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Piezo-optic and Dielectric Behavior of the Ferroelectric Lithium Heptagermanate Crystals

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1. Introduction

It is well known that piezo-optic and electro-optic effects in crystals find wide ranging applications in laser devices. The photoelastic behavior of crystals forms a necessary prelude to study the electro-optical effect of ferroelectric crystals. Lithium heptagermanate $Li_2Ge_7O_{15}$ (LGO) is regarded as a weak ferroelectric and its curie point T_c is 283.5K (Wada et al., 1981, 1983). Due to its intermediate behaviour between order-disorder and displacive types in a conventional grouping of ferroelectric materials LGO remains a subject of interest from both the theoretical and the application point of view. The paraelectric phase above T_c is orthorhombic $D_{2h}^{14} \sim pbcn$ and below T_c the ferroelectric phase is $C_{2v}^5 \sim pbc2_1$ with four formula units in a unit cell in both the phases. Below T_c LGO shows dielectric hysteresis loop and the permittivity shows a sharp peak at T_c (Preu, 1982; Wada et al., 1981, 1983). The Raman scattering spectrum shows a shoft mode whose frequency tends to zero as T_c is approached from below (Wada & Ishibashi, 1983). Below T_c the spontaneous polarization appears along the c-axis. The nature of the second order phase transition is not simple because according to Raman spectra the transition is suggested to be a displacive phase transition. But the temperature dependence of the permittivity ε is indicative of the order disorder character of the phase transition (Preu, 1982; Wada et al., 1981, 1983) and does not agree with the behaviour expected of a displacive phase transition.

Many interesting physical properties of LGO such as birefringence (Kaminsky & Haussühl, 1990), elastic (Haussühl et al., 1980), thermal expansion (Wada & Ishibashi, 1983), dielectric susceptibility (Preu, 1982; Kudzin, 1994a, 1995b), electron paramagnetic resonance (EPR) of doped ions Mn^{2+} and Cr^{+3} (Trubitsyn et al., 1992; Bain, 1994) and photoluminescence (Bain, 1994) exhibit strong anomalies around T_c. However, the optical properties vary only to such a small degree that the transition could not be detected with the aid of a standard polarization microscope (Kaminsky & Haussühl, 1990). Interestingly with the help of a high resolution polarization device, Kaminsky and Haussühl (Kaminsky & Haussühl, 1990) studied the birefringence in LGO near T_c and observed anomalies at the phase transition.

The study of piezo-optic dispersion of LGO (un-irradiated and irradiated) in the visible region of the spectrum of light at room temperature (RT=298 K) shows an optical zone/window in between 5400Å and 6200Å with an enhanced piezo-optical behavior (Bain et al., 2008). The temperature dependence of the photoelastic coefficients of the ferroelectric

crystals Li$_2$Ge$_7$O$_{15}$ (both un-irradiated and x-irradiated) in a cooling and a heating cycle between room temperature and 273K shows an interesting observation including the lowering of the T$_c$ under uniaxial stress contrary to the increase of T$_c$ under hydrostatic pressure and observation of thermal photoelastic hysteresis similar to dielectric behavior (Bain et al., 2009). The study of a.c. electrical impedance (Z) along the c-axis of the crystals LGO in the temperature range 283.5 K to 573 K at the frequency range 10kHz – 10,000 kHz shows a sharply decrease of the magnitude of |Z| with increasing frequency and tends to zero value at about the frequency 10,000kHz.

This chapter will include basic properties of the ferroelectric Lithium heptagermanate (Li$_2$Ge$_7$O$_{15}$) crystals, related experimental studies on this crystal including growth of single crystals, agreement and disagreement between the results of different experimental investigations. The brief description on the theory of photoelasticity, fabrication process of the ferroelectric Li$_2$Ge$_7$O$_{15}$ crystals, experimental methods of the photoelastic coefficients of LGO (un-irradiated and irradiated) at different wave length and temperatures around the phase transition temperature T$_c$ and also the practical applications of the LGO crystals in the opto-electronic devices will be discussed.

1.1 Growth and structure of Li$_2$Ge$_7$O$_{15}$ crystals

Single crystals of Li$_2$Ge$_7$O$_{15}$ are grown in an ambient atmosphere by Czochralski method from stoichiometric melt, employing a resistance heated furnace. Stoichiometric mixture of powdered Li$_2$CO$_3$ and GeO$_2$ in the ratio of 1.03 and 7.0 respectively was heated at 1100 K for 24 hours to complete the solid state reaction for the raw material for the crystal growth. The crystals were grown by rotating the seed at the rate of 50 rpm with a pulling rate of 1.2 mm/hour. The cooling rate of temperature in the process of growth was 0.8-1.2 K/hour. The crystals grown were colorless, fully transparent and of optical quality. The crystal axes were determined by x-ray and optical methods.

The desired impurities such as Cr^{+3}, Mn^{+2}, Bi^{+2} and Eu^{+2} etc are also introduced in desired concentration by mixing the appropriate amount of the desired anion salt in the growth mixture. The crystal structure of LGO above T$_c$ is orthorhombic (psedohexagonal) with the space group D_{2h}^{14} (Pbcn). The cell parameters are a: 7.406 Å, b: 16.696 Å, c: 9.610 Å, Z = 4 and b~√3c. Below T$_c$ a small value of spontaneous polarization occurs along c-axis and the ferro-phase belongs to C_{2v}^5 (Pbc2$_1$) space group. The crystal structure contains strongly packed layers of GeO$_4$ tetrahedra linked by GeO$_8$-octahedra to form a three dimensionally bridged frame work in which Li atoms occupy the positions in the vacant channels extending three dimensionally (Haussühl et al., 1980; Wada et al., 1984, 1988; Iwata et al., 1987). The size of the unit cell (Z = 4) does not change at the phase transition and ferroelectric phase transition is associated with a relaxational mode as well as the soft phonon (Wada, 1988).

1.2 Theory of photoelasticity

If a rectangular parallelepiped with edges parallel to x[100], y[010] and z[001] axes is stressed along z-axis and observation is made along y-axis, as shown in Fig.1, then the path retardation δ$_{zy}$ introduced per unit length due the stress introduced birefringence is given by

$$\delta_{zy} = (\Delta n_z - \Delta n_x) = C_{zy}P_{zz} \tag{1}$$

where Δn_z and Δn_x are the changes in the corresponding refractive indices, ($\Delta n_z - \Delta n_x$) is the corresponding stress induced birefringence, P_{zz} is the stress along z-axis and C_{zy} is a constant called the Brewster constant or the relative photoelastic coefficient. In general the Brewster constant is related to the stress optical and strain optical tensors of forth rank (Narasimhamurty, 1981) and is a measure of the stress induced (piezo-optic) birefringence. It is conveniently expressed in the unit of 10^{-13} cm^2/dyne per cm thickness along the direction of observation is called a Brewster (Narasimhamurty, 1981).
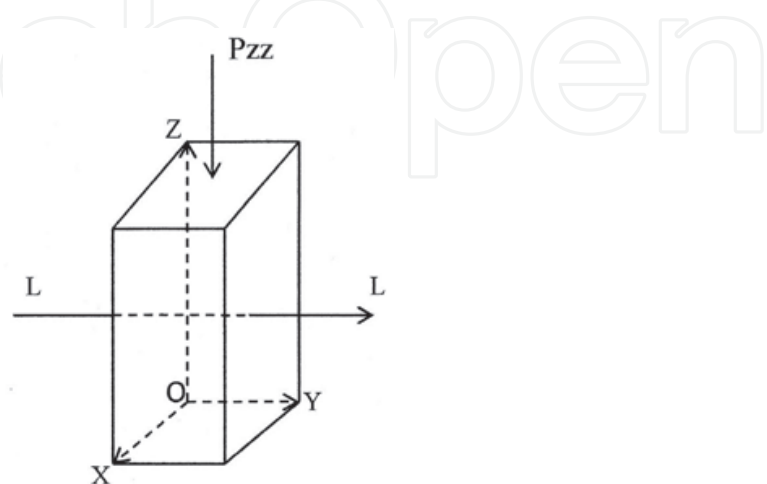

Fig. 1. A solid under a linear stress of stress-optical measurements (P_{zz} is the applied stress and LL is the direction of light propagation and observation).

1.3 Experimental method of determining the photoelastic constants

To study the piezo-optical birefringence the experimental set up consists of a source of light (S), a lens (L) to render the rays parallel, a polarizer (P), an analyzer Polaroid (A), a Babinet compensator (B) and a detector (D), as shown in Fig.2. The P and A combination are adjusted for optimal rejection of light. The sample with stressing arrangement and a Babinet compensator are placed between P and A. A monochromator and a gas flow temperature controlling device are used to obtain the piezo-optic coefficients (C_λ) at different wavelengths and temperature. The subscript λ in the symbol C_λ denotes that the piezo-optic coefficient depends on the wavelength of light used to measure it. The experiments are carried out for different wavelengths using white light and a monochromator and the monochromatic sodium yellow light. An appropriate stress along a desired direction of the sample is applied with the help of a stressing apparatus comprising a mechanical lever and load.
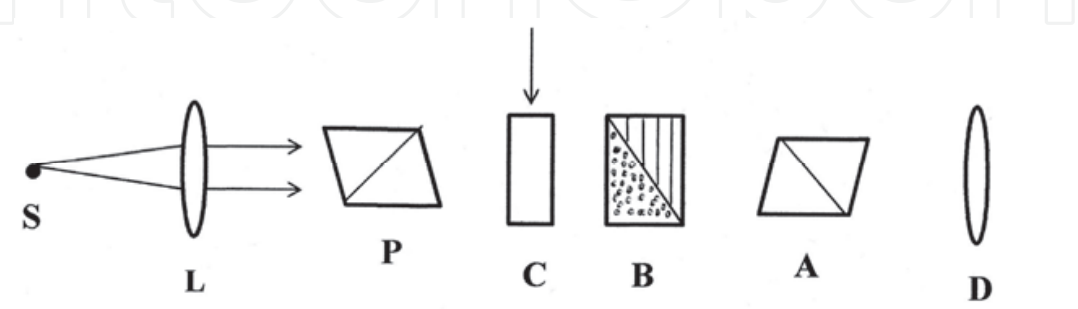

Fig. 2. A schematic diagram of the experimental setup for the measurement of photoelastic constants of the crystals at room temperature. Source of light (S), Lense (L), Polarizer (P), Crystals (C) under stress, Babinet Compensator (B), Analyzer (A) and Detector (D).

To start with, the Babinet compensator is calibrated and the fringe width is determined for different wavelengths of light in the visible region. The crystal specimen is placed on the stressing system so that the stress could be applied along vertical axis and observation made along horizontal axis. A load on the crystal shifts the fringe in the Babinet compensator and this shift is a measure of the piezo-optic behavior. The piezo-optic coefficients (C_λ) are now calculated using the calibration of the Babinet compensator. The experiment is repeated for other orientations of the crystals and the results are obtained.

1.4 Piezo-optic dispersion of $Li_2Ge_7O_{15}$ crystals

The experimental procedure for the piezo-optic measurements is described in section 1.3. The polished optical quality samples worked out to dimensions i) 5.9 mm, 9.4 mm and 5.0 mm; ii) 3.17 mm, 5.88 mm and 6.7 mm, along the crystallographic a, b and c axes respectively. The stress was applied with an effective load of ~23 kg in each case (Bain et al., 2008).

