (Mg/m^3)	4, 4.733
Radiation wavelength (Å)	0.71073
Absorption coefficient (mm^{-1})	25.052
$F(000)$	1096
Crystal size (mm)	0.8 × 0.4 × 0.12
θ range for data collection (deg)	2.30–29.98
Limiting indices	$-9 \leqslant h \leqslant 9$ $-9 \leqslant k \leqslant 9$ $-17 \leqslant l \leqslant 26$
Reflections collected/unique	6988/2423 [R(int) = 0.0650]
Completeness to $\theta = 30.01$	99.1%
Absorption correction	Face indexed
Max. and min. transmission	0.362 and 0.111
Data/restraints/parameters	2423/0/146
Goodness-of-fit on F^2	0.706
Final R indices [$I > 2\sigma(I)$]	
$R1$, w$R2$	0.0294, 0.0489
R indices (all data) $R1$, w$R2$	0.0484, 0.0526
Extinction coefficient	0.00192(10)
Largest diff. peak and hole (e Å^{-3})	0.959 and −0.872

$R1 = \Sigma||F_o|\text{-}|F_c||/\Sigma|F_o|$.w$R2 = [\Sigma w\ (F_o^2 – F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2)]$, where F_o is the observed structure factor, F_c is the calculated structure factor, σ is the standard deviation of F_c^2, and $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. $S = [\Sigma w(F_o^2 – F_c^2)^2/(n — p)]^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

3. Results and discussion

3.1. Phase relation

$CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ were prepared from the starting mixtures with the molar ratios, Ca:Y:Ge = 1:2:3 and 1:2:4, respectively. $CaY_2Ge_3O_{10}$ did not melt up to 1300 °C in the DTA–TGA analysis. Weight loss of the sample was less than 0.7 mass% and no change was observed in the XRD pattern taken after the analysis. A weight loss (total about 5 mass%) was observed above 1230–1250 °C for $CaY_2Ge_4O_{12}$ after heating and cooling with a rate of 10 °C/min from room temperature to 1380 °C. This sample melted partially and colorless and transparent platelet single crystals of $CaY_2Ge_3O_{10}$ with a size of 0.1–0.2 mm grew around the white grains of the sample on the Pt pan. Formation of $CaY_2Ge_3O_{10}$ phase after the thermal analysis was indicated by powder X-ray diffraction. The weight loss was probably caused by the evaporation of GeO_2 from the melt phase. The melting point of GeO_2 was confirmed at 1116 ± 5 °C that agreed with the reported one [17].

From these results, we propose a GeO_2–$CaY_2Ge_3O_{10}$ pseudo-binary phase diagram as shown in Fig. 1. We could not determine the incongruent melting point clearly by our

DTA analysis, but $CaY_2Ge_4O_{12}$ decomposes into a melt and $CaY_2Ge_3O_{10}$ at approximately 1230–1250 °C.

3.2. $CaY_2Ge_3O_{10}$

The crystal structure of $CaY_2Ge_3O_{10}$ was solved in the monoclinic space group $P2_1/c$, $a = 6.9060(8)$, $b = 6.8329(8)$, $c = 18.752(2)$ Å, $\beta = 109.14(3)^\circ$, $Z = 4$. Table 2 lists the final values of atomic positions, isotropic displacement parameters and occupations. Selected interatomic distances and bond angles are given in Table 3. All atom sites in the structure of $CaY_2Ge_3O_{10}$ are at 4e general positions. As far as we know, this structure is a new type and we could not find any compound with the isotypic structure.

