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THERMODYNAMIC STUDIES ON THE FERROELECTRIC PHASE TRANSITION IN NEUTRON IRRADIATED $(Li_xK_{1-x})_2SO_4$ CRYSTALS AT HIGH TEMPERATURE

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Thermodynamic studies of $(Li_xK_{1-x})_2SO_4$, LKS, mixed crystals have been made in the concentration range (x = 0.1, 0.2, ..., x = 0.5). The thermal behaviour has been investigated by differential thermal analysis, DTA, and differential scanning calorimeter, DSC, in the vicinity of high temperature phases. Also, the effect of the thermal neutron irradiations on the thermal properties of mixed crystals was studied. The results showed a change in the transition temperature T_c, as well as the value of specific heat C_p at transition temperature, due to the change of stoichiometric ratio and radiation doses. The change of enthalpy and entropy of mixed crystals have been estimated numerically.

In the last few years ferroelastic phase transition has been the subject of a considerable number of theoretical and experimental studies [1-2]. Crystals with the general formula $A'A''BX_4$ in several cases exhibit phase transformation associated with the onset of spontaneous strain in low [3-4] and high temperature phases [5]. Lithium potassium sulphate, $LiKSO_4$, crystal is pyroelectric [6] with a hexagonal symmetry at room temperature. The system corresponds to the space group $P6_3$ and there are two molecules in the hexagonal unit cell. Extensive studies on the physical properties of $LiKSO_4$ in various temperature ranges have been reported [7-10].

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No thermodynamic data for $(Li_xK_{1-x})_2SO_4$, (x = 0.1, ..., 0.5) irradiated with neutron pile have been reported in literatures.

The aim of this work is to show the defects induced by neutron pile irradiation and the corresponding changes which are produced in the thermodynamic properties in the vicinity of high phase transitions of $(Li_xK_{1-x})_2SO_4$ crystals.

Experimental

Sample preparation

Clear, colourless single crystal of $(Li_xK_{1-x})_2SO_4$ were grown isothermally at 315 K from aqueous solution containing the initial salts at different adapted stoichiometric ratios.

Neutrons irradiation technique

Samples were irradiated with neutrons using a special kind of polyethylene capsule known as Lazy Susan. Neutrons are produced from Triga Mark III, Berkeley research reactor, with steady state power 1000 KW. The neutron fluxes are determined by the activation of natural gold foils (1.2 cm diameter, 0.01 cm thickness). The resulting activity from $^{197}Au(n, \gamma)$ ^{198}Au reaction was measured and analyzed by using Ge (Li) gamma detector and pulse height analyzer connected to PDP 11/34 based data acquisition system. A normalization factor due to the degradation of the neutron flux through the samples during the irradiation process was considered. Crystals are irradiated to a flux $\varphi = 4.10^{12}$ n·cm^{-2}·S^{-1} through different time intervals from 2 minutes up to 10 minutes.

Thermal measurements

The thermal behaviour of irradiated mixed crystals was studied in the temperature range 300-970 K by applying the following techniques:

(a) The specific heat under constant pressure, C_p, was determined using a differential scanning calorimetry (DSC) technique, where a Heraeus DSC cell was connected to Heraeus DTA 500 thermal analyzer. Measurements were achieved by applying the base line method [11]. Lidded pans of aluminium were used to eliminate the sloping of the base line. A Pt 100 thermocouple was used as a temperature sensor, while a heating rate of 2 deg/min was applied.

(b) For differential thermal analysis, the sample was contained in a glass tube in the standard DTA cell connected to the DTA 500 analyzer. The

temperature sensor used was NiCrNi and the heating rate applied 5 deg/min.

(c) Thermogravimetric (TG) measurements were performed on a Heraeus TG 500 thermobalance with a Pt-Rh-Pt temperature sensor, and the heating rate was 10 deg/min. Dry nitrogen was allowed to flow at rate 15 ml/min, while the flow rate of cooling water was 10 l/h.

