Ferroelectrics

Dielectric, pyroelectric, and thermal properties of LiNH4SO4 and LiND4SO4

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DIELECTRIC, PYROELECTRIC, AND THERMAL PROPERTIES OF LiNH$_4$SO$_4$ AND LiND$_4$SO$_4$

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Measurements of optical second harmonic generation, specific heat, dielectric constant, and pyroelectric coefficient of LiNH$_4$SO$_4$ and its deuterated analog are reported over a temperature range which includes the two phase transitions near 283 K and 459 K. The results indicate that these materials are potentially useful as pyroelectric detectors. Pyroelectric and second harmonic generation data show that the phase below $\sim$283 K is polar.

INTRODUCTION

Lithium ammonium sulfate (LiNH$_4$SO$_4$) has generated considerable interest recently because of its unusual ferroelectric and ferroelastic properties.[1,2] The crystal has an orthorhombic symmetry (space group C_{2v}^9 – $Pna2_1$) at room temperature,[3] and undergoes two structural phase transitions near 283 K and 459 K respectively.[1,4] The symmetry of the high temperature phase (above $\sim$459 K) has been identified as orthorhombic D_{2h}^{16} – $Pmcn$.[1] The low temperature phase, which occurs below $\sim$283 K, has been reported to be monoclinic, however, an assignment of a space group is ambiguous. Yuzvak et al.[5] reported a step-wise increase in spontaneous polarization at the low temperature phase transition and proposed that the low temperature phase belongs to the space group $P2_1$. A study by Poulet and Mathieu[6] confirmed this polar assignment from measurements of piezoelectric response induced by stress along the two-fold axis below 283 K. However,

Mitsui et al.[7] and Aleksandrova et al.[7] concluded on a basis of second harmonic generation (SHG) measurements that the low temperature phase was centrosymmetric. This is supported by a recent X-ray analysis by Kruglik et al.[8] who found that the low temperature phase of LiNH$_4$SO$_4$ belongs to the space group $P2_1/a$.

In this paper we report on growth of single crystals of LiNH$_4$SO$_4$ (LAS) and LiND$_4$SO$_4$ (DLAS), and measurements of their optical SHG, specific heat, pyroelectric coefficient, and dielectric constant properties. For the purpose of studying the character of the phase transitions, measurements were performed over a temperature range which includes the two transition points. On the basis of the optical SHG and pyroelectric measurements, the center of symmetry problem of the low temperature phase is resolved. The results of the pyroelectric, dielectric, and specific heat measurements are used to assess the suitability of LAS and DLAS for use in pyroelectric detectors.

EXPERIMENTAL TECHNIQUE

Crystal Growth

Large (3 × 3 × 3 cm) colorless single crystals of LiNH$_4$SO$_4$ were grown from aqueous solution containing equimolar concentrations of

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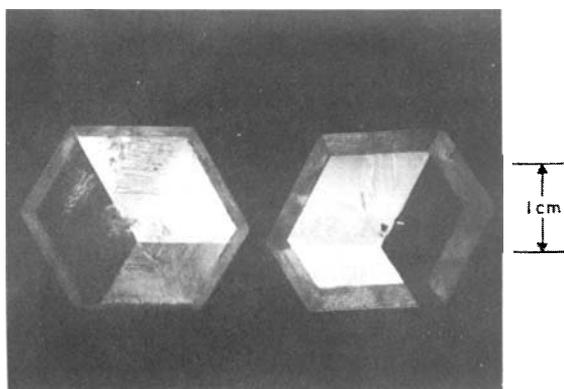‖ Present address: College of William and Mary, Williamsburg, Virginia, 23185.

FIGURE 1   Pseudo-hexagonal morphology of $LiNH_4SO_4$ (crossed polarizers).

$(NH_4)_2SO_4$ and $Li_2SO_4 \cdot H_2O$. The deuterated crystals were grown from D_2O (99.9 %D) solutions saturated with previously recrystallized $LiND_4SO_4$. The final growth solution had a deuteration level of 97.7 $\pm$ 0.03 %. The evaporation method of growth was employed using a nitrogen gas flow of 60 l/h, while the solution temperature was controlled at 318.00 $\pm$ 0.05 K and stirred at 25 rpm. Solvent removal was controlled at a rate of 2 cm^3/day. The saturated $LiNH_4SO_4$ and $LiND_4SO_4$ solutions were at pH 3.88 and 3.93, respectively. Single crystals from spontaneously nucleated seeds were always twinned and had a pseudohexagonal morphology (Figure 1). Untwinned sections of these crystals were selected and only c-axis plates were used as seeds for subsequent growth.