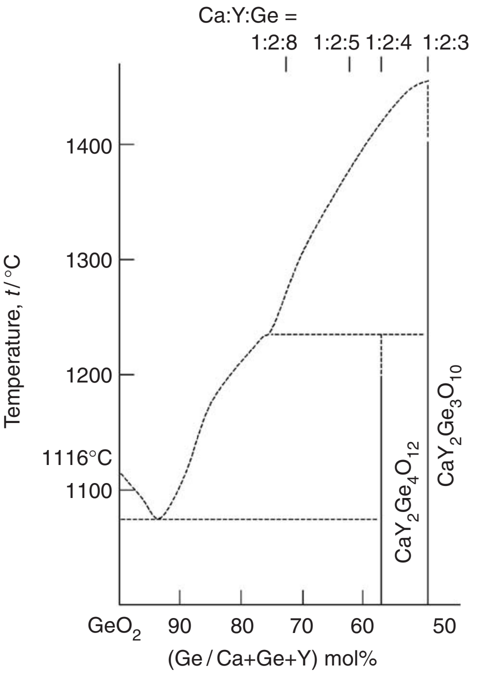

Fig. 1. Proposed pseudo-binary phase diagram of GeO_2–$CaY_2Ge_4O_{12}$.

As shown in Fig. 2, germanium atoms are coordinated by four oxygen atoms and three GeO_4 tetrahedra share apical oxygen atoms, forming a tritetrahedra germanate group Ge_3O_{10}. Similar Ge_3O_{10} groups were reported in the structures of $Ag_8Ge_3O_{10}$ [18] and $RE_2Ge_2O_7$ (RE = La, Nd, and Gd) [19–21]. The Ge–O bond distances of $CaY_2Ge_3O_{10}$ are in the range of 1.713(4)–1.789(4) Å, which are comparable to those reported for other compounds containing Ge_3O_{10} groups (1.626–1.902 Å).

In each GeO_4 tetrahedron in $CaY_2Ge_3O_{10}$, the distance between Ge and shared O atoms is longer than the distances between Ge and unshared O atoms. The shortest average Ge–O distances of 1.748(3) Å and smallest volume of 2.655(5) $Å^3$ were observed in Ge2–O_4 tetrahedron, which is in the middle of the tritetrahedra Ge_3O_{10} group. As shown in Table 3, the highest values of bond length distortion (BLD) [22] and bond angle variance (TVA) [23] indicate that Ge2–O_4 tetrahedron is distorted most.

The bond valence sums of Ge in Ge1, Ge2, and Ge3 sites, calculated with the bond valence parameter of Ge^{VI}–O^{II} (1.748 Å) [24] were 3.917, 4.026, and 3.942, respectively. These are close to the formal valence of Ge^{IV}. The Ge–O–Ge bond angles are 122.1(2)° and 120.9(2)°, which are also in the range of 112.1–137.0° reported for $Ag_8Ge_3O_{10}$ and $RE_2Ge_2O_7$ (RE = La, Nd, and Gd).