Results and discussion

$LiKSO_4$ crystals exhibit two structural phase transitions at 715 K and 960 K as shown in Fig. (1-a) which are in good agreement with the publish-

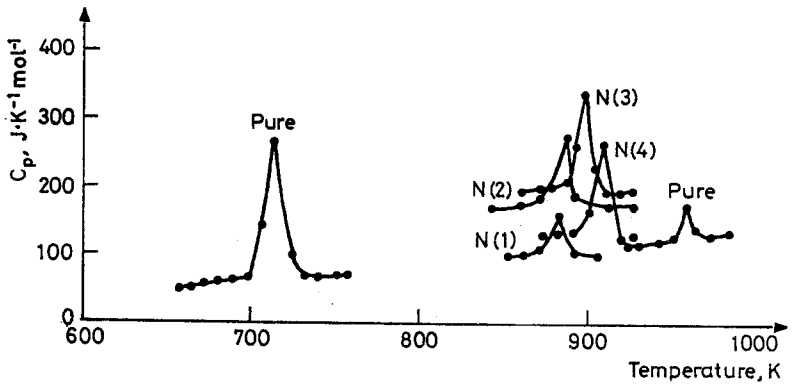

Fig. 1a Temperature dependence of C_p for $(Li_xK_{1-x})_2SO_4$ crystals for (x = 0.1, ... 0.5)

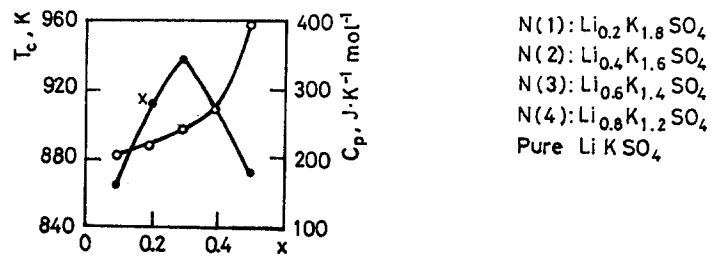

Fig. 1b The variation of T_c and C_p as a function of stoichiometric ratio

edvalues [12-13]. But with the change of stoichiometric ratio of such crystal according to the formula $(Li_xK_{1-x})_2SO_4$, where x = 0.1, 0.2, 0.3, and 0.4, it is observed that the anomaly in the temperature dependence of specific heat, C_p, at the first phase transition disappeared.

Table 1

Nuclide (Abundance)	Reaction	Product nucleus	Decay product	No of* defects
^{7}Li (92.48%)	(n, γ)	^{8}Li	^{8}Be	$2.8x10^{3}$
^{18}O (0.204%)	(n, γ)	^{19}O	^{19}F	$7.6x10^{-10}$
^{32}S (95.018%)	(n, γ)	^{33}S		
^{34}S (4.125%)	(n, γ)	^{35}S	^{35}Cl	$8.1x10^{-4}$
^{36}S (0.017%)	(n, γ)	^{37}S	^{37}Cl	$9.5x10^{-4}$
^{39}K	(n, γ)	^{40}K	^{40}Ca ^{40}Ar	0.046
(93.08%)	(n, P)	^{39}Ar	^{39}K	$1.46x10^{-5}$
^{41}K (6.91%)	(n, γ)	^{42}K	^{42}Ca	0.015

* For thermal neutrons per unit fluence per gram

While in the second transition, T_c shows a decrease in its value with the decrease of lithium content as presented in Fig. (1-b). Moreover, the value of specific heat, C_p, at transition shows a maximum at $x = 0.3$, Fig. (1-b).

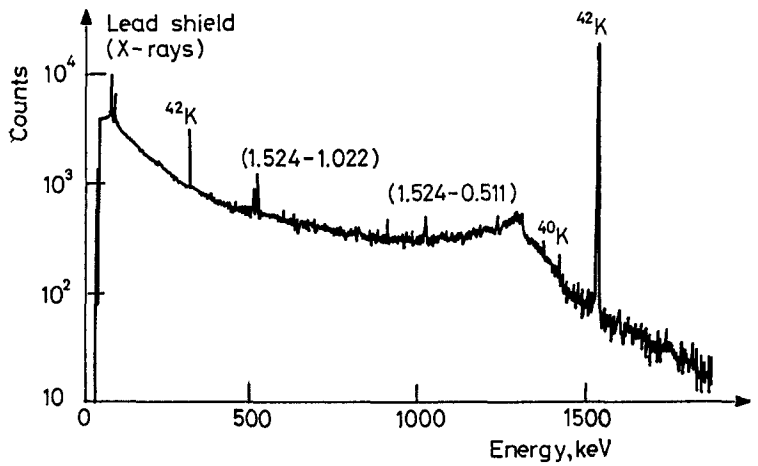

Fig. 2 γ-spectrum of irradiated $Li_{0.2}K_{1.8}SO_4$ for 10 minutes

This behaviour may be attributed to the enhancement of the phonon lattice vibrations due to the difference in cationic ratio $Li^+:K^+$ and phononic scattering.

