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Crystallographic study of $Ca_2BaSi_3O_9$

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Auszug

$Ca_2BaSi_3O_9$ ist triklin, Raumgruppe $P\bar{1}$, mit $a = 6{,}72$ Å, $b = 6{,}73$ Å, $c = 9{,}62$ Å, $\alpha = 88°22'$, $\beta = 111°03'$, $\gamma = 102°20'$; $Z = 2$. Tabelle 1 zeigt ein indiziertes Pulverdiagramm.

Abstract

$Ca_2BaSi_3O_9$ is triclinic, $a = 6.72$ Å, $b = 6.73$ Å, $c = 9.62$ Å, $\alpha = 88°22'$, $\beta = 111°03'$, $\gamma = 102°20'$, space group $P\bar{1}$, $Z = 2$. An indexed powder pattern is presented (Table 1).

Introduction

The compound $Ca_2BaSi_3O_9$ was first characterized by Eskola (1922) in a phase equilibrium investigation of the system $CaSiO_3$—$BaSiO_3$. We have repeated the preparation by heating weighed quantities of reagent grade $CaCO_3$, $BaCO_3$, and SiO_2. Large (0.2—1.0 mm) single crystals of $Ca_2BaSi_3O_9$ were readily prepared by heating the $Ca_2BaSi_3O_9$ composition just at or below the temperature of incongruent melting (1320 °C). The product was completely crystalline and free from α $CaSiO_3$. Rotation and Weissenberg photographs about all three axes showed that the crystals were triclinic and gave approximate unit-cell parameters. Powder data (Table 1) were obtained from a diffractometer trace run at 0.5° 2θ/minute. A silicon external standard was used to calibrate the diffractometer. Comparison of the diffractometer traces with powder photographs taken on a 6 cm diameter camera showed that the intensities of the peaks on the former were not affected by preferred orientation. The powder pattern was indexed down to about $d = 1.6$ Å by direct comparison of the powder photograph with single crystal rotation photographs; ambiguities were resolved by noting the strong reflections on indexed Weissenberg

Table 1. *Powder data for* $Ca_2BaSi_3O_9$

$d_{obs.}$	I	hkl	$d_{calc.}$	$d_{obs.}$	I	hkl	$d_{calc.}$	$d_{obs.}$	I	hkl	$d_{calc.}$	$d_{obs.}$	I	hkl	$d_{calc.}$
6.577	1	010	6.57	3.079	2	200	3.072	2.280	2	$1\bar{1}\bar{4}$	2.280			$20\bar{3}$	1.846
6.09 *	< 1	$10\bar{1}$	6.19	3.000	10	$00\bar{3}$	3.002	2.258	1	$02\bar{3}$	2.273	1.842 d	3	$1\bar{1}\bar{5}$	1.850
5.44 *	< 1	$01\bar{1}$	5.45	2.925	1	$1\bar{1}\bar{3}$	2.926	2.210	3	$21\bar{2}$	2.212			$11\bar{5}$	1.839
5.16 *	< 1	$1\bar{1}0$	5.07			$1\bar{2}\bar{1}$	2.895	2.161	2	$03\bar{1}$	2.153			$21\bar{3}$	1.834
4.43 d	1	$10\bar{2}$	4.44	2.792	5	$11\bar{3}$	2.792	2.124	1	122	2.122	1.818	1	$03\bar{3}$	1.813
		101	4.41			$1\bar{2}\bar{2}$	2.792	2.105	2	$22\bar{1}$	2.108			024	1.815
4.150	1	$11\bar{1}$	4.141			$0\bar{2}2$	2.720			014	2.098	1.778	1	114	1.781
3.902	1	$1\bar{1}\bar{2}$	3.886	2.71 d	4	$12\bar{1}$	2.703	2.058	1	$12\bar{3}$	2.056	1.757	2	$22\bar{4}$	1.757
3.516	1	$11\bar{2}$	3.515			$21\bar{1}$	2.712	2.041	2	300	2.048	1.695	1	222	1.694
3.386	1	111	3.388	2.663	1	$20\bar{3}$	2.666			[$21\bar{4}$	2.043]	1.676	1	$1\bar{4}0$	1.681
3.281	2	020	3.286			$2\bar{1}1$	2.639	2.007	2	$2\bar{2}2$	2.004	1.647	1		
		[$20\bar{1}$	3.283]	2.629	3	201	2.639			$03\bar{2}$	2.010	1.617	1		
3.211	2	$1\bar{2}0$	3.201			$22\bar{1}$	2.615	1.946	1	$13\bar{1}$	1.955	1.585 d	1		
		[211	3.227]	2.496	1	$2\bar{2}2$	2.494	1.907	1	$02\bar{4}$	1.902	1.503	1		
		$02\bar{1}$	3.138	2.451	7	121	2.432			$30\bar{4}$	1.879	1.464	1		
3.145	2	$12\bar{1}$	3.154	2.352	1	$1\bar{2}\bar{3}$	2.353	1.881	1	$31\bar{3}$	1.875	1.445	1		
		102	3.142			[$21\bar{3}$	2.355]			$2\bar{3}1$	1.878	1.404	1		
												1.379	1		
												1.251	1		