Recently, some new compounds $Cu_2M_2Ge_4O_{13}$ (M = Fe, Sc) [25,26] with structures related to the structure of $CuGeO_3$ [27], were reported. One-dimensional GeO_4 chain (GeO_3) in $CuGeO_3$, and two-thirds of GeO_4 tetrahedra of the Ge_4O_{13} isolated chain in $Cu_2M_2Ge_4O_{13}$ are connected to CuO_4 planes. The O–O–O angle for the two adjacent GeO_4 tetrahedra is equal or close to 180°. In the tritetrahedra Ge_3O_{10} group in $CaY_2Ge_3O_{10}$, angles of O1–O6–O9 and O6–O9–O3 are 155.2(2)° and 161.43(14)°, respectively.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $CaY_2Ge_3O_{10}$ U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	Site	x	y	z	U_{eq}	Occupancy
Ca/Y1	4e	0.02486(9)	0.90193(10)	0.41511(4)	0.0096(2)	0.450(3)/0.550(3)
Ca/Y2	4e	0.58216(9)	0.23583(10)	0.41494(4)	0.0095(2)	0.462(4)/0.538(3)
Ca/Y3	4e	0.12931(7)	0.12950(7)	0.25344(3)	0.00728(15)	0.088(4)/0.912(3)
Ge1	4e	0.09835(7)	0.37214(8)	0.42449(3)	0.00696(12)	1.0
Ge2	4e	0.45333(7)	0.22806(8)	0.07202(3)	0.00744(12)	1.0
Ge3	4e	0.65671(7)	0.11880(8)	0.24122(3)	0.00730(12)	1.0
O1	4e	0.0165(5)	0.0775(5)	0.12619(19)	0.0112(8)	1.0
O2	4e	0.0642(5)	0.7200(5)	0.0458(2)	0.0113(8)	1.0
O3	4e	0.1463(4)	0.4498(5)	0.21541(19)	0.0087(7)	1.0
O4	4e	0.1874(5)	0.8101(5)	0.2687(2)	0.0146(8)	1.0
O5	4e	0.2121(5)	0.2027(5)	0.3789(2)	0.0115(8)	1.0
O6	4e	0.3031(5)	0.0554(5)	0.00540(19)	0.0108(8)	1.0
O7	4e	0.3055(5)	0.4145(5)	0.0862(2)	0.0144(8)	1.0
O8	4e	0.4801(5)	0.1684(5)	0.2854(2)	0.0117(8)	1.0
O9	4e	0.5272(5)	0.0484(5)	0.14534(19)	0.0105(8)	1.0
O10	4e	0.6402(5)	0.3211(5)	0.04018(19)	0.0096(8)	1.0

Table 3
Bond lengths and angles for $CaY_2Ge_3O_{10}$

Ca/Y1–O10 (Å)	2.255(2)	Ca/Y2–O10 (Å)	2.282(3)	Ca/Y3–O4 (Å)	2.220(3)
Ca/Y1–O7 (Å)	2.275(3)	Ca/Y2–O2 (Å)	2.311(3)	Ca/Y3–O1 (Å)	2.282(3)
Ca/Y1–O1 (Å)	2.335(3)	Ca/Y2–O7 (Å)	2.331(3)	Ca/Y3–O5 (Å)	2.287(3)
Ca/Y1–O3 (Å)	2.366(3)	Ca/Y2–O8 (Å)	2.342(3)	Ca/Y3–O8 (Å)	2.312(3)
Ca/Y1–O2 (Å)	2.436(3)	Ca/Y2–O9 (Å)	2.419(3)	Ca/Y3–O3 (Å)	2.317(3)
Ca/Y1–O2 (Å)	2.517(3)	Ca/Y2–O5 (Å)	2.430(3)	Ca/Y3–O4 (Å)	2.426(3)
Ca/Y1–O5 (Å)	2.633(3)	Ca/Y2–O6 (Å)	2.617(3)	Ca/Y3–O3 (Å)	2.490(3)
<Ca/Y1–O> (Å)	2.403(3)	<Ca/Y2–O> (Å)	2.391(3)	<Ca/Y3–O> (Å)	2.334(3)
Volume ($Å^3$)	19.661(7)	Volume ($Å^3$)	19.791(7)	Volume ($Å^3$)	19.385(7)
BLD (%)	4.51(5)	BLD (%)	3.53(5)	BLD (%)	3.05(5)
Ge1–O5 (Å)	1.769(2)	Ge2–O10 (Å)	1.712(2)	Ge3–O8 (Å)	1.718(2)
Ge1–O6 (Å)	1.772(2)	Ge2–O7 (Å)	1.707(3)	Ge3–O4 (Å)	1.742(3)
Ge1–O1 (Å)	1.734(3)	Ge2–O6 (Å)	1.783(3)	Ge3–O3 (Å)	1.766(2)
Ge1–O2 (Å)	1.750(3)	Ge2–O9 (Å)	1.788(3)	Ge3–O9 (Å)	1.791(3)
⟨Ge1–O⟩ (Å)	1.756(3)	⟨Ge2–O⟩ (Å)	1.748(3)	⟨Ge3–O⟩ (Å)	1.754(3)
Volume ($Å^3$)	2.742(5)	Volume ($Å^3$)	2.655(5)	Volume ($Å^3$)	2.707(5)
BLD (%)	0.81(3)	BLD (%)	2.18(3)	BLD (%)	1.40(3)
TAV (deg^2)	39.3(2)	TAV (deg^2)	80.8(2)	TAV (deg^2)	66.3(2)
Ge1–O6–Ge2 (deg)	122.2(2)	Ge2–O9–Ge3 (deg)	120.7(2)		