The values of C_λ thus obtained at different wavelengths are given in Table 1 and the results are plotted in Fig. 3. Here C_{pq} is the piezo-optic coefficient with the stress direction being p and observation direction being q. The results show an interesting piezo-optic behavior. A survey of literature indicates that the piezo-optic behavior of materials studied till now shows a reduction of C_λ with increasing wavelength in the visible region (Narasimhamurty, 1981). In the present case, C_λ decreases with wavelength up to a certain wavelength as in other normal materials and then suddenly shows a peak and later on the usual behavior of reduction in the values of piezo-optic coefficients is observed.

Obs.	C_{pq}	Wavelenghts				
		4358Å	4880Å	5390Å	5890Å	6140Å
1	C_{xy}	4.024	3.819	3.722	4.328	3.677
2	C_{xz}	5.243	4.895	4.770	5.552	4.451
3	C_{yx}	4.084	3.525	3.092	3.562	2.913
4	C_{yz}	4.353	4.118	3.946	4.261	3.866
5	C_{zy}	4.179	2.814	3.177	3.713	3.172
6	C_{zx}	3.312	2.991	2.650	4.190	2.618

Table 1. Stress optical coefficients c_{pq} (in Brewster) for $Li_2Ge_7O_{15}$ at different wave lenghts.

To the best knowledge of the authors this behavior is unique to the LGO crystals. For the sake of convenience we denote C_λ measured at λ = 5890 Å as C_{5890} and so on. The results show that sometimes the value of C_{5890} is even higher than that at C_{4400}, the value of piezo-optic coefficient obtained at the lowest wavelength studied here. This is the case with C_{xy}, C_{zx} and C_{xz}. For other orientations the value is lower than that at 4400 Å. Further, C_λ is found to have increased to more than 50% in the case of stress along [001] and observation along [100]. Also, it is interesting to note that the value of C_{6140}, is less than that of C_{5390}, in tune with usual observation of piezo-optic dispersion. Thus one can see an "optical window" in between 5400 Å and 6200 Å. The height of this optical window is different for various orientations, though the width seems approximately the same. The maximum height of about 1.5 Brewster was found for C_{zx} followed by C_{xz} with about 0.9 Brewster. It should be noted here that Z-axis is the ferroelectric axis for LGO. It is also interesting to note that the change in height is more in the former while the actual value of C_λ is less compared to that of the latter. The percentage dispersion also is different for various orientations. It is very high, as high as 25% for C_{zy}, while it is just 10% for C_{xy}.
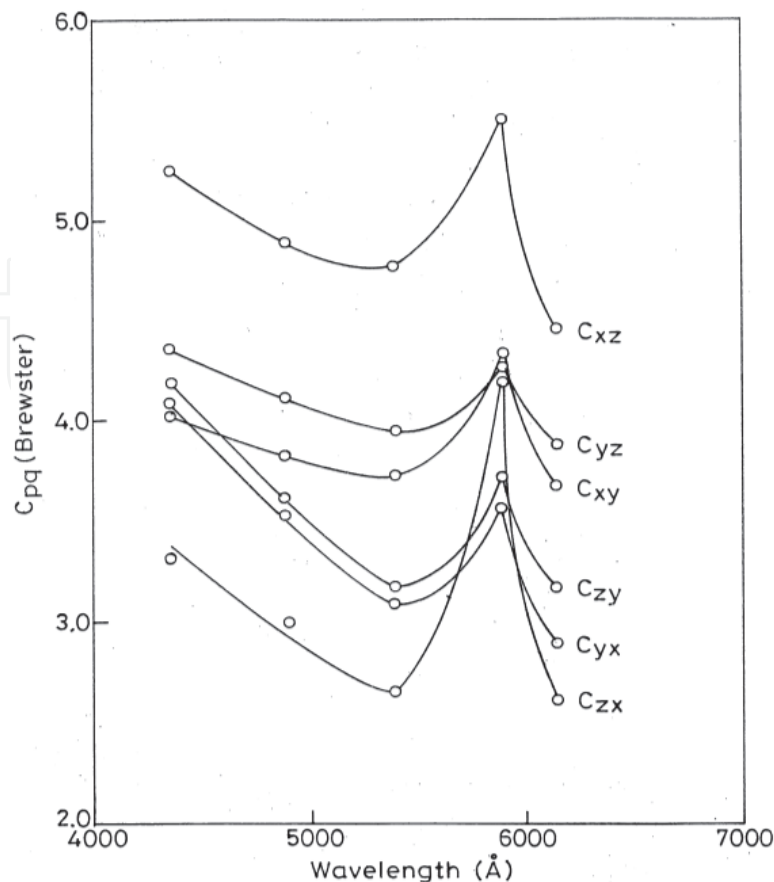
Fig. 3. Stress optical dispersion of $Li_2Ge_7O_{15}$ crystals with wavelength at room temperature (298 K).

Figure 4 shows the variation of $C_{zx}(\lambda)$ at the temperatures ranging from 298K to 283K on cooling process of the sample LGO. It is clear from the figure that the distinct peak of $C_{zx}(\lambda)$ appears only at the sodium yellow wavelength of 5890 Å for the whole range of temperatures (298 K–283 K) investigated. It is also interesting to note that a temperature anomaly is also observed around 283 K. LGO undergoes a second order phase transition at 283.5 K from the high temperature paraelectric phase to the low temperature ferroelectric phase. So this anomaly is related to this phase transition of the LGO crystal.

The observed peculiarity of piezo-optic behavior could be due to many factors, viz., i) anomalous behavior of refractive index or birefringence ii) anomalous ferroelastic transformation at some stage of loading iii) shift of absorption edge due to loading. The following have been done to identify the reasons for this peculiar behaviour.

Birefringence dispersion has been investigated in the visible region and no anomalies in its behavior has been observed. This rules out the first of the reasons mentioned. The reason due to ferroelastic behavior also is ruled out since the effect would be uniform over all the wavelengths investigated. It was not possible to investigate the effect of load on the absorption edge. Hence an indirect experiment has been performed. If there is a shift in the absorption edge due to loading the sample, the peak observed now at sodium yellow light would shift with load. No clear shift of the peak could be observed within the experimental limits. Another interesting experiment was done to identify the source of the anomaly. It is well known that T_c of LGO changes under uniaxial stress. The measurements were made near T_c under different stress (loads). Although T_c was found to shift a little with load the

dispersion peak did not show any discernible shift. No particular reason could be established as to why a dispersion peak appears around sodium yellow region. Another interesting work in this direction is on $Gd_2(MoO_4)_3$ — where an anomalous peak was recorded in spontaneous birefringence at 334.7 nm (Saito et al., 1994), an observation made for the first time.
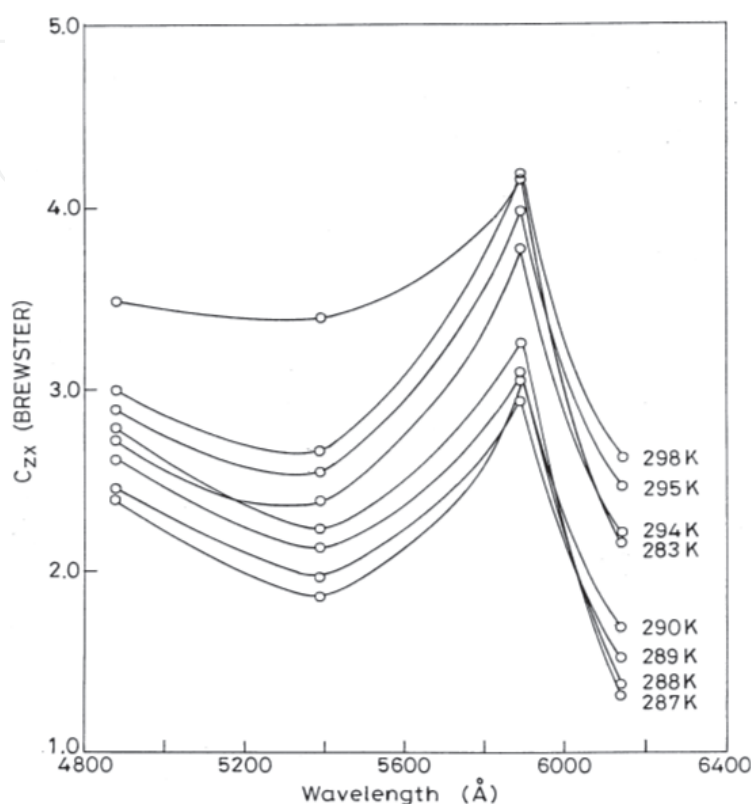

Fig. 4. The variation of $C_{zx}(\lambda)$ at the temperatures ranging from 298 K to 283 K on cooling process of the sample $Li_2Ge_7O_{15}$.

It is well known that the photoelasticity in crystals arises due to change in number of oscillators, effective electric field due to strain and the polarisability of the ions. In the present case, as the wavelength approaches around 5400 Å , the ionic polarisability seems to be changing enormously. There is no optical dispersion data available on LGO. We haveconducted an experiment on transmission spectra of LGO along x, y and z-axes, which shows a strong absorption around 5400 Å . The observed anomaly in the piezo-optic dispersion may be attributed to the absorption edge falling in this region. This explanation needs further investigation in this direction. It is also known that the strain optical dispersion arises due to the shift in absorption frequencies and a change in the oscillator strength caused by the physical strain in the crystal.

1.5 Irradiation effect on Piezo-optic dispersion of $Li_2Ge_7O_{15}$ crystals

The ferroelectric single crystals $Li_2Ge_7O_{15}$ was irradiated by x-ray for one hour and the experimental processes described in section 1.4 were repeated for the crystal (irradiated) LGO in order to understand the radiation effect on piezo-optical birefringence dispersion(Bain et al., 2008). The values of C_λ of the crystal (irradiated) LGO thus obtained at different wavelengths are given in Table 2 and the results are plotted in Fig. 5.

		Wavelenghts				
Obs.	$C/_{pq}$	4358Å	4880Å	5390Å	5890Å	6140Å
1	$C/_{xy}$	4.08	3.87	3.72	4.33	3.73
2	$C/_{xz}$	5.35	5.00	4.88	5.59	4.55
3	$C/_{yx}$	4.02	3.47	3.01	3.50	2.83
4	$C/_{yz}$	4.39	4.19	4.01	4.26	3.90
5	$C/_{zx}$	4.63	4.46	4.41	4.66	4.29
6	$C/_{zy}$	3.71	3.26	2.97	3.43	2.72

Table 2. Stress Optical Coefficients C_{pq} (in Brewsters) for $Li_2Ge_7O_{15}$ (irradiated) at different wavelenghts.

