High quality crystal in Space

An important discovery was made in space technology during the first Soviet attempt to weld materials on board the *Soyuz-6* ship in 1969. In outer space, under zero gravity, the newly formed crystal lattices have much less irregularities in their structure as compared to the crystals formed on the earth. The high quality crystals are of immense importance for many branches of science and technology. Some quite unusual things may happen in weightlessness, even though lasting for a short while. Specialists have not been able to explain them so far. For example crystals have been fabricated both in orbital laboratories, and also in space rockets. In the space rockets crystal has to be fabricated quickly in less than 10 min during which near zero environment can be achieved. This process involves taking the sample upto 1500°C and then crystallizing. There were instances when a crystal "baked" so quickly proved to be much more perfect and had an almost ideal lattice structure which is difficult to obtain even in an orbital laboratory.

An experiment proposed and prepared by the Indians involved the study of the pervasive nature of crystal formation in weightlessness. It boiled down to creating such conditions under which the mixture of smelted silver and germanium cooled below the solidification point remained in its liquid form. Such an unusual state is called the supercooling of liquid. During fast cooling a supercooled liquid may develop into a substance with some very unusual qualities, such as "metallic glass".

In its significance the experiment is not inferior to those involving the crystals of cadmium, mercury and tellurium which have been repeatedly conducted by Soviet cosmonauts and their colleagues from socialist countries. In weightlessness all the three components of the mixture merge into a single compound without any problems which would be there on the Earth because of the considerable differences in the density of cadmium, tellurium and mercury. Crystals thus obtained effectively transform infrared and thermal rays into visible images. The technology was used to manufacture heat sensors—the devices allowing a physician to diagnose a disease at an early stage and take appropriate measures.

The Soviet-Indian cooperation in outer space and on the earth has good prospects for the future, with both nations taking more joint steps to promote mutual interests and those of the entire mankind.

VIBRATIONAL SPECTROSCOPIC STUDY OF THE STRUCTURAL PHASE TRANSITION IN $LiCsSO_4$

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DOUBLE sulphate crystals with the general formula $M'M''SO_4$ ($M', M'' = Li^+, K^+, Cs^+, Rb^+$) show many interesting phase transitions. $LiCsSO_4$ which belongs to this family shows a structural phase transition at 202 K, from the room temperature (18–23°C) orthorhombic Pcmn phase to a low temperature monoclinic $P2_1/n$ phase. In the low temperature monoclinic phase the SO_4 ions lose their plane of site symmetry. Investigations[1–4] on its elastic and thermal properties and structure have been carried out on this crystal to understand this phase transition. In this brief note we report for the first time some interesting Raman spectroscopic results on the phase transition in $LiCsSO_4$.

A Spex Ramalog double monochromator spectrometer was used with an Argon ion laser (4880 A, at 250 mw power) to record the polarized Raman spectra. In the room temperature Pcmn symmetry phase, all the Li^+, Cs^+ and SO_4^{2-} ions occupy Cs sites. In both phases of the crystal the number of formula units in the primitive unit cell is $Z = 4$. In the room temperature phase, the modes of the species A_g, B_{1g}, B_{2g} and B_{3g} are Raman active. In six polarisation settings of the crystal, the Raman spectra were recorded both in the external and internal mode frequency regions. This enabled the identification of all the phonon modes of the crystal belonging to various symmetry species. Table 1 shows the correlation diagram for the free, site and unit cell symmetry of SO_4 ions in the orthorhombic and monoclinic phases.