$BLD = 100/n\ \Sigma_{i-1}^{n} |(X—O)_i–(\langle X—O\rangle)|/(\langle X–O\rangle)$ %, n = amount of cation–anion bonds and X–O = cation–anion (oxygen) distance [22].
$TVA = \Sigma_{i=1}^{6} (\Theta_i–109.47°)^2/5$ with Θ_i = O–M–O bonding angle [23].

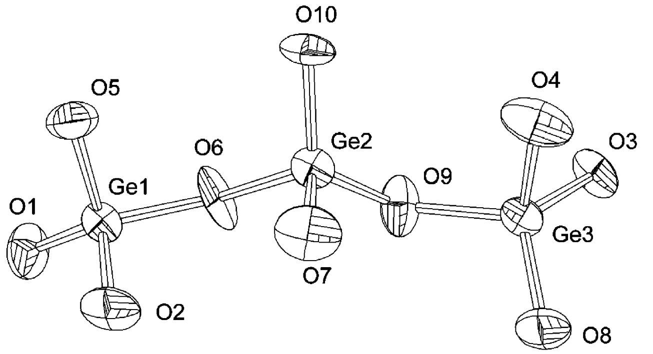

Fig. 2. Ge_3O_{10} group in $CaY_2Ge_3O_{10}$. Displacement ellipsoids are drawn at the 99% probability level.

The arrangement of Ge_3O_{10} groups is shown in Fig. 3(a). Calcium and yttrium atoms are located between the Ge_3O_{10} groups and coordinated by seven oxygen atoms of the groups. Ca and Y atoms occupy Ca/Y1, Ca/Y2, and Ca/Y2 sites statistically with occupations shown in Table 2. The structural formula of $CaY_2Ge_3O_{10}$ can be represented as $(Ca_{0.45}Y_{0.55})(Ca_{0.46}Y_{0.54})(Ca_{0.09}Y_{0.91})Ge_3O_{10}$. The bond valence sums of Y in Ca/Y1, Ca/Y2 and Ca/Y3 sites calculated with the bond valence parameter $R_{Y-O} = 2.014$ Å [24] were 2.585, 2.624, and 3.028, respectively. These values suggest the statistical occupations of Ca^{II} and Y^{III} at least for Ca/Y1 and Ca/Y2 sites. Similar statistical occupation of Ca and Y has been shown in the structures of $Ca_3Y_2Si_3O_{12}$: $(Ca_{0.84}Y_{0.16})(Ca_{0.41}Y_{0.59})(Ca_{0.67}Y_{0.33})_2(SiO_4)_3$ [3], $Ca_3Y_2Si_6O_{18}$: $(Ca_{0.89}Y_{0.11})_2(Ca_{0.54}Y_{0.46})_2(Ca_{0.14}Y_{0.86})(Si_3O_9)_2$ [2] and $Ca_2Y_2Si_2O_9$: $(Ca_{0.76}Y_{0.24})_2(Ca_{0.24}Y_{0.76})_2(Si_2O_7)O_2$ [4].