Some interesting results are obtained in the case of irradiated crystal LGO. The peak value of $C/_{zx}$ has decreased about 18% and that of $C/_{zy}$ has increased about 25% at the wave length λ= 5890 Å. Also, it is interesting to note that the value of C_{6140}, is less than that of C_{5390} for the un-irradiated and irradiated sample of LGO crystal, in tune with usual observation of piezo-optic dispersion.
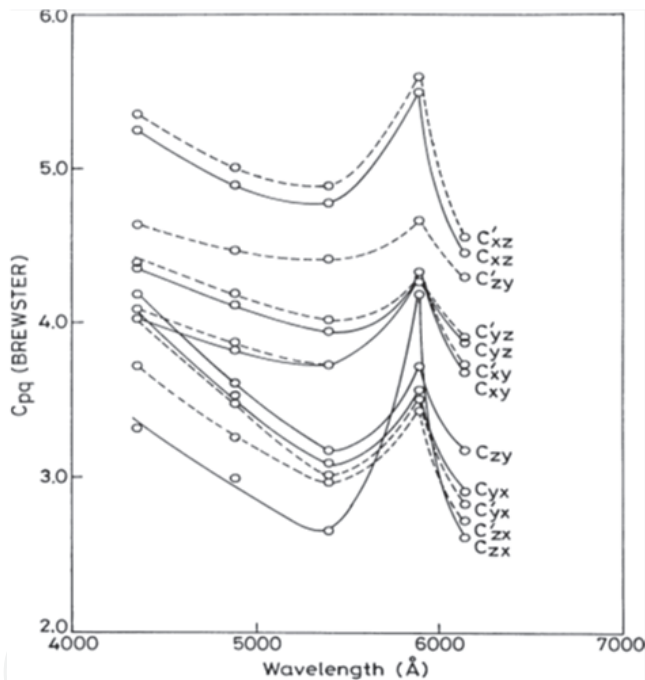
Fig. 5. Stress optical dispersion of $Li_2Ge_7O_{15}$ crystals (un-irradiated and irradiated) with Wavelength at room temperature (298 K).

Irradiation of crystals can change physical properties of the crystals. Irradiation brings about many effects in the crystal such as creating defects, internal stress and electric fields etc. These irradiation effects in turn are supposed to affect the physical properties of the irradiated crystal as compared to un-irradiated crystal. While there was no appreciable change in the lattice parameters, a significant drop in the value of dielectric constant and tan δ was observed upon x-irradiation of ferroelectric glycine phosphate. An appreciable shift in the phase transition temperature towards the lower temperature was observed. These changes are attributed to the defects produced in it by irradiation (Vanishi & Bhat, 2005). The studies of triglycine sulphate (TGS) showed that very small doses of x-irradiation

can give large changes of the ferroelectric properties. The direct evidence of domain clamping by defects was obtained from optical studies. With increasing dosage the dielectric constant peak and polarization curve broaden and move to lower temperatures. In our present studies, the x-irradiation is believed to produce internal stress and electric fields inside the crystals LGO due to defects that can change the values of piezo-optic constants (Lines & Glass, 2004).

2. Dielectric property of lithium heptagermanate crystals

Lithium heptagermanate $Li_2Ge_7O_{15}$ (LGO) belongs to weak ferroelectric crystals and it has a high nonlinearity of dielectric constant ε near T_c. The curie-Weiss law holds only within a narrow temperature interval close to T_c with a small value of the Curie constant. This high nonlinearity may be influenced by the external and internal electric field. The dielectric permittivity has been shown (Wada & Ishibashi, 1983) to be sensitive to sample history, so that reproducible results could be obtained only after a prolonged sample anneal at a temperature substantially above T_c. The nature of such behavior of ε is not clear.

2.1 Space charge effect in $Li_2Ge_7O_{15}$ crystals

An attempt is made to study the dielectric permittivity ε during the phase transition. The plate-like specimens for the electrical measurements were polished and then silver electrodes were deposited. The dielectric constants were measured along the c-axis at the frequency of 1 MHz by means of a LCR meter (E7-12) in the temperature range from 298 K to 273 K (Bain, 1994; Kudzin et. al., 1994, 1995).
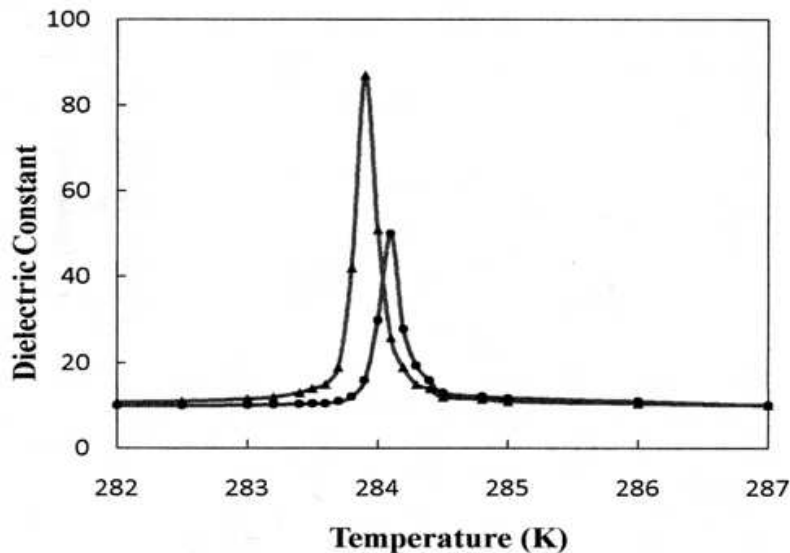

Fig. 6. The temperature dependence of dielectric constant ε of $Li_2Ge_7O_{15}$:0.7%Bi crystal at 1 MHz on cooling (▲) and heating (•) process.

Figure 6 shows the dielectric constant ε of $Li_2Ge_7O_{15}$:0.7% Bi measured on cooling and heating at 1 MHz as a function of temperature. It is found that the dielectric constant shows a sharp peak around T_c. The values at the peak are about 87 at cooling and about 50 at heating. The function ε (T) is represented after the sample heating up to 290 K during about an hour.

Sample	ε_{max}	$\Delta\varepsilon_{max}$	$\Delta\varepsilon_{max}/\varepsilon_{max}$, %
LGO	74.9	19.9	26
LGO: 0.2%Bi	114.1	44.1	38
LGO: 0.3%Bi	120.18	49.73	41
LGO: 0.5%Bi	39.41	9.03	23
LGO: 0.7%Bi	87.19	37.42	42.9
LGO: 0.6%Eu	79.51	27.25	34
LGO: 0.3%Cr	9.86	1.62	16

Table 3. The relative change of $\Delta\varepsilon_{max}/\varepsilon_{max}$ for $Li_2Ge_7O_{15}$ crystals and with different percentage of impurity ions Bi, Eu and Cr.

The Curie-Wess plot of ε of $Li_2Ge_7O_{15}$:0.7%Bi is shown in Figure 7, taking ε_0 as 7.1. It is found that the Curie-Wess law holds only within a narrow temperature region around T_c. The Curie constant is about 2.6 K above the phase transition temperature and 1.3 K below T_c. The characteristic behavior of ε appeared substantially different from the value ε_{max}, which is obtained under the sample heating and cooling. The relative change of $\Delta\varepsilon_{max}/\varepsilon_{max}$ for different percentage of impurity ions are shown in table. 3.

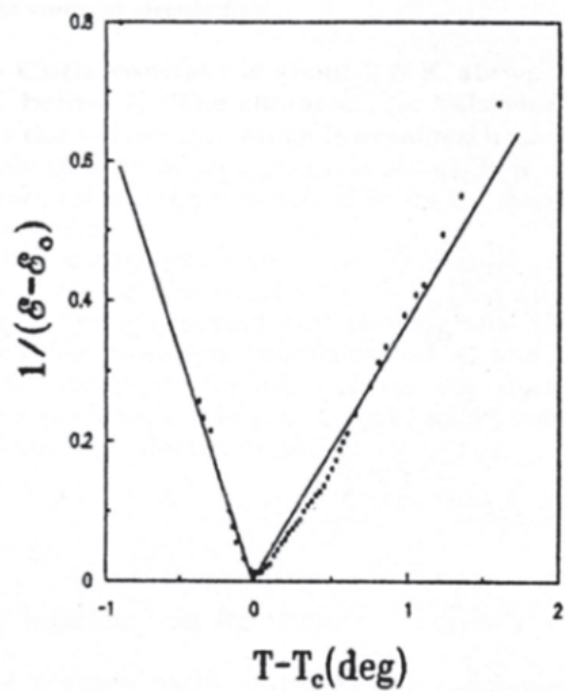Fig. 7. The temperature dependence of reciprocal dielectric constant along the c-axis of $Li_2Ge_7O_{15}$:0.7%Bi on cooling. Solid line shows $\varepsilon - \varepsilon_0 = C(T - T_c)^{-1}$, where $\varepsilon_0 = 7.1$, $T_c = 283.9$ K and C = 2.6 K above T_c, while C = 1.3 K below T_c.

The dielectric constant ε is also measured at the frequency of 1 MHz at a constant electric field. It is observed that the value of ε at T_c decreases with the increase of constant electric field during cooling and heating the sample and it is also observed that the difference between two values of ε decreases at T_c with the increase of constant electric field. Fig.8 shows the dielectric constant ε of $Li_2Ge_7O_{15}$:0.7%Bi measured on cooling at 1 MHz as a function of temperature for different values of constant electric field.

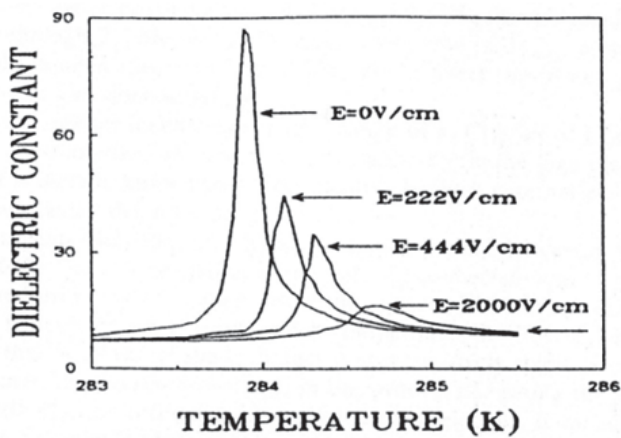Fig. 8. The temperature dependence of dielectric constant ε of Li₂Ge₇O₁₅:0.7%Bi at 1 MHz on cooling for different values of constant electric field.

The spontaneous polarization P_s and the coercive field E_c were studied at 50 Hz by the well known Sawyer-Tower technique. Both P_s and E_c were found to be independent of the Bismuth ion concentration in Li₂Ge₇O₁₅ (within the concentration range investigated). The temperature dependence of P_s for Li₂Ge₇O₁₅:0.7%Bi crystals is shown in Fig.9.
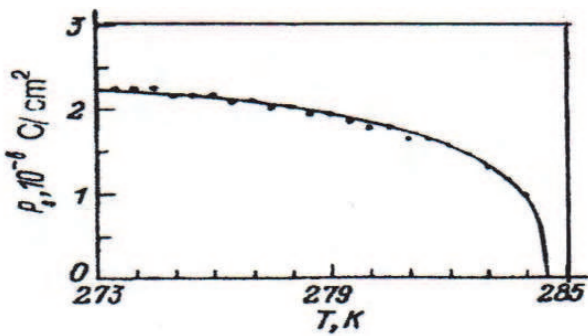
Fig. 9. Temperature dependence of the spontaneous polarization P_s in Li₂Ge₇O₁₅:0.7%Bi crystals.

Under heating, spontaneous polarization first falls off slowly until ~280 K, then faster, and vanishes at T_c, without revealing a noticeable discontinuity. Fig.10 displays the temperature dependence of the coercive field for Li₂Ge₇O₁₅:0.7%Bi crystals. It is seen to fall off linearly under heating up to ~280 K, then faster, to vanish at T_c.
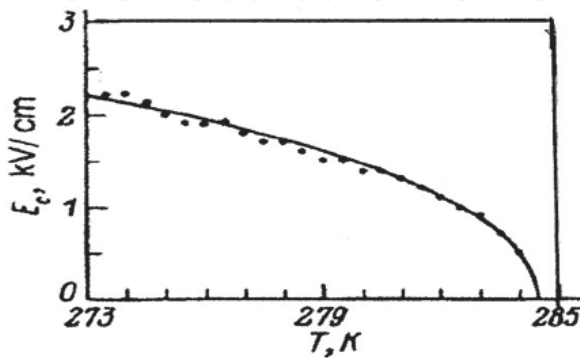
Fig. 10. Temperature dependence of the coercive field E_c in Li₂Ge₇O₁₅:0.7%Bi crystals.