Sample Preparation

Samples for electrical measurements were cut normal to the pyroelectric axis and polished with a water, ethanol and glycerin mixture to thicknesses from 0.05 to 0.1 mm. Electrodes were formed on the whole surface of the samples by vacuum deposition of antimony. Before each measurement, samples were poled with a steady field of ~ 5 kV/cm applied during slow cooling through the transition point down to room temperature.

Dielectric and Pyroelectric Measurements

The dielectric constant was measured by determining the ratio of the capacitance of a sample to that of a reference capacitor placed in series with

it. A small ac signal (typically 50 mV at 8 kHz) was applied to the sample and reference and synchronous detection was used to measure the voltage appearing across the reference capacitor.

Two different types of pyroelectric measurements were made. In the first method used the crystal was connected to a microvolt ammeter (Keithley model 150B) and heated slowly at a constant rate of 2°C/min. The pyroelectric current developed by the sample was recorded directly versus temperature using an X-Y recorder. The second method used was a dynamic technique[9] similar to that described by Chynoweth.[10] The sample was illuminated by a train of rectangular infrared pulses typically of 15 msec duration, so that the increase of its temperature did not exceed 0.01°C. A resulting pyroelectric voltage response was measured across a 10 MΩ load resistor connected in parallel to the sample. It has been shown[9] that when the period of the incident signal is larger than the electrical time constant of the sample (typically 1 msec) but smaller than the thermal time constant (~ 1 sec), the peak-to-peak value of the response is proportional to the ratio p/c, where p is the pyroelectric coefficient and c is the volume specific heat of the material.

Specific Heat Measurements

Measurements of the temperature dependence of the specific heat were performed with a Perkin-Elmer differential scanning calorimeter Model DSC-2. Sample weights were in the 10 to 40 mg range. Data were recorded at a scan rate of $10°$ min^{-1} and a sensitivity of 2 mcal sec^{-1}. The apparatus was calibrated with high purity indium ($T_M = 429.87$ K and $\Delta H = 6.80$ cal g^{-1}). The error in ΔH for indium was less than 0.1 % while the error in T_M was 0.3 K.

