REGULAR STRUCTURAL PAPERS

Refinement of the Structure of Sr_2RuO_4 with 100 and 295 K X-ray Data

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Abstract

The compound, with only a small mismatch between (001) and $YBa_2Cu_3O_{7-\delta}$ (001) crystallizes in the K_2NiF_4 structure type. The temperature dependence of the lattice parameters is reported and shows a comparable behaviour to that of epitaxially grown $YBa_2Cu_3O_{7-\delta}$.

Comment

For many device applications of high-T_c superconductors it is desirable to employ metals that are comparable with high-T_c materials. Such metals may be used in thin-film form for *SNS* heterostructures (S = superconductor, N = normal metal) or as substrates with high thermal conductivity. Recently, we described the single-crystal growth of Sr_2RuO_4 which has an excellent lattice match to $YBa_2Cu_3O_{7-\delta}$ (Lichtenberg, Catana, Mannhart & Schlom, 1992). Indeed, thin films of $YBa_2Cu_3O_{7-\delta}$ epitaxially grown on Sr_2RuO_4 could be obtained with high quality. Müller-Buschbaum & Wilkens (1990) have reported a single-crystal structure determination of Sr_2RuO_4; however, some inconsistencies therein with our results concerning crystal shape and structural parameters (up to 11σ), missing anisotropic displacement parameters, relatively high standard deviations, and no information concerning the temperature dependence of the lattice constants, encouraged us to report our investigations.

Sr_2RuO_4 crystallizes in the K_2NiF_4 structure type (Balz & Plieth, 1955) which is realized for a considerable number of compounds with the general composition A_2BX_4. The structure can be built up

theoretically by three perovskite monolayers stacked along the resulting c axis where the layers 1 and 3 are ABX_3 perovskite cells centred with atoms of the type A, while layer 2 is centred with B atoms. Removing two BX_2 layers leads to the K_2NiF_4 structure. In analogy to the perovskite structure, the ratio of the bond lengths $A—X:B—X = \sqrt{2}$ is essential. This is the case for the combination of oxides and halides (X) of alkali or alkali-earth metals (A) with those of transition metals (B). The resulting coordination polyhedra for A and B are different, as can be seen in Fig. 1. The Sr atom lies approximately in the basal plane of a quadratic pyramid of five O2 atoms, which forms a monocapped quadratic antiprism with four O1 atoms. The Ru atoms have distorted octahedral coordination. The ratio of the distances Sr1—O2 (2.736 Å) and Ru1—O1 (1.930 Å) is 1.418 and very close to the theoretical value $\sqrt{2}$.

The lattice constants show only a small variation with temperature. This is to be expected considering the comfortable atomic distances and the low displacement parameters. The lattice constants a and b of orthorhombic $YBa_2Cu_3O_{7-\delta}$ (Simon, Köhler, Borrmann, Gegenheimer & Kremer, 1988) and their variation with temperature agree well with those of Sr_2RuO_4 and show a distinctly smaller mismatch to other substrate materials, such as the frequently used $SrTiO_3$. Thus, Sr_2RuO_4 is an interesting compound for potential device applications.
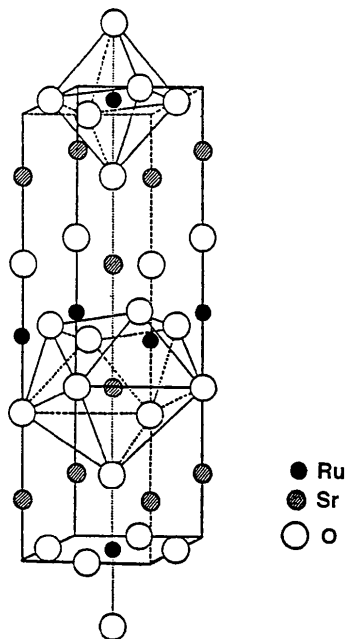

Fig. 1. Structure of Sr_2RuO_4 showing the octahedral coordination of Ru and the ninefold coordination of Sr.

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Experimental

RuSr₂O₄ at 100 K

Crystal data

$M_r = 340.31$
Tetragonal
$I4/mmm$
$a = 3.8603 (5)$ Å
$c = 12.729 (3)$ Å
$V = 189.69$ Å^3
$Z = 2$
$D_x = 5.958$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 136
  reflections
$\theta = 15–20°$
$\mu = 31.14$ mm^{-1}
Plate-like
$0.1 \times 0.1 \times 0.02$ mm
Black
Crystal source: modified
  floating-zone process

Data collection

Stoe Stadi-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
  analytical
  $T_{min} = 0.055, \; T_{max} = 0.485$
1110 measured reflections
156 independent reflections
156 observed reflections
  $[F_o > 3\sigma(F_o)]$

$R_{int} = 0.025$
$\theta_{max} = 40°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 6$
$l = -20 \rightarrow 20$
3 standard reflections
  frequency: 60 min
  intensity variation: <1%