Domain structure may influence on the dielectric permittivity by means of two mechanisms. 1) The crystals that contain many domains are mechanically (piezoelectric) stressed. The relation between dielectric permittivity at the mechanically stressed and at the mechanically free state is given by (Nye, 1957)

$$\varepsilon^{\varepsilon}_3 - \varepsilon^{\sigma}_3 = d^2_{33} c^E_{33} \ (T = \text{Constant}) \tag{2}$$

Here $\varepsilon^{\varepsilon}_3$ is the dielectric permittivity at the mechanically stressed state and ε^{σ}_3 is the dielectric permittivity at the mechanically free state, d_{33} is the piezoelectric modulus, and c^E_{33} is the modulus of elasticity at the constant electric field. This must cause the decrease of ε in multi domain crystals. But the estimation shows that this mechanism does not allow to explain the strong difference in ε_{max} at T_c. 2) The contribution to the dielectric permittivity may give displacements of 180^0 domain boundary (Nakamura et al., 1984). Crystals of LGO become multi domain near T_c during heating the sample. After heating the sample only at 1-2 K above T_c and by subsequent cooling through T_c, one obtains a very small value of $\Delta\varepsilon_{max}$, as crystals of LGO are multi domain. So, basically it does not connect the hysteresis of dielectric permittivity with domain structure.

There is another mechanism of the change of ε. Crystals of LGO have a small spontaneous polarization, which becomes apparent in the high dielectric nonlinearity. It is already known that a comparatively weak external electric field leads to the substantial decrease of ε_{max} (Kholodenko, 1971). Experiments show (Volnyanskii et. al., 1992) that the crystals of LGO are monodomain at the temperature $T_c - 10$ K. The compensation of the field E_p connected with P_s may take place by the redistribution of charges inside the crystals. These space charges create an electric field inside the crystals, which compensates the field E_p. It is possible to assume that this field of space charges is comparatively stable (electret state). In such a case, the decrement of ε_{max} in the process of heating the sample may be connected with the influence of internal field of electret. If we suppose that the effects of external and internal electric field are the same, then the field of electret is ~ 160 V/cm.

Consecutive heating and cooling of a sample from the temperatures 293, 289.25, 285.5 and 284.5 K shows the value of ε_{max} to decrease successively in the cooling runs while remaining constant during heating. This supports the existence of an internal electric field in the sample during the heating process.
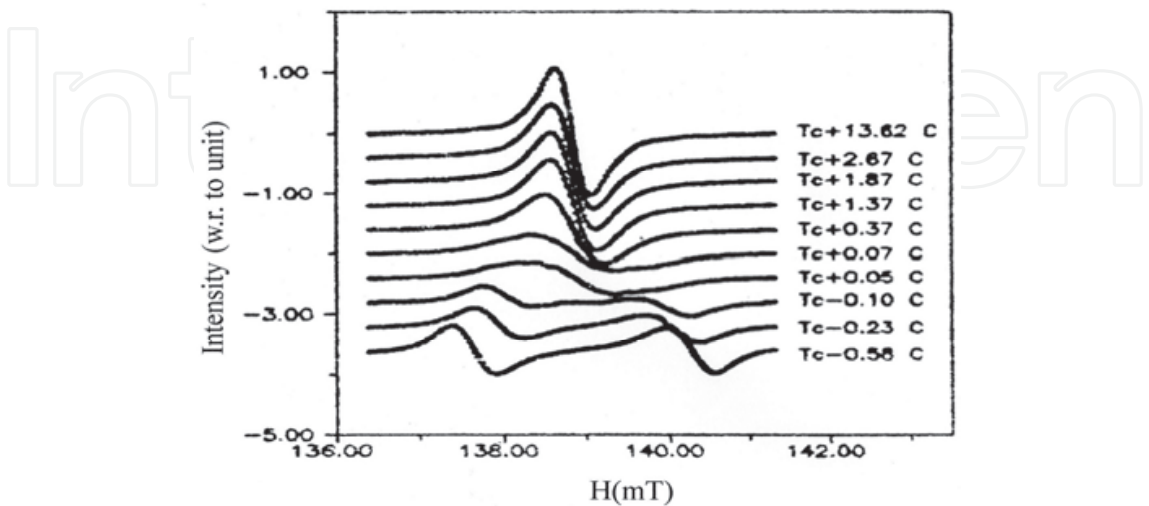

Fig. 11. Temperature dependence of EPR lines of $Li_2Ge_7O_{15}:Cr^{+3}$ crystals for $|M| = \frac{1}{2} \leftrightarrow 3/2$, $H\|a$, $H\perp c$ near T_c during cooling process.

The EPR (Electron Paramagnetic Resonance) spectroscopy of the transition metal ion doped crystals of LGO (Mn^{2+}, Cr^{3+}) has also been studied both in Paraelectric (PE) and ferroelectric (FE) phases in the temperature interval from 298 K to 279 K during cooling and heating cycles (Trubitsyn et. al., 1992; Bain, 1994). It is observed that on approaching T_c in a cooling cycle, the EPR lines are slightly shifted to the high field direction and undergo substantial broadening. At the temperature T_c ($\approx$ 283.4 K), the EPR lines are splitted into two components which are shifted to the higher and lower field directions progressively as a result of cooling the sample below T_c as shown in Fig.11.

During heating cycle (i.e. approaching T_c from below), the phenomena occurred were just opposite to the above processes observed in the cooling cycle. However, the EPR line width (peak to peak ΔH_{pp}) for H∥c, H⊥a was found to decrease to about one third of its value at T_c in a heating cycle as compared to its value in the cooling cycle. The shape of the EPR resonance lines far from T_c has a dominant Lorentzian character (a Lorentzian line shape) but very near to T_c, the line shape has been described mainly by Gaussian form of distribution (a Gaussian line shape). All the peculiarities observed are attributed to the PE ↔ FE phase transition of the LGO crystals. The line width reduction near T_c is attributed to the internal space charge (electret state) effects which produce an internal electric field inside the crystals on heating process from the ferroelectric phase. This observation is similar to the dielectric hysteresis behavior of the crystals LGO near T_c.

2.2 Study of impedance in $Li_2Ge_7O_{15}$ crystals

The temperature dependence of a.c. electrical impedance (Z) was studied along the c-axis in ferroelectric $Li_2Ge_7O_{15}$ (LGO) single crystals in 10 kHz – 10,000 kHz frequency range by means of impedance analyzer (Agilent HP4294A) in the temperature interval from 298 K to 273 K during cooling and heating process including T_c = 283.5 K is shown in Fig 12 (Bain et. al., "in print"). A rather temperature hysteresis of impedance is observed in a cooling and heating cycle at T_c = 283.5 K. The relative change of $\Delta|Z|_{(min)}/|Z|_{(min)}$ at the frequencies 100 kHz – 10,000 kHz is shown in Table 4. The relative change of $\Delta|Z|_{(min)}/|Z|_{(min)}$ is about 26% and it remains almost constant at the frequencies 100 kHz – 10,000 kHz. Here the value of $|Z|_{(min)} = |Z|_{room} - [|Z|_{Tc}$ (on cooling)] and $\Delta|Z|_{(min)} = [|Z|_{Tc}$ (on heating)] – [$|Z|_{Tc}$ (on cooling)].

Frequency (kHz)	$\|Z\|_{(min)}$ (K-Ω)	$\Delta\|Z\|_{(min)}$ (K-Ω)	$\Delta\|Z\|_{(min)}/\|Z\|_{(min)}$, %
100	3.895	0.97	25.0
200	2.275	0.6	26.4
500	0.374	0.1	26.5
1,000	0.229	0.06	26.2
10,000	0.0224	0.0056	25.0

Table 4. The relative change of $\Delta|Z|_{(min)}/|Z|_{(min)}$ for $Li_2Ge_7O_{15}$ crystal at different frequencies.

Like Fig.12, a similar kind of hysteresis was observed in the dielectric behavior of LGO, as described in section 2.1 and the appearance of the dielectric hysteresis is attributed to the internal space charge (electret state) effects which produce an internal electric field in LGO on heating from the ferroelectric phase. It was possible to compensate the internal electric field effects in dielectric measurements by an external electric field (Kudzin et al., 1994, 1995; Bain, 1994). It is suspected that the impedance (Z) hysteresis also occurs due to similar effects.

The frequency dependence of $|Z|$ of the crystal LGO was studied in the temperature range 283.5 K to 573 K, which covers the phase transition temperature (T_c) of 283.5 K as shown in Fig.13. It is observed that the magnitude of $|Z|$ decreases sharply with increasing of frequency and tends to zero value at about the frequency of 10,000 kHz. This may be due to the release of space charges. The curves also display single relaxation process and indicate an increase in a.c. conductivity with frequency. So, in the application point of view, LGO is suitable for conductivity even at the room temperature and frequency controlled switch.
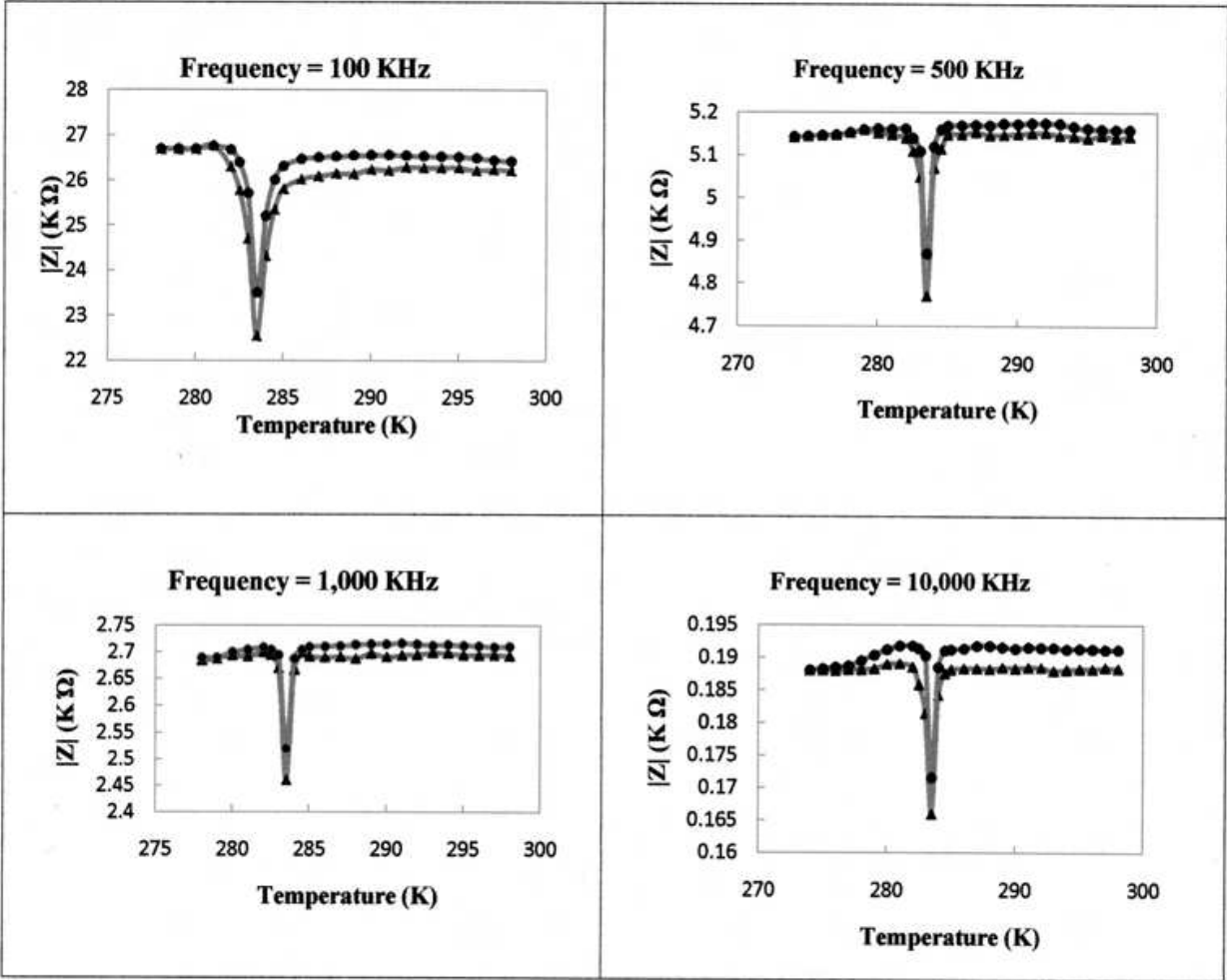

