JOURNAL OF MATERIALS SCIENCE 23 (1988) 1137–1140

Dielectric properties of selenite single crystals irradiated by X-rays or γ-rays

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Dielectric constant (K) and loss ($\tan\delta$) of selenite single crystals have been measured in the frequency region 10^2 to 10^7 Hz and in the temperature range 30 to 400° C. Measurements have also been taken after X-ray or γ-ray irradiation for these crystals. At 30° C, K, which has larger values at lower frequencies, decreases with frequency, reaching a constant value of 5.8 beyond 10^5 Hz; similar behaviour is exhibited by $\tan\delta$. Variation of K and $\tan\delta$ with temperature at different frequencies shows peaks around 120 and 265° C, the peak positions remaining the same at all frequencies. X-ray irradiation of the sample increases K and $\tan\delta$ values at lower frequencies significantly, but decreases them at the peaks. It is observed that the changes of K and $\tan\delta$ are greater with γ-ray irradiation than with X-ray irradiation. An attempt is made to understand the results.

1. Introduction

The physical properties of solids depend to a large extent on the nature and concentration of the lattice defects present in them in addition to the nature and bonding of their ions or molecules. Much of the understanding in the field of defect solid state physics has come out of the studies on alkali halides [1, 2]. The concepts developed from such studies have been utilized for understanding the behaviour of other materials such as alkaline earth halides and alkaline earth oxides [3, 4]. However, comparatively little attention has been paid to the study of optical and electrical properties of divalent metal sulphates. Some interest has been aroused, recently, in the investigation of the properties of some of these sulphates doped with various rare earths because of their utility as phosphors for dosimetry work.

Selenite is a naturally available single crystal having chemical composition $CaSO_4 \cdot 2H_2O$. The most transparent form of gypsum is called selenite. Luminescence and thermoluminescence of selenite have been well studied [5–10]. No data on systematic investigation of dielectric properties of selenite are available to the best of our knowledge. Selenite crystals have structural water molecules playing an important role in holding their different layers together, as well as the ions in the same layer [11]. Albuquerque and Isotani [12] have concluded, from EPR measurements, that two types of OH centres exist in selenite single crystals. These different types of OH centres are expected to produce interesting changes in the dielectric properties of selenite. It is the aim of the present communication to present the data of measurements on dielectric constant (K) and loss ($\tan\delta$) of selenite single crystals in the frequency region 10^2 to 10^7 Hz and in the temperature range 30 to 400° C before and after X-ray irradiation.

2. Experimental methods

The selenite single crystals used in the present investigation were obtained from Geological Syndicate, Calcutta, India. The samples were cleaved from sheets of selenite. Final dimensions of the samples were about $1.5 \times 1.5 \times 0.2\,\mathrm{cm}^3$. Silver paint was applied on either side of the samples for electrodes.

The dielectric measurements were taken on GR 716 capacitance bridge in the frequency range 10^2 to 10^5 Hz [13] and a Marconi Circuit Magnification Meter type TF329G in the frequency range 10^6 to 10^7 Hz [14] using the resonance curve principle. The samples were irradiated with X-rays from a Norelco unit operated at 35 kV, 10 mA or with γ-rays from ^{60}CO source of strength 10^3 giving a dose of $80\,\mathrm{krad\,h^{-1}}$.

3. Results and discussion

Fig. 1 presents the dielectric constant (K) and loss ($\tan\delta$) at room temperature ($\approx 30°$ C) as a function of frequency for selenite single crystals. The value of K gradually decreases with frequency and attains a constant value of 5.8 at 10^6 Hz; similar behaviour is exhibited by loss ($\tan\delta$). X-ray irradiation is found to increase the frequency-dependent K value of selenite single crystals significantly, but has practically no effect on its high-frequency value. The dielectric loss values increase considerably on irradiation with X-rays. The increases in K and $\tan\delta$ are more in the case of γ-ray irradiation.

