

Thermal expansion and a new phase transition in pyroelectric LiKSO_4

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Abstract. Single crystal macroscopic thermal expansion coefficient measurements have been made on uniaxial lithium potassium sulphate crystal both along and normal to the six fold axis, employing Fizeau's interferometer method. Measurements were made in the range of -120°C to 500°C . The results show that lithium potassium sulphate exhibits two major anomalies in its expansion coefficients around -95°C and 422°C respectively, the one at -95°C has been observed for the first time. The nature of dimensional changes of the crystal at the upper and lower transition points are opposite in nature. The crystal shows considerable lattice anisotropy. Megaw's tilt concept has been invoked to explain the relative magnitudes of expansion coefficients along a and c directions. Structural features responsible for the absence of ferroelectricity in this crystal have been pointed out.

Keywords. Thermal expansion; phase transition; ferroelectricity; pyroelectricity.

1. Introduction

Lithium potassium sulphate is a member of the family of crystals with the general formula, $\text{M}^{\text{I}}\text{M}^{\text{II}}\text{BX}_4$ (where $\text{M}^{\text{I}} = \text{Li, Na}$; $\text{M}^{\text{II}} = \text{Na, K, Rb, NH}_4, \text{Cs, N}_2\text{H}_5$; $\text{BX}_4 = \text{BeF}_4, \text{SO}_4, \text{SeO}_4$). It is isostructural with other members of this family, viz., LiNaSO_4 , LiNaSeO_4 and LiRbSO_4 . The latter group of crystals are all pyroelectric and belong to the hexagonal crystal system. These, in terms of the classification of Chung and Hahn (1972), can be regarded as the 'proper derivatives' of the well-known tridymite structure (space group $\text{Pm}\bar{3}$). Compounds with larger M^{II} ions in this family are generally orthorhombic and are said to belong to the 'improper derivatives' of the tridymite structure. Lithium ammonium sulphate (LAS) and lithium hydrazinium sulphate (LiHzS) are examples of the latter class. Both LAS and LiHzS are room temperature ferroelectrics (Mitsui *et al* 1975; Pepinsky *et al* 1958). Lithium potassium sulphate undergoes structural phase transformation at 435°C (Fischmeister and Roennquist 1960; Ando 1962; Blittersdorf 1928; Ranga Prasad *et al* 1978). The crystal structure above 435°C is not known yet. Ando (1962), employing 50 Hz a.c. field upto 5 kV/cm has shown that LPS does not exhibit typical ferroelectric D-E hysteresis curve. His pyroelectric experiments did not detect the reversal of pyroelectric currents, establishing thereby that the crystal is polar but not ferroelectric below 435°C .

Thermal expansion measurements have been carried out on this substance (Fischmeister and Roennquist 1960; Ando 1962; Ranga Prasad *et al* 1978). But none of these is a single crystal measurement. Ando has employed horizontal dilatometer

technique to get expansion data using fused and single crystal samples. His expansion data on LPS along the c axis seems to agree with the powder x-ray diffraction data of Fischmeister and Roennquist (1960). But none has extended his measurements below the room temperature. Further, the accuracy of the measurement of the temperature in the work of Fischmeister and Roennquist is rather low ($\pm 3^\circ\text{C}$). The heating/cooling rate of the crystal in Ando's dilatometric experiments is also rather high ($1^\circ\text{C}/\text{min}$) especially near the transition temperature.

It was therefore considered necessary to get fresh data on the expansion behaviour of lithium potassium sulphate by the more accurate Fizeau's interferometer method with a view to (i) get more reliable and accurate thermal expansion data over the extended temperature range (from -120°C to 500°C), (ii) look for any unsuspected/suspected expansion anomalies at low temperatures. It is suspected that crystals which are 'proper derivatives' of the tridymite structure may have more than one hettotype as evident in the case of 'improper derivatives' LiNH_4SO_4 , $\text{LiN}_2\text{H}_5\text{SO}_4$, etc. and in tridymite itself (Dallase 1967) and (iii) to compare the lattice anisotropies of lithium potassium sulphate with those of lithium ammonium sulphate and lithium hydrazinium sulphate, which are made up of similar structural building blocks (LiO_4 and SO_4 tetrahedra and monovalent cavity ions) and to point out structural features responsible for the absence of ferroelectricity in this crystal.

