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# Recognition on systems RbF–$GaF_3$ and CsF–$GaF_3$

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## Abstract

The systems RbF–$GaF_3$ and CsF–$GaF_3$ were re-investigated by DTA and XRD method. In the system RbF–$GaF_3$, with eutectic $E_1$ at 750°C in the location of 8.5 mol% $GaF_3$ and $E_2$ at 749°C in the location of 43.0 mol% $GaF_3$, three compounds $Rb_3GaF_6$, $RbGaF_4$ and RbF·2$GaF_3$ were identified and indexed by XRD. The indexed result of α-$Rb_3GaF_6$ could not be successfully obtained, β-$Rb_3GaF_6$ is tetragonal, $a = 6.324 \pm 0.004$, $c = 8.860 \pm 0.003$ Å. $RbGaF_4$ is orthorhombic, $a = 9.821 \pm 0.006$, $b = 9.517 \pm 0.005$, $c = 8.060 \pm 0.006$ Å; RbF·2$GaF_3$ is also orthorhombic, $a = 9.459 \pm 0.005$, $b = 9.336 \pm 0.005$, $c = 7.685 \pm 0.005$ Å. In the system CsF–$GaF_3$, with eutectic $E_1$ at 664°C in the location of 7.5 mol% $GaF_3$ and $E_2$ at 675°C in the position of 44.0 mol% $GaF_3$, two compounds were confirmed. α-$Cs_3GaF_6$ is orthorhombic with $a = 10.62 \pm 0.02$, $b = 9.959 \pm 0.006$ and $c = 5.607 \pm 0.005$ Å; β-$Cs_3GaF_6$ is also orthorhombic, $a = 10.356 \pm 0.003$, $b = 8.280 \pm 0.003$, $c = 7.621 \pm 0.005$ Å; γ-$Cs_3GaF_6$ is tetragonal, $a = 6.833 \pm 0.003$, $c = 9.869 \pm 0.002$ Å; $CsGaF_4$ is orthorhombic, $a = 8.571 \pm 0.007$, $b = 7.575 \pm 0.007$ and $c = 6.981 \pm 0.006$ Å. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* RbF; CsF; $GaF_3$; Phase diagram; Aluminum brazing

## 1. Introduction

The systems RbF–$GaF_3$ and CsF–$GaF_3$ have been investigated by Chassaing [1]. Minimal eutectic were located at 43 mol% at 548°C and 45 mol% at 500°C of $GaF_3$ in respective systems were determined. A system of type similar to that of RbF–$AlF_3$ and CsF–$AlF_3$ [2,3], along with their lower temperature of eutectics suggested at these compositions as a flux used in Nocolok method [4] for brazing aluminum and its alloys. But we could not repeat the reported temperatures of Chassaing. So we decided to re-study these two systems.

## 2. Experimental

### 2.1. Preparation of $GaF_3$

A certain amount of Ga metal with purity > 99.99% was reacted with excessive hydrofluoric acid in a polyvinyl beaker protected with $N_2$ flow. The beaker was heated on a water-bath. $H_2O_2$ was gradually dropped into the blend under continuous stirring. As the reaction was completed the product was vaporized until dry on the water-bath. The white crystal hydrate $GaF_3 \cdot xH_2O$ was obtained. The $GaF_3 \cdot xH_2O$ was put into a platinum crucible which was heated at 200°C for 2 h under HF-flow protection. The white mass obtained was confirmed as anhydrous $GaF_3$ by X-ray diffraction analysis.

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### *2.2. Preparation of the samples*

Samples were prepared from $GaF_3$ which was placed in a platinum crucible blending with a HF solution of RbF or CsF with known concentration and content. Twenty-three samples of RbF–$GaF_3$ and 18 samples of CsF–$GaF_3$ mixtures were prepared in this way and gradually heated until dry at 200°C, then annealed for 48 h at a higher temperature such that no melting of any phase could occur. During the annealing process, grinding and mixing of the samples were repeatedly carried out in order to obtain homogeneous and equilibrium samples.

### *2.3. Differential thermal analysis*

The high-temperature DTA equipment used (of the CR-G type, Beijing Optical Instruments, Inc.) was employed and calibrated using standard substances with known melting points. Both heating and cooling curves were calibrated. $Al_2O_3$ was used as a reference. The heating rate was 15 min. Temperatures were determined by the heating curve, and the cooling curve also was used to correct the liquidus temperature. Experiments were conducted in dry air (relative humidity <30%) in the static state. The error in measuring temperature was ± 3°C.