RESULTS

Second Harmonic Generation

The symmetry of the three phases in $LiNH_4SO_4$ and $LiND_4SO_4$ was investigated using standard optical second harmonic techniques.[11] Index matching oils were used only for temperatures in the range 293 to 313 K. The average index for $LiNH_4SO_4$ is 1.496 and for $LiND_4SO_4$ is 1.500. Both materials were found to be phase matchable for a 1.06 μm fundamental at room temperature.
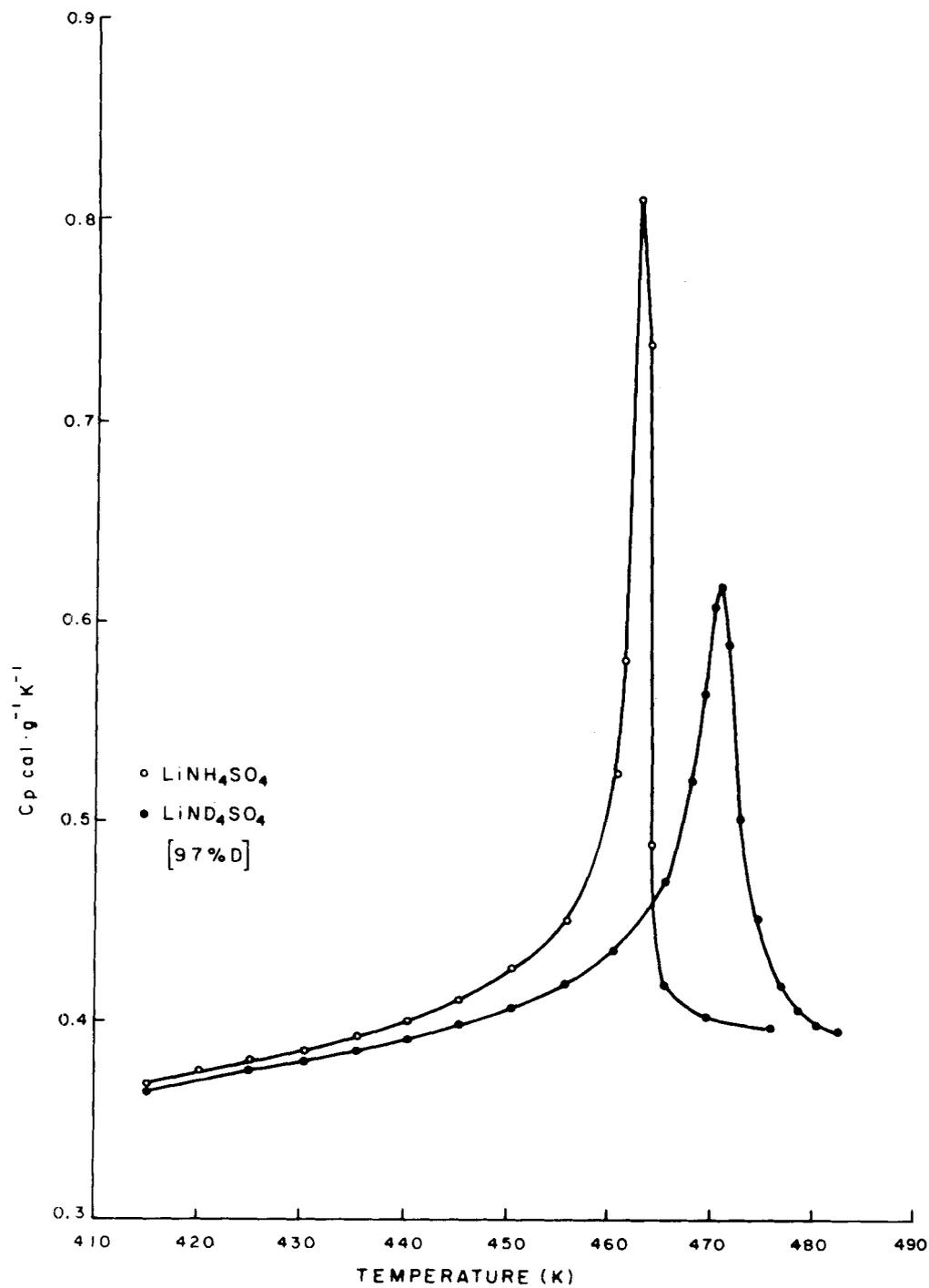
FIGURE 2 Temperature dependence of the specific heat in LiNH₄SO₄ and LiND₄SO₄.

TABLE I

Optical second harmonic powder analysis data (Particle size: 212–300 μm)

Crystal	Phase	Temperature interval (K)	$\bar{n}$ (5300 Å)	Single level relative α-SiO$_2$
LiNH$_4$SO$_4$	mmm	478–505	no oil	0.000
	mm 2	293–455	1.496	2.2
	2 or m	170–270	no oil	0.3
LiND$_4$SO$_4$	mmm	478–505	no oil	0.000
	mm 2	293–455	1.500	2.2
	2 or m	185–260	no oil	0.3

Table I summarizes the SHG analysis. Contrary to data previously reported,[1,7] the low temperature phase in both compounds is acentric. Therefore, the symmetry of this phase must be either m or 2 and confirms two previous assignments.[5,6]

At the low temperature phase transition, a thermal hysteresis of approximately 8K was observed. This is consistent with our dielectric and pyroelectric measurements. Near the high temperature phase transition, the SHG data also suggest a smaller thermal hysteresis, but the dielectric and pyroelectric measurements reveal no such hysteresis.

Specific Heat

The temperature dependence of the specific heat for LiNH$_4$SO$_4$ and LiND$_4$SO$_4$ is shown in Figure 2. Upon deuteration of LiNH$_4$SO$_4$, the peak in the specific heat is broadened and occurs about 8 K higher in temperature. The dielectric and pyroelectric measurements reveal an upward shift in the transition temperature upon deuteration of about 2 K.