Fig. 12. The temperature dependence of a.c. impedance ($|Z|$) of $Li_2Ge_7O_{15}$ at 100 kHz, 500 kHz, 1,000 kHz and 10,000 kHz on cooling(▲) and heating(•) processes.

Fig.14 shows the temperature dependence of impedance |Z| of the crystal LGO at frequency range 100 kHz – 10,000 kHz. It is observed that the value of impedance |Z| decreases gradually with increasing temperature. This may be related with the space charge relaxation at low frequencies.

At low temperatures the conductivity is dominated by short range hopping of charge carriers. Whereas at high temperatures, more space charges are accumulated at the electrode interfaces and grain boundaries, thus resulting in a strong space charge relaxation (Kim et al., 2002; James et al., 1999).
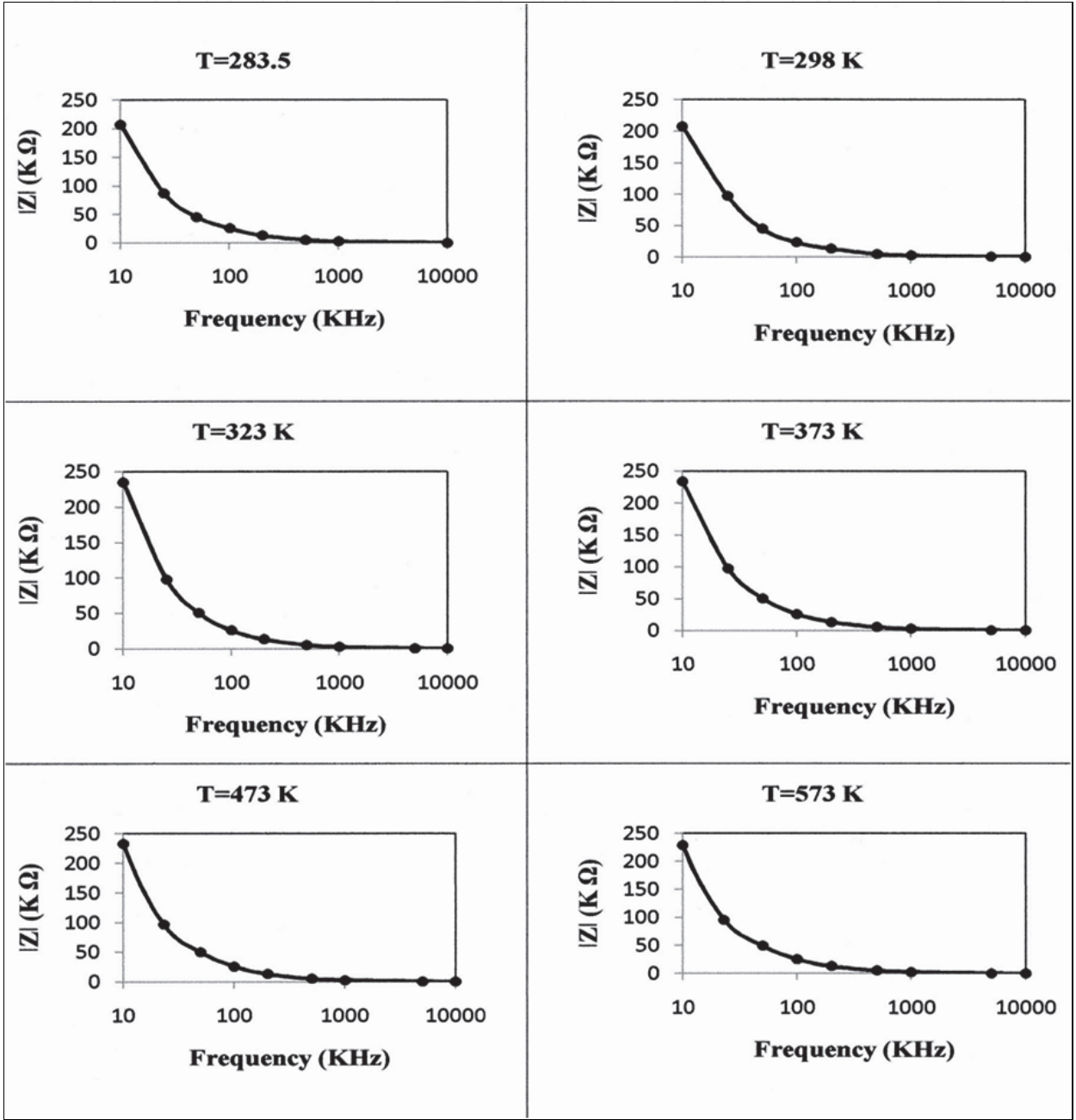
Fig. 13. The frequency dependence of impedance (|Z|) of $Li_2Ge_7O_{15}$ crystal at the temperature range 283.5 K to 573 K.

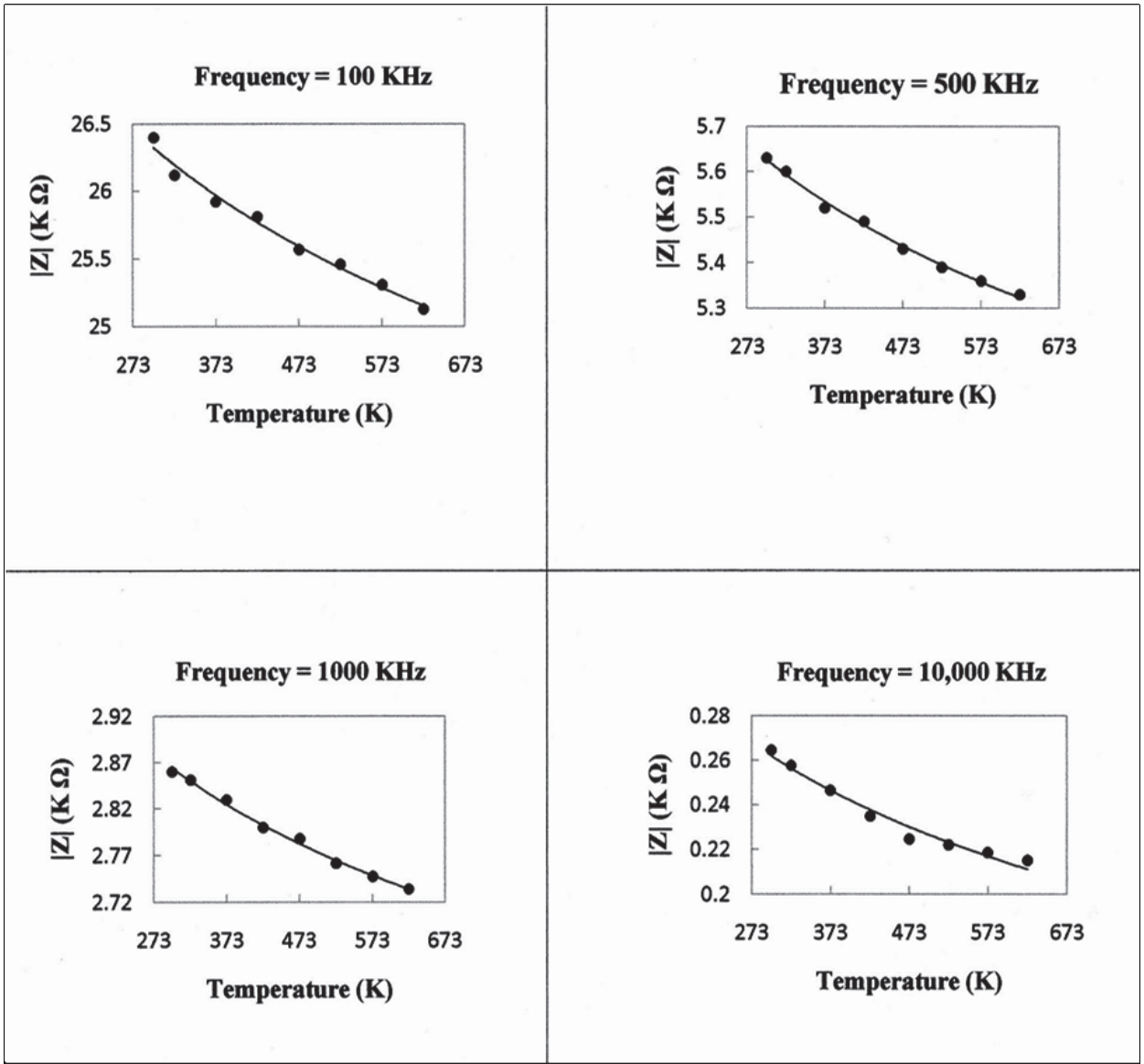Fig. 14. Temperature dependence of impedance (|Z|) of $Li_2Ge_7O_{15}$ crystal at Frequency range 100 kHz – 10,000 kHz.

3. Piezo-optic birefringence in $Li_2Ge_7O_{15}$ crystals

The temperature dependence of the photoelastic coefficients of the ferroelectric crystals $Li_2Ge_7O_{15}$ in a cooling and heating cycle between 298 K and 273 K was carried out with the experimental procedure described in section 1.4 (Bain et. al., 2009). A special arrangement was made to vary the temperature of the sample. The temperature was recorded with a digital temperature indicator and a thermocouple sensor in contact with the sample.