### *2.4. X-ray powder diffraction analysis*

The intermediate compounds in the system were determined by X-ray diffractometry (XRD, Model $D_{max}$ 2400, Rigaku Co., Tokyo, Japan) under Cu$K_\alpha$ radiation, with a nickel filter and $\lambda = 1.5409$.

## 3. Results and discussion

### *3.1. System RbF–$GaF_3$*

Phase diagram of the system RbF–$GaF_3$, based on DTA data is shown in Fig. 1. The invariant data is presented in Table 1.

Fig. 1 reveals three intermediate compounds formed in the system RbF–$GaF_3$:

1. $Rb_3GaF_6$ congruently melts at 860°C and transforms from $\alpha$ to $\beta$ form at 388°C. The compound reacts with RbF to form eutectic $E_1$ at 750°C in the location of 8.5 mol% $GaF_3$.
2. $RbGaF_4$ peritectic melts at 776°C and reacts with $Rb_3GaF_6$ to form $E_2$ at 749°C and in the location of 43.0 mol% $GaF_3$.
3. The existence of RbF·2$GaF_3$ is identified by X-ray diffraction powder analysis. Its formation temperature was at least over 900°C has not been determined yet.

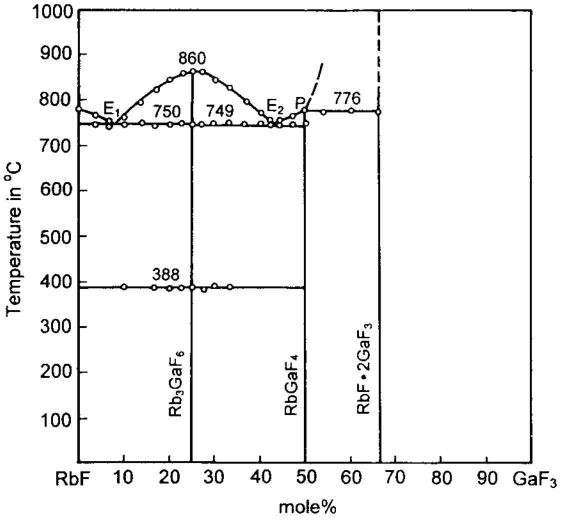

Fig. 1. Phase diagram of system RbF–$GaF_3$.

All these compounds were identified and indexed by X-ray diffraction analysis. The diffraction data of $\alpha$-$Rb_3GaF_6$ coincided with JCDPS(22–1275). Due to the data too complicated, the indexed result could not be successfully obtained. XRD data of $\beta$-$Rb_3GaF_6$ listed in Table 2 was indexed as tetragonal, the cell parameters being: $a = 6.324 \pm 0.004$, $c = 8.860 \pm 0.003$ Å. XRD data of $RbGaF_4$ are presented in Table 3. The compound is orthorhombic, with

Table 1
Invariant points of the system RbF–$GaF_3$

| Invariant point | Temperature (°C) | $GaF_3$ (mol%) |
|---|---|---|
| $E_1$ | 750 | 8.5 |
| $E_2$ | 749 | 43.0 |
| P | 776 | 50.0 |
| m.p. ($Rb_3GaF_6$) | 860 | 25.0 |

$a = 9.821 \pm 0.006$, $b = 9.517 \pm 0.005$, $c = 8.060 \pm 0.006$ Å. Compound RbF·2GaF$_3$ was also indexed (data listed in Table 4) as orthorhombic too, with $a = 9.459 \pm 0.005$, $b = 9.336 \pm 0.005$, $c = 7.685 \pm 0.005$ Å.

Table 2
Indexed data of β-Rb$_3$GaF$_6$[a]

| Observed $d$ (Å) | Calculated $d$ (Å) | $I/I_0$ | $h$ | $k$ | $l$ |
|---|---|---|---|---|---|
| 5.151 | 5.151 | 3 | 1 | 0 | 1 |
| | 3.162 | | 2 | 0 | 0 |
| 3.151 | 3.151 | 100 | 1 | 1 | 2 |
| 2.572 | 2.576 | 9 | 2 | 0 | 2 |
| 2.239 | 2.236 | 13 | 2 | 2 | 0 |
| 2.218 | 2.215 | 20 | 0 | 0 | 4 |
| 1.812 | 1.816 | 17 | 2 | 0 | 4 |
| 1.575 | 1.574 | 8 | 2 | 2 | 4 |
| 1.414 | 1.414 | 5 | 4 | 2 | 0 |
| | 1.412 | | 3 | 3 | 2 |
| 1.403 | 1.403 | 5 | 1 | 1 | 6 |
| 1.187 | 1.188 | 3 | 3 | 1 | 6 |

[a] Tetragonal cell: $a = 6.324 \pm 0.004$; $c = 8.860 \pm 0.003$ Å.