A linear least squares fit of these data over the range 415 K to 445 K yields, for LiNH$_4$SO$_4$

$$C_p(\text{cal g}^{-1}\text{ K}^{-1}) = -0.118 + 1.17(10^{-3})T,$$

and for LiND$_4$SO$_4$

$$c_p(\text{cal g}^{-1}\text{ K}^{-1}) = 0.054 + 1.01(10^{-3})T.$$

Figure 3 illustrates a high precision scan of LiNH$_4$SO$_4$ ($dT/dt = 0.6°$ min^{-1} and 1 mcal/sec sensitivity) which revealed multiple peaking behavior near the high temperature phase transition. Similar behavior has been observed in Gd$_2$(MoO$_4$)$_3$, Tb$_2$(MoO$_4$)$_3$, Cr$_3$B$_7$O$_{13}$Cl and Ni$_3$B$_7$O$_{13}$Br, and can be attributed to bulk strains in the crystalline samples.[12] The specific heat
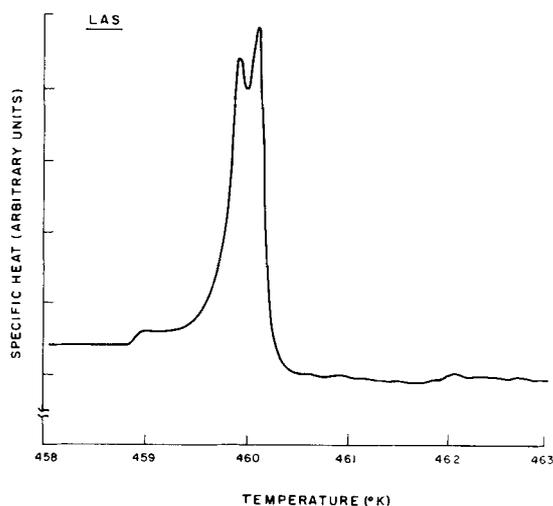

FIGURE 3   High-resolution scan of specific heat vs. temperature in LiNH$_4$SO$_4$.

measurements also show that both LiNH$_4$SO$_4$ and LiND$_4$SO$_4$ are stable in air up to at least 548 K. This contradicts an earlier report that LiNH$_4$SO$_4$ decomposes at 465 K.[13]

Dielectric Constant

Figure 4 shows the temperature dependence of the dielectric constant, ε_c, along the pyroelectric axis of DLAS. A step-wise change of ε_c accompanies the low temperature phase transition, and a sharp peak is obtained at the high temperature phase transition. Between the two transition points, ε_c depends weakly on temperature and varies only within 20% of its room temperature value which is about 11. Within 1 K of the low temperature transition an unstable behavior of the dielectric constant was observed. A change of the measuring frequency between 80 Hz and 8 kHz did not influence the unstable behavior of ε_c in that region. In a narrow temperature region (~ 4 K) above 461 K, ε_c follows a Curie-Weiss law: $\varepsilon_c = 13.2 + 1.8$ K/(T-459 K). The dielectric constant of LAS shows a similar behavior, with the high transition point shifted downward by ~ 2 K, and the low transition point shifted upward by ~ 4 K.

