

Thermal and Dielectric Properties of LiKSO_4 and LiCsSO_4

M. DELFINO,* G. M. LOIACONO, AND W. A. SMITH

Philips Laboratories, Briarcliff Manor, New York 10510

AND A. SHAULOV,† Y. H. TSUO,‡ AND M. I. BELL§

Yeshiva University, New York, New York 10033

Received October 18, 1978; in final form March 9, 1979

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 orthorhombic 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

* Present address: Fairchild Research and Development Laboratory, Palo Alto, CA 94304.

† Present address: Philips Laboratories, Briarcliff Manor, N.Y. 10510.

‡ Present address: College of William and Mary, Williamsburg, Va. 23185.

§ Present address: National Bureau of Standards, Washington, D.C. 20234.

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 $\pm 1.5\%$ 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 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 $300^\circ\text{K} \leq T \leq 520^\circ\text{K}$ is

$$C_p \text{ (J mole}^{-1} \text{ }^\circ\text{K}^{-1}\text{)}$$

$$= 81.1 + 0.1247 T + 7.2 \times 10^{-6} T^2.$$

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 $7.2 \pm 10\%$ at room temperature which increases to a value of $7.6 \pm 10\%$ 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 cm^2) were fully electroded with silver paint. The measurements were performed under a helium atmosphere at a heating rate of $6.5^\circ\text{K min}^{-1}$. The pyroelectric coefficient was found to be $1.6 \pm 10\% \times 10^{-9} \text{ C cm}^{-2} \text{ }^\circ\text{K}^{-1}$ 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 the sign upon cooling, clearly demonstrating pyroelectric behavior. Early work by Ackermann (9) showed a pyroelectric coefficient of $1.61 \times 10^{-9} \text{ C cm}^{-2} \text{ }^\circ\text{K}^{-1}$ at

293°K which rises slowly to $1.78 \times 10^{-9} \text{ C cm}^{-2} \text{ } ^\circ\text{K}^{-1}$ 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 LiKSO₄. This suggests that LiKSO₄ is not ferroelectric in agreement with the observations of Ando (8).

LiKSO₄ exhibited a temperature-independent ($\pm 10\%$) second harmonic signal on the order of $0.5 \alpha\text{-SiO}_2$ 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. LiCsSo₄

Least-squares fitting of the specific heat data for LiCsSO₄ in the temperature interval $300^\circ\text{K} \leq T \leq 520^\circ\text{K}$ yields the relation

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

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

Pyroelectric measurements in LiCsSO₄ 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 $10^{-10} \text{ C cm}^{-2} \text{ } ^\circ\text{K}^{-1}$, suggesting that the structure is nonpolar.

In crystals of LiCsSo₄, no detectable second harmonic signal at a level of $10^{-4} \alpha\text{-SiO}_2$ 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 LiKSO₄ and LiCsSo₄ reflect similar

interatomic bonding energies in the two materials. The temperature slope of the molar heat capacities are quite different, namely, for LiKSO₄, $0.132 \text{ J mole}^{-1} \text{ } ^\circ\text{K}^{-2}$, and for LiCsSo₄, $0.160 \text{ J mole}^{-1} \text{ } ^\circ\text{K}^{-2}$ over the temperature range measured. This difference can be attributed to dissimilar crystal structures, namely, LiKSO₄ is hexagonal (space group $P6_3$) while LiCsSO₄ is orthorhombic.

The absence of a measurable SHG signal and pyroelectric coefficient in LiCsSO₄ indicates that the correct space group is $Pcmm$ 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 LiKSO₄ as a pyroelectric detector. The figure of merit of a pyroelectric material used as a vidicon target is $M(1) = p/\epsilon c$, while $M(\frac{1}{2}) = p/\epsilon^{1/2} c$ is the figure of merit for a noise-limited detector made of that material (10). Combining a density of $2.39 \text{ g} \cdot \text{cm}^{-3}$ for LKS obtained from the lattice parameter measurements with the values of the pyroelectric coefficient, dielectric constant, and specific heat described above, one obtains $M(1) = 1.25 \times 10^3 \text{ cm}^2 \text{ C}^{-1}$ and $M(\frac{1}{2}) = 9.9 \times 10^{-4} \text{ cm}^{-3/2} \text{ J}^{-1/2}$ 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 LiKSO₄ does not have attractive properties for these applications.

Acknowledgments

The authors wish to thank W. N. Osborne and G. Kostecky for the growth of the materials. This research was sponsored by USAECOM, Night Vision and Electro-Optics Laboratories under Government Contract DAAG53-76-C-0053.

References

1. A. J. BRADLEY, *Phil. Mag.* **49**, 1225 (1925).
2. TH. HAHN, G. LOHRE, AND S. J. CHUNG, *Naturwissenschaften* **56**, 459 (1969).
3. M. DELFINO, G. M. LOIACONO, AND J. A. NICOLosi, *J. Solid State Chem.* **23**, 289 (1978).
4. D. C. GINNINGS AND G. T. FURUKAWA, *J. Amer. Chem. Soc.* **75**, 522 (1953).
5. R. L. BYER AND C. B. ROUNDY, *Ferroelectrics* **5**, 267 (1973).
6. A. G. CHYNOWETH, *J. Appl. Phys.* **27**, 78 (1956).
7. J. P. DOUGHERTY AND S. K. KURTZ, *J. Appl. Crystallogr.* **9**, 145 (1976).
8. R. ANDO, *J. Phys. Soc. Japan* **17**, 937 (1962).
9. W. ACKERMANN, *Ann. Phys. (Leipzig)* **46**, 197 (1915).
10. L. E. GARN AND E. J. SHARP, *IEEE Trans. Parts Hybrids Packag.* **PHP-10**, 208 (1974).