Table 3
Indexed data of RbGaF$_4$[a]

| Observed $d$ (Å) | Calculated $d$ (Å) | $I/I_0$ | $h$ | $k$ | $l$ |
|---|---|---|---|---|---|
| 4.197 | 4.192 | 13 | 2 | 0 | 1 |
| 4.073 | 4.092 | 15 | 0 | 2 | 1 |
| 3.735 | 3.735 | 9 | 1 | 0 | 2 |
| 3.418 | 3.424 | 54 | 2 | 2 | 0 |
| 3.276 | 3.276 | 23 | 3 | 0 | 0 |
| 2.919 | 2.938 | 43 | 1 | 2 | 2 |
| 2.316 | 3.313 | 17 | 1 | 4 | 0 |
| | 2.279 | | 4 | 1 | 1 |
| | 2.276 | | 3 | 3 | 0 |
| 2.271 | 2.274 | 9 | 1 | 2 | 3 |
| 2.197 | 2.194 | 24 | 3 | 3 | 1 |
| 2.102 | 2.106 | 12 | 4 | 2 | 1 |
| | 2.097 | | 4 | 0 | 2 |
| 2.026 | 2.029 | 16 | 3 | 1 | 3 |
| | 2.008 | | 1 | 3 | 3 |
| 2.004 | 2.006 | 14 | 1 | 4 | 2 |
| 1.765 | 1.767 | 6 | 5 | 0 | 2 |
| 1.705 | 1.708 | 18 | 4 | 4 | 0 |
| 1.489 | 1.489 | 8 | 5 | 4 | 1 |
| 1.460 | 1.460 | 28 | 1 | 6 | 2 |
| | 1.458 | | 2 | 2 | 5 |
| 1.297 | 1.297 | 7 | 4 | 2 | 5 |
| | 1.299 | | 2 | 0 | 6 |
| 1.265 | 1.265 | 8 | 4 | 6 | 2 |
| 1.149 | 1.149 | 5 | 6 | 0 | 5 |

[a] Orthorhombic cell: $a = 9.821 \pm 0.006$; $b = 9.517 \pm 0.005$; $c = 8.060 \pm 0.006$ Å.

Table 4
Indexed data of RbF·2GaF$_3$[a]

| Observed $d$ (Å) | Calculated $d$ (Å) | $I/I_0$ | $h$ | $k$ | $l$ |
|---|---|---|---|---|---|
| 5.961 | 5.980 | 8 | 1 | 0 | 1 |
| | 5.941 | | 0 | 1 | 1 |
| 4.679 | 4.667 | 3 | 0 | 2 | 0 |
| | 3.326 | | 1 | 1 | 2 |
| 3.318 | 3.324 | 5 | 2 | 2 | 0 |
| | 2.986 | | 3 | 1 | 0 |
| | 2.985 | | 2 | 0 | 2 |
| 2.966 | 2.966 | 12 | 0 | 2 | 2 |
| | 2.957 | | 1 | 3 | 0 |
| 2.928 | 2.919 | 15 | 3 | 0 | 1 |
| 2.816 | 2.829 | 34 | 1 | 2 | 2 |
| 2.623 | 2.612 | 23 | 3 | 2 | 0 |
| 2.523 | 2.513 | 23 | 2 | 2 | 2 |
| 2.412 | 2.418 | 10 | 0 | 3 | 2 |
| 2.351 | 2.360 | 15 | 3 | 1 | 2 |
| | 2.342 | | 1 | 3 | 2 |
| 2.231 | 2.233 | 5 | 0 | 4 | 1 |
| 2.132 | 2.130 | 7 | 3 | 3 | 1 |
| 2.026 | 2.030 | 4 | 2 | 2 | 3 |
| | 2.021 | | 2 | 4 | 1 |
| 1.971 | 1.967 | 3 | 4 | 1 | 2 |
| 1.922 | 1.922 | 100 | 0 | 0 | 4 |
| | 1.920 | | 3 | 3 | 2 |
| 1.890 | 1.892 | 3 | 5 | 0 | 0 |
| 1.840 | 1.840 | 3 | 2 | 4 | 2 |
| | 1.836 | | 5 | 0 | 1 |
| | 1.826 | | 2 | 3 | 3 |
| 1.823 | 1.823 | 3 | 3 | 4 | 1 |
| | 1.694 | | 2 | 5 | 1 |
| 1.692 | 1.691 | 8 | 4 | 3 | 2 |
| 1.665 | 1.663 | 12 | 2 | 2 | 4 |
| | 1.623 | | 4 | 4 | 1 |
| 1.621 | 1.622 | 5 | 2 | 4 | 3 |
| 1.552 | 1.555 | 4 | 6 | 1 | 0 |
| 1.478 | 1.478 | 11 | 2 | 6 | 0 |
| | 1.466 | | 2 | 0 | 5 |
| 1.461 | 1.461 | 15 | 0 | 2 | 5 |
| | 1.460 | | 6 | 0 | 2 |
| 1.420 | 1.420 | 3 | 4 | 2 | 4 |
| 1.406 | 1.407 | 6 | 6 | 3 | 0 |

