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γ - IRRADIATION EFFECT ON THE FERROELASTIC HIGH TEMPERATURE PHASE IN $LiKSO_4$ CRYSTALS

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تأثير إشعاعات جاما على التحول الطوري الفرومرن لبللورات من كبريتات الليثوم والبوتاسيوم

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تم دراسة تأثير جرعات ومعدل الجرعات من أشعة جاما على بارامترات الديناميكا الحرارية لبللورات احادية من كبريتات الليثوم والبوتاسيوم في مدى حراري ٣٠٠ ـ ١٠٠٠ درجة مطلقة ، وقد أظهرت النتائج أن درجة حرارة التحويل الطوري T_C وكذلك الحرارة النوعية تحت ضغط ثابت C_P تقل بزيادة جرعات الاشعاع . وعند جرعات اشعاعية أكبر من ١٠ ميجاراد يكون T_C . C_P في زيادة مع الجرعة الاشعاعية . وبتحليل النتائج وجد أن التصادمات بين الشوائب يكون السائد ويسبب ثبات الطور المنخفض . كذلك حسبت كل من طاقة الترتيب الفرومرن u وكذلك عدد الذرات المزاحة N ووجد أن طاقة الترتيب تزداد مع زيادة معدل الجرعة الاشعاعية بينما يقل عدد الذرات المزاحة .

Key Words: γ - Radiation, Ferroelastic phase, Energy of ordering, $LiKSO_4$.

ABSTRACT

The effect of γ -irradiation on the thermodynamic parameters of $LiKSO_4$ single crystals, in the high temperature range 300-1000 K, is investigated. The results show that T_c as well as C_p decrease with dose rate. However, when the dose is greater than 10 MRad, both C_p and T_c increase with increasing dose. The analysis indicators that for high dose the interaction of defects is prominent, causing the stabilization of the low temperature phase. The energy of ferroelastic ordering (U), as well as the number of displaced atoms (N), were also estimated. It was found that, with increasing dose rate, U decreases while N increases.

INTRODUCTION

The problem of defects and impurity influence upon the phase transition temperature of ferroelectric and ferroelastic crystals has received significant attention. (Thomas, 1981), Gamma-irradiation causes defects of ionizing type which are introduced due to internal radiation with photo or compton electrons. As a result of irradiation, the chemical bonds are damaged and various kinds of radicals are created. Moreover, it has been found that irradiation with high energy γ rays introduces point defects as a result of collision of compton electrons with lattice atoms. The influence of these defects is, however, small in comparison with that of ionizing type. (Pawlaczyk, 1975) The crystal of $LiKSO_4$ was found to be hexagonal and belongs to $C^6_6(P6_3)$ space group with two formula per unit cell. (Sandomirskii *et al*, 1983 It was observed an incommensurate phase between 470 and 670°C and a commensurate phase between 435 and 470°C. (Pimenta et al, 1989) The thermal properties of $LiKSO_4$ crystals were studied in low (Sharma, 1979; Mahmoud *et al*, 1985; Abello *et al*, 1985; Tomasczwski *et al*, 1983; Piskunowicz *et al*, 1988) as well as in high temperature regions (Kandil *et al*, 1986; Kassem *et al*, 1984, 1990; Okaz *et al*, 1988). Incommensurate phases were found to be highle sensitive to the presence of defects. (Levedev *et al*, 1988) The aim of the present work is to study the effect of dose and dose rate on the thermodynamic parameters of $LiKSO_4$ crystals in the high temperature region.

EXPERIMENTAL

Lithium Potassium Sulphate crystals were grown from aqueous solution, containing the initial salts as stoichio-metric ratio, using isothermal and dynamical methods, (Kassem *et al*, 1984) Differential scanning calorimeter has been used to evaluate C_p in the temperature range 300-1000 K. The details of the experimental procedures were previously reported. (Kassem *et al*, 1991, 1992) The samples were γ irradiated at room temperature using ^{60}Co gamma cell manufactured by Atomic Energy of Canada. The dose rate was between 0.7 and 1.9 MRad/h while the accumulated dose was 10-250 MRad.

RESULTS AND DISCUSSION

Lattice defects in crystals affects the values of various physical parameters such as dielectric, electrical, mechanical and thermal. The defects in any crystal lattice cause a deformation of the local structure which changes the local field. Ferroelastic ordering (spontaneous strain) results in an excess of heat capacity over the lattice. The specific heat in the transition region may be separated into two components: one due to lattice contribution (C_o) while the other is associated with the ordering of the tetrahedron (C_a). Hence the effective specific heat could be given by $C_p = C_o + C_a$.