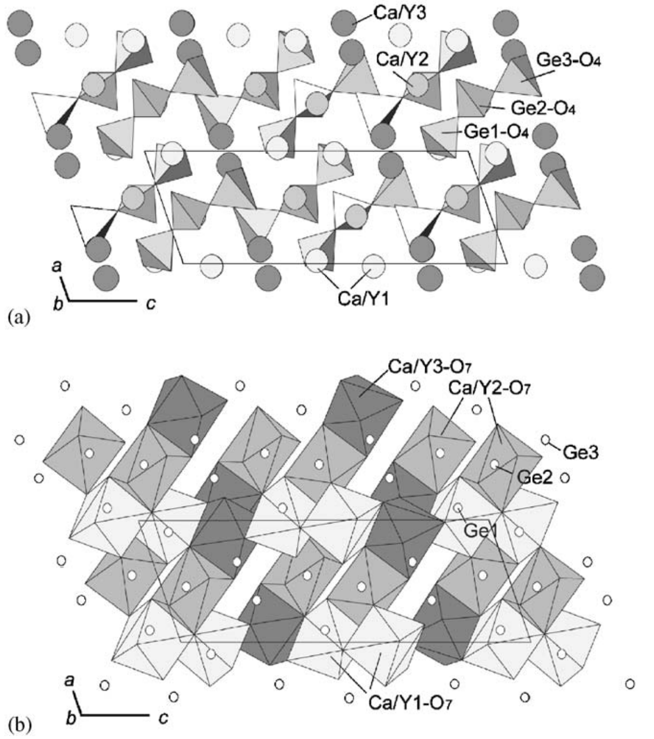

Fig. 3. Crystal structure of $CaY_2Ge_3O_{10}$ showing with the Ge–O_4 tetrahedra (a) and Ca/Y atom-centered oxygen polyhedra (b).

Fig. 3(b) shows the crystal structure of $CaY_2Ge_3O_{10}$ illustrated with Ca/Y centered oxygen decahedra, which connect each other by sharing edges and apexes of the polyhedra. The volume and BLD of Ca/Y3–O_7 polyhedron are smallest in $CaY_2Ge_3O_{10}$ (Table 3).

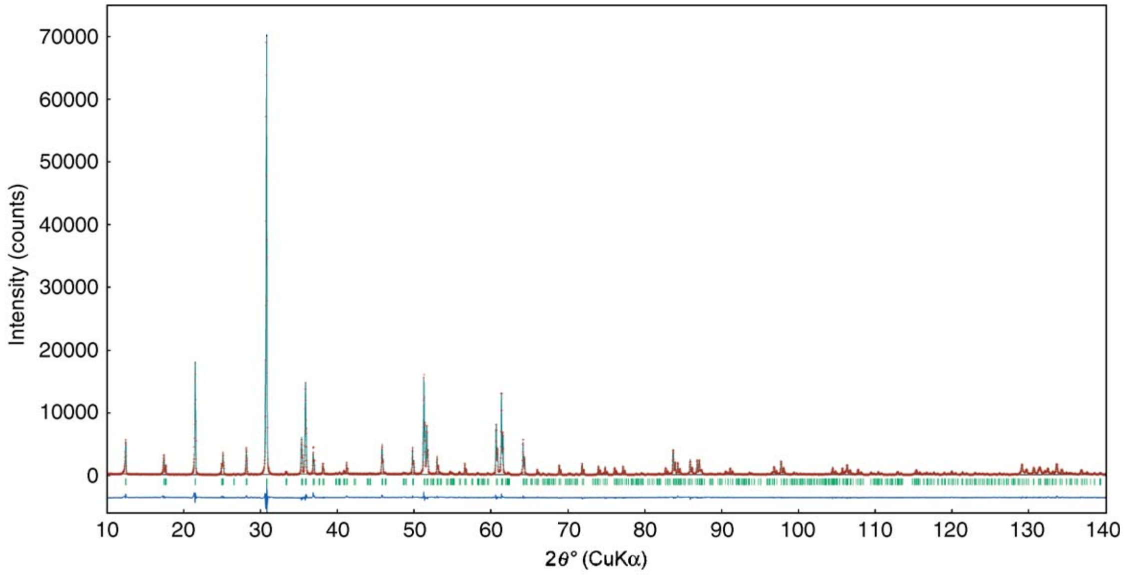

Fig. 4. Observed (dots) and calculated (solid) X-ray diffraction profiles of $CaY_2Ge_4O_{12}$.

