Crystal Structure of $Sr_{0.2}Ca_{2.8}Tl_2O_6$

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Crystal Structure, X-Ray

The crystal structure of $Sr_{0.2}Ca_{2.8}Tl_2O_6$ has been determined by single crystal X-ray diffraction. The compound crystallizes in space group Pbam (No. 55) with a = 11.228(1), b = 16.471(1) and c = 3.3326(3) Å. It is isostructural with $Ca_3In_2O_6$ and $SrCa_2In_2O_6$.

Introduction

Only a few alkaline earth oxothallates are known. $SrTl_2O_4$ was shown by X-ray powder diffraction [1] to crystallize in the $CaFe_2O_4$ type. The only other known oxothallates – $Sr_4Tl_2O_7$ [2] and $Ba_2Tl_2O_5$ [3] – have completely different crystal structures. To our knowledge a calcium oxothallate has not yet been described. Due to the sizes of the Tl(III) and Ca(II) cations a $CaFe_2O_4$ structure type is not expected. Here we report the structure of the oxothallate $Sr_{0.2}Ca_{2.8}Tl_2O_6$.

Experimental

The title compound was formed as a by-product in the preparation of Tl-based high T_c superconductors. A mixture of oxides Tl_2O_3, BaO_2 and $Ca_{1.85}Sr_{0.15}CuO_2$ was reacted in a closed gold tube, sealed in a quartz-glass ampoule, and heated for 3 h at 920 °C. After cooling to room temperature at a rate of 1.7 °/h, light-brown, transparent needles were obtained. EDAX investigations of one needle indicated the presence of Tl, Ca and Sr (trace). A structural analysis was carried out by single crystal X-ray diffraction. The crystal data are summarized in Table I**.

Table I. Single crystal data and X-ray intensity collection for $Sr_{0.2}Ca_{2.8}Tl_2O_6$.

Formula	$Sr_{0.2}Ca_{2.8}Tl_2O_6$
Molar weight	634.5 g mol^{-1}
Lattice constants	a = 11.228(1), b = 16.471(1), c = 3.3326(3) Å
Space group	Pbam, Z = 4
d_{calc}	7.251 g cm^{-3}
μ(MoKα), λ	62.51 mm^{-1}, 0.71069 Å
Data collection	CAD4 diffractometer, graphite monochromator, scintillation counter
Range of data, method	$4° \leq 2\theta \leq 60°$, ω-scan
Scan speed	variable depending on I
Number of reflections	2111; 1041 independent with 777 $F_o > (4\sigma)F_o$
Absorption correction	empirical on psi-scans
Refinement	SHELXL-93, full matrix least squares; extinction correction x = 0.000983
Number of parameters	80
R(aniso)	5.32% (related to all independent data)

Results and Discussion

The atomic coordinates and isotropic displacement parameters for $Sr_{0.2}Ca_{2.8}Tl_2O_6$ are given in Table II. The polyhedron model of the structure is shown in Fig. 1, the shades of the octahedra indicating different kinds of metal atoms in the centers. $Sr_{0.2}Ca_{2.8}Tl_2O_6$ was found to be isostructural with $Ca_3In_2O_6$ [4] and $SrCa_2In_2O_6$ [5]. These oxides form a special structure type related to $CaFe_2O_4$. In contrast to the oxoindates, which show a random distribution of Ca and In, all the different metal atom positions in the structure of $Sr_{0.2}Ca_{2.8}Tl_2O_6$ are predominantly occupied by one kind of atom. The refinement of the Tl atom positions gives evidence for a small, but significant substitution by Ca atoms and vice versa. Such a disorder of Ca and Tl is a well-known feature in the Tl based HTC materials, *e.g.* $Tl_2Ba_2CaCu_2O_8$.

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** Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD 400514, the names of the authors, and the journal citation.

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Table II. Atomic parameters of $Sr_{0.2}Ca_{2.8}Tl_2O_6$.