Refinement

Refinement on F
Final $R = 0.0146$
$wR = 0.0129$
156 reflections
13 parameters
$w = 2.13/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.76$ e Å^{-3}

$\Delta\rho_{min} = -1.05$ e Å^{-3}
Extinction correction: as
  *SHELX*76 (Sheldrick,
  1976)
Extinction coefficient:
  6.81×10^{-3}
Atomic scattering factors
  from Cromer & Mann
  (1968)

RuSr₂O₄ at 295 K

Crystal data

$M_r = 340.31$
Tetragonal
$I4/mmm$
$a = 3.8694 (4)$ Å
$c = 12.746 (2)$ Å
$V = 190.84$ Å^3
$Z = 2$
$D_x = 5.922$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 136
  reflections
$\theta = 15–20°$
$\mu = 30.95$ mm^{-1}
Plate-like
$0.1 \times 0.1 \times 0.02$ mm
Black
Crystal source: modified
  floating-zone process

Data collection

Stoe Stadi-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
  analytical
  $T_{min} = 0.055, \; T_{max} = 0.485$
268 measured reflections
155 independent reflections
152 observed reflections
  $[F_o > 3\sigma(F_o)]$

$R_{int} = 0.0214$
$\theta_{max} = 40°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 20$
3 standard reflections
  frequency: 60 min
  intensity variation: <1%

Refinement

Refinement on F
Final $R = 0.0197$
$wR = 0.0168$
152 reflections
13 parameters
$w = 0.9/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.40$ e Å^{-3}
$\Delta\rho_{min} = -1.93$ e Å^{-3}

Extinction correction: as
  *SHELX*76 (Sheldrick,
  1976)
Extinction coefficient:
  9×10^{-3}
Atomic scattering factors
  from Cromer & Mann
  (1968)

Table 1. *Fractional atomic coordinates and displacement parameters* (Å^2)

$$U_{12} = U_{13} = U_{23} = 0.$$

		x	y	z	U_{11}	U_{22}	U_{33}
Sr1	(100 K)	0	0	0.14684 (5)	0.0042 (2)	U_{11}	0.0039 (3)
	(295 K)	0	0	0.14680 (7)	0.0074 (3)	U_{11}	0.0077 (4)
Ru1	(100 K)	0	0	½	0.0024 (2)	U_{11}	0.0036 (4)
	(295 K)	0	0	½	0.0029 (3)	U_{11}	0.0066 (5)
O1	(100 K)	0	½	0	0.004 (2)	0.010 (2)	0.006 (2)
	(295 K)	0	½	0	0.004 (2)	0.013 (3)	0.011 (3)
O2	(100 K)	0	0	0.3381 (4)	0.009 (1)	U_{11}	0.004 (2)
	(295 K)	0	0	0.3389 (5)	0.011 (2)	U_{11}	0.007 (3)

Table 2. *Distances* (Å)

	100 K	295 K	
Sr1—O1	2.687 (1)	2.691 (1)	(4×)
Sr1—O2	2.434 (5)	2.449 (6)	(1×)
Sr1—O2	2.736 (5)	2.742 (5)	(4×)
Ru1—O1	1.930 (1)	1.935 (1)	(4×)
Ru1—O2	2.061 (5)	2.053 (6)	(2×)

Single crystals were prepared by a modified floating-zone process as described recently (Lichtenberg, Catana, Mannhart & Schlom, 1992). Rods several cm in length and 0.5 cm in diameter were pressed from a well ground SrCO₃/RuO₂ mixture and treated by infrared zone-melting conditions. A black crystal with dimensions 0.114 ($\bar{1}$30), 0.103 ($\bar{2}$30), 0.122 ($4\bar{1}$0), 0.009 (001) and 0.009 (00$\bar{1}$) mm (distances from common centre to crystal faces) was used for data collection. Lattice parameters were obtained by least-squares refinement of 136 strong reflections with $2\theta > 30°$ using the double step-scan technique at 100, 200 and 295 K yielding $a = 3.8603 (5)$, 3.8638 (4), 3.8694 (4) Å and $c = 12.729 (3)$, 12.736 (2), 12.746 (2) Å, respectively. Numerical absorption and Lp corrections were applied. Starting values for the refinement were taken from the structure of Na₄OI₂ (Sabrowsky, Hippler, Sitta, Vogt & Walz, 1990). Refinement was by full-matrix methods (Sheldrick, 1976).

References

Balz, D. & Plieth, K. (1955). *Z. Elektrochem.* **59**, 545–551.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
Lichtenberg, F., Catana, A., Mannhart, J. & Schlom, D. G. (1992). *Appl. Phys. Lett.* **60**, 1138–1140.
Müller-Buschbaum, Hk. & Wilkens, J. (1990). *Z. Anorg. Allg. Chem.* **591**, 161–166.