[a] Orthorhombic cell: $a = 9.459 \pm 0.005$; $b = 9.336 \pm 0.005$; $c = 7.685 \pm 0.005$ Å.

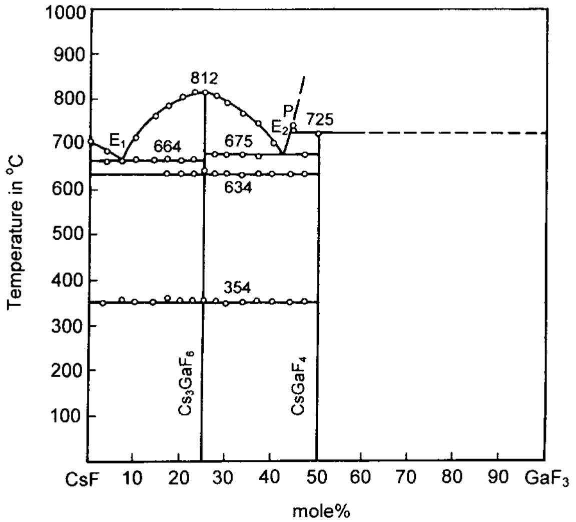

Fig. 2. Phase diagram for the system CsF–$GaF_3$.

### 3.2. System CsF–$GaF_3$

The phase diagram of the CsF–$GaF_3$ system, based on the results of DTA is displayed in Fig. 2. Invariant points can be seen in Table 5.

Fig. 2 reveals two intermediate compounds formed in the system.

1. $Cs_3GaF_6$ congruently melts at 812°C and transforms from $\alpha$ to $\beta$ and $\gamma$ form at 354°C and 634°C, respectively. $Cs_3GaF_6$ reacts with CsF to form eutectic $E_1$ at 664°C in the location of 7.5 mol% $GaF_3$.
2. Peritectic reaction of $CsGaF_4$ takes place at 725°C. The compound reacts with $Cs_3GaF_6$ to form eutectic $E_2$ at 675°C and in the position of 44.0 mol% $GaF_3$.

A technique of quenching in liquid $N_2$ flow was used to keep the structure for determining the sample by X-ray diffractometry.

Table 5
Invariant points of the system CsF–$GaF_3$

| Invariant point | Temperature (°C) | $GaF_3$ (mol%) |
|---|---|---|
| $E_1$ | 664 | 7.5 |
| $E_2$ | 675 | 42.0 |
| P | 725 | 44.0 |
| m.p. ($Cs_3GaF_6$) | 812 | 25.0 |

$\alpha$-$Cs_3GaF_6$ was indexed as orthorhombic with $a = 10.62 \pm 0.02$, $b = 9.959 \pm 0.006$, and $c = 5.607 \pm 0.005$ Å; $\beta$-$Cs_3GaF_6$ is also orthorhombic with $a = 10.356 \pm 0.003$, $b = 8.280 \pm 0.003$, $c = 7.621 \pm 0.005$ Å; $\gamma$-$Cs_3GaF_6$ is tetragonal with $a = 6.833 \pm 0.003$, $c = 9.869 \pm 0.002$ Å. The indexed results of these compounds are listed in Tables 6–8.