As a results of the neutron irradiation of $(Li_xK_{1-x})_2SO_4$ crystals, where $x = 0.1, 0.2, 0.3$ and 0.4, radioisotope ^{42}K is detected by means of the γ-spectrometer while the other radioisotopes are not detected either due to their short half-lives or very small yields. Figure (2) represents the γ-spectrum of the activated crystal and Table (1) shows the possible produced radioisotopes with their decay products and the number of induced defects due to neutron irradiations. $(Li_xK_{1-x})_2SO_4$ crystals are irradiated to neutron pile of different integrated flux Φt doses, ranging from $4.8 \cdot 10^{14}$ to $2.4 \cdot 10^{15}$ $n \cdot cm^{-2}$.

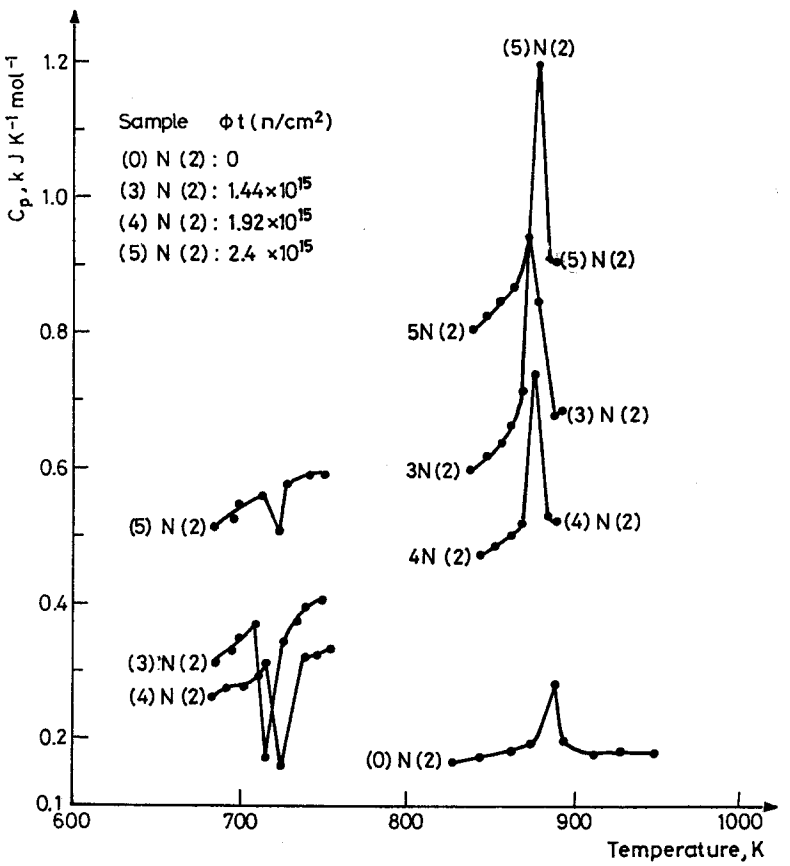

Fig. 3 Variation of C_p of $Li_{0.4}K_{1.6}SO_4$ crystal *vs.* temperature for different neutron fluences

As an example the variation of the temperature dependence of specific heat, C_p, of $Li_{0.4}K_{1.6}SO_4$ crystal under the action of neutron fluence is presented in Fig. (3). It is observed that the anomaly in the first high temperature phase appears again showing an endothermic behaviour. In general, the values of specific heat, C_p for irradiated samples increase as a result of irradiation [14]. From Fig. (3) one can conclude that the dependence of C_p on the neutron integrated flux Φt shows a decrease to a minimum at neutron fluence $\varphi t = 1.92 \times 10^{15}$ n.cm^{-2} and increases to 1200 J·K^{-1} mole^{-1} at $\Phi t = 2.4.10^{15}$ n·cm^{-2}. This behaviour may be attributed to the decomposition induced by irradiation, as well as the generation of new species [15].

