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Reference
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ALUMINATE SODALITE \(\text{Sr}_8[\text{Al}_{12}\text{O}_{24}](\text{CrO}_4)_2\) - A NEW FERROELECTRIC MATERIAL

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Abstract On flux grown polydomain single crystals of \(\text{Sr}_8[\text{Al}_{12}\text{O}_{24}](\text{CrO}_4)_2\) exploratory domain studies and measurements of birefringence, polarization, dielectric constant and transition enthalpy demonstrate the existence of a first order ferroelectric phase transition at about 295\(^\circ\) - 299\(^\circ\)K.

INTRODUCTION

The general formula of the members of the sodalite family is \(\text{M}_8[\text{T}_{12}\text{O}_{24}]\text{X}_2\). Corner-sharing tetrahedra \(\text{T}\text{O}_4\) (\(\text{T} = \text{Si}^{4+}, \text{Al}^{3+}, \ldots\)) form an open framework, in the cavities of which are contained the cage cations \(\text{M} (\text{Na}^+, \text{Ca}^{2+}, \text{Sr}^{2+}, \ldots)\) and the cage anions \(\text{X} (\text{Cl}^-, \text{SO}_4^{2-}, \text{CrO}_4^{2-}, \ldots)\). Aluminate sodalites contain only \(\text{Al}^{3+}\) as \(\text{T}\) cations. The sodalite framework is flexible and adapts itself to the sizes and shapes of the cage ions. Displacive phase transitions have been found to occur in most aluminate sodalites containing tetrahedral cage anions\(^1\),\(^2\). The result of the first structure determination of a non-cubic sodalite has recently been reported\(^2\),\(^3\). Symmetry considerations made it conceivable that ferroelectricity might occur in at least some of the aluminate sodalites. Because of its convenient transition temperature, the title compound has been chosen for a first search for ferroelectricity amongst aluminate sodalites.

EXPERIMENTS

Crystal growth and samples
Light green single crystals of 1 - 2 mm size and imperfect (110) and (112) facets - the rhombic dodecahedron is usually dominating - have been grown from a \(\text{Bi}_2\text{O}_3\) flux\(^9\). Platelets parallel to (100) and (110) have been prepared with a thickness of 40 - 60\(\mu\)m and electroded with a transparent gold layer.
Polarized light microscopy of the domain structure.

Using a polarizing microscope in conjunction with an optical helium flow cryostat, observation of (100) platelets showed two kinds of domains, one with extinction parallel [100], the other parallel [110], suggesting orthorhombic symmetry. Domains with extinction parallel [100] are separated by (110) walls, whereas those with extinction parallel [110] are linked to the former by walls having traces on (100) along [100]. Cooling of the sample through $T_c$ with 20 kV cm$^{-1}$ applied perpendicular to the surface, increased the amount of domains with extinction parallel [100]. This behaviour is consistent with mm2 symmetry with the spontaneous polarization parallel [110] (Aizu species m3mF2mm(sp)). Because the domains did not change the orientation of the indicatrix upon reversal of polarization, the high temperature symmetry $43m$ can be excluded. Application of the same field below $T_c$ had no visible effect on the domain pattern.

Spontaneous birefringence.

On a (100)-cut platelet (thickness 74μm), the spontaneous birefringence $\Delta n$ has been measured on a domain with extinction parallel [100] from $T$ down to 4K, using a tilting compensator (Fig.1). The discontinuous onset of $\Delta n$ and the thermal hysteresis at $T_c$ clearly show the transition to be of first order (hysteresis of measured domains: $T_c=295K$ on cooling, $T_c=299K$ on heating; hysteresis of the entire platelet: $+285 - 299K$). No further transition appeared below $T_c$.

Spontaneous polarization.

Platelets cut parallel (110) and (100) have been cooled in a field of 20 kV cm$^{-1}$ through $T$, and the remanent polarization has been measured by charge integration upon heating using an electrometer (Keithley 616). The charge integration was possible owing to the very high resistivity of the samples. Maximum polarizations of 7 and 5μC cm$^{-2}$ (at 248K) have been achieved on (110) and (100) cuts, respectively (Fig.2). Reversal of the poling field reversed the sign of the remanent polarization (Fig.3). After a second cooling of the poled samples in zero field strong depolarization was observed. Therefore, the slope $\partial P / \partial T$ is certainly not intrinsic and the apparent second order type vanishing of the polarization at $T_c$ can be attributed to smooth depoling effects. Although the samples were not fully saturated, the ratio $P[110]/P[100] = \sqrt{7/5} \approx \sqrt{2}$ is also consistent with $P_s$ lying along [110].

Dielectric constant and loss tangent.

Figure 4 shows the dielectric constant and loss tangent measured at 100 kHz on a polydomain (100) platelet between 240 and 300K by
means of a LF Impedance Analyzer (HP 4192A). For a heating/cooling rate of 1 deg/min the maximum of $\varepsilon$ ($\varepsilon_{\text{max}} \approx 90$) was found at 292K and 287K, respectively. The temperature dependence of $\varepsilon$ below T and its independence of temperature above T are typical for an improper ferroelectric, reminiscent of, e.g., Gd$_2$(MoO$_4$)$_3$. In the range 1 to 1000 kHz $\varepsilon$ is nearly independent of frequency. Measurement of $\varepsilon$ in a bias field of 20 kV·cm$^{-1}$ decreased $\varepsilon_{\text{max}}$ by about 20% without changing T($\varepsilon_{\text{max}}$), an effect probably due to partial poling. The dielectric loss, $\tan \delta$, was extremely low (Fig.4): above T lower than the detection limit of the bridge (<0.0001), whereas the maximum of $\tan \delta$ was still lower than 0.0001 for $f = 1$ kHz and increased with frequency to 0.003 for 100 kHz and to 0.01 for 1MHz.

Calorimetric measurement.
With a differential scanning calorimeter the enthalpy of the transition could be determined to be 5.76 kJ·mol$^{-1}$.

CONCLUSIONS.

Although the different results are of preliminary character — owing to the insufficient size and quality of the crystals — the observed polarization and its reversal upon cooling in an electric field through T clearly demonstrate that Sr$_8$[Al$_{12}$O$_{24}$](CrO$_4$)$_2$ is ferroelectric. Herewith it is the first example of ferroelectricity occurring in the aluminate sodalite family in which many more ferroelectrics and ferroelastics are to be expected. The dielectric anomaly suggests that the compound is an improper ferroelectric and the domain pattern and poling behaviour show that the most probable Aizu species is m3mP2mm(sp). The apparent sluggishness of the phase transition needs further study.

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REFERENCES
4. to be published
5. V. Dvořák, Ferroelectrics 7, 1 (1974)
FIGURE 1 Spontaneous birefringence vs. temperature.

FIGURE 2 Remanent polarization vs. temperature.

FIGURE 3 Sign reversal of the remanent polarization on reversal of the poling field.

FIGURE 4 Dielectric constant and loss tangent vs. temperature, (100) platelet, 100kHz.