$CsGaF_4$ was indexed (see Table 9) by X-ray diffraction as orthorhombic with $a = 8.571 \pm 0.007$, $b = 7.575 \pm 0.007$ and $c = 6.981 \pm 0.006$ Å.

Except for two compounds $Rb_3GaF_6$ ($Cs_3GaF_6$) and $RbGaF_4$ ($CsGaF_4$) being only commonly recognized, these re-investigated phase diagrams are quite different from that reported in Chassaing's research. The compounds $Rb_2GaF_5$ and $Rb_2Ga_5F_{17}$ in system RbF–$GaF_3$, $Cs_5Ga_3F_{14}$ and $CsGa_2F_7$ in the system CsF–$GaF_3$ reported by Chassaing, could not confirm their existence in this research. Another compound RbF·2$GaF_3$ was indexed in our research but no infor-

Table 6
Indexed data of $\alpha$-$Cs_3GaF_6$[a]

| Observed *d* (Å) | Calculated *d* (Å) | $I/I_0$ | *h* | *k* | *l* |
|---|---|---|---|---|---|
| 4.993 | 4.985 | 36 | 0 | 2 | 0 |
| | 4.960 | | 1 | 0 | 1 |
| 4.447 | 4.436 | 43 | 1 | 1 | 1 |
| 3.743 | 3.720 | 35 | 0 | 2 | 1 |
| 3.594 | 3.601 | 34 | 2 | 1 | 1 |
| | 3.336 | | 3 | 1 | 0 |
| 3.312 | 3.323 | 84 | 0 | 3 | 0 |
| | 2.712 | | 1 | 0 | 2 |
| 2.700 | 2.696 | 27 | 0 | 1 | 2 |
| 2.608 | 2.612 | 21 | 1 | 1 | 2 |
| 2.428 | 2.427 | 21 | 1 | 4 | 0 |
| | 2.421 | | 3 | 3 | 0 |
| 2.342 | 2.342 | 33 | 4 | 2 | 0 |
| | 2.331 | | 4 | 1 | 1 |
| 1.930 | 1.931 | 21 | 4 | 0 | 2 |
| 1.911 | 1.912 | 29 | 3 | 4 | 1 |
| 1.653 | 1.652 | 18 | 3 | 0 | 3 |
| 1.641 | 1.641 | 100 | 1 | 6 | 0 |
| | 1.481 | | 1 | 4 | 3 |
| | 1.480 | | 6 | 1 | 2 |
| 1.479 | 1.479 | 16 | 3 | 3 | 3 |
| 1.392 | 1.391 | 16 | 1 | 0 | 4 |
| | 1.335 | | 2 | 7 | 1 |
| 1.333 | 1.333 | 15 | 7 | 0 | 2 |

[a] Orthorhombic cell: $a = 10.62 \pm 0.02$; $b = 9.959 \pm 0.006$; $c = 5.607 \pm 0.005$ Å.

Table 7
Indexed data of β-$Cs_3GaF_6$[a]