The temperature variation of K at different frequencies (Fig. 2) for selenite single crystals shows a slight increase of K with temperature up to 100° C, and exhibits two peaks at 120 and 265° C; the K values at the peaks are frequency dependent having smaller values at higher frequencies; similar behaviour is exhibited by $\tan\delta$. Fig. 3 presents the results of K and

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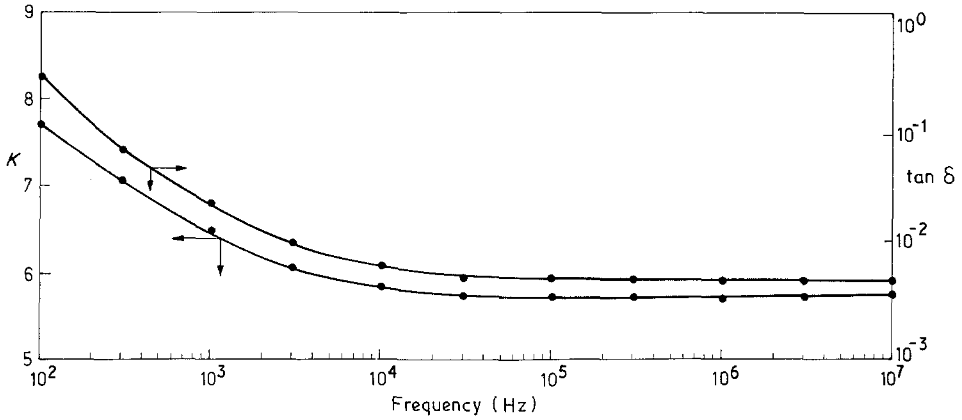

Figure 1 Dielectric constant (K) and loss (tan δ) at 30° C as functions of frequency for selenite single crystals.

tan δ measurements as functions of temperature for selenite crystals as-supplied and also on X-ray and γ-ray irradiation taken at two frequencies, 10^2 and 10^5 Hz. X-ray irradiation of the samples increases K and tan δ values at lower frequencies significantly, but decreases them at the peaks. γ-ray irradiation increases K and tan δ values more at lower frequencies but decreases them at the peaks.

Fig. 4 gives the variation of K and tan δ values with temperature at different frequencies, of selenite single crystals heated initially to 150° C for 30 min and then cooled to room temperature. Fig. 5 gives similar measurements where the crystals were initially heated to 350° C (the crystals become opaque when they are heated beyond 350° C), for 30 min and then cooled to room temperature. These results show that when the crystals were initially heated to 150° C and then cooled to room temperature, the peaks in K and tan δ values at 120° C disappeared and their values at the peak positions decreased slightly at 265° C. However, when the crystals were heated initially to 350° C and then cooled to room temperature, the peaks in K and tan δ values at both 120 and 265° C disappear. It may be mentioned that when selenite crystals heated around 350° C and cooled to room temperature were kept in a desiccator with a dehydrant like $CaCl_2$, the peaks in K and tan δ were not observed even after one week.

The dielectric constant of a material is composed of four contributions: electronic, ionic, dipolar and space-charge polarizations. All these may be active at low frequencies. The nature of the variation of dielectric constant with frequency indicates which contributions are present. The space charge contribution depends on the purity and perfection of the crystals. Its influence is negligible at very low temperatures and is observable in the low-frequency region. The dipolar orientation effect can sometimes be seen in some materials up to 10^{10} Hz. The electronic and ionic polarizations always exist below 10^{13} Hz.

