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Thermal and Dielectric Properties of $LiKSO_4$ and $LiCsSO_4$

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Measurements of the thermal and dielectric properties of single crystals of the double sulfates $LiKSO_4$ and $LiCsSO_4$ are reported. Uncertainty in the determination of the space group of $LiCsSO_4$ is resolved on the basis of optical second harmonic generation and pyroelectric measurements; the correct space group is *Pcmn*. Measurements of the pyroelectric coefficient, dielectric constant, and specific heat of $LiKSO_4$ permit an assessment of the suitability of this material for use in pyroelectric detectors.

Introduction

There has been considerable interest in the thermal and dielectric properties of $LiNH_4SO_4$ and related compounds. Therefore, the synthesis, crystal growth, and evaluation of the thermal and dielectric properties of the K and Cs substituted Li analog compounds were investigated.

Preparation and Characterization of Materials

The double sulfates $LiKSO_4$ and $LiCsSO_4$ were prepared by combining aqueous solutions of the appropriate high-purity (99.9+%) alkali sulfates according to stoichiometry. Single crystals were grown from aqueous solution via isothermal evaporation at 313°K. Lattice parameters were obtained from X-ray precession photographs. For $LiKSO_4$, the hexagonal unit cell has $a_0 = 5.15$ and $c_0 = 8.63$ Å, and for $LiCsSO_4$, the orthorhomic unit cell has $a_0 = 9.45$, $b_0 = 5.45$, and $c_0 = 8.80$ Å. These values are in good agreement with the previously reported work of Bradley (*1*) and Hahn *et al.* (*2*). Impurity analysis of $LiKSO_4$ and $LiCsSO_4$ crystals (flame emission) showed Na to be present at 300 and 500 ppm, respectively. The only other impurity detected in significant concentration was 300 ppm Rb in the $LiCsSO_4$ by atomic absorption spectroscopy.

Measurements Performed

Single crystals of $LiKSO_4$ and $LiCsSO_4$ were examined from 280 to 580°K with a computer-controlled Perkin–Elmer differential scanning calorimeter, Model DSC-2. The instrument calibration, operating parameters, and data refinement were

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performed as previously described (*3*). Two specific heat determinations were made on two different samples of each material. The four measurements on each material agreed within 1%. The C_p values are considered accurate to ±1.5% relative to the NBS values for sapphire (*4*).

The dielectric constant ε_{33} of $LiKSO_4$ 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 (at most $10\ \mathrm{V\ cm^{-1}}$ at 8 kHz) was applied to the sample and reference, and synchronous detection (i.e., a lock-in amplifier) was used to measure the voltage appearing across the reference capacitor. The capacitance of the reference was measured with an accuracy of 2%, and the sample dimensions determined to within 5%, so that the dielectric constant was obtained with an accuracy of better than 10%.

Pyroelectric measurements were performed on single crystals using either the direct method of Byer and Roundy (*5*) or a modification of the dynamic technique introduced by Chynoweth (*6*).

Powders ground from single-crystal samples of $LiKSO_4$ and $LiCsSO_4$ were examined by optical second harmonic analysis (*7*) from 260 to 560°K.

Results

1. $LiKSO_4$

Specific heat measurements failed to detect any phase transition in the temperature range examined. The molar heat capacity is given in Table I at intervals of 20°K. Using a least-squares curve fit, the temperature dependence of the molar heat capacity in the temperature interval $300°\mathrm{K} \leq T \leq 520°\mathrm{K}$ is

$$C_p\ (\mathrm{J\ mole^{-1}\ °K^{-1}}) = 81.1 + 0.1247\ T + 7.2 \times 10^{-6}\ T^2.$$

TABLE I

ISOBARIC MOLAR HEAT CAPACITIES OF $LiKSO_4$ (MW = 142.10) AND $LiCsSO_4$ (MW = 235.91)

T (°K)	C_p (J mole^{-1} °K^{-1}) $LiKSO_4$	$LiCsSO_4$
300.0	119.0 ± 1.5%	111.0 ± 1.5%
320.0	121.7	114.0
340.0	123.8	116.9
360.0	126.9	120.9
380.0	128.8	123.6
400.0	130.7	126.5
420.0	132.9	128.5
440.0	135.3	131.5
460.0	138.0	135.7
480.0	142.0	139.7
500.0	145.8	143.2
520.0	148.0	146.9

For the dielectric constant ε_{33} of $LiKSO_4$ we measure a value of 7.2 ± 10% at room temperature which increases to a value of 7.6 ± 10% at 473°K. Ando (*8*) measured a value of about 6 for ε_{33} at 100 kHz over the same temperature interval. This small discrepancy may be attributed to the dispersion of the dielectric constant in $LiKSO_4$.

