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Dielectric properties and optical absorption of X-ray irradiated KD_2PO_4

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The effects of X-ray irradiation on the dielectric constant (K) and loss ($\tan \delta$) in the frequency range 10^2 to 3×10^5 Hz, temperature range 30 to 105° C, and on optical absorption, have been studied. All these parameters are found to be decreased considerably with increasing doses of X-ray irradiation. The effects of irradiation on these parameters for KD_2PO_4 crystals are found to be greater than those of KH_2PO_4.

1. Introduction

Potassium dihydrogen phosphate KH_2PO_4 (KDP) and its deuterated crystals KD_2PO_4 (DKDP) are prototypes of an important class of H-bonded ferroelectrics [1]. In the high-temperature paraelectric phase, these crystals are isomorphous. It is observed that KDP shows remarkable dielectric dispersion [1, 2] associated with the domain wall motion below the Curie temperature. Recently, a new dielectric dispersion in KDP below 10 K has been observed, where the contribution of the domain wall motion to the dielectric constant [3] is considered to be in 'freezing'. Unusually large isotope effects on the transition temperature [4] and saturated spontaneous polarization of KDP [5, 6] have been observed. Remarkable variation in electrical and optical properties [7–9] in most of the H-bonded ferroelectrics has been observed due to impurities and radiation damage. Excitation of this type of material with moderately strong ionizing radiation (X-rays or γ-rays) affects both surface and bulk properties of the materials. This irradiation effect can change the contribution of space charge layers as a whole on the surface of the crystal, which reflects the deformation of the surrounding volume and modification of the local field. Here we report the effect of X-ray irradiation on the dielectric and optical properties of DKDP in the paraelectric phase.

2. Experimental procedures

DKDP crystals were grown by slow evaporation of a supersaturated solution of KDP and heavy water (99.4%, supplied by the Heavy Water Division, B.A.R.C., Bombay). The quality and deuteration level of the crystals were improved by recrystallizing from D_2O, and analysed by high-power polarising microscope and X-ray diffraction techniques. Crystals were cut perpendicular to the c-axis and silver paint was applied on either side of the sample for electrodes. The dielectric constant (K) and loss ($\tan \delta$) measurements were carried out on a GR 716 capacitance bridge in the frequency range 10^2 to 3×10^5 Hz and in the temperature region 30 to 110° C. The estimated accuracy of the measurements in K was found to be 2% and 4% in $\tan \delta$. The optical absorption measurements were taken at room temperature using a Beckman-26 spectrophotometer in the wavelength region 200 to 800 nm where the optical absorption coefficient α, could be measured to an accuracy of 0.05 cm^{-1}. A Philips X-ray tube running at 30 kV and 10 mA was used for X-ray irradiation for the time stated at room temperature (30° C) on either side of the sample, keeping it at a distance of 1 cm from the copper target window of the X-ray tube.

3. Results

Fig. 1 gives the variation of K and $\tan \delta$ as a function of frequency at 25° C ($\pm$ 1). The maximum value of K at 10^2 Hz for the as-cleaved crystal is 188. All the higher doses of X-ray irradiation decreased the K value considerably. The value of K for 1 and 2 h of X-ray irradiation at 1×10^2 Hz are 162 and 138, respectively. K becomes frequency independent beyond 10^4 Hz · $\tan \delta$ of as-cleaved crystal, was found to decrease from 10^2 to 10^4 Hz, and then takes a constant value beyond 10^5 Hz. The value of $\tan \delta$ at 10^5 Hz for 1 and 2 h of X-ray irradiated DKDP are 7.3×10^{-3} and 3.5×10^{-3}, respectively. X-ray irradiation has decreased the $\tan \delta$ value (Fig. 2).