Atom	Position	k	*x*	*y*	*z*	U_{eq}
Tl(1) Ca(1)	4g	0.418(2) 0.078(6)	0.13389(4)	0.45470(3)	0.0	0.0096(2)
Tl(2) Ca(2)	4g	0.462(2) 0.037(6)	0.41531(4)	0.35086(3)	0.0	0.0095(1)
Tl(3) Ca(3)	4h	0.055(2) 0.443(6)	0.1361(1)	0.0389(1)	0.5	0.0097(5)
Tl(4) Ca(4)	4h	0.065(2) 0.435(6)	0.1715(1)	0.2758(1)	0.5	0.0099(5)
Ca(5) Sr(5)	4h	0.41(1) 0.09(1)	0.3976(1)	0.1442(1)	0.5	0.0095(6)
O(1)	4g	0.5	0.0559(6)	0.3409(5)	0.0	0.011(2)
O(2)	4h	0.5	0.0439(7)	0.1666(5)	0.5	0.012(2)
O(3)	2d	0.25	0.0	0.5	0.5	0.014(3)
O(4)	4h	0.5	0.2846(7)	0.4049(5)	0.5	0.017(2)
O(5)	4g	0.5	0.2792(7)	0.0643(5)	0.0	0.014(2)
O(6)	4h	0.5	0.3079(6)	0.2393(5)	0.0	0.013(2)
O(7)	2a	0.25	0.0	0.0	0.0	0.027(3)

Equivalent isotropic U_{eq} [Å^2] are defined as one third of the trace of the orthogonalized U_{ij} tensor. Standard deviations are in parentheses. The sum of the site occupation factors of every split position and the number of Tl atoms per unit cell are restrained to be a constant.

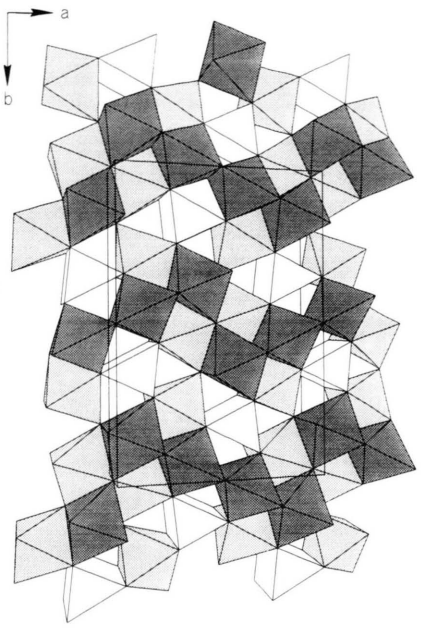

Fig. 1. Crystal structure of $Sr_{0.2}Ca_{2.8}Tl_2O_6$ viewed along the *c*-axis. TlO_6 and CaO_6 are drawn as dark and light octahedra, respectively. The trigonal prisms are occupied with Ca and Sr.

Linear groups of four edge-sharing TlO_6 octahedra are connected *via* corners to build up two independent zigzag chains. Every TlO_6 unit also shares edges with the oxygen octahedra surrounding the Ca atoms. The resulting network forms tunnels of bicapped trigonal prisms, centered by Ca and Sr atoms.

The octahedra around the Ca atoms compare well with those in the structure of $CaCu_2O_3$ [6]. The bond lengths Ca/Sr–O (Table III) in the trigonal prismatic coordination, which range from 2.449(5) to 2.639(2) Å, lie between the values observed for Ca–O [4] and Sr–O [5]. The oxygen octahedra around Tl are strongly distorted as in $SrTl_2O_4$.

Besides the octahedral coordination around Tl(III) in $Sr_{0.2}Ca_{2.8}Tl_2O_6$, a tetrahedral coordination as in $Ba_2Tl_2O_5$ or a square planar coordination as in $Sr_4Tl_2O_7$ have also been observed with alkaline earth oxothallates. For alkali oxothallates a tetrahedral coordination around Tl(III) is known with the alkali-rich K_5TlO_4 [7], $K_2Na_3TlO_4$ [8] or $Rb_6Tl_2O_6$ [9], while otherwise octahedral coordination [10] is more common.

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Table III. Bond lengths of $Sr_{0.2}Ca_{2.8}Tl_2O_6$ in Å.

Tl/Ca(1)–O	2.053(7)	1×	2.069(8)	1×	2.365(1)	2×	2.513(6)	2×
Tl/Ca(2)–O	2.198(8)	1×	2.224(5)	2×	2.392(6)	2×	2.634(1)	1×
Ca/Tl(3)–O	2.344(8)	1×	2.350(1)	4×	2.381(8)	1×		
Ca/Tl(4)–O	2.300(8)	1×	2.342(5)	2×	2.369(5)	2×	2.475(8)	1×
Ca/Sr(5)–O	2.449(5)	2×	2.498(6)	4×	2.639(2)	2×		

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