2. Crystal structure and other studies

Bradley (1925) has approximately solved the crystal structure of lithium potassium sulphate. Its space group is C_6^2 and it has two molecules in its unit cell. The structure essentially is made up of the corner sharing of two kinds of tetrahedra LiO_4 and SO_4 , the framework enclosing large cavities occupied by potassium ions. The pattern of the sharing of the corners of the tetrahedra is tridymite-like. The sulphur and lithium atoms are on the special positions on the triad axes but they are ordered, occupying alternate tetrahedra. Every oxygen atom has one lithium neighbour and one sulphur neighbour. The lithium-oxygen-sulphur bond is mostly linear and is along the six-fold axis of the structure. A consequence of the sulphur/lithium ordering is that the structure is polar.

Reports on other physical properties viz., static dielectric constant (Ando 1962), pyroelectricity (Ando 1962; Hayashi 1912), piezoelectricity (Elings 1928), refractive index (Blittersdorf 1928), Raman spectra (Schaefer *et al* 1930; Rao *et al* 1975), electro-optic effect (Slicker 1960) are also available in the literature.

3. Experimental details

Good optical quality single crystals of LiKSO_4 in the form of transparent hexagonal discs were grown at constant temperature of 30°C from an aqueous solution containing Li_2SO_4 and K_2SO_4 in their stoichiometric proportions. The crystal axes were identified by optical crystallographic technique. Typical dimensions of the crystal were $1.5\text{ cm} \times 1.5\text{ cm} \times 0.7\text{ cm}$. Fizeau's interferometer, employed by the author to measure the expansion coefficients, is a well-recognised method of determining length changes

in solids. Detailed descriptions of the method are available from several papers (e.g. Yates 1972). In the present measurements, wavelength of the light used was 5462.2 \AA . The crystal specimens were pyramidal in shape. The error in grinding the pyramids along the c -axis was almost nil because the bases of the pyramids were natural crystal faces. Along the a axis, there might be an error of $\pm 1^\circ$ from the original axis. Measurements were made in the temperature range of -120°C to 500°C . The accuracy of the temperature measurement was better than $\pm 0.5^\circ\text{C}$. The rate of heating of the specimens was in the range of 0.3°C to 0.6°C per minute. Crystals remained undamaged after the experiments were over. Measurements were reproducible. The error in coefficient of thermal expansion in any direction is estimated to be around 3 to 5%.

4. Results

The linear thermal expansion coefficients α_a and α_c were calculated by using the formula

$$\alpha = (1/2l) (dN/dT), \quad (1)$$

where α is the linear expansion coefficient along a or c direction, l is the length of the crystal pyramid along a or c axis, dN is $N\lambda$ (where $\lambda = 5462.2 \text{ \AA}$) and dT is the temperature interval of passage of N fringes across the reference mark in the field of view.

Expansion coefficients along a and c axes have been designated α_a and α_c respectively. The graphs showing the variation of α with temperature along the c and a