Table 4
Crystal data and structure refinement for $CaY_2Ge_4O_{12}$

Chemical formula	$CaY_2Ge_4O_{12}$
Formula weight (g/mol)	700.32
Temperature (°C)	20(2)
Crystal system, space group	Tetragonal, *P*4/*nbm* (Origin choice 2)
Unit cell dimensions	
a(Å)	9.99282(6)
c(Å)	5.06701(4)
Volume (Å^3)	505.97(6)
Z, Calculated density (Mg/m^3)	2, 4.597
Radiation wavelength (Å)	1.540562, 1.544390
θ range for data collection (deg)	5.01–70.00
Increment in 2θ	0.02°
Final *R* indices[a]	
R_{wp}, R_p,	0.0919, 0.0668
R_I, , R_F	0.0421, 0.0413
S[a]	2.1090

[a] Young [28].

3.3. $CaY_2Ge_4O_{12}$

The observed, calculated, and difference patterns of the Rietveld analysis for the X-ray powder diffraction data of $CaY_2Ge_4O_{12}$ are shown in Fig. 4. The final results of the refined lattice parameters and *R*-factors [28] are given in Table 4. The reliability factors R_{wp} and R_p for the full pattern data were 9.19% and 6.68%, respectively. Table 5 lists the final positional, isotropic displacement and occupation parameters of $CaY_2Ge_4O_{12}$. Selected interatomic distances and bond angles are given in Table 6.

Table 5
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $CaY_2Ge_4O_{12}$

Atom	Site	*x*	*y*	*z*	U_{eq}	Occupancy
Ca/Y1	2*b*	1/4	1/4	1/2	0.0039(4)	0.005(5)/0.995(5)
Ca/Y2	4*f*	0	0	1/2	0.0068(4)	0.498(5)/0.502(5)
Ge	8*k*	0.52113(7)	1/4	0	0.0048(2)	1.00
O1	8*m*	−0.3731(3)	0.3731(3)	0.1511(8)	0.0049(11)	1.00
O2	16*n*	0.1753(3)	0.0622(3)	0.2620(5)	0.0029(8)	1.00

$CaY_2Ge_4O_{12}$ is $SrNa_2P_4O_{12}$-tpye structure [16], and isostructural with $CeMn_2Ge_4O_{12}$ [29] and $A_2Sr(VO_3)_4$ ($A = $ Na, K, and Rb) [30]. It crystallizes in the tetragonal space group *P*4/*nbm*. In the Rietveld analysis of $CaY_2Ge_4O_{12}$, the calculated pattern did not fit well to the observed one and the displacement parameter was refined to be a very small value when Ca atom was placed at 2*b* site and Y atom at 4*f* site. Therefore, we placed Ca and Y atoms at both sites and refined the occupation parameters. As shown in Table 5, 2*b* site is almost fully occupied with Y atom, and 4*f* site is statistically occupied by Y and Ca atoms. The structure formula is expressed as $(Ca_{0.5}Y_{0.5})_2Y(Ge_4O_{12})$.

Fig. 5 shows the crystal structure of $CaY_2Ge_4O_{12}$ projected on the *a*–*a* plane. Two O1 atoms of every GeO_4 tetrahedron being shared with other GeO_4 tetrahedra results in a quaternary Ge_4O_{12} ring. The bond length of Ge–O1 (1.793(3) Å) is longer than that of Ge–O2 (1.736(2) Å), where O2 atom is bonded to one Ge atom. Ge–O1 and Ge–O2 bond lengths in the Ge_4O_{12} ring of $CeMn_2Ge_4O_{12}$ are 1.783 and 1.728 Å, respectively. The bond valence sum of the Ge atom in $CaY_2Ge_4O_{12}$ was 3.836 and close to the formal valence of Ga^{IV}.