Sabrowsky, H., Hippler, K., Sitta, S., Vogt, P. & Walz, L. (1990). *Acta Cryst.* C46, 368–369.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Simon, A., Köhler, J., Borrmann, H., Gegenheimer, B. & Kremer, R. (1988). *J. Solid State Chem.* 77, 200–203.

Structure Cristalline du Sulfure d'Ytterbium et d'Indium: $Yb_{4/3}In_{4/3}S_4$

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Abstract

The title compound was prepared as part of a study of the Yb–In–S system. It belongs to a cubic solid solution with formula In[tetra $8(a)]_{1-x}$(In,Yb)[octa $16(d)]_{2-y}$Yb[octa $16(c)]_{1-z}S_4$ ($0.23 \leq x \leq 0.50$) ($0 \leq y \leq 2$) ($0 \leq z \leq 0.666$). Tetrahedral sites are occupied by In^{3+} ions and octahedral sites $16(d)$ by In^{3+} and Yb^{3+} ions with statistically incomplete occupancy. The structure is intermediate between the spinel and NaCl type.

Commentaire

Poursuivant nos recherches concernant les sulfures mixtes formés par l'indium et les terres rares (Guittard, Carré & Kabré, 1978), nous avons étudié le ternaire Yb–In–S. Sur la ligne Yb_2S_3–In_2S_3, nous n'observons qu'une solution solide cubique à faces centrées qui s'appuie sur le sulfure In_2S_3. Le composé de formule $YbInS_3$ orthorhombique décrit par Karaev, Kejserukhskaya, Alieva & Gadymov (1966) correspond en réalité non à un composé situé sur la ligne Yb_2S_3–In_2S_3, mais au composé $Yb_{18}In_{7,33}S_{36}$ dont nous venons de décrire la structure cristalline (Lemoine, Tomas, Carré, Guittard & Likforman, 1989). Abdullaev, Ivanovemin & Karaev (1968) font mention de l'existence d'un composé $YbInS_3$ de type spinelle ce qui nous a conduit à préparer des échantillons correspondant à cette composition. Nous avons déterminé sur monocristal la structure du composé obtenu et nous en donnons ici la description.

Ce composé a été préparé à partir d'un mélange à parties égales de In_2S_3 et Yb_2S_3, chauffé en ampoule de silice scellée sous vide une heure à 1473 K, ce chauffage est suivi d'un recuit de deux jours à 1073 K puis d'un refroidissement lent.

Le sulfure d'indium est obtenu par action du sulfure d'hydrogène sur l'oxyde In_2O_3 vers 873 K, son diffractogramme de poudre s'interprète dans une maille cubique de type spinelle, mais il existe des raies faibles supplémentaires correspondant à une surstructure. Ce sulfure est de couleur rouge. Le sulfure d'ytterbium Yb_2S_3 de couleur jaune est obtenu par action du sulfure d'hydrogène sur Yb_2O_3 a 1373 K. Ce sulfure est rhomboédrique.

Le Tableau 1 donne les valeurs des coordonnées et les facteurs d'agitation thermique équivalents des atomes. Dans le Tableau 2 ont été relevées les distances métal-soufre.

L'indium occupe partiellement le site $8(a)$ tétra-édrique avec des distances In—S de 2,47 Å corre-spondant à la somme des rayons ioniques (Shannon, 1976) In^{3+}(VI)—S^{2-}: 2,46 Å. Cet environnement de l'indium est classique dans les sulfures. L'indium occupe également partiellement le site $16(d)$ comme dans plusieurs autres composés spinelles $In_2S_3\beta$ et $InS_{1,44}$ (Likforman, Guittard, Tomas & Flahaut, 1980).

L'ytterbium se répartit sur deux sites octaédriques, le site $16(c)$ et le site $16(d)$ qu'il partage en désordre statistique avec l'indium. Du fait des valeurs rela-tivement proches de leurs rayons ioniques l'ytter-bium et l'indium trivalents peuvent partager les mêmes sites octaédriques. La distance M^{3+}(Yb/In)—S^{2-} de 2,72 Å en moyenne correspond bien à la somme des rayons ioniques donnée par Shannon (1976), soit Yb^{3+}(VI)—S^{2-}: 2,71 Å et In^{3+}(VI)—S^{2-}: 2,64 Å. On retrouve cet environnement pour l'ytterbium avec des distances comparables dans $FeYb_2S_4$ (Tomas, Brossard & Guittard, 1980).

Ces deux sites octaédriques ne sont que partiel-lement occupés; il y a ainsi une répartition homogène des lacunes dans la structure.

Les octaèdres centrés sur les atomes d'indium et d'ytterbium partagent avec les tétraèdres centrés sur les atomes d'indium des sommets communs.

En l'absence de traînées de diffusion sur les clichés de Weissenberg, nous concluons que nous sommes en présence d'une maille dans laquelle la répartition des cations est intermédiaire entre la structure spinel-le [sites occupés $8(a)$ et $16(d)$] et la structure de type NaCl [sites occupés $16(c)$].

Partie expérimentale