

contain pairs of Li atoms alternating with pairs of Ga atoms. The puckered (220) sheets govern the registration between the strings. In Cu_3AsS_4 the [010] strings are of two kinds, all copper and alternating copper and arsenic; the [210] and $[2\bar{1}0]$ strings are all of the same kind and have the sequence three coppers and one arsenic.

The present compound is strictly isostructural with LiGaO_2 (Marezio, 1965) and with $\beta\text{-NaFeO}_2$ (Bertaut & Blum, 1954). In the former case the similarity extends to the displacement of the gallium from the centroid of the tetrahedron (only 0.016 Å in the oxide) and the deviations of bond angles from the ideal tetrahedral values.

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Structure and Phase Transition of $\text{K}_3\text{Na}(\text{CrO}_4)_2$

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Abstract. Tripotassium sodium chromate, $M_r = 372.27$, trigonal, $P\bar{3}m1$, $a = 5.8580$ (6), $c = 7.523$ (2) Å, $V = 223.57$ (7) Å³, $Z = 1$, $D_m = 2.77$ (2), $D_x = 2.77$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 3.837$ mm⁻¹, $F(000) = 180$, $T = 293$ K, $R = 0.030$ for 709 unique observed reflections. A decrease in the elastic stiffness tensor component C_{44} near 239 K reveals a phase transition at this temperature. The configuration of the domain structure confirms the ferroelastic character of the low-temperature phase and the sequence of point groups $\bar{3}m$ and $2/m$.

Introduction. The $\text{K}_3\text{Na}(\text{CrO}_4)_2$ crystal belongs to a family of compounds, with the common chemical formula $A_3C(\text{BX}_4)_2$ (where $A, C = \text{Li, Na, K, Rb, Cs, NH}_4$; $\text{BX}_4 = \text{SO}_4, \text{SeO}_4, \text{CrO}_4$), which frequently exhibit ferroic phases.

In $\text{K}_3\text{Na}(\text{CrO}_4)_2$ a second-order phase transition, at 239 K, has recently been detected by thermal, elastic and dielectric measurements performed in the temperature range 100–300 K (Krajewski, Mroz, Piskunowicz & Breziewski, 1990). The phase below 239 K is ferroelastic as the above authors have confirmed by the direct observation of a domain structure, reorientable under the action of external mechanical stress.

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Following the structural work carried out by Okada & Osaka (1980) and given the structural isomorphism between this compound and the corresponding sulfate, $\text{K}_3\text{Na}(\text{SO}_4)_2$, the point symmetry $\bar{3}m$ was assumed for the room-temperature phase of $\text{K}_3\text{Na}(\text{CrO}_4)_2$ (Krajewski, Mroz, Piskunowicz & Breziewski, 1990). This point group, together with the orientation of the domain walls observed below 239 K, allowed these authors to assign the point group $2/m$ to the ferroelastic phase (Sapriel, 1975).

With the aim of confirming this suggested point-symmetry change at the transition temperature, we have determined the crystal structure of $\text{K}_3\text{Na}(\text{CrO}_4)_2$ at 293 K and performed ultrasonic measurements in the temperature range 200–300 K.

Experimental. Yellow well shaped crystals of $\text{K}_3\text{Na}(\text{CrO}_4)_2$ were grown from aqueous solutions by the steady-state method at 315 K. The reagents used for synthesis were chemically pure sodium and potassium hydroxides and chromic acid anhydride. The crystals obtained displayed a hexagonal prism shape with an edge length of about 10 mm (density measured by flotation); one of the crystals was ground to a sphere of radius 0.12 mm and mounted on an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used. Unit-cell parameters were refined using a set of 25 reflections ($10 < \theta < 50^\circ$). Intensity data were collected by

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Table 1. Positional and equivalent atomic displacement parameters ($\times 10^2$) of $K_3Na(CrO_4)_2$

Standard deviations of the last significant digits are given in parentheses. U_{eq} is defined as: $U_{eq} = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* a_i a_j$.

| | x | y | z | $U_{eq}(\text{\AA}^2)$ |
|------|-------------|--------|---------------|------------------------|
| O(2) | -0.8188 (1) | 0.8188 | 0.3025 (2) | 2.88 (3) |
| O(1) | | | 0.0114 (4) | 3.85 (3) |
| Cr | | | 0.22657 (5) | 0.825 (5) |
| K(1) | | | 0.66767 (8) | 1.571 (8) |
| Na | 0 | 0 | $\frac{1}{2}$ | 1.17 (2) |
| K(2) | 0 | 0 | 0 | 3.25 (1) |

