Crystal structure of samarium-strontium-calcium orthoaluminotantalate, $(Sm_{0.40}Sr_{0.50}Ca_{0.10})(Al_{0.70}Ta_{0.30})O_3$

Thorsten M. Gesing[*,I], Reinhard Uecker[II], Wei Zheng[II] and J.-Christian Buhl[III]

[I] Universität Bremen, FB05 Kristallographie, Klagenfurter Straße, 28359 Bremen, Germany
[II] Leibnitz Institut für Kristallzüchtung, Max-Born-Straße 2, 12489 Berlin, Germany
[III] Leibnitz Universität Hannover, Institut für Mineralogie, Callinstraße 3, 30167 Hannover, Germany

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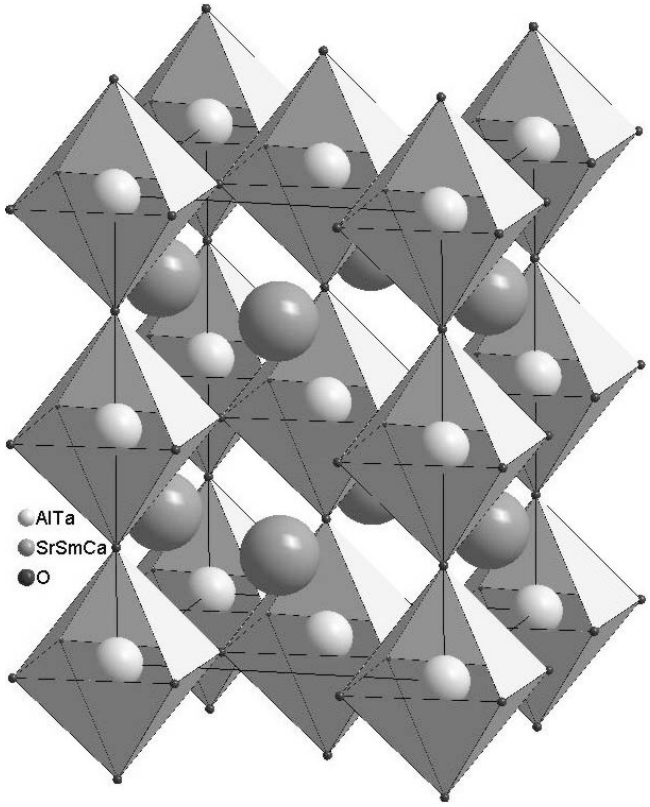

Abstract

$Al_{2.90}Ca_{0.45}O_{12}Sm_{1.59}Sr_2Ta_{1.10}$, tetragonal, $I\bar{4}$ (no. 82), a = 5.4174(8) Å, c = 7.643(2) Å, V = 224.3 Å^3, Z = 1, $R_{gt}(F)$ = 0.039, $wR_{ref}(F^2)$ = 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 The starting materials Sm_2O_3, $SrCO_3$, $CaCO_3$, Al_2O_3 and Ta_2O_5 were of 99.99 % purity or higher. They were mixed according to the formula $Sm_{0.418}Sr_{0.491}Ca_{0.089}Al_{0.718}Ta_{0.284}O_{2.994}$ (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_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 2*c* and 2*d* with mixed occupation as well as aluminum and tantalum on 2*a* and 2*b*. 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 2*c* position. On the 2*d* 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 Sr^{2+}, Ca^{2+}, Ta^{5+}, and 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 $Sm_{0.418}Sr_{0.491}Ca_{0.089}Al_{0.718}Ta_{0.284}O_{2.994}$ nearly the same composition $Sm_{0.398(4)}Sr_{0.499(8)}Ca_{0.113(10)}Al_{0.725(2)}Ta_{0.275(2)}O_{2.938(32)}$ was refined from the single crystal (C) data. We have refined Sm, Sr and Ca (2*c* and 2*d*) as well as Al and Ta on the same position (2*a* and 2*b*). 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 Sm^{+3}, Sr^{+2}, Ca^{+2}, Al^{+3} and 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.

* Correspondence author (e-mail: gesing@uni-bremen.de)

Table 1. Data collection and handling.

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

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

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

1. Mateika, D.; Kohler, H.; Laudan, H.; Voelkel, E.: Mixed-perovskite substrates for high-Tc superconductors.. J. Crystal Growth **109** (1991) 441-446.
2. Sheldrick, G. M.: SHELXS-86. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1986.
3. Sheldrick, G. M.: SHELXL-93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1993.
4. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.2. Crystal Impact, Bonn, Germany 1998.