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Abstract

The ferroelec. orthorhombic phase and a new nonpolar tetragonal phase of yellow Sr₈[Al₁₂O₂₄](CrO₄)₂ single crystals were studied by polarized light microscopy, DSC, permittivity measurements, spontaneous birefringence, and spontaneous polarization. The high perfection of the title crystals relative to the green form was demonstrated. The symmetry and microtwinning of the crystals are discussed.

Reference

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OPTICAL, DIELECTRIC AND DSC STUDIES OF "YELLOW-TYPE" ALUMINATE SODALITE Sr₈[Al₁₂O₂₄](CrO₄)₂

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Abstract The ferroelectric orthorhombic phase and a new non-polar tetragonal phase of yellow single crystals of Sr₈[Al₁₂O₂₄](CrO₄)₂ are studied by polarized light microscopy, differential scanning calorimetry (DSC), measurements of permittivity, spontaneous birefringence and spontaneous polarization.

INTRODUCTION
On green single crystals of the aluminate sodalite Sr₈[Al₁₂O₂₄](CrO₄)₂ (abbreviated SACR) an improper ferroelectric phase transition was found at (295K± 299K)\(^{±}\)\(^{(1)}\). Measurements on ceramics\(^{(2)}\) confirmed the ferroelectric phase. The present paper reports some properties of better quality crystals of yellow colour, typical of the pure chromate ion, and those of a new tetragonal phase not observed on the green crystals and ceramics.

EXPERIMENTS

Crystal Growth and Samples.
Yellow single crystals (1-3 mm) of SACR were grown from a Bi₂O₃ flux by using SrCrO₄ (instead of CrO₃)\(^{(1,2)}\), SrO and β-Al₂O₃ directly as solutes. The shiny (110)\(_C\) and (112)\(_C\) facets served as reference for preparing (110)\(_C\) and (100)\(_C\) platelets for the measurements.

Domains and poling.
In polarized light two sharp first order transitions, cubic ↔ tetragonal and tetragonal ↔ orthorhombic, have been evidenced. The tetragonal phase is optically
negative, has ferroelastic domain walls //\((110)_c\) moving easily under stress and showing no response to electric fields up to \(40 \text{kV.cm}^{-1}\). Aizu species \(m\overline{3}mF4/mmm\) is probable. The orthorhombic phase has tiny intricate domains at zero field, strong birefringence, parallel and 45 degrees extinction on (100)\(_c\)-cuts. With a field of \(\approx 40 \text{kV.cm}^{-1} \parallel [110]_c\), ferroelastic/ferroelectric single domains were obtained proving Aizu species \(m\overline{3}mFmm2(ss)\).

**Differential Scanning Calorimetry.**

By using a Mettler FP800, an Al-crucible, 28.26mg of small crystals and a heating rate of 4 deg.min\(^{-1}\), the transition temperatures and enthalpies were obtained (Fig. 1):

\[
T_1(\text{orth.} \leftrightarrow \text{tetr.}) = (12.1^\circ C \pm 14.9^\circ C \uparrow) ; \Delta H_1 = 3.9 \text{ J.g}^{-1} \\
T_2(\text{tetr.} \leftrightarrow \text{cub.}) = (26.6^\circ C \pm 27.1^\circ C \uparrow) ; \Delta H_2 = 1.4 \text{ J.g}^{-1}
\]

**Spontaneous birefringence** \(\Delta n_s\).

Figure 2 shows \(\Delta n_s\) of the orthorhombic and tetragonal principal sections, measured on (100)\(_c\) and (110)\(_c\) mono-domain platelets upon heating from 4K to 310K, using a Babinet-Soleil compensator. The discontinuous onsets of \(\Delta n_s\) clearly show the transitions to be of first order.

**Spontaneous polarization** \(P_s\).

On a platelet (110)\(_c\) cooled in a field of 30kVcm\(^{-1}\) from the cubic to the orthorhombic phase, the remanent polarization has been measured by charge integration upon heating (electrometer Keithley 616). A spontaneous polarization of \(2.5 \mu \text{C.cm}^{-2}\) (below 260 K) has been measured on a ferroelastic mono-domain platelet (Fig. 3). Reversal of the poling field reversed the sign of the remanent polarization.

**Dielectric constant and loss tangent.**

The dielectric constant was measured at 300kHz on a poled (110)\(_c\) platelet between 200 and 300K upon heating, using a LF Impedance Analyzer (HP 4192A). In the entire temperature range of the mm2 phase the sample remained single domain up to the maximum \(\varepsilon_{33} (//P_s) (\approx 24)\) at 286K, but it became polydomain in the tetragonal phase, simulating a 2\(^{nd}\) order transition to the cubic phase. At variance with green polydomain crystals\((1)\), the dielectric loss, \(tg\delta\), was extremely low, lower than the
OPTICAL, DIELECTRIC AND DSC STUDIES

FIGURE 1
Differential scanning calorimetry.

FIGURE 2
Spontaneous birefringence vs. temperature; sample: (001)c, (110)c and (110)c parallelepiped (thickness: 0.450 mm x 0.470 mm x 0.470 mm).

FIGURE 3
Remanent polarization on reversal of the poling field; sample: (110)c-cut, thickness (0.063 mm).

FIGURE 4
Dielectric constant vs. temperature; sample: (110)c-cut, thickness (0.063 mm).
CONCLUSION
The high perfection of yellow SACR crystals relative to the green ones has been demonstrated by i) the detection of a new non-polar tetragonal phase, ii) the great ease of tetragonal ferroelastic wall motion, iii) the achievement of fully poled orthorhombic single domains permitting reliable measurements of $P_s(T)$, $\Delta n_s(T)$ and $\epsilon_{33}(T)$. In the green crystals (1) of SACR the Cr$^{6+}$ ions seem to be reduced to Cr$^{3+}$ to some extent, leading to defects that tend to smear the two transitions to an apparent single one(1,2). Recent X-ray structural work on a green single crystal, was unable to decide between space group $I\bar{m}3m$ and $I\bar{4}3m$ for the cubic phase(3). The fact that $P_s$ lies along [110]$_c$ unequivocally requires the prototype to be of point group $m\bar{3}m$, hence of space group $I\bar{m}3m$. However, the cubic phase is eventually $I\bar{4}3m$ microtwinned with the prototype remaining hypothetical. Microtwinning might be demonstrated by successful ferroic switching with simultaneous electric field and mechanical stress as proposed for a similar problem in the case of spinels(4).

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