From the data presented, the slightly larger values

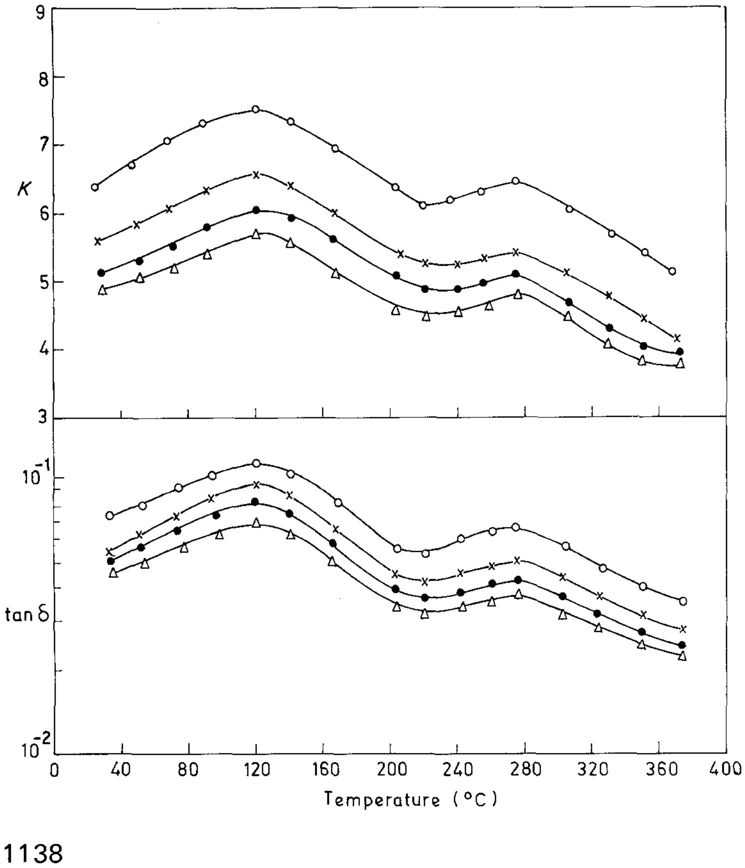

Figure 2 Variation of dielectric constant (K) and loss (tan δ) as functions of temperature at different frequencies for selenite single crystals. Frequency: (○) 10^2 Hz, (x) 10^3 Hz, (●) 10^4 Hz, (△) 10^5 Hz.

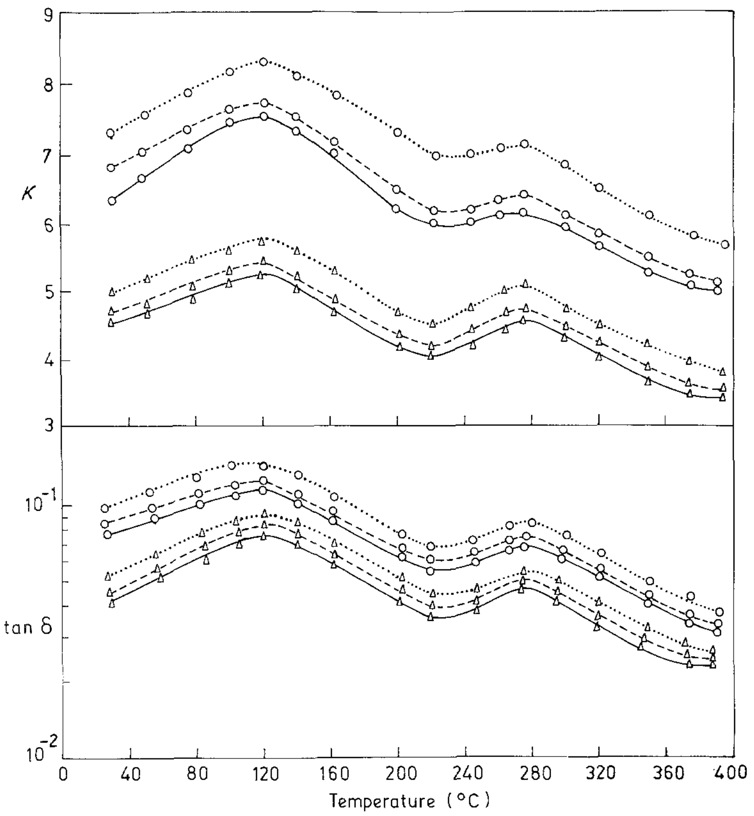

Figure 3 Variation of dielectric constant (K) and loss (tan δ) as functions of temperature at different frequencies for selenite single crystals with X-ray and γ-ray irradiation. Frequency: (○) 10^2 Hz, (△) 10^5 Hz. (——) As-grown crystal, (– – –) 1.5 h X-ray irradiation, (· · · ·) 40 h γ-ray irradiation.

cooled to room temperature. Optical absorption measurements, etc., of these selenite crystals may give more information which will enable better understanding of the nature of the defects involved.

of K and tan δ at low frequencies at room temperature shown by selenite single crystals may be associated with space-charge polarization due to charged lattice defects [15]. X-ray or γ-ray irradiation is expected to increase the lattice defects. This increase in concentration of lattice defects increases the space-charge polarization and hence the K and tan δ values are increased in the low-frequency region.

Selenite crystals contain water of crystallization. These water molecules present in selenite crystals are known to be related to two types of bonds [11]. Selenite crystals have a layered lattice consisting of sheets of Ca^{2+} and $(SO_4)^{2-}$ ions. The water molecules which hold different layers in these crystals form comparatively weaker bonds while the water molecules involved in holding ions in the same layer make the comparatively stronger bonds. The former may be responsible for the K and tan δ peaks at 120° C whereas the latter may give rise to the corresponding peaks at 265° C. X-ray or γ-ray irradiation may destroy