Variations of K and $\tan \delta$ as a function of temperature are shown in Figs 2 and 3. The value of K (for a particular frequency) is temperature independent up to 75° C and then slowly rises relative to higher values. X-ray irradiation has decreased the K value considerably. The value of $\tan \delta$ has increased from room temperature to high temperature. X-ray irradiation has also decreased the loss values and becomes frequency dependent. The value of $\tan \delta$ at 75° C for 10^2, 10^3 and 10^4 Hz for as-cleaved DKDP crystals are 7.5×10^{-1}, 2.0×10^{-1} and 3.6×10^{-2}, respectively. After 2 h of X-ray irradiation at the above frequencies $\tan \delta$ decreased, and the values become 2.0×10^{-1}, 1.5×10^{-2} and 5.3×10^{-3}, respectively. Comparative data on KDP and DKDP for K and $\tan \delta$ at various conditions are given in Table I. It is observed that the values of K and $\tan \delta$ are always more in case of DKDP crystals.

Fig. 4 presents the variation of α as a function of wavelength for as-cleaved and X-ray-irradiated

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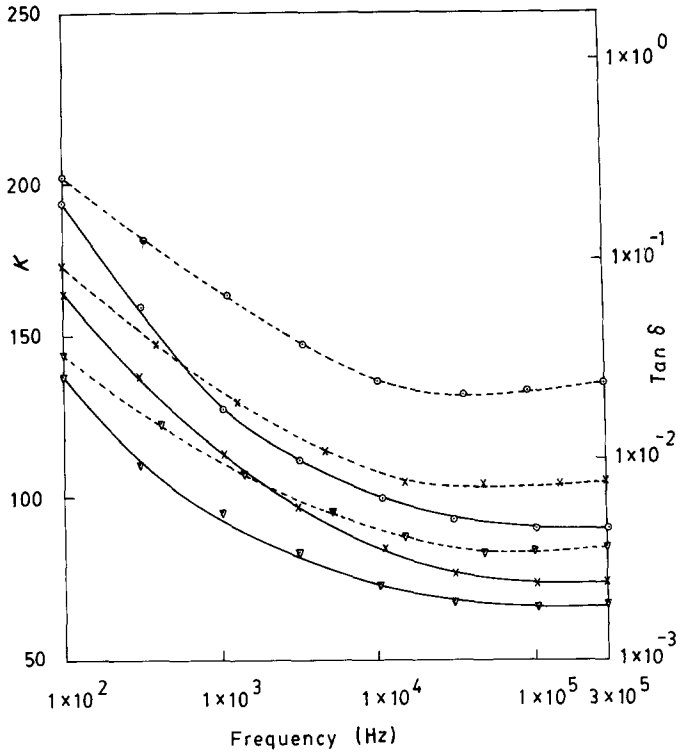

Figure 1 K (——) and tan δ (– – –) as a function of frequency for as-grown and different X-ray-irradiated DKDP crystal. ⊙, As-grown; ×, X-ray 1 h; ▽, X-ray 2 h.

(at different times) DKDP single crystals. X-ray irradiation decreases the α value in the higher wavelength region and increases the peak value on the lower wavelength side. The value of α has decreased from 4 (as-cleaved) to 3 (after 2 h of X-ray irradiation) on the higher wavelength (800 nm) side. The peak value of α for 2 h of X-ray irradiated DKDP crystals at 220 nm is found to decrease from 9.1 to 6.3, which is around 30%. The magnitude of α at 220 nm (peak position) in DKDP and KDP crystals is 8.5 and 7.85, respectively, which shows the value of α has increased 7% at 220 nm from that of KDP as compared with its as-cleaved condition.