Table 2. Interatomic distances (\AA) and angles ($^\circ$) of $K_3Na(CrO_4)_2$

The standard deviations of the last significant digits are given in parentheses. For each polyhedron, symmetry equivalent distances can be identified by their multiplicity. Distances, corrected for thermal-riding motion, are given in square brackets.

| | | | |
|--------------------------------------|------------|--------------------------------------|------------|
| CrO₄ tetrahedron | | | |
| Cr—O(1) | 1.619 (3) | O(1)—Cr—O(2) | 110.31 (6) |
| | [1.646] | | |
| Cr—O(2) \times 3 | 1.6459 (8) | O(2)—Cr—O(2) | 108.63 (5) |
| | [1.661] | | |
| Mean distance | 1.639 (1) | | |
| NaO₆ octahedron | | | |
| Na—O(2) \times 6 | 2.364 (1) | | |
| K(1)O₁₀ polyhedron | | K(2)O₁₂ polyhedron | |
| K(1)—O(1) | 2.586 (3) | K(2)—O(2) \times 6 | 2.926 (2) |
| K(1)—O(2) \times 6 | 2.941 (1) | K(2)—O(1) \times 6 | 3.3834 (4) |
| K(1)—O(2) \times 3 | 3.151 (2) | Mean distance | 3.155 (1) |
| Mean distance | 2.969 (2) | | |

the ω - 2θ scan technique up to $\sin\theta/\lambda = 0.993 \text{ \AA}^{-1}$. Range of hkl : $-11 \rightarrow 11$, $-11 \rightarrow 11$, $-14 \rightarrow 14$. Three check reflections were measured every 1 h, without significant variation. 6137 reflections collected; 733 unique reflections ($R_{int} = 0.035$) of which 715 with $I > 3\sigma(I)$ were labelled as observed. Lorentz and polarization corrections were applied but no absorption correction. Full-matrix refinement based on $|F|$, using the positional parameters of the isomorphous compound $K_3Na(SO_4)_2$ (Okada & Ossaka, 1980) as starting values and anisotropic atomic displacement parameters for all atoms. In the final stages of the refinement process six reflections (002 , $10\bar{2}$, 110 , 202 , 220 and 300) suspected of extinction were omitted. Final agreement factors were $R = 0.030$, $wR = 0.039$ with $w = 1/\sigma^2(F_o)$; $S = 2.67$, $(\Delta/\sigma)_{max} = 0.015$, $\Delta\rho = \pm 0.63 \text{ e \AA}^{-3}$. Scattering factors for neutral atoms from Cromer & Mann (1968) and anomalous-dispersion corrections for Cr and K atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computer programs: *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), *PLUTO* (Motherwell & Clegg, 1978) and *STRUPLO84* (Fischer, 1985).

The samples used for the ultrasonic measurements were cut from the single crystals and prepared in the

form of rods oriented along the crystallographic direction [001]. The measurements were performed using the pulse-echo overlap technique with a Matec 6600 system. The velocity of transversal ultrasonic waves (10 MHz) propagating along the [001] direction was measured. The elastic stiffness tensor component C_{44} was calculated from the wave velocity and the crystal density.

Discussion. Final positional coordinates and equivalent atomic displacement parameters are given in Table 1.* The most relevant interatomic distances and bond angles are listed in Table 2.

The structure is made up of CrO_4 tetrahedra, NaO_6 octahedra and two different, $K(1)O_{10}$ and $K(2)O_{12}$, more complicated polyhedra stacked along the c axis. A projection of the structure parallel to the [001] direction showing the coordination of the

* Lists of structure factors and anisotropic atomic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53130 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

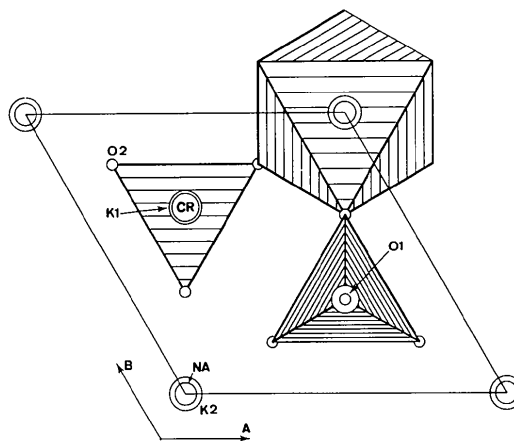


Fig. 1. Projection of the structure on to the (001) plane showing the two CrO_4 tetrahedra inside the unit cell and the octahedral coordination of the Na atoms.