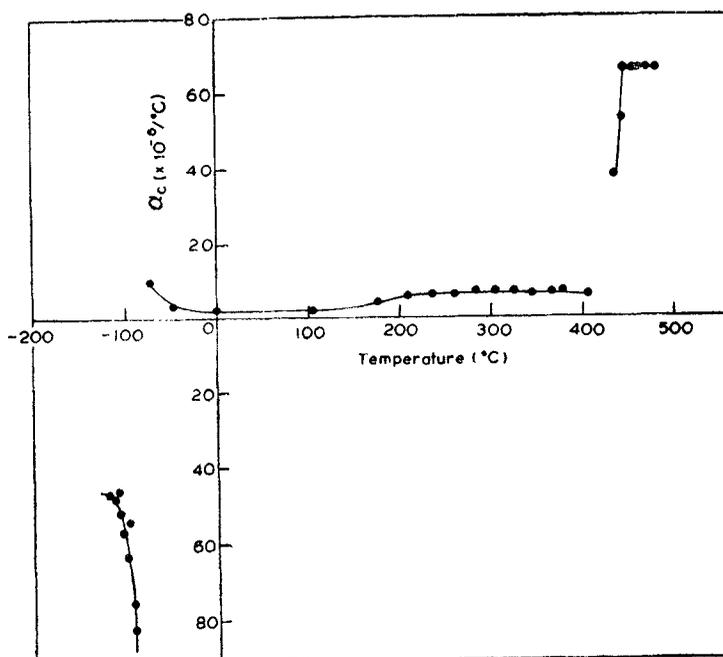


Figure 1. Linear thermal expansion α_c of LiKSO_4

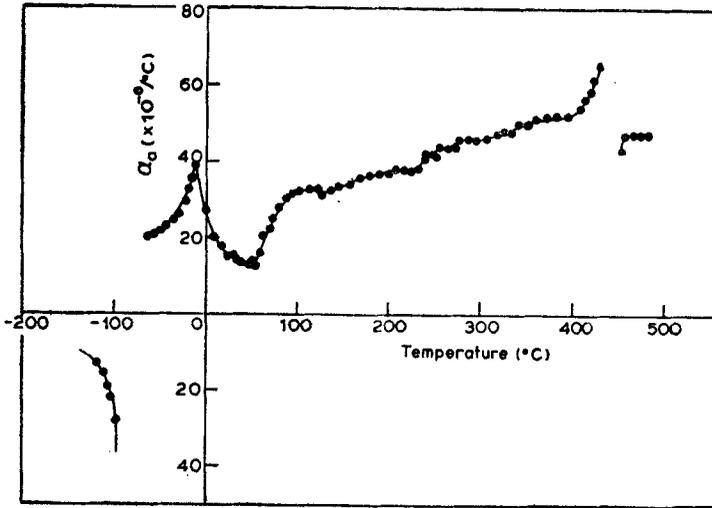


Figure 2. Linear thermal expansion coefficient α_a of LiKSO_4

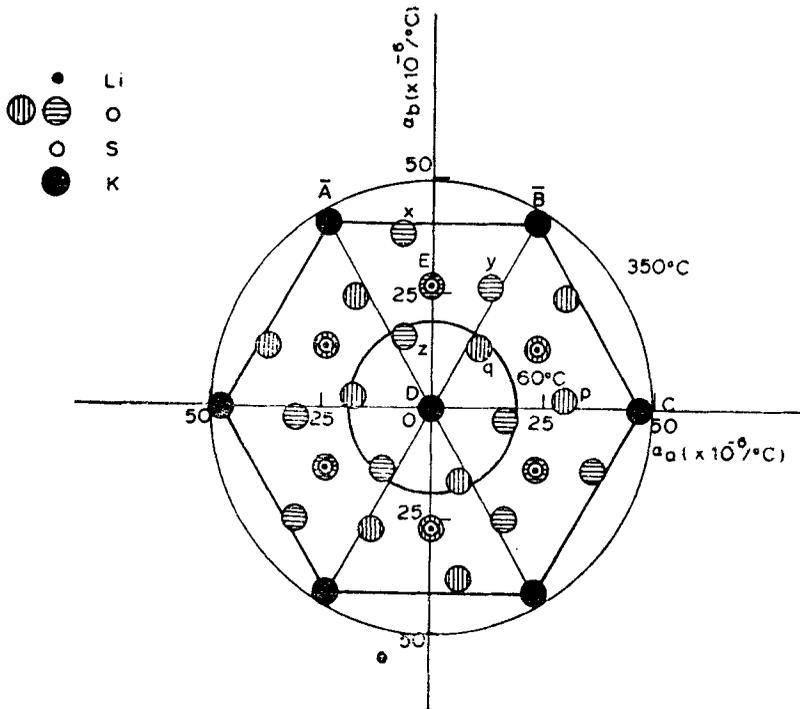


Figure 3. Polar diagram of LiKSO_4 in (001) plane

directions have been drawn in figures 1 and 2 respectively. Figures 3 and 4 illustrate the variation of the expansion coefficients with orientations on (0001) and (0100) planes. These polar diagrams have been drawn on the projection of the crystal structures on these planes as given in Bradley (1925).

Figures 1 and 2 reveal that LPS exhibits two major anomalies in its expansion coefficients around -95°C and 422°C respectively. The anomalous nature of the

variation of α at -95°C has been observed for the first time. Since the symmetries below -95°C and above 422°C are unknown, the expansion coefficients in the lowest and the highest temperature phases may not be the principal coefficients. The nature of the dimensional changes of the crystal at the upper and lower transition points are opposite both along a and c axes. As the lower transition point is approached from the high temperature phase, at $T_{c_2}(-95^\circ\text{C})$, the crystal suddenly contracts. Below T_{c_2} , there is a steep rise in both α_a and α_c . At $T_{c_1}(422^\circ\text{C})$, the crystal expands along the a direction but shows sudden contraction along the optic axis. Another feature of the expansion behaviour of LPS along the a axis is the presence of a minimum around 60°C followed by a peak at -9°C . Since there is no brisk movement of the fringe system at these temperatures, nor is there any sudden change in orientation, it is concluded that at these two temperatures there is no major structural change in the crystal.