From the first correlation diagram, it is seen that at room temperature (D_{2h}^{16} symmetry), in the three A_g (aa, bb, cc) settings only one symmetric stretching mode (ν_1), only one of the two symmetric bending modes (ν_2), two of the asymmetric stretching triplet (ν_3) modes and two of the asymmetric bending triplet (ν_4) modes should be seen if there is no observable correlation splitting on account of $Z = 4$. The same number of Raman lines should be observed in the B_{2g}(ac) polarisation setting also. This is borne out fully since the spectra showed one ν_1 line (1018 cm^{-1}), one of the ν_2 lines (450 cm^{-1}) and two lines each of ν_3 and ν_4 modes (628 cm^{-1}, 650 cm^{-1}, 1124 cm^{-1}, 1158 cm^{-1}), in the

Table 1 *Correlation diagrams of $LiCsSO_4$ in (a) the orthorhombic phase and (b) the monoclinic phase.*

(a)

T_d	C_s	D_{2h}	Raman activities
ν_1 A_1	A′	A_g	aa, bb, cc
		B_{2g}	ac
ν_2 E		B_{1u}	
		B_{3u}	
	A″	A_u	
		B_{2u}	
ν_3, ν_4 F_2		B_{1g}	ab
		B_{3g}	bc

(b)

T_d	C_1	C_{2h}	Raman activities
ν_1 A_1	A	A_g	aa, bb, cc, ac
ν_2 E		A_u	
		B_g	bc, ab
ν_3, ν_4 F_2		B_u	

c(aa)b, a(bb)c, a(cc)b and c(ac)b settings.

The spectra corresponding to c(ba)b (B_{1g}) and c(bc)b (B_{3g}) should be identical and show one line of ν_2 mode and one each of ν_3 and ν_4 modes. These were also observed at 460 cm^{-1} (ν_2), 1110 cm^{-1} (ν_3) and 620 cm^{-1} (ν_4).

In the low temperature monoclinic C_{2h} phase, all the ions occupy C_1 sites. In the low temperature Raman spectra taken in the two polarisation settings c(aa)b (A_g) and c(ba)b (B_g) all the expected Raman lines were observed (that is, one totally symmetric line, two lines in the symmetric bending region, three lines each, in the asymmetric stretching and asymmetric bending regions).

The total integrated intensity of the Raman line due to ν_1 mode in two polarisation settings c(aa)b and c(ac)b at various temperatures was measured across the phase transition. The total intensity of the ν_1 mode in both the settings individually showed anomalous increase near the phase transition. The intensities of the ν_1 line under the two polarisation settings were added up and plotted against the temperature. As can be seen from figure 1, the total intensity is temperature dependent and shows an anomalous increase across the phase transition. This type of

