Crystal structure of barium selenate, $BaSeO_4$

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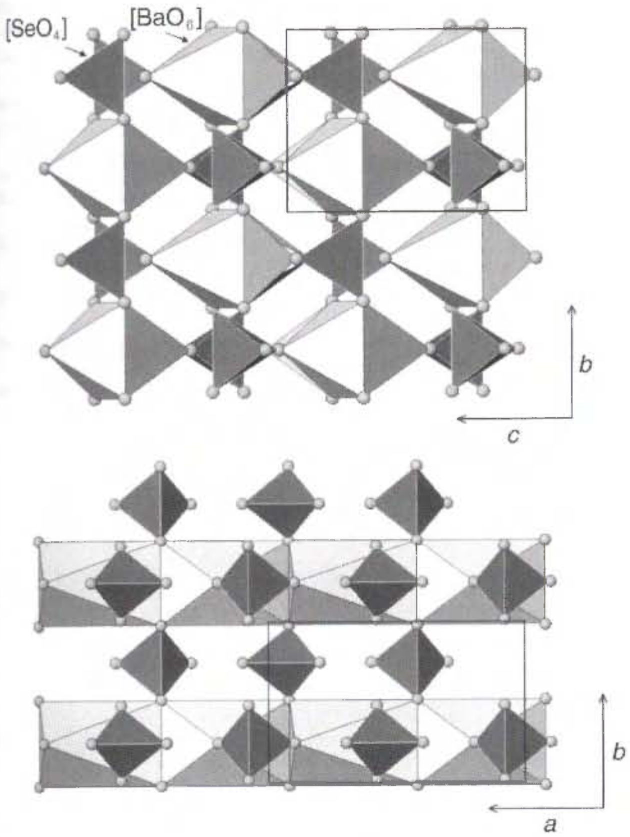

Abstract

BaO_4Se, orthorhombic, *Pnma* (no. 62), $a = 8.993(8)$ Å, $b = 5.675(6)$ Å, $c = 7.349(4)$ Å, $V = 375.1$ Å^3, $Z = 4$, $R_{gt}(F) = 0.042$, $wR_{ref}(F^2) = 0.116$, $T = 293$ K.

Source of material

Crystallization of $BaSeO_4$ single crystals was carried out in a double-diffusion system where parent aqueous solutions of two reagents are separated by a column of silica hydrogel. Crystal growth in gels is in fact solution growth, although nucleation and growth conditions are quite different from those in conventional solution growth methods. The gel is a porous medium that suppresses convection and advection, only allowing diffusion of reacting ions, which eventually meet in the gel column where precipitation occurs. This method has been used extensively as a way of growing crystals of sparingly soluble salts from aqueous solutions [1]. In the present experiments, the two parent solutions (0.5 M $BaCl_2$ and 0.5 M Na_2SeO_4) were separated by a 28 cm column of silica hydrogel in a U-shaped tube. The gel was prepared by acidification of a sodium silicate solution with 1 M HCl to the desired pH of 5.5. The acidified solution was poured into the U-tube, where it polymerized to form a solid gel. In all the aqueous solutions reagent grade chemicals (Merck) were used. During the experiment the temperature was maintained to 25.0±0.1 °C.

Experimental details

The high main residual electron density, ca. 4 eÅ^{-3}, located near Ba and the odd thermal parameters for O1 and O2 reflect the low quality of the only available barium selenate crystals.

Discussion

Selenate is the predominant form of Se in soils and water. Selenate and sulfate ions have similar chemical properties and structures and, when both are present, compete in many processes such are sorption on mineral surfaces, absorption by plants and incorporation into plant and animal tissues [2-4]. Because of selenate's toxicity and its mobility the relationship between selenate and sulfates in soils has been the subject of attention by researchers, mainly in the context of agricultural sciences [5,6]. However, the relationship between selenate and common sulfates mineral crystal structures are not always clear.

The crystal structure studies of $BaSeO_4$ in the literature indicate that is isomorphous with barite, the corresponding sulfate [7]. The sulfate and selenate anions are both tetrahedral and even though the selenate anion is larger, the structures of many selenates are isomorphous with those of the corresponding sulfates [8,9]. These studies are limited to the determination of the cell parameters and space group, but the determination and refinement of the structure of $BaSeO_4$ have not been completed until now. $BaSeO_4$ crystallizes orthorhombically and its structure is isomorphous with barite (β-$BaSO_4$). The structure consists of isolated SeO_4 tetrahedra joined by barium atoms coordinated to twelve oxygen atoms forming irregular BaO_{12} polyhedra. The structure is easier to visualize by considering the six closest oxygen atoms to each barium. These atoms form chains of distorted BaO_6 octahedra parallel the *a*-axis, in the direction that those are linked by SeO_4 tetrahedra.

Table 1. Data collection and handling.

Crystal:	colorless, prismatic, size 0.11 × 0.14 × 0.14 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	201.44 cm^{-1}
Diffractometer, scan mode:	Nonius CAD-4, $\omega/2\theta$
$2\theta_{max}$.	63.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	705, 705
Criterion for I_{obs}, $N(hkl)_{gt}$.	$I_{obs} > 2\,\sigma(I_{obs})$, 651
$N(param)_{refined}$:	34
Programs:	SHELXL-97 [10], ATOMS [11]

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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}
Ba	4*c*	0.18200(5)	¼	0.15865(7)	0.0062(3)	0.0185(3)	0.0100(3)	0	0.0000(1)	0
Se	4*c*	0.06357(8)	¼	0.6850(1)	0.0067(4)	0.0122(4)	0.0071(4)	0	−0.0004(2)	0
O(1)	4*c*	0.8995(8)	¼	0.594(1)	0.017(3)	0.045(5)	0.035(4)	0	−0.023(3)	0
O(2)	4*c*	0.1984(7)	¼	0.5369(9)	0.017(3)	0.033(4)	0.009(3)	0	0.011(2)	0
O(3)	8*d*	0.0797(5)	0.0172(8)	0.8154(6)	0.018(2)	0.013(2)	0.015(2)	0.001(2)	0.003(1)	0.004(2)

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