Pyroelectric Coefficient

Figure 5 describes results of a dynamic measurement of the ratio p/c as a function of temperature in a sample of LAS. The existence of pyroelectric
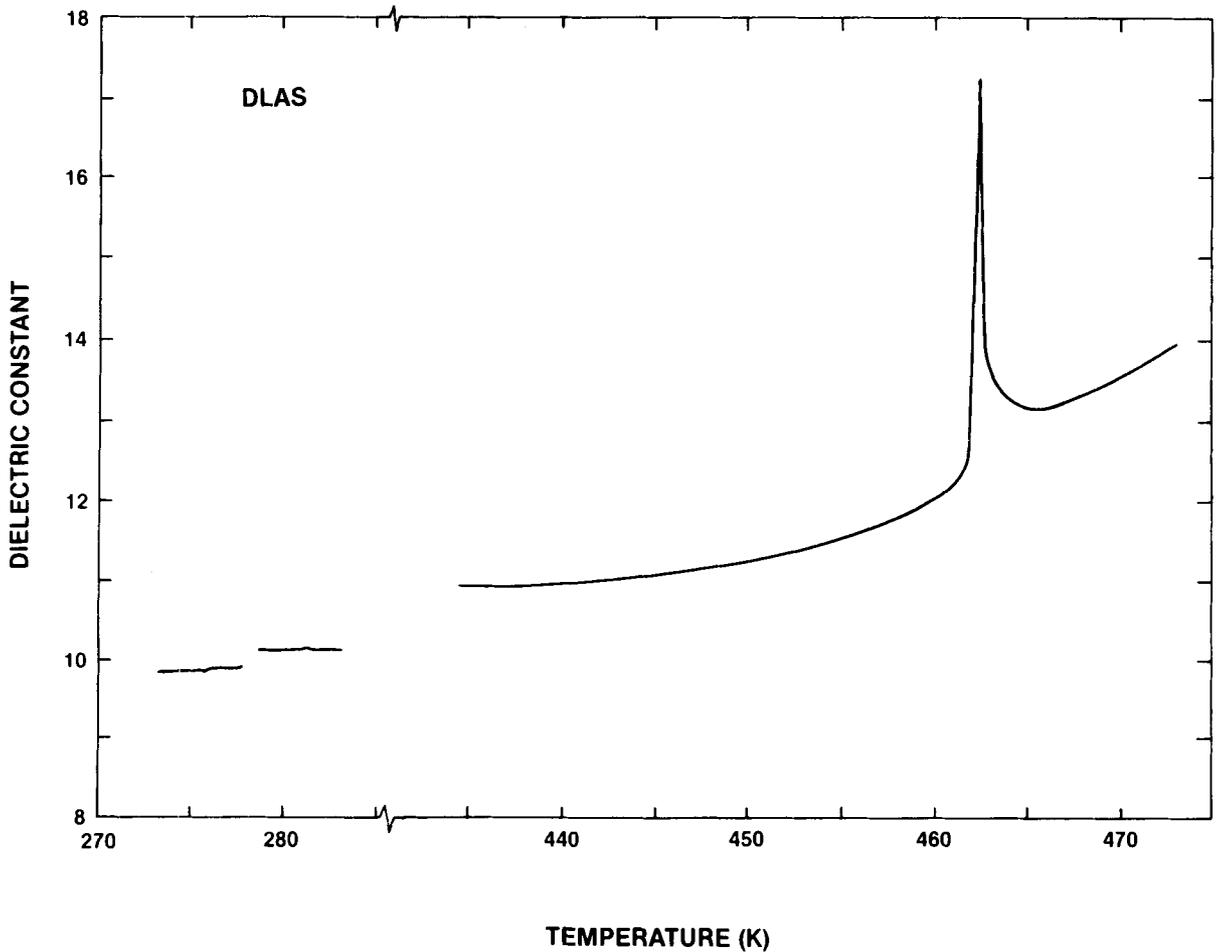
FIGURE 4   Temperature dependence of dielectric constant in LiND$_4$SO$_4$.

response in the low temperature phase is in accordance with the observation of Yuzvaket et al.[5] Upon heating, the pyroelectric response decreases slowly and becomes unstable in the vicinity of the transition point. A sharp increase is observed at 284 K after which the response again becomes stable. Between 284 K and 445 K, p/c behaves in an unusual manner: it decreases as the temperature increases. In the vicinity of the high temperature phase transition, p/c passes through a minimum, and then rises rapidly to a sharp peak at the transition point. A thermal hysteresis of the order of 5 K was found for the low temperature transition. For the high temperature transition no detectable hysteresis was observed. Similar results were obtained in the deuterated crystal.