5. Discussion

The sudden and discontinuous nature of the transition at -95°C and 422°C suggests that the crystal undergoes a transformation of first order at these temperatures. Ando's static dielectric constant experiments detect an anomaly at 445°C .

Figures 1, 2, 3 and 4 show that LPS exhibits considerable lattice anisotropy. The anisotropy is pronounced in the (0100) plane. Figure 4 shows that along the six-fold polar axis, the expansion coefficient is very small at 60°C ($\sim 2 \times 10^{-6}/^\circ\text{C}$) and reaches a value of $6 \times 10^{-6}/^\circ\text{C}$ around 350°C .

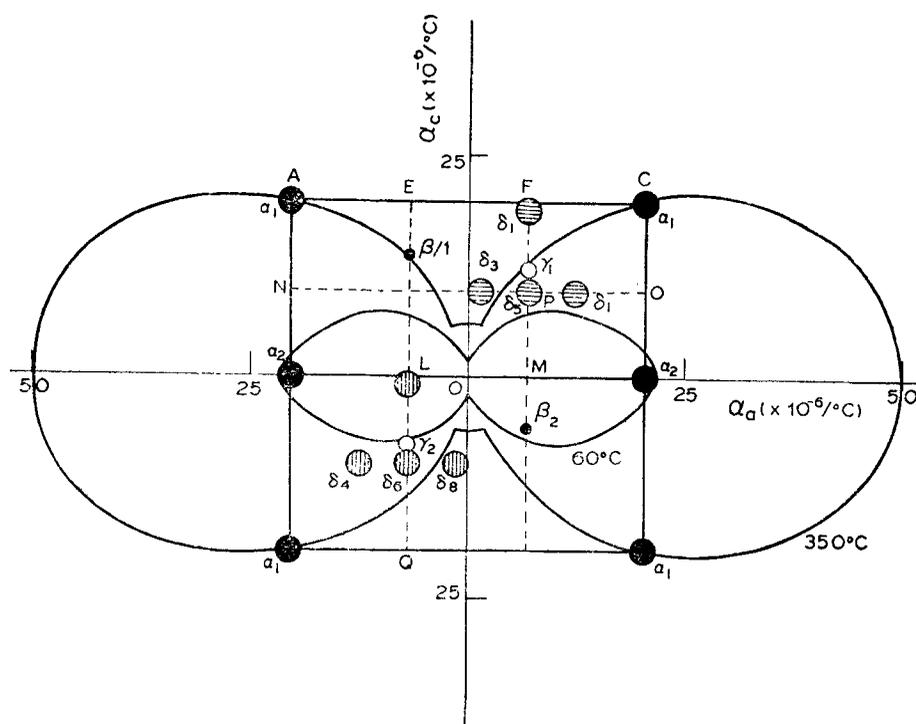


Figure 4. Polar diagram of LiKSO_4 in (0100) plane

The small value of the expansion coefficient of the crystal along the unique axis can be explained by applying the 'tilt concept' of Megaw (1971). As can be seen from Bradley's (1925) structure work, the tilt between Li-O and S-O tetrahedra is zero along the *c*-axis making Li-O-S bond linear along the polar axis. Thus the framework of tetrahedra is almost straightened out along this direction and thus the only significant contribution to α_c is from the bond-length expansion and practically nothing from the crumpling of the framework. This indeed is seen from figure 1, where at 0°C, $\alpha_c = 1.7 \times 10^{-6}/^\circ\text{C}$ and at 407°C, $\alpha_c = 6.8 \times 10^{-6}/^\circ\text{C}$. Such a small increase over a temperature range of 400°C can be associated with the bond-length expansion of a *hard* sulphate tetrahedron. The projection of the crystal structure diagram on the (0001) plane shows (figure 3) that on this plane LiO₄ and SO₄ tetrahedra are tilted against each other by as much as 60°. Therefore, the structural units on the (0001) plane have enough elbow room to straighten themselves out with the increase of temperature. This explains the progressive increase of expansion coefficient along the *a* axis as one approaches the transition temperature T_{c1} . In the absence of the data on the r.m.s. thermal amplitudes of various atoms that make the structure, it is not possible to elucidate the transition mechanism at T_{c1} .