The obtained results of the specific heat for pure and γ irradiated $LiKSO_4$ crystals for different irradiation dose rates are presented in (Fig. 1) A clear anomaly in C_p appeared in the

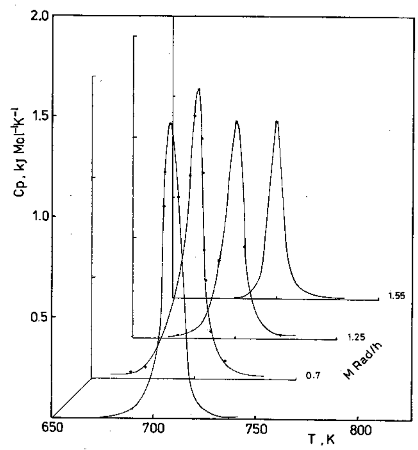

Fig. 1: Temperature dependence of the specific heat C_p of $LiKSO_4$ crystals for different values of γ - irradiation dose rate.

neighbourhood of T_c = 705 K for pure $LiKSO_4$ crystal which is in agreement with published data. (Kassem *et al*, 1984) Since energy in domain walls could be considered as sort of imperfection; the local damage centers, certainly the local strain in the vicinity of such centers, must cause a greater distribution than substantial impurity. Radiation defects introduced homogeneously into the bulk ferroelastic sample (e.g. γ -rays) were found to cause rounding of the phase transition, which is clearly visible in (Fig. 1). This phenomena may be related to irradiation effect in the ferroelastic temperature range which has many imperfections to trap damage products. It seems logical to assume that the local damage centers tend to upset these stability conditions while the crystal tends to stabilize its structure. The net result will be a decrease in the maximum value C_p with the increase of the dose rate (Fig. 2). A shift in the phase transition temperature T_c is also observed (Fig. 2). The downward shift in

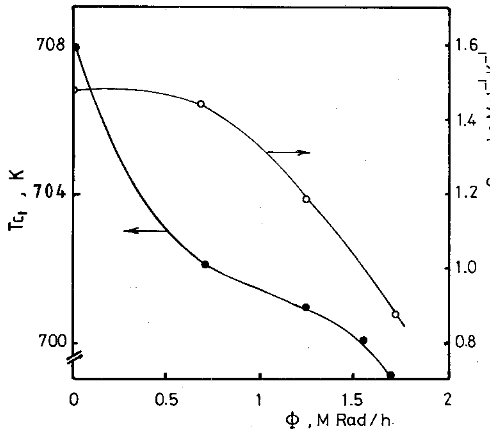

Fig. 2: Variation of T_c and C_p at transition of $LiKSO_4$ crystals with γ - irradiation dose rate.

T_c due to irradiation can be explained according to the statistical theory (Gonzalo and Lopez Alonzo, 1964).

(Blinc and Lewanyuk, 1985), and (Burtseva *et al*, 1988), discussed the changes in the structure of defects and the resultant anomalies in the phase transition region within the framework of a phenomenological theory. They used the non-interacting defects approximation, which assumes that the correlation radius of the order parameter is smaller than the distance between defects. They also observed that the rounding effect of C_p should appear due to defects. The calculation shows that to the first approximation, the influence of polar defects on the anomalies in the thermodynamic quantities can be reduced to the appearance of the effective field conjugated to the order parameter and to the normalization of the transition temperature.

The temperature dependence of the specific heat heat near the phase transition obey an experimental law. (Burtseva *et al*, 1988)

$$\triangle C_p = Z\ (NU^2 / RT^2)\ \exp\ (-U / RT)$$

where N is the number of displayed atoms from the equilibrium position, U is the activation energy, R is the universal gas constant and Z is the co-ordination number, i.e. the number of neighbours of each atom. The dependence of ln $\triangle C_pT^2$ on 1/T for pure and irradiated $LiKSO_4$ crystals is given in (Fig. 3). The

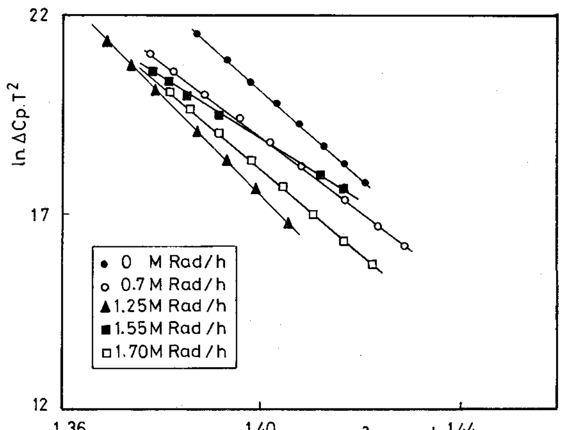

Fig. 3: Dependence of Ln (ΔC_pT^2) on 1/T in $LiKSO_4$ crystals for different γ - irradiation dose rate.

activation energy U was evaluated from the slope of the straight line for each crystal. The obtained values give the changes in the thermal energy, related with the ferroelastic ordering, as a function of dose rate. The results are shown in (Fig. 4) and it is