The lower phase transition of LAS and DLAS was also studied by measuring the pyroelectric current while cooling and heating the samples through the transition. The pyroelectric current of a partially electroded sample exhibited multiple peaking near the transition. Using a fully electroded sample resulted in a marked reduction of the number of multiple peaks but did not completely eliminate this behavior (Figure 6). From the sign of the pyroelectric current released near the transition, we deduced that the spontaneous polarization on the low temperature side of the transition is smaller than that on the high temperature side. The jump in spontaneous polarization, measured by integration of the pyroelectric current released is $0.27 \pm 0.03 \ \mu C/cm^2$.
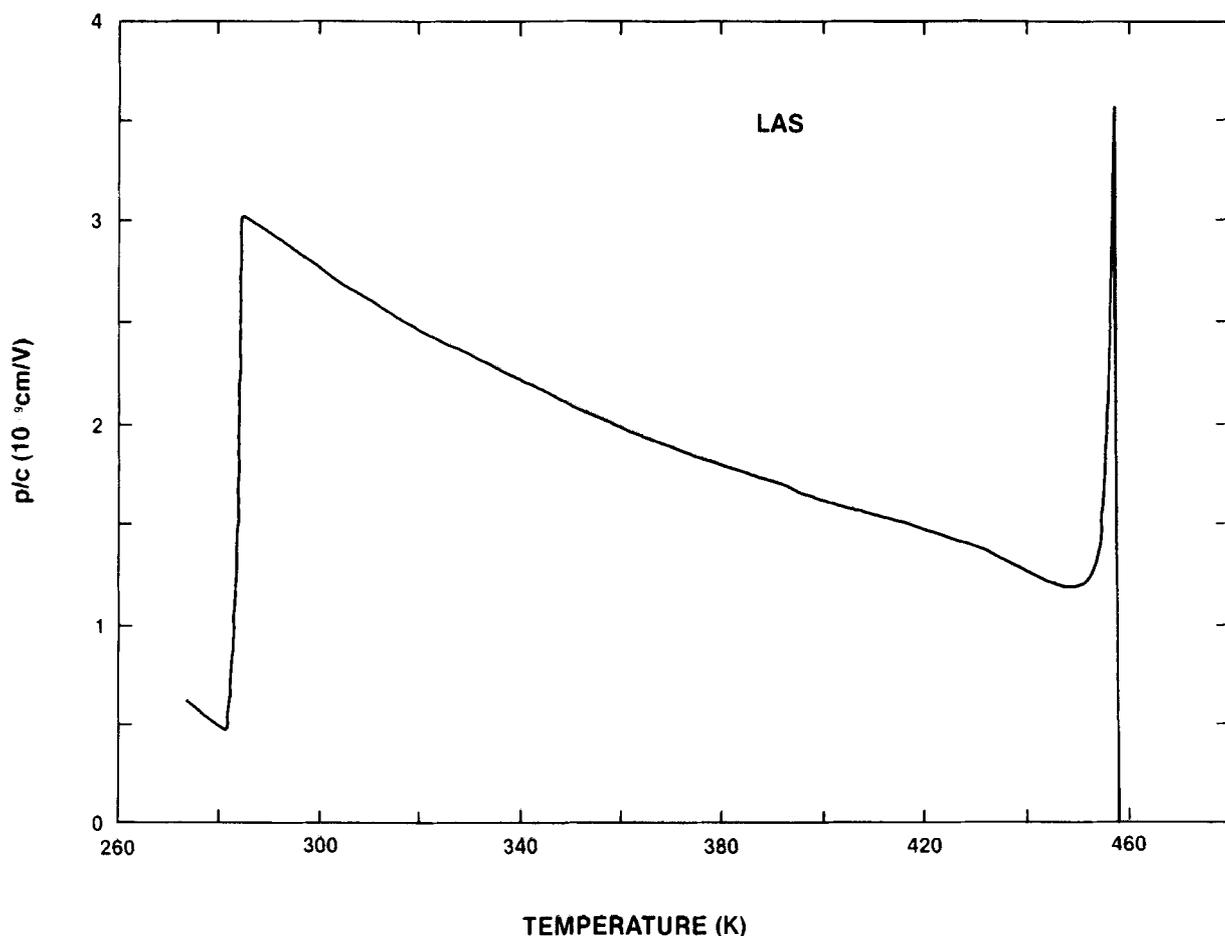
FIGURE 5   Temperature dependence of p/c in $LiNH_4SO_4$.

DISCUSSION AND CONCLUSIONS

Lithium ammonium sulfate and its deuterated analog exhibit almost identical properties. This result suggests that the hydrogen bonding in these crystals is only weakly coupled to the ferroelectric transition.

Pyroelectric and second harmonic generation measurements show the low temperature phase of these materials to be polar, thus clarifying an ambiguity in the literature.