Table 6
Bond lengths and angles for $CaY_2Ge_4O_{12}$

Y1–O2 (Å)	2.352(2) × 8
Volume (Å^3)	22.391(6)
BLD (%)	0.0
Ca/Y2–O2 (Å)	2.216(2) × 4
⟨Ca/Y2–O⟩ (Å)	2.317(3)
Volume (Å^3)	16.001(6)
BLD (%)[a]	5.81(3)
OAV (°^{2})	63.8(2)
Ge–O1 (Å)	1.793(3) × 2
Ge–O2 (Å)	1.736(2) × 2
⟨Ge1–O⟩ (Å)	1.765(3)
Volume (Å^3)	2.777(5)
BLD (%)[a]	1.63(3)
TAV (deg^2) [a]	45.5(2)
Ge–O1–Ge (deg)	128.8(2)

$\mathrm{OAV} = \Sigma_{i=1}^{12} (\Theta_i - 90°)^2/11$ with Θ_i = O–M–O bonding angle [23].

[a] See footnote of Table 3.

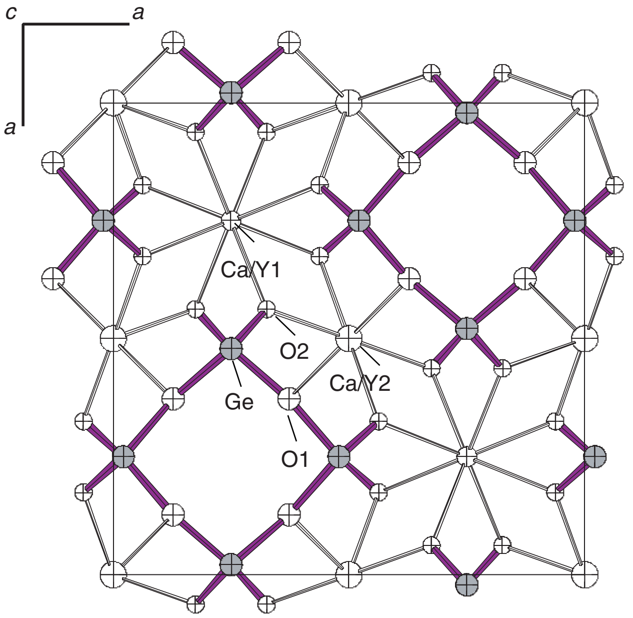

Fig. 5. Projective view of $CaY_2Ge_4O_{12}$ along the *c*-axis direction illustrated with 99% probability displacement spheres.