4. Discussion

Four polarizations usually contribute to the K of a material (i.e. electronic, ionic, dipolar and space charge). The nature of the variation of K with frequency indicates the presence of the contribution of a particular polarization. The space charge contribution

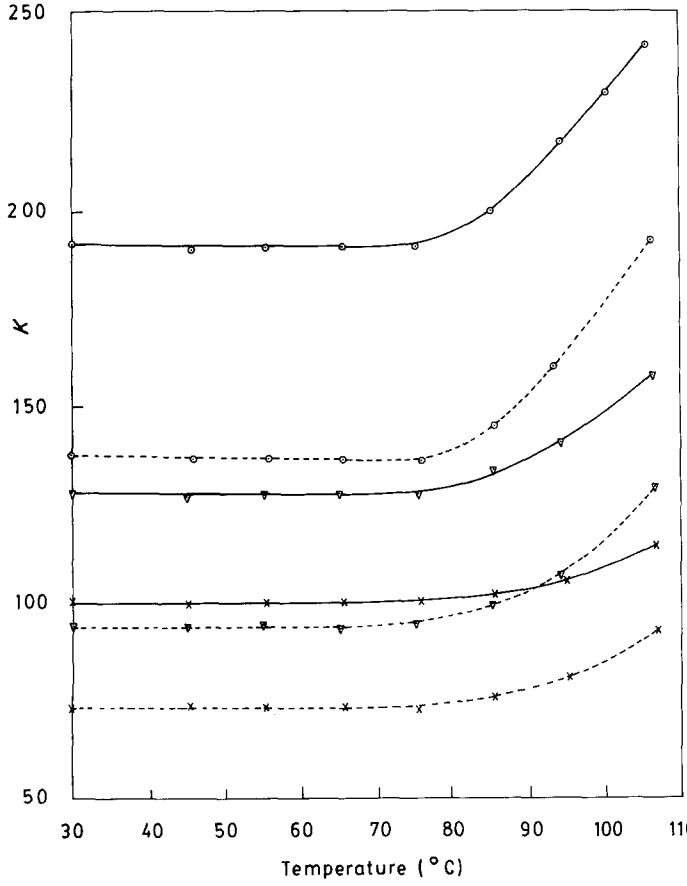

Figure 2 K as a function of temperature for as-grown (——) and X-ray-irradiated (2 h) (– – –) DKDP crystal. ⊙, 10^2; ×, 10^3; ▽, 10^4 Hz.

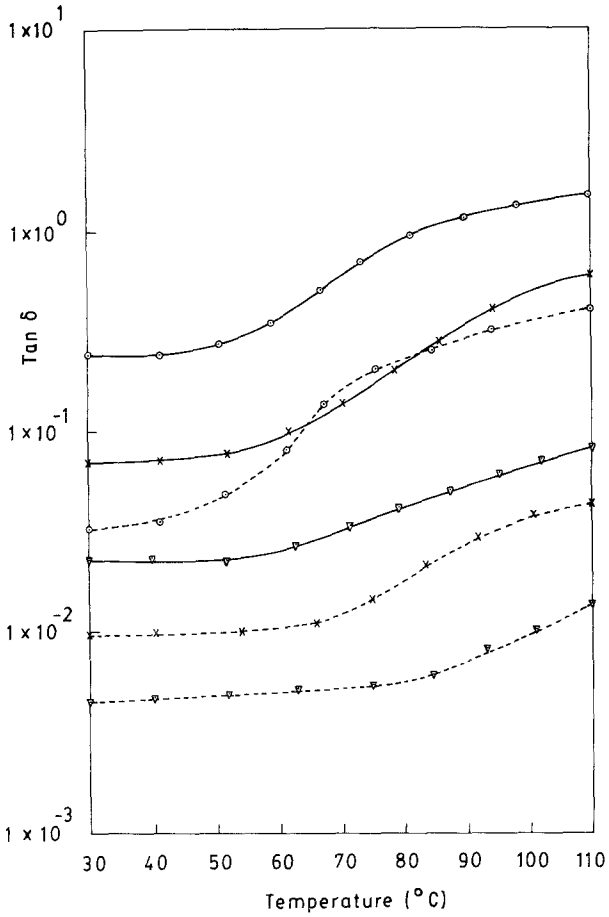

Figure 3 Tan δ as a function of temperature for as-cleaved (——) and X-ray-irradiated (2 h) (– – –) DKDP crystals. ⊙, 10^2; ×, 10^3; ▽, 10^4 Hz.

