Crystal structure of tricalcium tantalum trigallium disilicon oxide, $Ca_3TaGa_3Si_2O_{14}$

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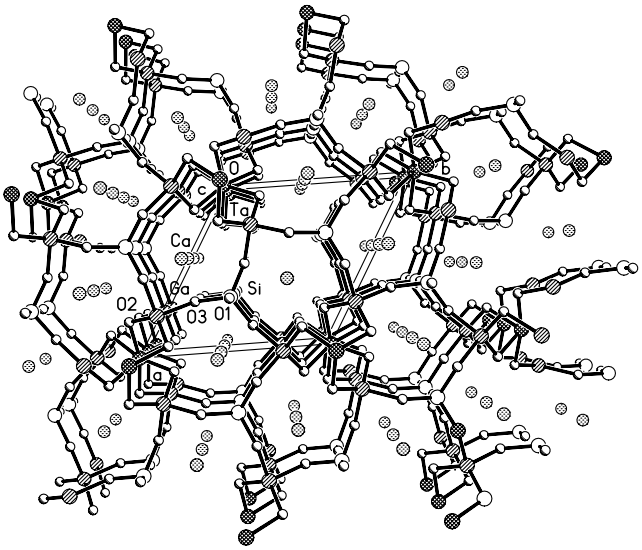

Abstract

$Ca_3Ga_3O_{14}Si_2Ta$, trigonal, $P321$ (No. 150), a = 8.1081(4) Å, c = 4.9850(4) Å, V = 283.8 Å^3, Z = 1, $R_{gt}(F)$ = 0.025, $wR_{ref}(F^2)$ = 0.064, T = 293 K.

Source of material

$Ca_3TaGa_3Si_2O_{14}$ (CTGS) was prepared by solid-state reaction of a stoichiometric mixture of 99.99% $CaCO_3$, Ta_2O_5, SiO_2 and 98% Ga_2O_3 powders. The powders were ground, mixed for 12 h and pressed into tablets. The latter were heated at 1373 K for 6 h to decompose $CaCO_3$ completely and produced CTGS ceramics. The ceramic materials were put into an Ir crucible and melted by RF-heating using an atmosphere of pure nitrogen plus a small amount of oxygen in order to avoid the evaporation of gallium suboxide from the melt during growth. The crystal pulling and rotation rates were 1-3 mm/h and 15-30 rpm, respectively. When the length of the crystal was sufficient, the temperature was lowered to room temperature at a rate of 30-180 K/h. The colorless and transparent single crystals of CTGS (16-14 mm in diameter and 37 mm in length) suitable for X-ray structure analysis were obtained.

Discussion

In the structure of $Ca_3TaGa_3Si_2O_{14}$, the Ca—O bond lengths in the CaO_8 dodecahedra are 2.363(3) Å, 2.394(3) Å, 2.679(2) Å and 2.867(4) Å. Two of them are shorter and the two other are longer than the sum of the ionic radii (2.47 Å) [1]. The O–Ca–O bond angles (between adjacent atoms) are in the ranges of 57.8(2)° – 153.87(6)°, which are remarkably different from the typical dodecahedral angle (41.81°, 70.53°, 114.97°, 138.20°, 180°). Summing up, the bond lengths of Ca—O and bond angles of O–Ca–O, one can conclude that the CaO_8 dodecahedron is a distorted one. In the TaO_6 octahedron, all Ta—O bonds have the length 1.985(3) Å, which is slightly shorter than the sum of the ionic radii (2.02 Å [1]). The bond angles of O–Ta–O (between adjacent atoms) are 167.1(2)°, 83.6(2)°, 88.3(1)° and 83.6(2)°, which is significantly different from ideal octahedron. In the GaO_4 tetrahedron, two bond lengths are 1.827(3) Å, the others are 1.856(4) Å, which are all longer than the sum of the ionic radii (1.82 Å [1]); and the bond angles of O–Ga–O (between adjacent atoms) [102.2(2)° – 127.7(2)°] deviate clearly from the tetrahedral angle. However, in the SiO_4 tetrahedron, one bond length is shorter (1.594(5) Å) and the others (1.637(4) Å) are longer than the sum of the Shannon ionic radii (1.61 Å [1]). Among the bond angles of O–Si–O (between adjacent atoms), three bond angles (114.6(1)°) are larger than the remaining (103.9(2)°), which are slightly different from the ideal value for a tetrahedron. From the above discussion, it is clear that the CaO_8, TaO_6, GaO_4 and SiO_4 polyhedra of the CTGS structure are all distorted, which leads to a high efficiency of second harmonic generation (SHG) in CTGS crystals. The distortion of polyhedra in CTGS crystal is somewhat higher than that of the $Ca_3NbGa_3Si_2O_{14}$ crystals [2], the more polyhedrons distortion, the higher the SHG efficiency. The SHG efficiency was studied by the powder technique and emission of a strong green light (532 nm) was observed, with an intensity weaker than that generated by $LiNbO_3$ and $La_3Ga_5SiO_{14}$ crystals but stronger than that obtained from $Ca_3NbGa_3Si_2O_{14}$ crystals.

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.10 × 0.16 × 0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	183.02 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	69.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4938, 835
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 834
$N(param)_{refined}$:	38
Program:	SHELXTL [3]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta	1*a*	0	0	0	0.0136(2)	U_{11}	0.0104(2)	$U_{11}/2$	0	0
Ga	3*f*	0.74569(8)	0	1/2	0.0150(2)	0.0151(2)	0.0120(2)	$U_{22}/2$	–0.00057(8)	$2U_{13}$
Ca	3*e*	0.4241(1)	0	0	0.0171(3)	0.0255(5)	0.0134(4)	$U_{22}/2$	–0.0011(2)	$2U_{13}$
Si	2*i*	2/3	1/3	0.4498(3)	0.0143(4)	U_{11}	0.0116(6)	$U_{11}/2$	0	0
O(1)	2*i*	2/3	1/3	0.7695(9)	0.024(1)	U_{11}	0.012(2)	$U_{11}/2$	0	0
O(2)	6*l*	0.7750(4)	–0.1401(4)	0.2367(6)	0.017(1)	0.018(1)	0.0152(9)	0.0077(9)	0.0034(8)	–0.0015(8)
O(3)	6*l*	0.6806(5)	0.1572(5)	0.3129(6)	0.025(1)	0.018(1)	0.017(1)	0.013(1)	–0.004(1)	–0.004(1)

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