JOURNAL OF MATERIALS SCIENCE 23 (1988) 1416–1418

Dielectric properties of $LaPO_4$ ceramics

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Dielectric constant (K) and loss ($\tan\delta$), and hence conductivity (σ), have been measured for $LaPO_4$ ceramics prepared by a molten urea process in the frequency region 10^2 to 10^7 Hz and in the temperature range −193 to 280° C. At room temperature (~30° C), K decreases with frequency up to 10^5 Hz, beyond which it attains a constant value; $\tan\delta$ behaves in a similar way. The values of K and $\tan\delta$ at 30° C and 10^6 Hz for this material are 14 and 2.7×10^{-3}, respectively. As a function of temperature, K exhibits two stages of increase: (i) a slow stage up to −30° C and (ii) a fast one beyond −30° C which is considerably frequency dependent, K having larger values at lower frequencies. Similar behaviour is exhibited by $\tan\delta$. Plots of σ against $1/T$ for $LaPO_4$ exhibit the usual extrinsic and intrinsic regions; the activation energy for conduction in the intrinsic region is calculated to be 0.61 eV. It seems possible to understand the results through space charge polarization effects due to lattice defects in $LaPO_4$.

1. Introduction

Analogues of the mineral monazite, a mixed lanthanide orthophosphate ($LnPO_4$) are potentially important primary containment forms for the isolation actinide nuclear wastes [1, 2]. A method of preparing this material by precipitation in molten urea has been reported by Abraham *et al.* [3]. In this paper details of preparation of high quality $LaPO_4$ in sintered pellet form using the above method are reported; a systematic study of the dielectric properties, e.g. dielectric constant (K), and loss ($\tan\delta$), and hence conductivity (σ), has been carried out on such $LaPO_4$ samples and the results are reported. The frequency range covered was 10^2 to 10^7 Hz, and the temperature range was −193 to 280° C. As far as is known to the authors, such a detailed study on this material has not yet been reported.

2. Experimental methods

Lanthanum phosphate was prepared by mixing La_2O_3 with $HNO_3 + H_2O$ (1:1) and then a stoichiometric amount of diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] was added to this mixture. The mixture was heated at 200° C and granular urea simultaneously added until a white precipitate was formed. Later, the entire mixture was heated to 400° C and kept at this temperature for about 2 h. The white powder was collected in a platinum crucible and calcination was done at 770° C. After this, the sample was ground to a fine powder and samples were prepared in pellet form using hydraulic press at a pressure of about $4.5 \times 10^6\,\mathrm{g\,cm^{-2}}$. Then sintering of these pellets was carried out at 1000° C for 10 h. The d-spacing of these samples was determined by X-ray diffraction studies and was found to be in good agreement with standard data; for $LaPO_4$ for (2 0 0) or (1 1 0) plane ($I/I_0 = 100$), the d-spacing was calculated to be 0.306 nm (the standard value is 0.304 nm). In the above procedure the concentration of the solutions and the treatment temperatures etc., seem to be quite critical, otherwise the samples obtained are not of high quality. The density was found to be 97.8% of the theoretical value.

The dimensions of $LaPO_4$ samples which were circular in shape were 1.1 cm diameter and 0.15 cm thick. A thin coating of silver paint applied to the large area faces of the samples served as electrodes for dielectric measurements.

The dielectric measurements were taken on a GR 716 type capacitance bridge in the frequency range 10^2 to 10^5 Hz [4] and on a Marconi circuit magnification metre type TF 329G in the range 10^6 to 10^7 Hz using the resonance curve principle [5]. The accuracy of measurement of the dielectric constant was 3% and of the loss ($\tan\delta$), 6%. Measurements were carried out on at least three samples and the agreement was within the limits mentioned.

3. Results

Fig. 1 shows K and $\tan\delta$ of $LaPO_4$ at room temperature (~30° C) as a function of frequency. K, having larger values at lower frequencies, decreases with frequency, attaining a constant value beyond 10^5 Hz; similar behaviour is exhibited by $\tan\delta$. The values of K and $\tan\delta$ at 10^6 Hz and 30° C for $LaPO_4$ are 14 and 2.7×10^{-3}, respectively.

The temperature variation of K and $\tan\delta$ at different frequencies for $LaPO_4$ is shown in Fig. 2. K increases with temperature in two stages: (i) a slow stage up to about −30° C, and (ii) a fast stage beyond −30° C which is considerably frequency dependent, K having larger values at lower frequency. Similar behaviour is exhibited by $\tan\delta$ (Fig. 3).

Using, instead of dielectric loss, the conductivity, σ ($= WK \tan\delta\, K_0$, where $W = 2\pi f$, f is the frequency and K_0 the vacuum dielectric constant), of the samples at different frequencies for various temperatures has been calculated and plots of $\log\sigma$ against $1/T$ drawn