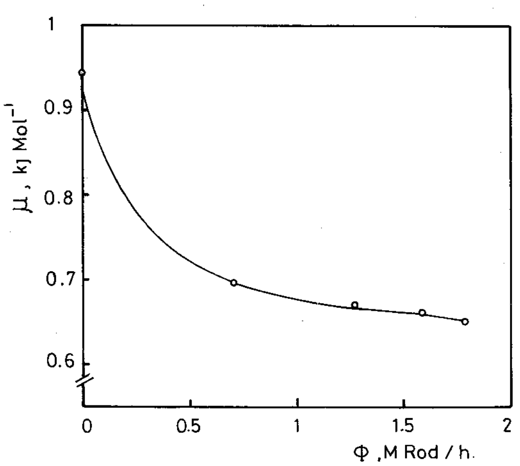

Fig. 4: Variation of the activation energy U with dose rate for $LiKSO_4$ crystals.

clear that the energy of ferroelastic ordering decreases with dose rate. This is to be expected and is more exemplified by the changes of displaced atoms, N, due to irradiation. The number of displaced atoms, N, is estimated from the intersection of the straight lines (Fig. 4) for each crystal. Taking Z = 4 for the crystal (Mroz *et al*, 1989) the relative increase in N, ($\triangle N/N$) as a function of dose rate is given in (Table 1).

Table 1

Dose Rate MRad/h	0.7	1.25	1.55	1.75
$\triangle N/N$	0.027	0.028	0.037	0.043

The behaviour of T_c and C_p at the transition with high irradiation dose (10 MRad) is, however, different. The changes in T_c and C_p with irradiation dose are given in (Fig. 5 and 6) respectively. An upward shift in T_c is observed as the dose increases (Fig. 5). This could be explained by the fact that, the

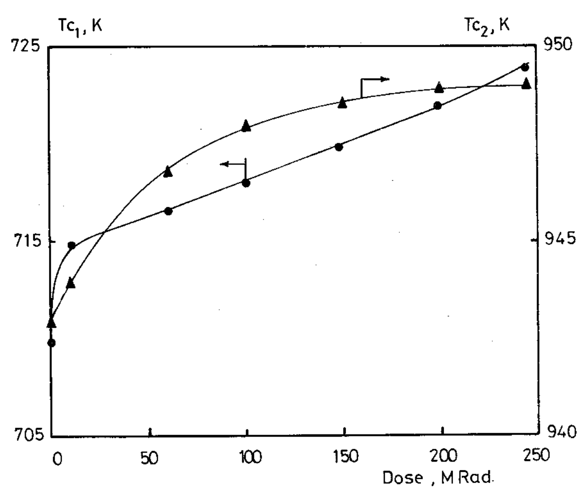

Fig. 5: Variation of T_{c1} and T_{c2} with dose for $LiKSO_4$ crystals, (Dose Rate = 1.7 MRad/h).

interaction between tend to order themselves in a way to favour the orientation parameter. (Halperin and Varma, 1974) This causes the stabilization of the low temperature phase and in consequence tends to raise T_c.

An interesting and significant treatment of the problem of point defects in ferroelectric materials has been presented by (Thomas, 1981). It was proposed that the symmetry of defects determines the type of coupling with the ferroelectric lattice. Moreover, (Thomas, 1981) pointed out that for high concentration of defects (high γ irradiation dose), the interaction between defects, mediated by the order parameter co-ordinates, may give rise to a phase transition in the impurity system. Moreover, as the irradiation dose increases, greater than 10 MRad, it gives rise to a dynamic interaction between defects and soft phonons resulting in an increase in C_p at transition (Fig. 6).

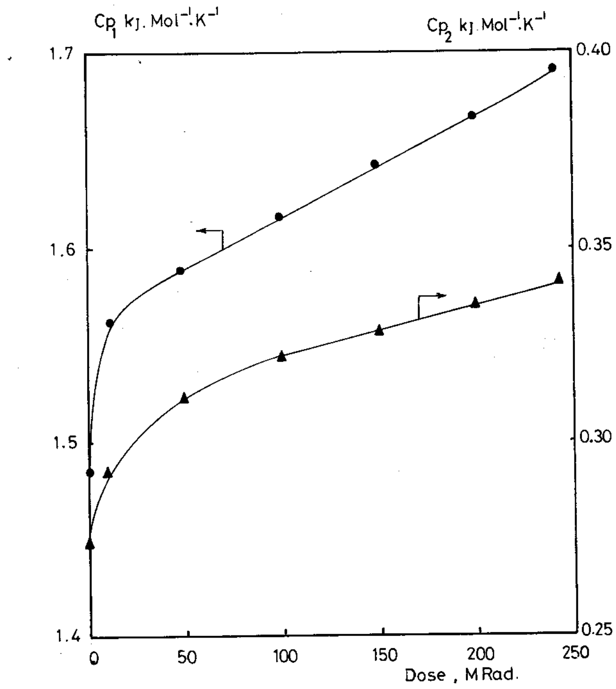

Fig. 6: Variation of C_{p1} and C_{p2} with dose rate for $LiKSO_4$ crystals (Dose Rate = 1.7 MRad/h).

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