Lithium potassium sulphate belongs to the polar point group class 6; this symmetry allows it to show pyroelectric behaviour. Pyroelectric constants of LPS have been determined by Hayashi (1912) and more recently by Ando (1962). The temperature ranges of their measurements are from 88°K to 357°K and 593°K to 773°K respectively. From well below room temperature to the upper transition point T_{c1} , the pyroelectric current versus temperature curve follows the expansion coefficient versus temperature behaviour of the crystal (Ando 1962) (figure 2). The static dielectric constant versus temperature curve also follows the expansion coefficient versus temperature curve along the *c*-axis of the crystal (Ando 1962). The results of these two experiments lead to the following conclusions: (i) the nature of the chemical binding along the six-fold axis in LPS is predominantly of ionic type; (ii) although the temperature variation of the elastic constant and the piezoelectric moduli of LiKSO₄ are not available, the persistence of a very small value of the thermal expansion coefficient of this substance right upto the upper transition temperature T_{c1} along the polar axis suggests that the pyroelectricity in this substance is of secondary nature, i.e., it is brought about by the mechanism of piezoelectric polarisation.

Now, what are the structural features in LiKSO₄ crystal which make it only pyroelectric at the room temperature? Why is it not possible to reverse the spontaneous polarisation in LPS even at 350°C and with a field as large as 5 kV/cm (Ando 1962)? It looks as though the existence of ferroelectricity is simply dependent on the presence of an ion of the right size at the large cavities of these structures. Members of LiMeBX₄ family, LiNaSO₄, LiNaSeO₄, LiKSO₄ are all linear pyroelectrics. Na, K (with ionic radii 97, 133 pm) are relatively smaller ions than NH₄, N₂H₅, Cs (167 pm) whose presence at the cavities of these structures results in LAS and LiHzS becoming ferroelectrics. Compounds with smaller Me^{II} ions are hexagonal closed-packed structures with smaller thermal expansions and larger force constants along the polar directions; whereas those members having larger Me^{II} cations are essentially linkage structures, having large thermal expansions and lower force constants along their polar directions. The former (proper derivatives) expand very little along the polar direction because the smaller cavity cations do not control the interpolyhedral tilts as effectively

as the large cavity cations in their improper counterparts. The tilted structures are vulnerable to the presence of large cations at their cavities. Thus, whereas the proper derivatives LPS crystal expands from $1.73 \times 10^{-6}/^\circ\text{C}$ to $6 \times 10^{-6}/^\circ\text{C}$ along the c -axis, in a temperature interval of about 400°C (figure 1); in less than half of that temperature interval, LAS, along its polar axis, has an average expansion coefficient of about $40 \times 10^{-6}/^\circ\text{C}$ (Sharma 1978). The expansion coefficient figures for $\text{LiN}_2\text{H}_5\text{SO}_4$ are $40 \times 10^{-6}/^\circ\text{C}$ and $95 \times 10^{-6}/^\circ\text{C}$ at 0°C and 200°C respectively (Devanarayanan and Easwaran 1966). The role of these cations in bringing about ferroelectricity can be understood in the following manner. It is known that a structure is ferroelectric if the displacements are sufficiently small to be reversed by an electric field; otherwise it is pyroelectric. The 'displacement' in these alkali double sulphates should be the off-centering of Me or B cations. The improper derivatives LiNH_4SO_4 and $\text{LiN}_2\text{H}_5\text{SO}_4$ are ferroelectrics because the LiO_4 and SO_4 tetrahedra are slightly distorted as is evidenced from the magnetic resonance studies of Aleksandrov *et al* (1977). The lowest temperature phase of LiNH_4SO_4 (below 10°C) remains polar and is *not* ferroelectric because there appear two types of Li-O tetrahedra below 10°C ; one of them is highly distorted and all aligned along the conserved two-fold polar axis of the structure (Yuzvak 1975). Thus, since the displacements of lithium ions within their tetrahedra are quite large (Yuzvak 1975), Li-O-S bond does not form a reversible dipole. The crystal shows a jump in spontaneous polarisation but no ferroelectricity.

It is suggested that the same situation exists in LiKSO_4 at the room temperature. Bradley (1925) has not been able to accurately determine the positions of lithium atom in the structure. He observes that Li atoms are 'somewhere' along the line joining the sulphur and the oxygen atoms along the six-fold axis. The author conjectures that lithium atoms must be very much away from the centre of their tetrahedra like their counterparts in LAS below 10°C . This implies that lithium ions in LPS sit in a field of single minimum potential. This suggests that the point-group symmetry of the phase existing above the upper transition temperature should be polar. Polar to polar transition is a necessary condition for the non-existence of ferroelectric domains in the crystal (Zheludev 1977).

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