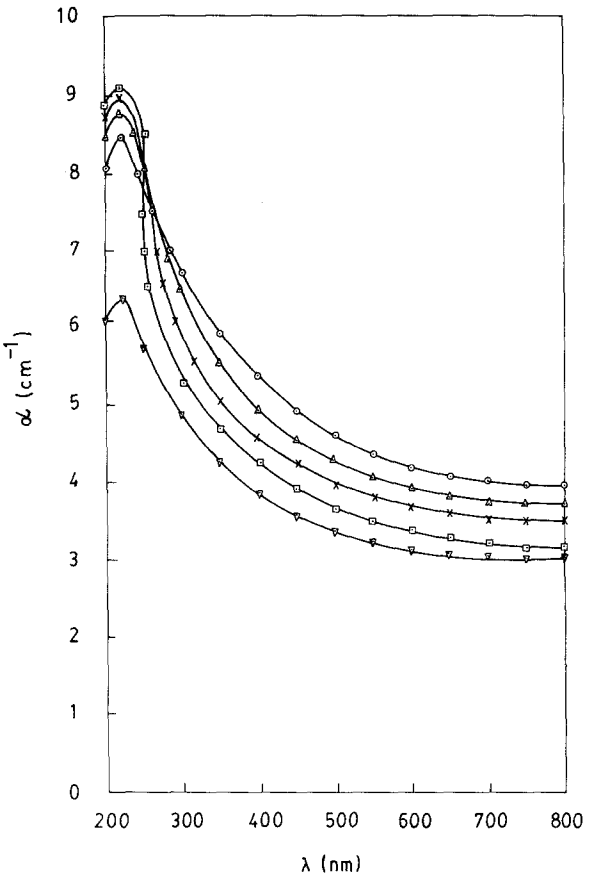

Figure 4 Variation of α as a function of wavelength for DKDP in different conditions. ⊙, As-cleaved; △, X-ray 0.5 h; ×, X-ray 1 h; □, X-ray 1.5 h; ▽, X-ray 2 h.

depends on the purity and perfection of the crystals, and generally its influence is neglibible at low temperature and is observable in the low frequency region. The dipolar orientational effect can sometimes be noticeable up to 10^{10} Hz. The ionic and electronic polarizations always exist below 10^{13} Hz. The effect of space charge and surface charge on the static domain structure of insulating ferroelectrics has been considered by Selyuk [10]. The total dipole moment, and hence the polarization of the crystal, may be changed by the movement of the domain walls between domains or by the annihilation and nucleation of new domains.

The larger values of K at room temperature and low frequency in DKDP may be ascribed to the space-charge polarization [11]. From the optical absorption measurements, the peak value of α at low frequency indicates that there are defects which may be due to the vacancies (i.e. OH/OD radicals in a specific configuration). Relatively larger values of tan δ at low frequency and at room temperature can be understood in similar ways.

X-ray irradiation causes the release of free electrons and holes from the exposed specimen, and these charged entities are trapped at the charge defect region, resulting in the partial neutralization of charged defect concentration. Finally, this partial neutralization leads to a decrease in the space-charge polarization and is thus responsible for the low values of K and tan δ at different X-ray doses. Similarly, the free-charge entity may be trapped at the defect region inside the sample, which influences the variation