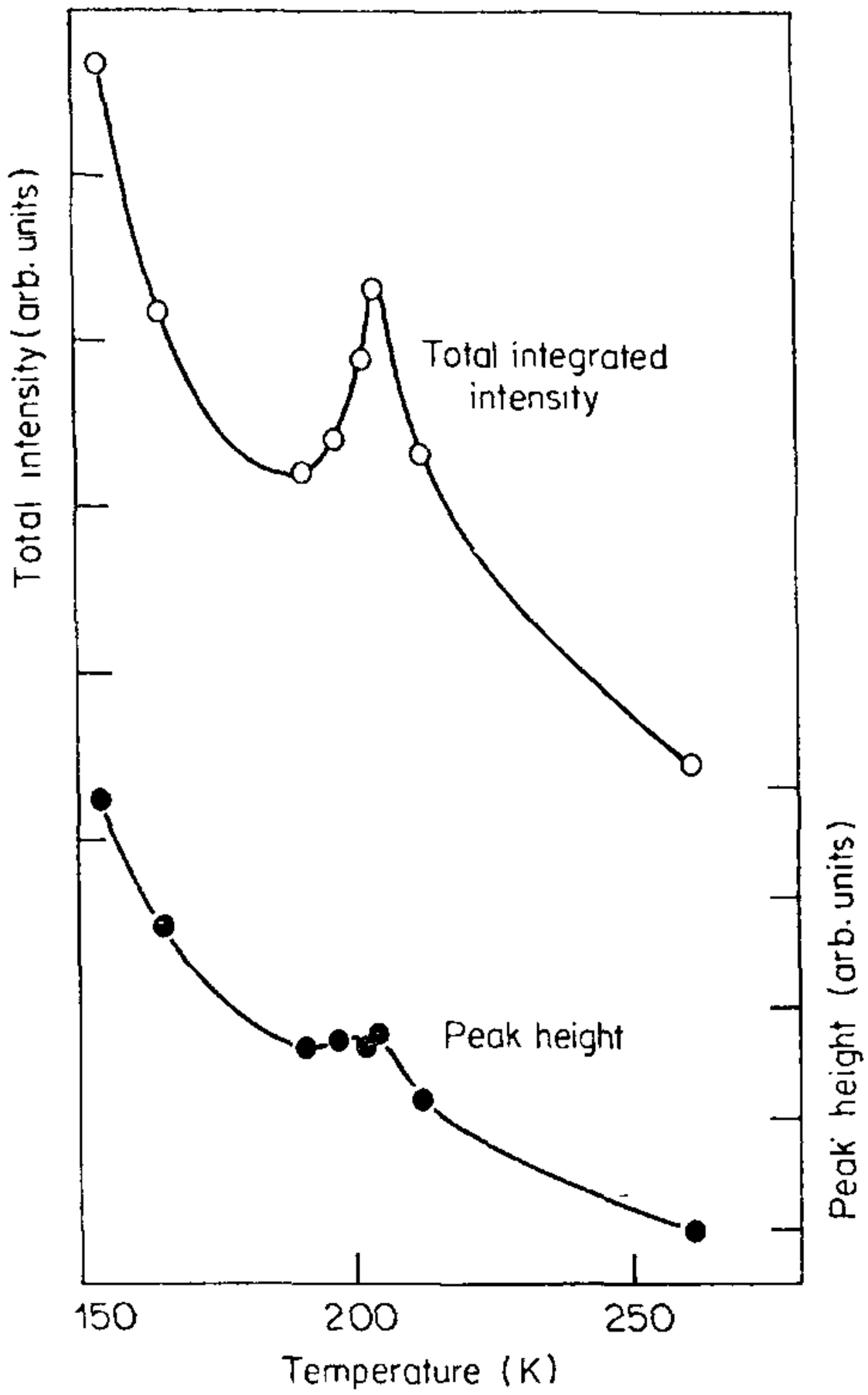

Figure 1. *Plots of total intensity and peak height of the totally symmetric stretching mode against temperature.*

anomaly indicates the second order nature of the phase transition as is also evidenced by the nature of anomalies in the specific heat and dielectric constant studies[1]. This anomaly can be attributed to the increase of fluctuations in the changes of polarisability of the scattering SO_4 species and the disappearance of the plane of symmetry near the phase transition. The peak height versus temperature also shows a similar anomaly. The absence of any change in the width is interpreted to indicate only a very small anharmonic coupling between the various SO_4 ions in the unit cell.

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DISCOVERY OF TUFFACEOUS MUDSTONES IN THE PINJOR FORMATION OF PANJAB SUB-HIMALAYA, INDIA

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SEVERAL volcanic ash and tuffaceous mudstone layers have been reported in recent years from the Siwalik Group of Pakistan[1,2]. Fission track dating of the zircons from these layers in combination with the remanent-polarity-stratigraphy of the sequences has resulted in building up of temporal constraints for the Siwalik Group in Pakistan. From the Siwalik Group in India, bentonitic beds have been known from the locality of Parmandal in the Jammu region.

We report, the occurrence of four levels of tuffaceous mudstones from the Pinjor Formation of the Upper Siwalik Subgroup in the area east of Chandigarh (figure 1). Two of the tuffaceous mudstones occur in the Ghaggar section and two others occur in the Khetpurali section (figures 1, 2). Detailed stratigraphic measurements of the Siwalik sequences in which they occur are published elsewhere[3].

Ghaggar Section: The tuffaceous mudstones occur 75 m above the base of the section as a couplet in the overbank interval of the ninth alternative (figure 2).