The temperature dependence of piezo-optic coefficients C_{pq} of the crystals $Li_2Ge_7O_{15}$ between 298 K and 273 K were determined and are shown in Fig. 15 and Fig. 16. The values of C_{pq} at 291 K and 278 K were reported in paper (Bain et.al., 1998) and it was observed that there were large changes in the values of C_{zy} and C_{yz} at 278 K and 291 K as compared to other components and C_{zy} did not show a peak in its temperature dependence between 291K and 278 K.
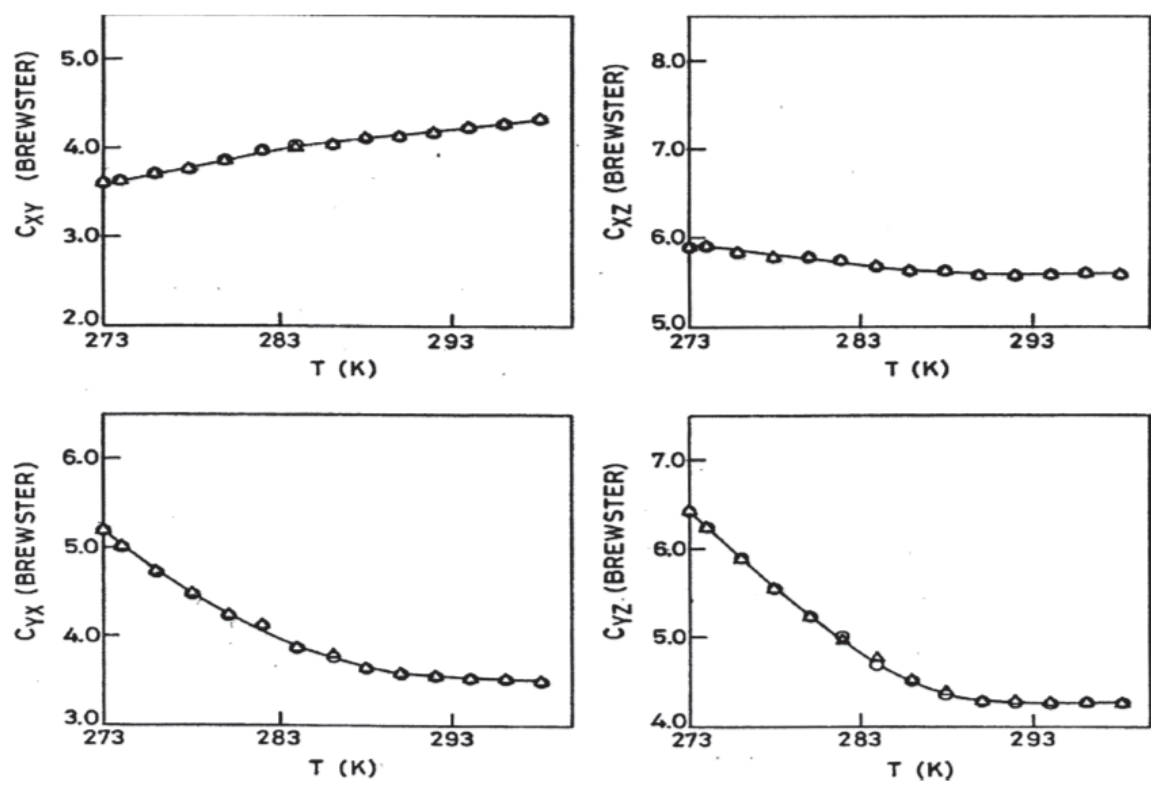
Fig. 15. Temperature dependence of the piezo-optic coefficients C_{xy}, C_{xz}, C_{yz} and C_{yx} of the crystals LGO in a cooling (0) and heating (Δ) cycle.
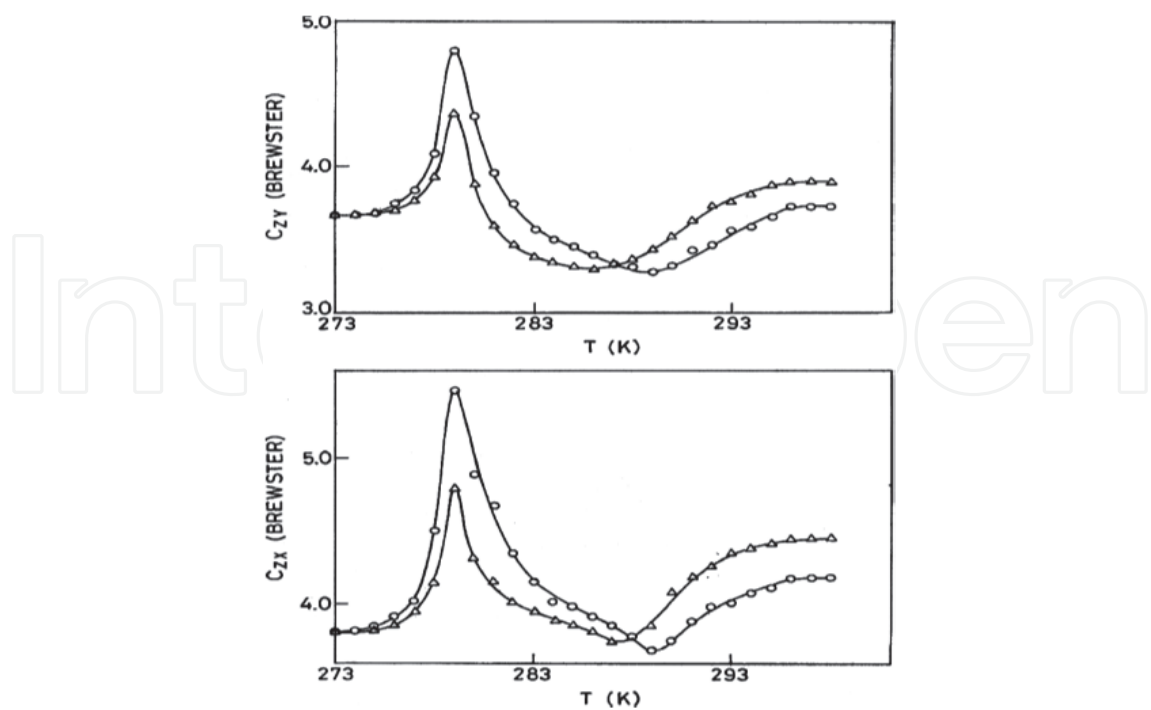

Fig. 16. Anomalous temperature dependence of the piezo-optic coefficients C_{zx} and C_{zy} of the crystals LGO in a cooling (0) and heating (Δ) cycle.

Here in contrast we observed a peak in the temperature dependence of both C_{zy} and C_{zx} at 279 K. The temperature dependence of C_{pq} are quite interesting, for example the piezo-optic coefficients C_{yz}, C_{yx} and C_{xz} have negative temperature derivatives but C_{xy} has a positive temperature derivative. In complete contrast both C_{zy} and C_{zx} have both positive and negative temperature derivatives at different temperature intervals between 298 K and 273 K (Table: 5). Besides a clear thermal hysteresis is observed in C_{zy} and C_{zx} in a complete cooling and heating cycle (Fig. 16) whereas no discernible hysteresis is observed in rest of the piezo-optic coefficients (Fig. 15). The two distinct anomalies in the temperature dependence of C_{zy} and C_{zx} are characterized by a valley at T_m (~289 K) and a peak at T_c (~279 K). Anomalous temperature dependence of C_{zx} at different wave lengths is also shown in Fig. 17. The temperature dependence of the dielectric permittivity along the c-axis of LGO shows a sharp peak at T_c (283.5 K) and the Curie-Weiss law holds only for a narrow range of temperature ($T_c \pm 4$ K) (Wada & Ishibashi, 1983; Kudzin et al., 1994, 1995) as shown in Fig. 6 and Fig. 7. The peak for piezo-optic coefficient is attributed to the paraelectric to ferroelectric phase transition of LGO at T_c. To check the curie-Weiss law like dependence near T_c the following relation is used.

$$C^T_{pq} - C^0_{pq} = K_{pq}/(T - T_c) \tag{3}$$

Where C^T_{pq} and C^0_{pq} denote the value of the corresponding piezo-optic coefficients at temperature T and 273 K respectively and K_{pq} is a constant. Figure 18 shows the $(C^T_{pq} - C^0_{pq})^{-1}$ vs $(T-T_c)$ curve for C_{zx} and C_{zy}. It is clear from these curves that like dielectric constant the relation fits well only within a narrow range of temperature near T_c($T_c\pm 4$ K). The solid lines denote the theoretical curves with the following values.

$$K_{zx} = 1.05; \qquad K_{zy} = 0.92 \qquad \text{for } T > T_c$$

$$K_{zx} = -0.40; \qquad K_{zy} = -0.34 \qquad \text{for } T < T_c$$

$$T_c = 279 \text{ K}$$

Further more the magnitudes of the ratio of the temperature derivatives below and above T_m and T_c are given in Table 5 and we can see that the ratio near T_c comes out to be about 2. Therefore it satisfies the law of two for the ratio of such derivatives of quantities which are coupled with the spontaneous polarization in second order ferroelectric phase transition such as in the case of triglycine sulphate (Haussuhl & Albers, 1977) and LGO. Therefore the peak around T_c is (Kaminsky & Haussühl, 1990; Kudzin et al., 1994, 1995) attributed to the paraelectric to ferroelectric phase transition of LGO. The smallness of K_{pq} and the applicability of relation (3) above only in a narrow range of temperature suggest that LGO may be an improper ferroelectric. The law of two does not hold for the ratio at T_m (Table 5). Therefore this anomaly is not related to the spontaneous polarization.

From the behaviour that only C_{zx} and C_{zy} show anomalous it is obvious that birefringence $(\Delta n_z - \Delta n_y)$ and $(\Delta n_z - \Delta n_x)$ show steep increase around T_c and below T_c show a $(T - T_c)^{1/2}$ behaviour correlated to the spontaneous polarization which is parallel to the z-axis (crystallographic c-axis). From the behaviour of C_{xy} and C_{yx} which do not show any temperature anomaly we may say that only n_z is responsible for the anomaly in accordance with the behaviour of the dielectric properties where only ε_{33} is strongly affected by the phase transition. These observations are in accordance with the results of Faraday effect and birefringence in LGO (Kaminsky & Haussühl, 1990).

C_{pq}	Value of Derivative (Brewster/K)	Temperature Range	Ratio
C_{zx}	0.013 -0.022 -0.090 0.181 ~0	296K-289K 289K-283K 282K-279K 279K-276K 276K-273K	-1.69 -2.0
C_{xz}	-0.003	293K-273K	
C_{zy}	0.020 -0.015 -0.095 0.179 ~0	296K-289K 289K-283K 282K-279K 279K-276K 276K-273K	-0.75 -1.9
C_{yz}	-0.026	293K-273K	
C_{xy}	0.007	293K-273K	
C_{yz}	-0.023	293K-273K	

Table 5. The temperature derivative [$dl_n C_{pq}/dT$] of the piezo-optic coefficients of $Li_2Ge_7O_{15}$.
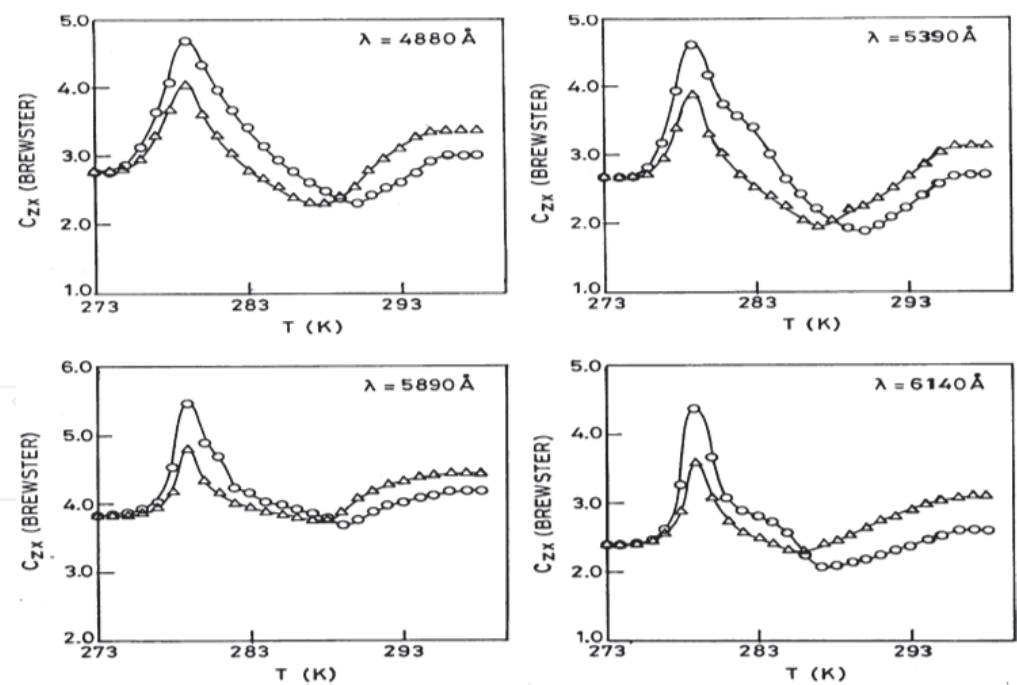
Fig. 17. Anomalous temperature dependence of piezo-optic coefficient C_{zx} of the crystals LGO at different wave lengths in a cooling (0) and heating (Δ) cycle.

