

# Crystal structure of samarium-strontium-calcium orthoaluminotantalate, $(\text{Sm}_{0.40}\text{Sr}_{0.50}\text{Ca}_{0.10})(\text{Al}_{0.70}\text{Ta}_{0.30})\text{O}_3$

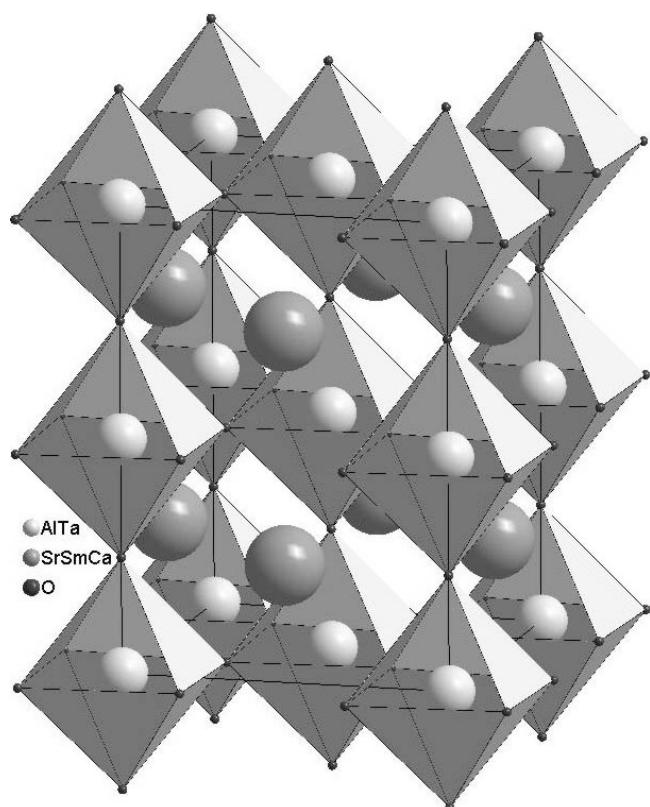
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## Abstract

$\text{Al}_{2.90}\text{Ca}_{0.45}\text{O}_{12}\text{Sm}_{1.59}\text{Sr}_2\text{Ta}_{1.10}$ , tetragonal,  $\bar{4}$  (no. 82),  $a = 5.4174(8)$  Å,  $c = 7.643(2)$  Å,  $V = 224.3$  Å<sup>3</sup>,  $Z = 1$ ,  $R_{\text{gt}}(F) = 0.039$ ,  $wR_{\text{ref}}(F^2) = 0.1258$ ,  $T = 298$  K.

## Source of material

A samarium-strontium-calcium orthoaluminotantalate single crystal of 35 mm in length and 16 mm in diameter was grown by the Czochralski technique with RF-induction heating and automatic diameter control. The starting materials  $\text{Sm}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  were of 99.99 % purity or higher. They were mixed according to the formula  $\text{Sm}_{0.418}\text{Sr}_{0.491}\text{Ca}_{0.089}\text{Al}_{0.718}\text{Ta}_{0.284}\text{O}_{2.994}$  (this composition corresponds to the crystal composition of no. 11 which is practically the same as the used melt composition [1]). Due to its high melting temperature ( $T_{\text{f}} > 1400$  °C) the crystal was grown from an Ir crucible under flowing nitrogen atmosphere. The pulling rate was 1 mm/h with the rotation of 10 rpm.

## Experimental details

During the refinement, samarium, strontium and calcium were refined on the same crystallographic position 2c and 2d with mixed occupation as well as aluminum and tantalum on 2a and 2b. All crystallographic positions were refined fully occupied. In the case of aluminum and tantalum the occupation of one atom type was calculated as one minus the occupation of the second atom. For samarium, strontium and calcium the occupancy sum was calculated to be one for each crystallographic position, whereas the ratio between the different atom types was freely refined. During this refinements all atom types were found on the 2c position. On the 2d position the calcium atom occupation was refined to be zero and were therefore removed in the final refinement runs.