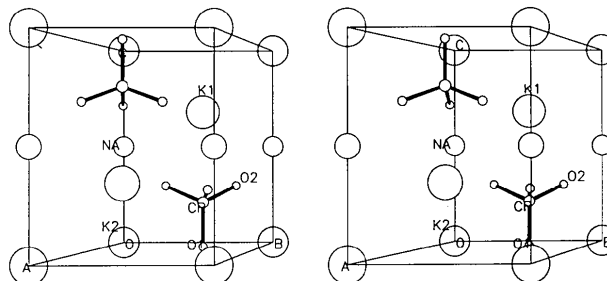


Fig. 2. *PLUTO* stereoview of the unit cell at 293 K.

Cr and Na atoms, can be seen in Fig. 1. The two CrO_4 tetrahedra, inside each unit cell, are disposed with their apices in opposite directions along the c axis (Figs. 1 and 2). This kind of packing is the same as that of the isomorphous compound $\text{K}_3\text{Na}(\text{SO}_4)_2$ (Okada & Ossaka, 1980).

The Na—O distances in the NaO_6 octahedron are symmetry restricted to a single value of 2.364 Å. The mean distances in the $\text{K}(1)\text{O}_{10}$ and $\text{K}(2)\text{O}_{12}$ polyhedra are 2.969 and 3.155 Å respectively.

The Cr—O distances range from 1.613 to 1.6459 Å with a mean value of 1.639 Å. The values of the two possible bond angles O—Cr—O, in the CrO_4 group (110.31 and 108.63°), indicate a very small distortion with respect to the ideal tetrahedral configuration. The rigidity of this group was revealed by means of a librational thermal-motion analysis based on the anisotropic atomic displacement parameters of the Cr, O(1) and O(2) atoms. The results show that the thermal motion of the CrO_4 groups can be completely described by the **T** and **L** tensors (Schomaker & Trueblood, 1968). The residual deformation deduced from the comparison between the observed and calculated atomic displacement parameters is practically zero for this tetrahedron. The corrected bond lengths involving Cr—O(1) and Cr—O(2) atom pairs (see Table 2) exhibit, therefore, closer values (1.646 and 1.661 Å respectively).

The elastic stiffness tensor component C_{44} shows a usual decrease with increasing temperature from about 250 K up to room temperature. Below 250 K, in the vicinity of the phase transition, the C_{44} component strongly decreases and acoustic phonon softening is quite evident (Gómez-Cuevas & Breczewski, 1990). The strong damping of ultrasound waves by the ferroelastic domain walls prevents measurement below the phase transition.

In the present case, the softening of C_{44} is necessary only for the appearance of $2/m$ symmetry in the ferroelastic phase (Toledano, Fejer & Auld, 1983). In

fact, such a symmetry change, as probed by ultrasonic measurements, would also require similar behaviour in C_{11} – C_{12} (equal to $2 \times C_{66}$ for this point group) at the transition temperature. Unfortunately, the morphology of the samples hindered the study of C_{11} – C_{12} as a function of temperature.

Nevertheless, previous results published by Krajewski, Mroz, Piskunowicz & Breczewski (1990) concerning the domain structure of the ferroelectric phase, together with the X-ray measurements presented above and the behaviour of the elastic tensor component C_{44} confirm, as expected from Landau theory (Toledano, Fejer & Auld, 1983; Sapriel, 1975), the change of point symmetry in the phase transition from $\bar{3}m$ to $2/m$.

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Structure of $\text{Li}_4\text{Ge}_5\text{O}_{12}$ – a New Compound in the Li_2O – GeO_2 System

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Abstract. Tetralithium pentagermanate $\text{Li}_4\text{Ge}_5\text{O}_{12}$, $M_r = 582.7$, triclinic, $P\bar{1}$, $a = 5.120$ (1), $b = 9.143$ (2), $c = 9.586$ (2) Å, $\alpha = 72.95$ (3), $\beta = 77.74$ (3), $\gamma =$

78.81 (3)°, $V = 415.02$ (15) Å³, $Z = 2$, $D_m = 4.63$, $D_x = 4.663$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 17.74$ mm⁻¹, $F(000) = 536$, $T = 295$ (2) K, $R =$

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