Single-crystal samples oriented along the [001] were studied by the Byer–Roundy technique (*5*). The sample plates were polished on both sides to a thickness of 0.66 mm using 3 μm alumina grit and mineral oil. Both faces of the sample (area $0.32\ \mathrm{cm^2}$) were fully electroded with silver paint. The measurements were performed under a helium atmosphere at a heating rate of $6.5°\mathrm{K\ min^{-1}}$. The pyroelectric coefficient was found to be $1.6 \pm 10\% \times 10^{-9}\ \mathrm{C\ cm^{-2}\ °K^{-1}}$ and temperature independent from 313 to 343°K. The measurement above 343°K was impeded by a large background current.

However, the current measured below 343°K reversed sign upon cooling, clearly demonstrating pyroelectric behavior. Early work by Ackermann (*9*) showed a pyroelectric coefficient of $1.61 \times 10^{-9}\ \mathrm{C\ cm^{-2}\ °K^{-1}}$ at

293°K which rises slowly to 1.78×10^{-9} C cm^{-2} $°\mathrm{K}^{-1}$ at 352°K, in reasonable agreement with our measurements.

The application of a dc field of 5 kV cm^{-1} for 1 hr and 2 kV cm^{-1} for an additional 12 hr did not produce a change in sign of the polarization in $LiKSO_4$. This suggests that $LiKSO_4$ is not ferroelectric in agreement with the observations of Ando (*8*).

$LiKSO_4$ exhibited a temperature-independent (±10%) second harmonic signal on the order of 0.5 α-SiO_2 from 260 to 560°K. This is consistent with the reported non-centrosymmetric crystal structure, space group $P6_3$ (*1*), and indicates the absence of any phase transitions in the temperature range.

2. $LiCsSo_4$

Least-squares fitting of the specific heat data for $LiCsSO_4$ in the temperature interval $300°\mathrm{K} \leqslant T \leqslant 520°\mathrm{K}$ yields the relation

$$C_p\,(\mathrm{J\ mole^{-1}\ °K^{-1}}) = 63.0 + 0.1585\,T + 4.8 \times 10^{-6}\,T^2.$$

Again, no phase transitions were detected in this temperature range.

Pyroelectric measurements in $LiCsSO_4$ were performed by a modification of the Chynoweth technique (*6*). All three principal crystallographic directions were studied from room temperature to about 473°K. No pyroelectric response was observed. This result places an upper limit on the pyroelectric coefficient of 10^{-10} C cm^{-2} $°\mathrm{K}^{-1}$, suggesting that the structure is nonpolar.

In crystals of $LiCsSo_4$, no detectable second harmonic signal at a level of 10^{-4} α-SiO_2 was observed from 260 to 560°K, indicating the absence of a non-centrosymmetric phase in this temperature interval.

Discussion

The similarities of the molar heat capacities of $LiKSO_4$ and $LiCsSo_4$ reflect similar interatomic bonding energies in the two materials. The temperature slope of the molar heat capacities are quite different, namely, for $LiKSO_4$, 0.132 J mole^{-1} $°\mathrm{K}^{-2}$, and for $LiCsSo_4$, 0.160 J mole^{-1} $°\mathrm{K}^{-2}$ over the temperature range measured. This difference can be attributed to dissimilar crystal structures, namely, $LiKSO_4$ is hexagonal (space group $P6_3$) while $LiCsSO_4$ is orthorhombic.

The absence of a measurable SHG signal and pyroelectric coefficient in $LiCsSO_4$ indicates that the correct space group is $Pcmn$ and not $Pc2_1n$, thus resolving any ambiguity (*2*) in the determination of the structure of this material. Since this is not a polar space group, we conclude that this material has no pyroelectric effect.

It is interesting to consider the use of $LiKSO_4$ 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 noise-limited detector made of that material (*10*). Combining a density of $2.39\ \mathrm{g \cdot cm^{-3}}$ for LKS obtained from the lattice parameter measurements with the values of the pyroelectric coefficient, dielectric constant, and specific heat described above, one obtains $M\ (1) = 1.25 \times 10^3\ \mathrm{cm^2\ C^{-1}}$ and $M\ (\frac{1}{2}) = 9.9 \times 10^{-4}\ \mathrm{cm^{-3/2}\ J^{-1/2}}$ at room temperature. These values vary only slightly from room temperature up to 343°K. Both values are significantly smaller than the corresponding figures of merit of triglycine sulfate, and we conclude that $LiKSO_4$ does not have attractive properties for these applications.

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