As mentioned by Lines and Glass (Lines & Glass, 2004), under an external pressure T_c of a ferroelectric phase transition may be shifted. This shift may be to the higher or the lower side of normal T_c. Wada et al. (Wada et al., 1981) studied the pressure effect on the

ferroelectric phase transition in LGO through the dielectric and Raman scattering measurements and found a positive pressure coefficient dT_c/dp = 14.6 K/kbar. Preu and Haussühl (Preu and Haussühl, 1982) studied the dependences of dielectric constants on hydrostatic and uniaxial pressure as well as temperature. They observed a shift of T_c at a rate of 14.02 K/kbar for the hydrostatic pressure and ~7 K/kbar for the uniaxial pressure. In the present case the position of the peak of C_{zy} is found to depend on the stress applied. If the peak position is believed to represent the T_c, it appears to shift to the lower side under the uniaxial stress. To see whether T_c shifts linearly with uniaxial stress similar to the earlier observations (Preu and Haussühl, 1982; Wada et al., 1981), we used different stresses within the elastic limits of LGO for C_{zx} and found a linear relationship (Fig. 19). However, a negative stress coefficient dT_c/dp ~−22 K/kbar is obtained in this case which agrees only in magnitude with the hydrostatic pressure coefficient. The linear curve (Fig. 19) extrapolates to a T_c = 281.5 K in the unstressed state instead of 283.5K as determined by dielectric measurements (Wada & Ishibashi, 1983; Kudzin et al., 1994, 1995). This may be due to a non linear dependence of shift of T_c under stress near 283.5 K.

Now we turn to the anomaly around T_m. Morioka et al. (Morioka et al., 1988) proposed that there is an interaction between the soft phonon mode and a relaxational mode in the paraelectric phase in the temperature interval 300 K to T_c. The critical slowing down of the relaxational mode near T_c is expected to cause the increase of the fluctuation of the spatially homogeneous polarization and thereby the increase of the fluctuation of the hyperpolarizability with k_c = 0. Wada et al. (Wada et al., 1991) measured the soft phonon mode with the help of their newly designed FR-IR spectrometer and proposed that as T_c is approached from above soft phonon mode becomes over damped and transforms to a relaxational mode.
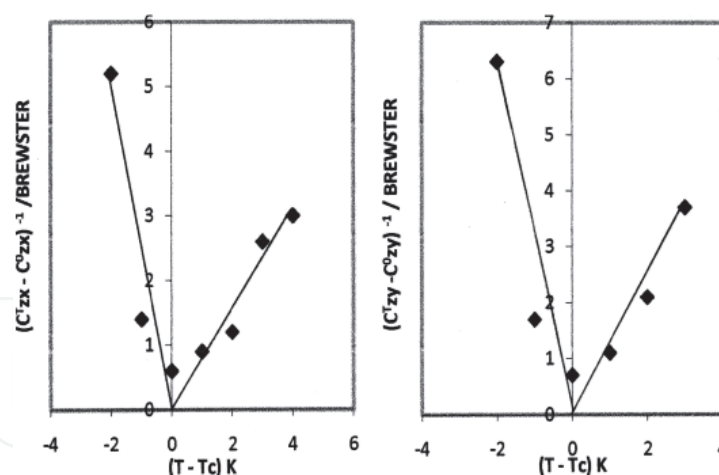

Fig. 18. Plots of $(C^T_{pq} - C^o_{pq})^{-1}$ vs $(T-T_c)$ curve for C_{zx} and C_{zy}.

On the other hand there may exist a relaxational mode with an independent degree of freedom as well as the soft phonon mode and the character of the softening transfers from the phonon to the relaxational mode. This is an important problem in determining the dynamics of the peculiar ferroelectric phase transition of LGO, where both the dielectric critical slowing down characteristic of the order-disorder phase transition and the soft phonon mode characteristic of the displacive phase transition are observed (Wada & Ishibashi, 1983; Haussühl et al., 1980). In the light of the above discussion we may say that the change up to T_m is caused by the softening of mode and the softening character

transforms to the relaxations mode near T_m causing a change in the trend below T_m and near T_c the relaxational mode becomes dominant. The valley around T_m is perhaps caused by the interplay between the competitive relaxational mode and the soft phonon mode. It has been observed that softening of the velocity and rise of the damping of acoustic phonon occur in the paraelectric phase of LGO even quite far from T_c, i.e.($T-T_c$) ~ 30 K and the effect is attributed to the fluctuation induced contributions (Sinii et al., 1990).
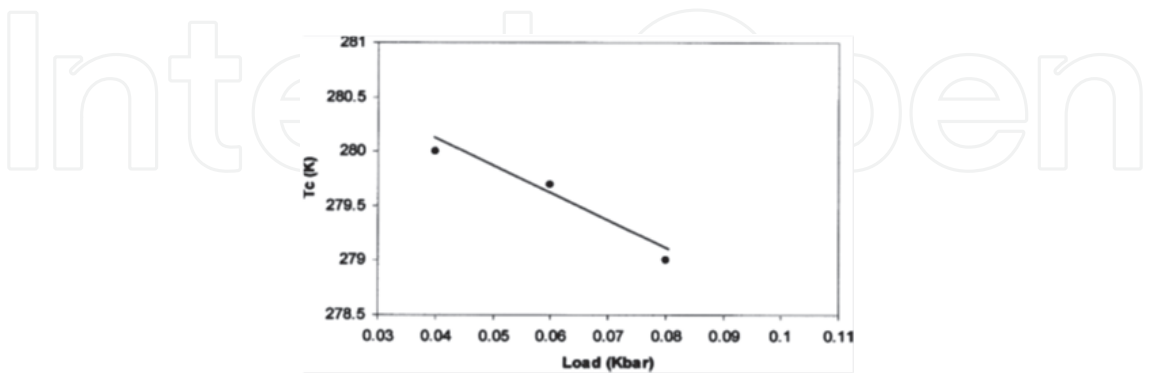
Fig. 19. The stress dependence of the shift of T_c for C_{zx}.

Another interesting aspect is the observation of a significant thermal photoelastic hysteresis (Fig. 16). Although the peak position does not shift in the heating cycle the values of the photoelastic constants get reduced significantly in the heating cycle as compared to the corresponding values in a cooling cycle. A similar kind of hysteresis was observed in the dielectric behaviour of LGO (Kudzin et al., 1994, 1995; Bain, 1994) and the appearance of the dielectric hysteresis is attributed to the internal space charge (electrets state) effects which produce an internal electric field in LGO on heating from the ferroelectric phase as described in section 2.1. It was possible to compensate the internal electric field effects in dielectric measurements by an external electric field (Kudzin et al., 1994, 1995; Bain, 1994). It is suspected that the photoelastic hysteresis also occurs due to similar effects. Although it was not possible to try to compensate the electric field effects in the present investigation, it is possible to attempt experiment under the simultaneous application of a suitable electric field and stress along z-direction.

Obs.	C_{pq}	Paraelectric (PE)	At T_c = 279 K phase (RT)
1	C_{xy}	4.38	3.85
2	C_{xz}	5.55	5.85
3	C_{yx}	3.60	4.46
4	C_{yz}	4.26	5.50
5	C_{zy}	3.71	4.83
6	C_{zx}	4.19	5.45

Table 6. Stress optical coefficients c_{pq} (in brewsters) of $Li_2Ge_7O_{15}$ at RT=298 K and at T_c = 279 K.

The Stress optical coefficients C_{pq} of the crystals $Li_2Ge_7O_{15}$ at paraelectric phase (RT = 298 K) and at T_c = 279 K are presented in Table 6. It is important to compare the values of C_{pq} for $Li_2Ge_7O_{15}$ with other ferroelectric crystals given in Table 7 particularly with Rochelle-salt (RS) which belongs to the orthorhombic class like LGO (Bain et.al., 1998).

Obs	C_{pq}	Rochelle Salt (RS)	KDP	ADP	Remarks
1	C_{xz}	3.74	0.28	1.25	Ref. [9] for RS
2	C_{yz}	4.29	0.28	1.25	a- polar axis
3	C_{yx}	3.56	1.04	4.30	Ref. [26] for KDP
4	C_{zx}	0.85	1.54	3.50	Ref. [27] for ADP
5	C_{zy}	2.61	1.54	3.50	
6	C_{xy}	3.04	1.04	4.30	

Table 7. Piezo-optic coefficients c_{pq} (in Brewsters) for some ferroelectric crystals in their paraelectric (PE) phases.

The values of C_{pq} are significantly higher for LGO as compared to these ferroelectric systems. So, the large photoelastic coefficients and the other properties like good mechanical strength, a transition temperature close to room temperature and stability in ambient environment favour LGO as a potential candidate for photoelastic applications.