TABLE I Comparison of K and tan δ for KDP and DKDP in various conditions

Sample condition	At room temperature 10^2 Hz		At room temperature 10^4 Hz		At 75° C, 10^2 Hz		At 75° C, 10^4 Hz	
	K	tan δ	K	tan δ	K	tan δ	K	tan δ
KDP As-cleaved	165	1.0×10^{2}	82	6.5×10^{-4}	169	2.9×10^{-2}	89	1.7×10^{-3}
DKDP As-cleaved	188	2.7×10^{-1}	89	2.8×10^{-2}	195	7.5×10^{-1}	129	3.6×10^{-2}
KDP 2 h X-ray irradiation	104	6.8×10^{-4}	53	1.2×10^{-4}	102	1×10^{-3}	65	3.0×10^{-4}
DKDP 2 h X-ray irradiation	138	2.8×10^{-2}	61	4.2×10^{-3}	138	2.0×10^{-1}	95	5.3×10^{-3}

in domain size depending on the influence of the individual interactions between them. The present measurements seem to indicate that there may be a contraction of the domain wall as more and more free-charged entities interact with them, as a result of which one may expect a relatively small domain after certain X-ray doses. With a decrease in the volume of domains which are favourably oriented relative to the depolarizing field at the expense of free charge in the surrounding medium, the decrease in net polarization in the system will yield a low K value.

The rise in K at higher temperature (80° C) may be attributed to the larger space-charge polarization [11, 12]. It is observed from our data that the polarizability due to the deuterion in the DKDP crystal is larger than that due to hydrogen in KDP, and therefore DKDP has relatively higher K and tan δ values compared to KDP in the paraelectric phase. Finally, we conclude that the effect of X-ray irradiation has decreased the K and tan δ values considerably. Low-temperature work along these lines is in progress to learn more about the above observation for this important class of H-bonded ferroelectric materials.

From the optical absorption characteristics, the low value of α at higher wavelength is indicative of the high-quality DKDP crystals. The presence of some defects like ionic vacancies is found to be due to the increase of α at about 220 nm [13]. The absorption band with a peak at 220 nm in indicative of the presence of OD/OH radicals that are normally present in water-solution-grown crystals [13]. X-ray irradiation is found to decrease the absorption in the high-wavelength region, presumably due to the clustering of vacancies. However the increase in the absorption band at 220 nm up to 1 and 1.5 h of X-ray irradiation seems to show that more OD radicals are produced from the absorbed D_2O molecules. From experiments, it is observed that the peak value of α at 220 nm for DKDP is more than KDP, which is due to the large variation of deuterion size as compared to the hydrogen in KDP. As the time of X-ray irradiation is prolonged, the OD/OH radicals that are initially present, and also those that are converted from H_2O/D_2O molecules by X-ray irradiation, seem to be converted to a slightly different species resulting in a considerable decrease in the optical absorption band.

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References

1. B. PAUL, J. ALBERS and H. E. MIISEX, *Ferroelectrics* **14** (1976) 707.
2. Z. MALAK, L. A. SHUVALOV, I. FIALA and Y. A. SHTRADIBLOVA, *Kristallografiya* **13** (1968) 825 (translation in *Sov. Phys. Crystallogr.* **13** (1969) 713).
3. H. MOTEGI, K. KURAMATO and E. NAKAMURA, *J. Phys. Soc. Jpn.* **52** (1983) 1131.
4. G. M. LOIACONO, J. F. BALASCIO and W. OSBORNE, *Appl. Phys. Lett.* **24** (1974) 455.
5. P. S. PEEREY, *Phys. Rev. B.* **12** (1975) 2725.
6. G. A. SAMARA, *Ferroelectrics* **5** (1972) 25.
7. K. L. BYE and E. T. KEVE, *ibid.* **4** (1972) 87.
8. E. T. KEVE, K. L. BYE, P. W. WHIPPS and P. D. ANNIS, *ibid.* **3** (1971) 39.
9. H. BOUTIN, B. C. FRAZER and F. JONA, *J. Chem. Solids* **24** (1969) 341.
10. B. V. SELYUK, *Kristallografiya* **16** (1971) 564.
11. K. V. RAO and A. SMAKULA, *J. Appl. Sci.* **37** (1966) 319.
12. S. GOVINDA and K. V. RAO, *Ind. J. Pure Appl. Phys.* **13** (1975) 175.
13. A. K. GUPTA and K. V. RAO, *J. Mater. Sci.* **16** (1981) 564.

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