| Observed $d$ (Å) | Calculated $d$ (Å) | $I/I_0$ | $h$ | $k$ | $l$ |
|---|---|---|---|---|---|
| 5.157 | 5.180 | 26 | 2 | 0 | 0 |
| 3.639 | 3.644 | 6 | 0 | 2 | 1 |
| 3.581 | 3.575 | 9 | 1 | 0 | 2 |
| 3.466 | 3.463 | 4 | 0 | 1 | 2 |
|  | 3.451 |  | 3 | 0 | 0 |
| 3.411 | 3.410 | 6 | 1 | 2 | 1 |
| 3.300 | 3.288 | 100 | 1 | 1 | 2 |
| 3.140 | 3.145 | 15 | 3 | 0 | 1 |
| 3.083 | 3.066 | 5 | 2 | 0 | 2 |
| 2.693 | 2.704 | 11 | 1 | 2 | 2 |
| 2.595 | 2.597 | 4 | 0 | 3 | 1 |
|  | 2.590 |  | 4 | 0 | 0 |
|  | 2.453 |  | 4 | 0 | 1 |
| 2.442 | 2.446 | 4 | 3 | 1 | 2 |
|  | 2.434 |  | 2 | 3 | 0 |
| 2.328 | 2.324 | 18 | 2 | 3 | 1 |
| 2.151 | 2.154 | 5 | 3 | 3 | 0 |
| 1.922 | 1.922 | 26 | 2 | 4 | 0 |
|  | 1.905 |  | 0 | 0 | 4 |
| 1.902 | 1.902 | 18 | 4 | 2 | 2 |
| 1.856 | 1.857 | 4 | 0 | 1 | 4 |
|  | 1.852 |  | 5 | 2 | 0 |
| 1.826 | 1.827 | 4 | 1 | 1 | 4 |
|  | 1.819 |  | 5 | 0 | 2 |
| 1.817 | 1.818 | 4 | 0 | 4 | 2 |
|  | 1.816 |  | 4 | 0 | 3 |
| 1.799 | 1.799 | 4 | 5 | 2 | 1 |
| 1.780 | 1.776 | 4 | 5 | 1 | 2 |
| 1.770 | 1.771 | 4 | 4 | 1 | 3 |
| 1.730 | 1.730 | 3 | 0 | 2 | 4 |
| 1.730 | 1.729 | 5 | 3 | 4 | 1 |
|  | 1.726 |  | 6 | 0 | 0 |
| 1.649 | 1.649 | 6 | 6 | 1 | 1 |
|  | 1.640 |  | 2 | 2 | 4 |
| 1.638 | 1.636 | 4 | 3 | 1 | 4 |
|  | 1.636 |  | 1 | 5 | 0 |
| 1.478 | 1.478 | 4 | 7 | 0 | 0 |
| 1.473 | 1.471 | 7 | 6 | 2 | 2 |
| 1.358 | 1.358 | 4 | 0 | 6 | 1 |
| 1.246 | 1.247 | 16 | 1 | 1 | 6 |

[a] Orthorhombic cell: $a = 10.356 \pm 0.003$; $b = 8.280 \pm 0.003$; $c = 7.621 \pm 0.005$ Å.

mation was indicated in the Chassaing's report. The difference in our study is that the original material $GaF_3$ was prepared from supper-pure metal gallium and the samples used for DTA analysis were prepared by total solution synthesis. This, we believe, may be the best way for preparing the real homogeneous and equilibrium samples.

Table 8
Indexed data of γ-$Cs_3GaF_6$[a]

| Observed $d$ (Å) | Calculated $d$ (Å) | $I/I_0$ | $h$ | $k$ | $l$ |
|---|---|---|---|---|---|
| 3.288 | 3.287 | 47 | 0 | 0 | 3 |
| 3.054 | 3.070 | 11 | 2 | 1 | 0 |
| 2.966 | 2.966 | 15 | 1 | 0 | 3 |
| 2.919 | 2.930 | 12 | 2 | 1 | 1 |
| 2.740 | 2.724 | 7 | 1 | 1 | 3 |
| 2.321 | 2.321 | 10 | 1 | 0 | 4 |
| 1.920 | 1.924 | 100 | 2 | 1 | 4 |
| 1.898 | 1.897 | 12 | 1 | 0 | 5 |
|  | 1.600 |  | 1 | 0 | 6 |
| 1.599 | 1.599 | 6 | 3 | 3 | 1 |
| 1.520 | 1.518 | 6 | 4 | 2 | 1 |

[a] Tetragonal cell: $a = 6.833 \pm 0.003$; $c = 9.869 \pm 0.002$ Å.

Table 9
Indexed data of $CsGaF_4$[a]

| Observed $d$ (Å) | Calculated $d$ (Å) | $I/I_0$ | $h$ | $k$ | $l$ |
|---|---|---|---|---|---|
| 3.645 | 3.647 | 26 | 2 | 0 | 1 |
| 3.336 | 3.330 | 15 | 0 | 2 | 1 |
| 3.306 | 3.290 | 100 | 2 | 1 | 1 |
| 2.829 | 3.837 | 23 | 2 | 2 | 0 |
| 2.704 | 2.704 | 22 | 2 | 0 | 2 |
| 2.527 | 2.526 | 20 | 0 | 3 | 0 |
| 2.328 | 2.328 | 27 | 0 | 0 | 3 |
| 1.907 | 1.908 | 25 | 3 | 2 | 2 |
| 1.646 | 1.646 | 8 | 4 | 2 | 2 |
| 1.461 | 1.461 | 16 | 3 | 1 | 4 |
|  | 1.460 |  | 1 | 5 | 1 |

[a] Orthorhombic cell: $a = 8.571 \pm 0.007$; $b = 7.575 \pm 0.007$; $c = 6.981 \pm 0.006$ Å.

## Acknowledgements

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