4. Irradiation effect on photoelastic coefficients in $Li_2Ge_7O_{15}$ crystals

The photoelastic coefficients C_{pq} of the ferroelectric crystals $Li_2Ge_7O_{15}$ (x-irradiated) in a cooling and heating cycle between 298 K and 273 K was carried out with the experimental procedure described in section 1.4 and are shown in Fig. 20 (Bain et.al., "in print"). The results show an interesting photoelastic behaviour.
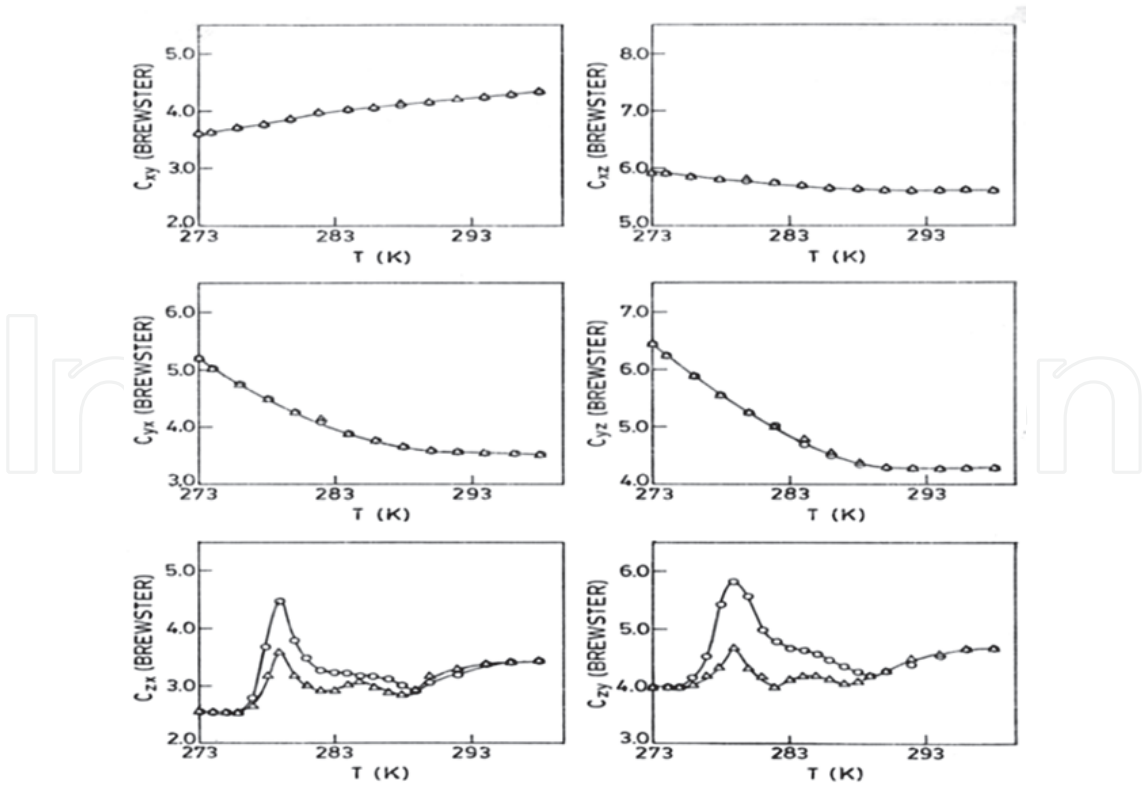

Fig. 20. Temperature dependence of photoelastic coefficients C_{xy}, C_{xz}, C_{yz}, C_{yx}, C_{zx} and C_{zy} of the crystal (x-irradiated) LGO in a cooling (0) and heating (Δ) cycle.

Peaks are observed in the temperature dependence of the photoelastic coefficients C_{zy} and C_{zx} at temperature ~ 279 K in a complete cooling and heating cycle whereas no discernible hysteresis is observed in rest of the photoelastic coefficients. Anomalous temperature dependence of C_{zx} of the crystal (x-irradiated) LGO at different wave lengths are shown in Fig.21.

It is observed that the peak value of C_{zy} has increased about 25% and that of C_{zx} has decreased about 18% at the wave length λ=5890 Å during cooling process of the crystal (Fig.16 and Fig.20). The peak value of C_{zx} of the crystal (un-irradiated and x-irradiated) LGO thus obtained at different wave lengths (Fig.17 and Fig.21) are given in Table 8 and the results are plotted in Fig.22.
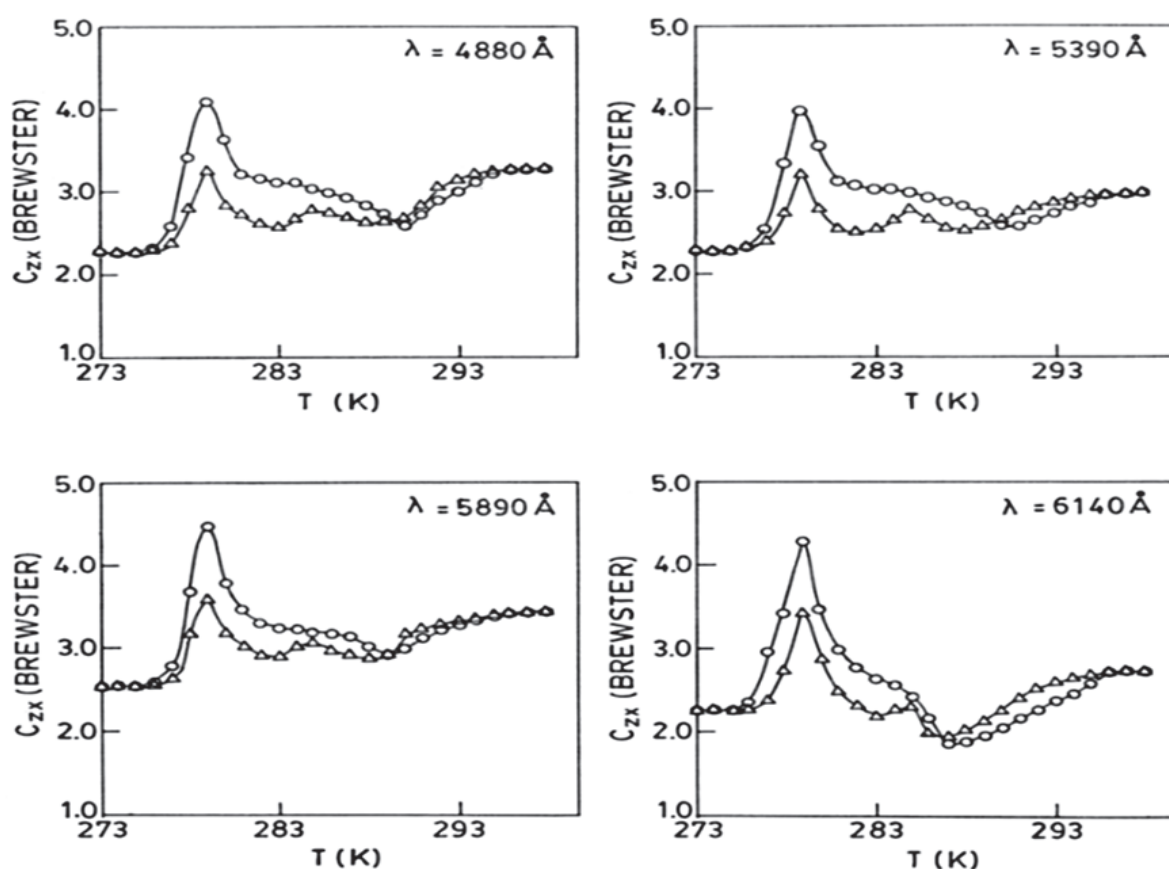
Fig. 21. Temperature dependence of photoelastic coefficient C_{zx} of the crystal (x-irradiated) LGO at different wave lengths in a cooling (0) and heating (Δ) cycle.

It has been observed that the changes in the value of photoelastic coefficients C_{zy} and C_{zx} of the crystal (x-irradiated) LGO in a cooling and heating cycle occur only if the crystal is stressed along the polar axis (c-axis). It is known that the irradiation of crystals can change physical properties of the crystals.

Irradiation brings about many effects in the crystal such as creating defects, internal stress and electric fields etc (Lines & Glass, 2004). In our present studies, the x-irradiation is believed to produce internal stress and electric fields inside the crystals $Li_2Ge_7O_{15}$ due to defects that can change the values of photoelastic coefficients.

Wave lengths (Å)	C_{zx} (un-irradiated)		C_{zx} (x-irradiated)	
	Cooling	Heating	Cooling	Heating
4880	4.8	4.0	4.05	3.3
5390	4.7	3.9	3.95	3.2
5890	5.6	4.8	4.6	3.7
6140	4.5	3.6	4.3	3.4

Table 8. The peak value of C_{zx} (in Brewster) for the Crystal (un-irradiated and x-irradiated) LGO at different wave lengths in the cooling and heating cycles.
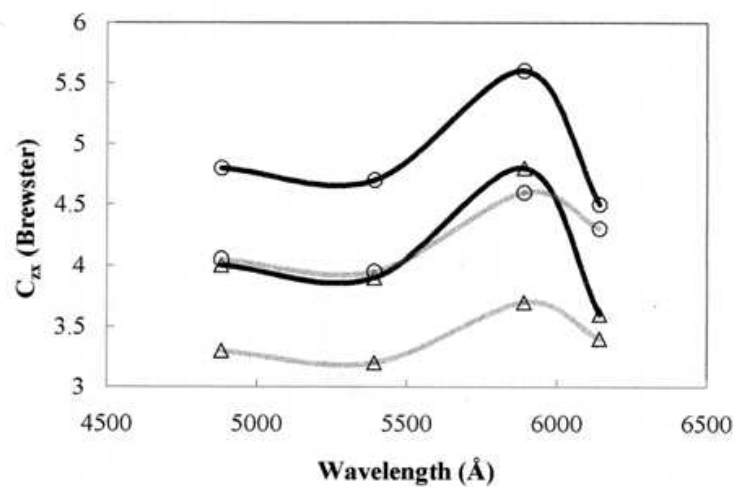

Fig. 22. The peak value of C_{zx} for the un-irradiated (black colour) and x-irradiated (ash colour) crystal LGO at different wave lengths in a cooling (0) and heating (Δ) cycle.

5. Summary

It is known that the high optical quality, good mechanical strength and stability in ambient environment, large photoelastic coefficients in comparison with other ferroelectric crystals like Rochelle-salt, KDP and ADP favors the crystals LGO as a potential candidate for photoelastic applications.

The piezo-optic dispersion of the crystals (un-irradiated and x-irradiated) LGO in the visible region of the spectrum of light at room temperature (298 K) have been described in section 1.4 and 1.5. It shows an "optical zone or optical window" in between 5400 Å and 6200 Å with an enhanced piezo-optical behavior. This peculiar optical window can have a technical importance. This window region can act as an optical switch for acousto-optical devices. From the studies undertaken it may be concluded that LGO is an attractive acousto-optic material which deserves further probe. It may be possible to understand the observed behavior if extensive piezo-optic and refractive index data become available over an extended range of wavelengths.

It has been observed in section 2.2 that the value of impedance of the crystals LGO decreases sharply with increasing frequency and tends to zero value at about the frequency 10,000 kHz. So, in the application point of view, LGO is also suitable for conductivity even at room temperature and frequency controlled switch.

The temperature dependence of the photoelastic coefficients of the crystals (un-irradiated and x-irradiated) LGO in a cooling and heating cycle between room temperature (298 K) and

273 K have been studied in section 3 and 4. It shows an interesting observation including the lowering of the T_c under uniaxial stress contrary to the increase of T_c under hydrostatic pressure and observation of thermal photoelastic hysteresis similar to dielectric hysteresis behavior. In our studies, the x-irradiation is believed to produce internal stress and electric fields inside the crystals LGO due to defects that can change the values of photoelastic coefficients, as described in section 1.5 and 4.

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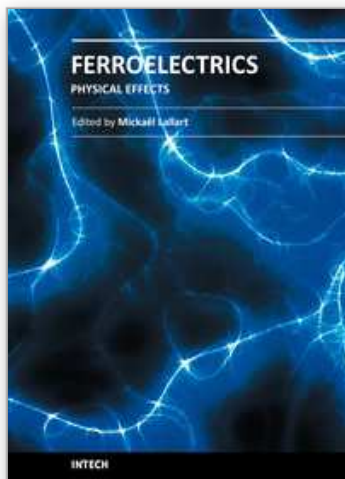
Ferroelectrics - Physical Effects

Edited by Dr. Mickaël Lallart

Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on the underlying mechanisms of ferroelectric materials, including general ferroelectric effect, piezoelectricity, optical properties, and multiferroic and magnetoelectric devices. The aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric systems, allowing a deep understanding of the physical aspect of ferroelectricity.

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