Crystal structure of rubidium tetrachlorogallate, $RbGaCl_4$

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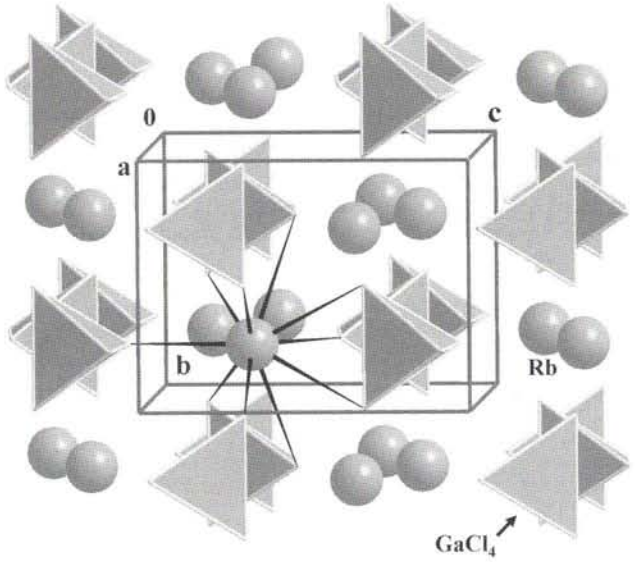

Abstract

Cl_4GaRb, orthorhombic, *Pnma* (No. 62), $a = 11.1699(4)$ Å, $b = 7.0882(2)$ Å, $c = 9.3003(4)$ Å, $V = 736.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.035$, $wR_{ref}(F^2) = 0.071$, $T = 293$ K.

Source of material

The title compound was synthesized in a hydrochloric acid solution. The reaction was carried out with a mixture of RbCl (2.418 g) and $GaCl_3$ (obtained from metal gallium, 1.05g, dissolved in HCl) with the molar ratio of 4:3 adding excess of HCl (37%) in aqueous solutions. All starting materials were of analytical grade purity and used without further purification. The mixture was heated to the boiling point on an electric stove, then cooled down to the room temperature. Colorless crystals were grown up after vaporizing for 5 days in air.

Discussion

Although most of tetrahalides were synthesized in a period of later half of the last century[1-3], structural researches were not carried out for some of them. The compound of $RbGaCl_4$ was synthesized as a midcourse product in order to synthesize borophosphates. Its atomic paremeters have not been reported until now. After completing the structural refinement, the anisotropic displacement parameters of Rb and Cl atoms showed to be slightly larger than those in non-chlorogallate compounds. The abnormal anisotropic displacement parameters of Cl could not be refined better by using the method of changing elements (e.g. oxygen) or occupacies. It was believed to be associated with the low melting point of gallium and its halides. In the structure, gallium was bonded by four chlorine atoms, so it had relatively normal anisotropic displacement parameters. The abnormal anisotropic displacement parameters could also be evidenced from the rapid decrease of the intensities of X-ray powder diffraction patterns and the single crystal data on Image Plate with the increase of 2θ angles. Abnormal anisotropic displacement parameters were also observed in its isotypic compound, $Ga[GaCl_4]$ at room temperature structure [4], and become normal by synchrotron X-ray anomalous scattering or at low temperature X-ray diffraction [5,6]. The structure is characterized by isolated $GaCl_4$ tetrahedra linking with rubidium atoms by chlorines to form a three dimensional structure. The distances of the rubidium to their ten chlorine neighbours range from 3.366 Å to 3.893 Å. The first coordination circle can also be considered as a deformed octahedron. Each rubidium links with seven $GaCl_4$ tetrahedra. The bond distances of Ga—Cl in $GaCl_4$ tetrahedra range from 2.129 Å to 2.158 Å, being similar to those in the Cs anologue (2.12 Å to 2.17 Å) [2,3]. The bond angles range from 107.5° to 113.1°, showing quite regular tetrahedral coordination for $GaCl_4$. Similar bond angles were found for the Cs compound (107.0° to 114.0°) [2,3].

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.05 × 0.06 × 0.10 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	116.31 cm^{-1}
Diffractometer, scan mode:	Rigaku R-axis RAPID, $\varphi = 0°, 90°$; $\Delta\omega = 5°$
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1598, 911
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 529
$N(param)_{refined}$:	35
Programs:	SHELXL-97 [7], DIAMOND [8]

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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}
Rb(1)	4*c*	0.18196(7)	3/4	0.6713(1)	0.0463(4)	0.1069(6)	0.0809(7)	0	–0.0021(5)	0
Ga(1)	4*c*	0.43269(7)	1/4	0.68855(8)	0.0443(4)	0.0385(3)	0.0378(4)	0	–0.0003(4)	0
Cl(1)	8*d*	0.4217(1)	0.4955(2)	0.8252(2)	0.0734(9)	0.0558(6)	0.084(1)	0.0032(7)	–0.0084(9)	–0.0292(8)
Cl(2)	4*c*	0.2817(2)	1/4	0.5464(3)	0.108(2)	0.099(2)	0.073(2)	0	–0.056(2)	0
Cl(3)	4*c*	0.5997(2)	1/4	0.5782(4)	0.095(2)	0.170(3)	0.131(3)	0	0.073(2)	0

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