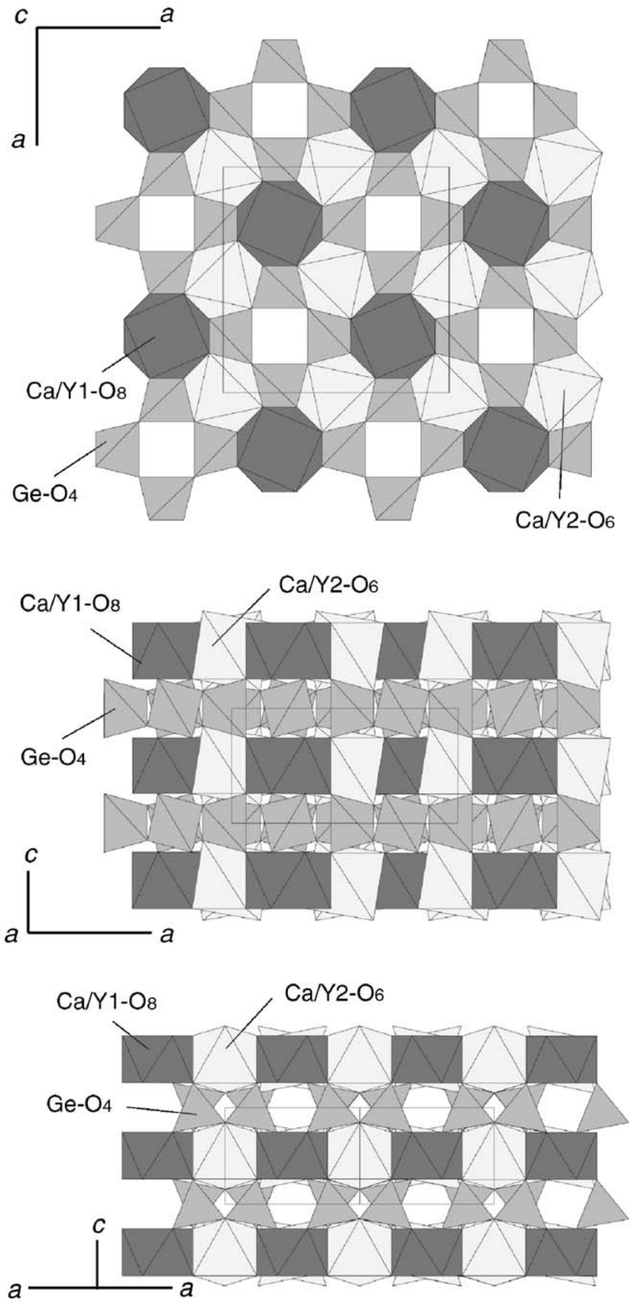

Fig. 6. Projective views of $CaY_2Ge_4O_{12}$ along the *c*-axis, *a*-axis, and [110] directions, illustrated with Ge–O_4 tetrahedra, Ca/Y1–O_8 square anti-prisms, and Ca/Y2–O_6 octrahedra.

The crystal structure of $CaY_2Ge_4O_{12}$ illustrated with oxygen polyhedra is shown in Fig. 6. The structure can be described as Ca/Y1 and Ca/Y2 atom layers and Ge_4O_{12} ring layers stacking along the [0 0 1] direction. Ca and Y atoms connect the Ge_4O_{12} rings. Eight-fold coordination sites of Ca/Y1 are in oxygen square antiprisms. Ca/Y2 site is in an oxygen octahedron. Ca/Y1–O2 distance in the square antiprism is 2.352(2) Å and the average Ca/Y2–O distance in the octahedron is 2.317(3) Å. The bond valence sums calculated with the $R_{\mathrm{Y-O}}$ parameter for Ca/Y1 and Ca/Y2 sites were 3.206 and 2.831, respectively. This result suggests that Ca/Y2 sites cannot be occupied by $\mathrm{Y^{III}}$ atoms only and a statistical occupation of $\mathrm{Ca^{II}}$ and $\mathrm{Y^{III}}$ is necessary.

4. Conclusions

In CaO–Y_2O_3–GeO_2 system, we prepared two new compounds $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$. $CaY_2Ge_3O_{10}$ is stable at 1300 °C. $CaY_2Ge_4O_{12}$ decomposes into a melt and $CaY_2Ge_3O_{10}$ around 1230–1250 °C and GeO_2 evaporates from the melt. The germanates found in the present study are not isostructural with the silicates in

$CaO–Y_2O_3–SiO_2$ system. Triple GeO_4 tetrahedral units of Ge_3O_{15} and four-membered Ge_4O_{12} rings were found in their structures in contrast to the silicates containing isolated monotetrahedra SiO_4, ditetrahedra Si_2O_7, or three-membered Si_3O_9 rings. Ca atoms statistically occupy the sites in $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ with Y atoms. Such statistical occupation of Ca and Y atoms is also seen in the calcium yttrium silicates.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2005.10.023.

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