* = inaccurate d value
d = diffuse

Table 2. *Unit cell of* $Ca_2BaSi_3O_9$

Triclinic, $P\bar{1}, Z = 2$			
$a = 6.71_8$ Å	$a^* = .1627$ Å^{-1}	$\alpha = 88°22'$	$\alpha^* = 87°08'$
$b = 6.73_3$ Å	$b^* = .1522$ Å^{-1}	$\beta = 111°03'$	$\beta^* = 67°27'$
$c = 9.61_7$ Å	$c^* = .1111$ Å^{-1}	$\gamma = 102°20'$	$\gamma^* = 77°27'$

photographs. The unit-cell parameters were refined by using the indexed powder pattern; the final values are given in Table 2.

A small, equant crystal was selected for further study. Zero-layer Weissenberg photographs were taken about the *a* and *c* axes, using Mo radiation and multiple film packs. Intensities were estimated visually. The statistical methods of HOWELLS, PHILLIPS and ROGERS (1950) were applied to about 225 0*kl* reflections and to about 165 *hk*0 reflections. The results show that both the *yz* and *xy* projections are centrosymmetric, and the space group is therefore $P\bar{1}$.

The unit cell parameters strongly suggest that $Ca_2BaSi_3O_9$ belongs to the group of compounds based on X_3O_9 rings, where X = Si or Ge. Table 3 shows data for some of these compounds. In all cases where the structure is known, the Si_3O_9 rings occur in layers normal to the *c* axis, interleaved by cations. Benitoite, $BaTiSi_3O_9$ has the smallest unit cell. $BaTiGe_3O_9$ appears to be isostructural with it at high temperatures; at low temperatures the appearance of weak extra lines in the powder pattern indicates a slight modification of the structure. α-$CaSiO_3$ and $SrGeO_3$ are basically isostructural with one another, but differences in the way the layers are stacked cause their *c* axes to be multiples of the basic unit; furthermore both appear to show polytypism (HILMER, 1960).

Table 3. *Some compounds based on* X_3O_9 *rings*

Formula	Symmetry	a	b	c	Reference
$BaTiSi_3O_9$	Hexagonal	6.60		9.71	ZACHARIASEN (1930)
$BaTiGe_3O_9$	Hexagonal	$6.77 \times \sqrt{3}$ *		10.02	ROBBINS (1960)
$SrGeO_3$	Rhombo-hedral	7.29		10.55×3	HILMER (1958)
α-$CaSiO_3$	Triclinic-Pseudo-hexagonal	6.82		9.825×2	JEFFERY and HELLER (1953)
$Ca_2BaSi_3O_9$	Triclinic	6.72	6.73	9.70	

* At high temperatures, $a = 6.77$.

The axial lengths of $Ca_2BaSi_3O_9$ are very similar to those of the above compounds, and it is probably a triclinic member of this structural family. A full structure determination is being undertaken to check this.

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