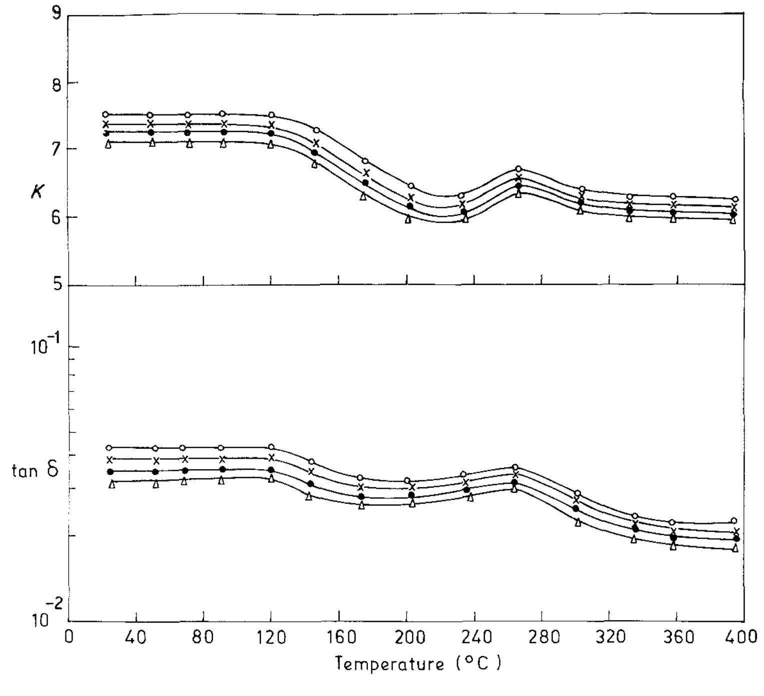

Figure 4 Dielectric constant (K) and loss (tan δ) as functions of temperature at different frequencies for selenite heated to 150° C and cooled to room temperature. Frequency: (○) 10^2 Hz, (x) 10^3 Hz, (●) 10^4 Hz, (△) 10^5 Hz.

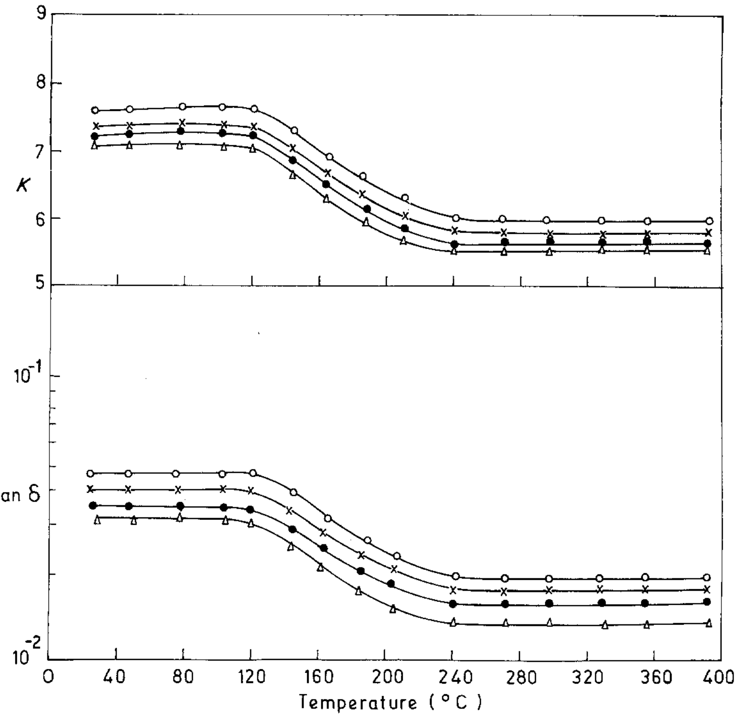

Figure 5 Dielectric constant (K) and loss (tan δ) as functions of temperature at different frequencies for selenite heated to 350° C and cooled to room temperature. Frequency: (○) 10^2 Hz, (x) 10^3 Hz, (●) 10^4 Hz, (△) 10^5 Hz.

some of the bonds connected to the water molecules and increase the number of lattice defects. This may be responsible for the general increase in K and tan δ values at low frequencies, but a decrease in the peak values of K and tan δ as observed in the present investigation. The inference that the peaks in K and tan δ values at 120 and 250° C may be related to the water molecules forming two types of bond, a weaker and stronger bond respectively, is also borne out by the fact that these peaks disappear in crystals which are heated to 150 and 350° C, respectively, and then

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Received 10 July
and accepted 9 October 1987