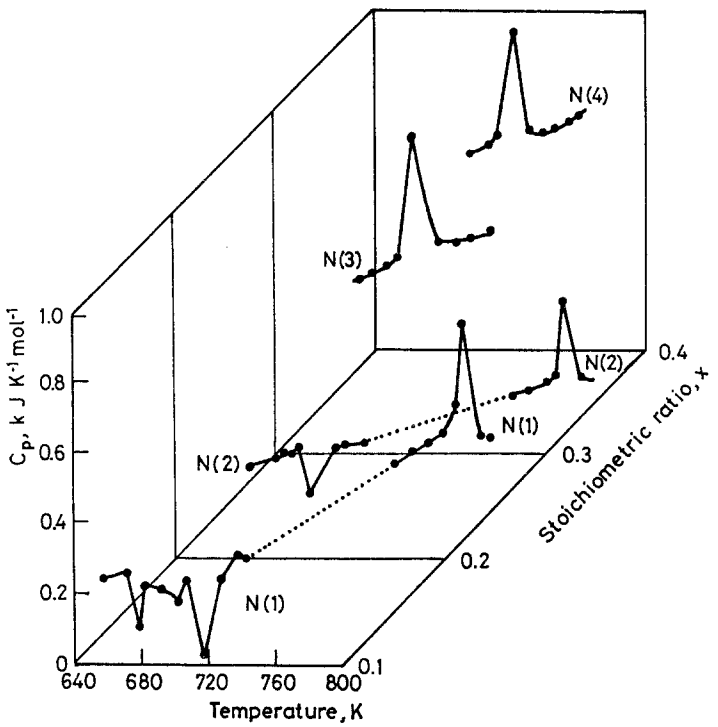

Fig. 4 Temperature dependence of C_p for $(Li_xK_{1-x})_2SO_4$ crystals irradiated with neutron fluence 1.92×10^{15} n·cm^{-2}

The three-dimensional diagram (temperature-concentration-specific heat), for the system under consideration in the whole range of concentration (x = 0.1, 0.2, 0.3, 0.4) irradiated with neutrons of fluence

$1.92.10^{15}$ n·cm^{-2}, is presented in Fig. (4). As one can see [16], the further increase of x results in disappearance of the second high temperature phase besides the increase in the value of specific heat C_p at the first high temperature phase the same neutron fluence.

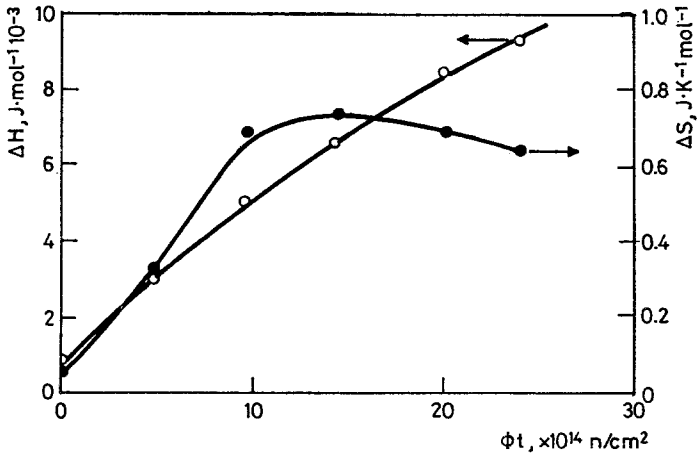

Fig. 5 Variation of the changes of enthalpy and entropy for $Li_{0.4}K_{1.6}SO_4$ crystal as a function of neutron fluence

Furthermore, the changes in enthalpy ΔH and entropy ΔS of $Li_{0.6}K_{1.4}SO_4$ crystal are plotted *vs.* the neutron fluence Φt as shown in Fig. (5). It is clear from Fig. (5) that ΔH and ΔS increase as a function of the increase of the fluence. The non linearity in the ΔH and ΔS depends on the interactions of defects induced by neutrons irradiation.

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Zusammenfassung — Im Konzentrationsbereich ($x = 0.1$, 0.2, ..., $x = 0.5$) wurden thermodynamische Untersuchungen an $(Li_xK_{1-x})_2SO_4$, LKS, Mischkristallen durchgeführt. Mittels DTA und DSC wurde das thermische Verhalten in der Nähe von Hochtemperatur-Phasen untersucht. Weiterhin wurde der Einfluß von thermischer Neutronenbestrahlung auf die thermischen Eigenschaften der Mischkristalle beleuchtet. In Zusammenhang mit der stöchiometrischen Zusammensetzung und der Strahlungsdosis zeigen die Ergebnisse sowohl eine Änderung der Umwandlungstemperatur T_c als auch der spezifischen Wärme C_p im Umwandlungspunkt. Die Enthalpie- und Entropieänderung der Mischkristalle wurde annähernd auch numerisch bestimmt.