It is interesting to consider the use of LAS as a pyroelectric detector. The figure of merit of a pyroelectric material used as a vidicon target is $M(1) = p/\varepsilon c$, while $M(\frac{1}{2}) = p/\varepsilon^{1/2} c$ is the figure of merit for a small-area detector made of that

materials.[14] Combining the values of p/c and ε given above, one obtains $M(1) = 3000 \text{ cm}^2/\text{C}$ and $M(\frac{1}{2}) = 2.8 \times 10^{-3} \text{ cm}^{3/2} \text{ J}^{-1/2}$ at room temperature. These are relatively high values ($M(1)$ is about 70% of that of TGS) and we examined related materials to see if any further improvement could be obtained. Our investigation of $LiKSO_4$ and $LiCsSO_4$[15] shows them to be essentially different from $LiNH_4SO_4$. Other sulfates examined, i.e. $LiRbSO_4$, $LiTlSO_4$, $CsNH_4SO_4$, and KNH_4SO_4, were found to be centrosymmetric at room temperature. While it is difficult to determine precisely what direction should be taken, further study of related materials is merited on the basis of the high figure of merit obtained for LAS and DLAS.
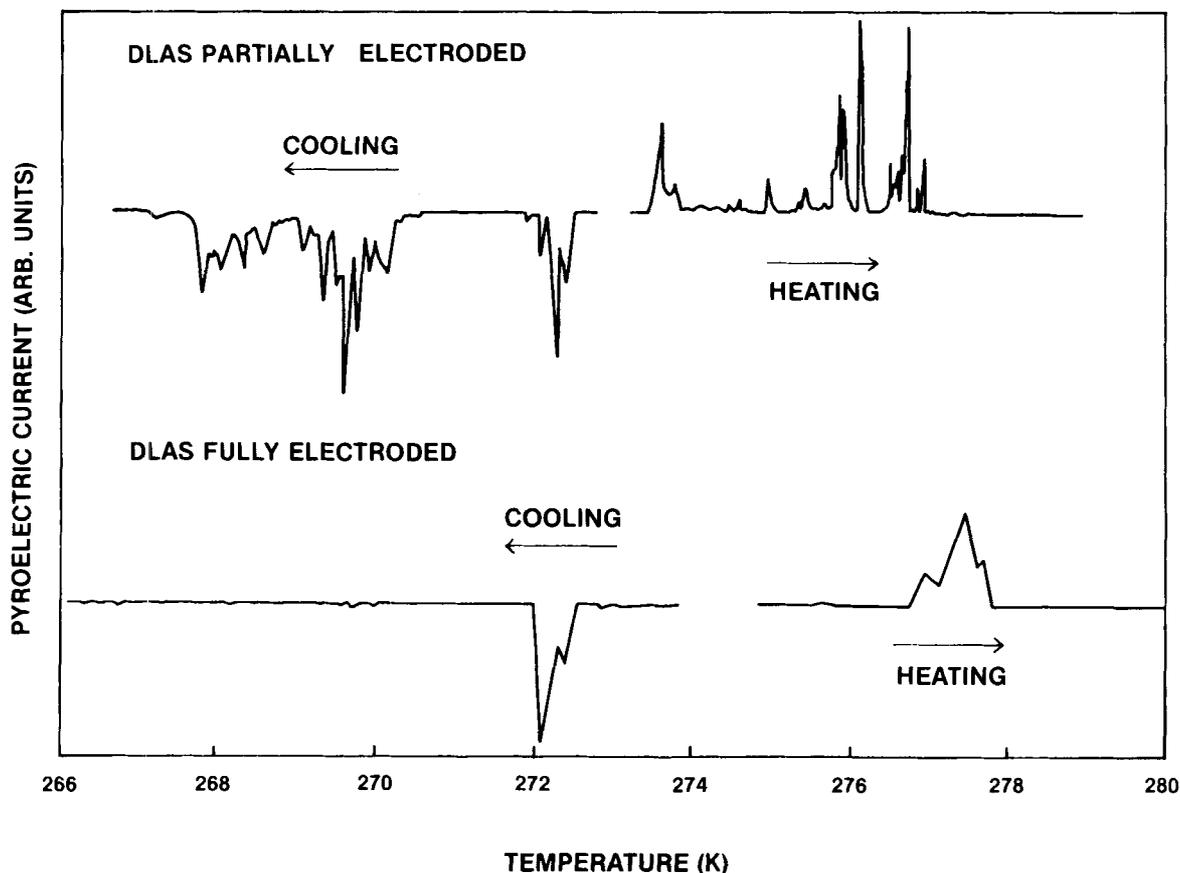
FIGURE 6 Multiple peaking in the pyroelectric current of partially and fully electroded samples of LiND₄SO₄ as seen during both heating and cooling through the low temperature transition.

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