The thickness of the alternation in which the tuffaceous mudstones occur is 10 m. The channel sandstone facies measures 2 m and the overbank interval 8 m. The two tuffaceous mudstone layers are 13 cm and 5 cm thick respectively and are separated by about 1.35 m of stratigraphic thickness (figure 2). The tuffaceous mudstones have a sharp lower contact and occur as easily distinguishable units within the pedogenetically modified overbank deposits. The tuf-

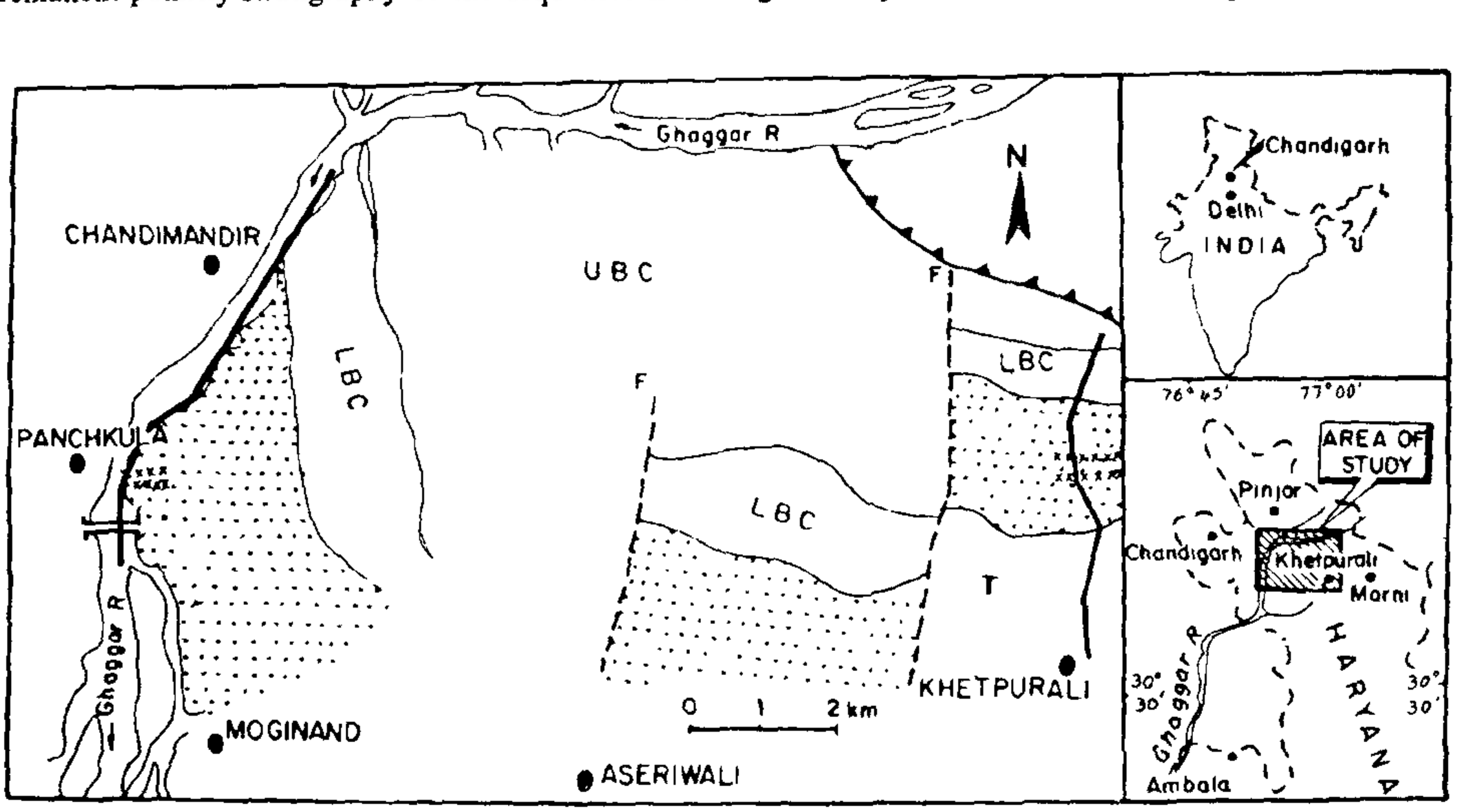

Figure 1. Sketch geological map of the Pinjor Formation, east of Chandigarh, Panjab Sub-Himalaya.