

**No. 40A-2 RbHSO<sub>4</sub>, Rubidium hydrogen sulfate***(M* = 182.54; [*D*: 183.55])

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| 1a | Ferroelectricity of RbHSO <sub>4</sub> was found by Pepinsky et al. in 1960.                                                                                                                                                                                                                                                                                                                   |                                |                                                 | 60Pep        |
| b  | phase                                                                                                                                                                                                                                                                                                                                                                                          | II                             | I                                               | 60Pep        |
|    | state                                                                                                                                                                                                                                                                                                                                                                                          | F                              | P                                               |              |
|    | crystal system                                                                                                                                                                                                                                                                                                                                                                                 | monoclinic                     | monoclinic                                      |              |
|    | space group                                                                                                                                                                                                                                                                                                                                                                                    | Pc-C <sub>s</sub> <sup>2</sup> | P2 <sub>1</sub> /c-C <sub>2h</sub> <sup>5</sup> |              |
|    | Θ [°C]                                                                                                                                                                                                                                                                                                                                                                                         | −9.4                           |                                                 | 75Chi        |
|    | Θ <sub>I-I</sub> of deuterated crystal was reported as −22 °C.                                                                                                                                                                                                                                                                                                                                 |                                |                                                 | 74Kas        |
|    | P <sub>s</sub>    [001]                                                                                                                                                                                                                                                                                                                                                                        |                                |                                                 |              |
|    | ρ <sub>X</sub> = 1.734 · 10 <sup>3</sup> kg m <sup>−3</sup> .                                                                                                                                                                                                                                                                                                                                  |                                |                                                 | 75Ash        |
|    | Transparent, colorless.                                                                                                                                                                                                                                                                                                                                                                        |                                |                                                 | 60Pep        |
|    | Cleavage plane: (001).                                                                                                                                                                                                                                                                                                                                                                         |                                |                                                 | 60Pep        |
|    | Before 1960, the crystal was believed to belong to the orthorhombic system. In this pseudoorthorhombic lattice, the space group is B2 <sub>1</sub> /a and the volume of the pseudo-unit cell is twice that of the true unit cell. The ferroelectric transition temperature is first reported to be 5 °C by Pepinsky et al. Chihara et al. reported −9.4 °C from the heat capacity measurement. |                                |                                                 | 60Pep, 75Chi |
| 2a | Crystal growth: slow cooling or slow evapolation from aqueous solution containing equimolar ratio of Rb <sub>2</sub> SO <sub>4</sub> and H <sub>2</sub> SO <sub>4</sub> .                                                                                                                                                                                                                      |                                |                                                 | 62Mya        |
| 3a | Unit cell parameters at RT: <i>a</i> = 14.354(14) Å, <i>b</i> = 4.618(7) Å, <i>c</i> = 14.808(13) Å, β = 120.92(16)°. In the pseudoorthorhombic lattice, the crystallographic axes designated as <i>a'</i> , <i>b'</i> and <i>c'</i> lie along the [201], [010] and [001] directions, respectively. <i>a'</i> = 24.612 Å, <i>b'</i> = 4.622 Å, <i>c'</i> = 14.807 Å, β = 90°3'.                |                                |                                                 | 75Ash        |
|    |                                                                                                                                                                                                                                                                                                                                                                                                |                                |                                                 | 95Ito        |
| b  | <i>Z</i> = 8 in phase I.                                                                                                                                                                                                                                                                                                                                                                       |                                |                                                 | 70Ash        |
|    | Crystal structure of phase I:                                                                                                                                                                                                                                                                                                                                                                  |                                |                                                 |              |
|    | Projection on (010): Fig. 40A-2-001.                                                                                                                                                                                                                                                                                                                                                           |                                |                                                 |              |
|    | Geometry of the two hydrogen bonds: Fig. 40A-2-002.                                                                                                                                                                                                                                                                                                                                            |                                |                                                 |              |
|    | Fractional coordinates: Table 40A-2-001.                                                                                                                                                                                                                                                                                                                                                       |                                |                                                 |              |
|    | Anisotropic temperature factors: Table 40A-2-002.                                                                                                                                                                                                                                                                                                                                              |                                |                                                 |              |
|    | Interatomic distances and angles: Table 40A-2-003, Table 40A-2-004.                                                                                                                                                                                                                                                                                                                            |                                |                                                 |              |
|    | Distances between rubidium and oxygen at 23 °C: Table 40A-2-005.                                                                                                                                                                                                                                                                                                                               |                                |                                                 |              |
|    | Arrangement of SO <sub>4</sub> (1) ion: Fig. 40A-2-003.                                                                                                                                                                                                                                                                                                                                        |                                |                                                 |              |
| 5a | Dielectric constant:                                                                                                                                                                                                                                                                                                                                                                           |                                |                                                 |              |
|    | Temperature dependence at 10 kHz: Fig. 40A-2-004, Fig. 40A-2-005, Fig. 40A-2-006.                                                                                                                                                                                                                                                                                                              |                                |                                                 |              |
|    | Frequency dependence from 10 · 10 <sup>3</sup> Hz to 9.5 · 10 <sup>9</sup> Hz: Fig. 40A-2-007, Fig. 40A-2-008.                                                                                                                                                                                                                                                                                 |                                |                                                 |              |
|    | Frequency dependence from 8.72 · 10 <sup>9</sup> Hz to 7.85 · 10 <sup>10</sup> Hz: Fig. 40A-2-009, Fig. 40A-2-010.                                                                                                                                                                                                                                                                             |                                |                                                 |              |
|    | Frequency dependence from 1.18 · 10 <sup>11</sup> Hz to 3.66 · 10 <sup>11</sup> Hz: Fig. 40A-2-011.                                                                                                                                                                                                                                                                                            |                                |                                                 |              |
|    | Frequency dependence from 1.18 · 10 <sup>11</sup> Hz to 5.10 · 10 <sup>11</sup> Hz: Fig. 40A-2-012.                                                                                                                                                                                                                                                                                            |                                |                                                 |              |
|    | Frequency dependence at constant temperature: Fig. 40A-2-013, Fig. 40A-2-014.                                                                                                                                                                                                                                                                                                                  |                                |                                                 |              |
|    | For deuterated crystal: Fig. 40A-2-015, Fig. 40A-2-016.                                                                                                                                                                                                                                                                                                                                        |                                |                                                 |              |
|    | Dielectric relaxation time τ: Fig. 40A-2-017.                                                                                                                                                                                                                                                                                                                                                  |                                |                                                 |              |
|    | κ = C/( <i>T</i> − Θ <sub>p</sub> ): <i>T</i> ≥ Θ <sub>f</sub> , <i>C</i> = 144 K, Θ <sub>p</sub> = −8 °C.                                                                                                                                                                                                                                                                                     |                                |                                                 | 77Kaj        |
|    | See also                                                                                                                                                                                                                                                                                                                                                                                       |                                |                                                 | 78Nak        |
|    | Effect of hydrostatic pressure: Fig. 40A-2-018.                                                                                                                                                                                                                                                                                                                                                |                                |                                                 |              |