## Discussion

Mixed perovskite crystals are of great importance as substrates for several advanced perovskite thin films because they develop a wide range of lattice constants and the possibility of their fine tuning. E.g., the coupled substitution of cations in rare earth aluminates by  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ta}^{5+}$ , and  $\text{Nb}^{5+}$  provides mixed perovskite crystals with lattice parameters between 3.78 and 3.88 [1]. Depending on the melting behavior of a compound, i.e. whether it is congruently or incongruently, the composition of the melt either has to coincide with that of the crystal or it has to differ, sometimes even to a large extend. In the case of slight deviations the crystal often finds the target composition itself during growth. Because of segregation to be expected here, the growth process has to be performed particularly careful and only a small amount of the melt should be crystallized. Using a mixture (M) according to the composition  $\text{Sm}_{0.418}\text{Sr}_{0.491}\text{Ca}_{0.089}\text{Al}_{0.718}\text{Ta}_{0.284}\text{O}_{2.994}$  nearly the same composition  $\text{Sm}_{0.398(4)}\text{Sr}_{0.499(8)}\text{Ca}_{0.113(10)}\text{Al}_{0.725(2)}\text{Ta}_{0.275(2)}\text{O}_{2.938(32)}$  was refined from the single crystal (C) data. We have refined Sm, Sr and Ca (2c and 2d) as well as Al and Ta on the same position (2a and 2b). The cation sum ratio for each group is 1.00/1.00 (M) and 1.01/1.00 (C) which confirms the same composition in melt and crystal. Calculating the cation sum assuming  $\text{Sm}^{+3}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Al}^{+3}$  and  $\text{Ta}^{+5}$  leads to 5.968 positive charges which are then compensated by 2.984 oxygen atoms which is within one e.s.d. fully occupied.

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**Table 1.** Data collection and handling.

Crystal:	yellow triangle, size 0.05 × 0.08 × 0.11 mm
Wavelength:	Mo $K_{\alpha}$ radiation (0.71073 Å)
$\mu$ :	360.73 cm <sup>-1</sup>
Diffractometer, scan mode:	STOE IPDS I, imaging plate dynamic profile integration
$2\theta_{\max}$ :	60.08°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$ :	902, 341
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 254
$N(\text{param})_{\text{refined}}$ :	33
Programs:	SHELXS-86 [2], SHELXL-93 [3], DIAMOND [4]

**Table 2.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	Occ.	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ta(1)	2a	0.136(2)	0	0	0	0.0020(5)	$U_{11}$	0.0032(6)	0	0	0
Al(1)	2a	0.864	0	0	0	0.0020	$U_{11}$	0.0032	0	0	0
Ta(2)	2b	0.415(2)	0	0	½	0.0106(3)	$U_{11}$	0.0092(4)	0	0	0
Al(2)	2b	0.585	0	0	½	0.0106	$U_{11}$	0.0092	0	0	0
Sm(1)	2c	0.355(4)	0	½	¼	0.0236(5)	$U_{11}$	0.0203(8)	0	0	0
Sr(1)	2c	0.420(7)	0	½	¼	0.0236	$U_{11}$	0.0203	0	0	0
Ca(1)	2c	0.227(10)	0	½	¼	0.0236	$U_{11}$	0.0203	0	0	0
Sm(2)	2d	0.441(4)	0	½	¾	0.0182(4)	$U_{11}$	0.0193(6)	0	0	0
Sr(2)	2d	0.579(8)	0	½	¾	0.0182	$U_{11}$	0.0193	0	0	0
O(1)	4e		0	0	0.2477(6)	0.028(4)	0.069(6)	0.011(3)	-0.007(5)	0	0
O(2)	8g		0.2463(8)	0.2497(7)	1.003(2)	0.030(3)	0.025(3)	0.046(3)	-0.012(3)	-0.015(3)	0.012(3)

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