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| $\Theta$ - $p$ phase diagram: Fig. 40A-2-019, Fig. 40A-2-020.<br>$d\Theta_{II-I}/dp = 12.0(1) \cdot 10^{-8} \text{ K Pa}^{-1}$ .<br>For deuterated crystal: $d\Theta_{II-I}/dp = 12.7(2) \cdot 10^{-8} \text{ K Pa}^{-1}$ . |                                                                                                                                                                                                                                                                             |
| b                                                                                                                                                                                                                           | Nonlinear dielectric properties: $\xi = 7.2 \cdot 10^{14} \text{ V C}^{-3} \text{ m}^5$ , $\zeta = 4.2 \cdot 10^{19} \text{ V C}^{-5} \text{ m}^9$ .<br>Spontaneous polarization: Fig. 40A-2-021, Fig. 40A-2-022, Fig. 40A-2-023.<br>Coercive field: Fig. 40A-2-024.        |
| 6a                                                                                                                                                                                                                          | Heat capacity: Fig. 40A-2-025.<br>$\Delta S = 0.91(8) \text{ J K}^{-1} \text{ mol}^{-1}$ .<br>See also                                                                                                                                                                      |
| 8a                                                                                                                                                                                                                          | Elastic stiffness constant at $10 \cdot 10^6 \text{ Hz}$ : Fig. 40A-2-026.<br>Ultrasonic velocity: at $5 \cdot 10^6 \text{ Hz}$ : Fig. 40A-2-027; at $10 \cdot 10^6 \text{ Hz}$ : Fig. 40A-2-028.<br>Ultrasonic attenuation at $10 \cdot 10^6 \text{ Hz}$ : Fig. 40A-2-029. |
| 9a                                                                                                                                                                                                                          | Refractive index: $n_\beta = 1.473$ for $\lambda = 589 \text{ nm}$ .<br>Optical axial angle: $2V = 55^\circ 52'$ .<br>Infrared spectra, see                                                                                                                                 |
| b                                                                                                                                                                                                                           | Electrooptic effect: see                                                                                                                                                                                                                                                    |
| 10a                                                                                                                                                                                                                         | Raman scattering spectra in a low frequency region: Fig. 40A-2-030;<br>in a high frequency region: Fig. 40A-2-031.                                                                                                                                                          |
| b                                                                                                                                                                                                                           | Brillouin scattering frequency shifts and widths: Fig. 40A-2-032.                                                                                                                                                                                                           |
| 13a                                                                                                                                                                                                                         | NMR: Table 40A-2-006, Table 40A-2-007, Table 40A-2-008.<br>Spin-lattice relaxation time of $^1\text{H}$ : Fig. 40A-2-033.<br>$^{85}\text{Rb}$ nuclear quadrupole resonance: Table 40A-2-009.                                                                                |
| 15a                                                                                                                                                                                                                         | Striped domains were observed by X-ray topography.                                                                                                                                                                                                                          |