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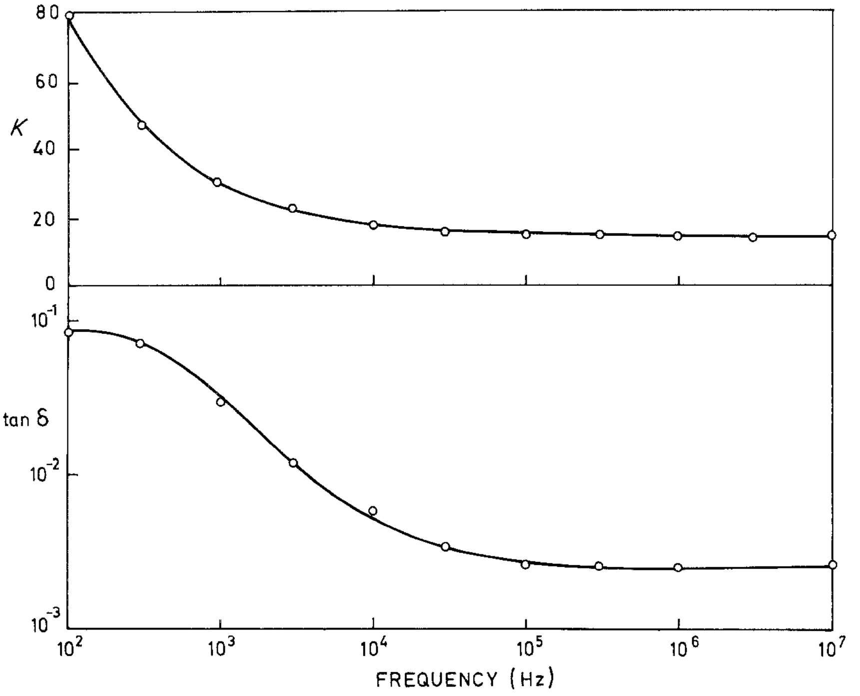

Figure 1 Dielectric constant (K) and loss ($\tan\delta$) at 30° C as a function of frequency for $LaPO_4$ ceramic.

(Fig. 4). The graphs exhibited intrinsic conductivity above 60° C. The activation energy for conduction in the intrinsic region is calculated to be 0.61 eV.

4. Discussion

The dielectric constant of a material is composed of four contributions: electronic, ionic, orientational and space charge polarizations. All these may be active at low frequencies. In fact, the nature of the variation of dielectric constant with frequency indicates which contributions are present.

The space-charge contribution will depend on the purity and perfection of the material. Its influence is small at low temperature and is noticeable in the low-frequency region. The dipolar orientational effect can sometimes be seen in some materials even up to 10^{10} Hz. Ionic and electronic polarizations always exist below 10^{13} Hz.

Recalling our data, the larger values of K and $\tan\delta$ at lower frequencies may be attributed to space-charge polarization due to charged lattice defects [6].

Temperature has a complicated influence on the dielectric constant. In general, increasing the temperature of this type of material decreases the electronic polarization. The increase of the ionic distance due to the temperature, influences the ionic and electronic polarizations. The decrease in electronic dielectric constant is found to be less than 3% for a temperature change of about 400° C [7], similarly it appears that the changes in ionic polarizations are not very large. Even assuming the presence of a small number of dipoles and their contributions to dielectric constant, we know from Debye's theory that K is inversely proportional to temperature. As such, it is expected

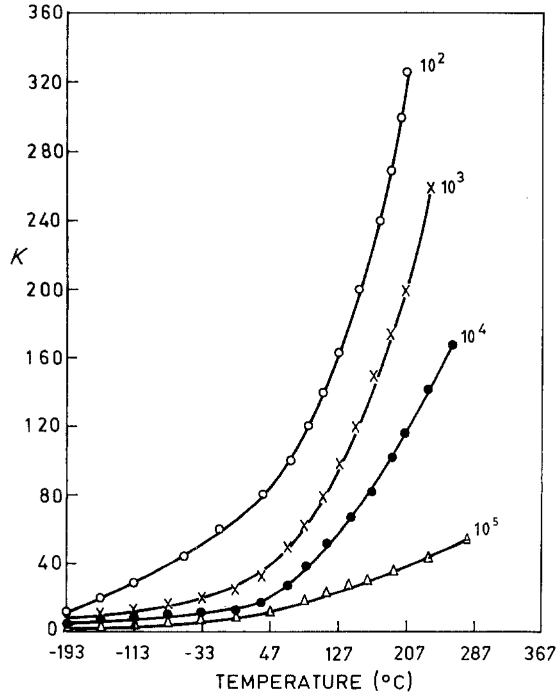

Figure 2 Variation of dielectric constant (K) with temperature at different frequencies for $LaPO_4$ ceramic.

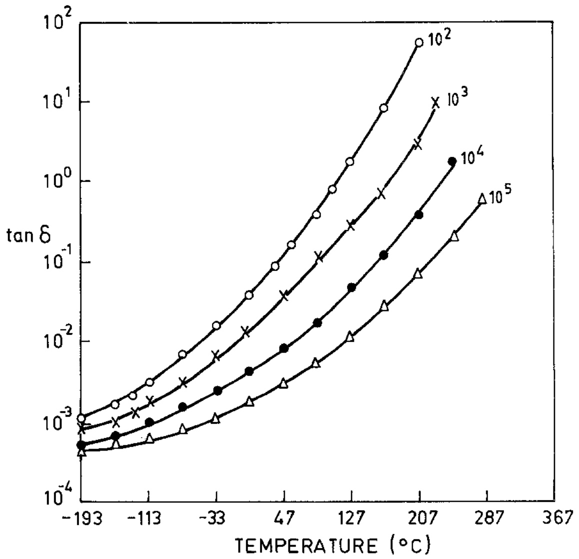

Figure 3 Variation of dielectric loss ($\tan\delta$) with temperature at different frequencies for $LaPO_4$ ceramics.

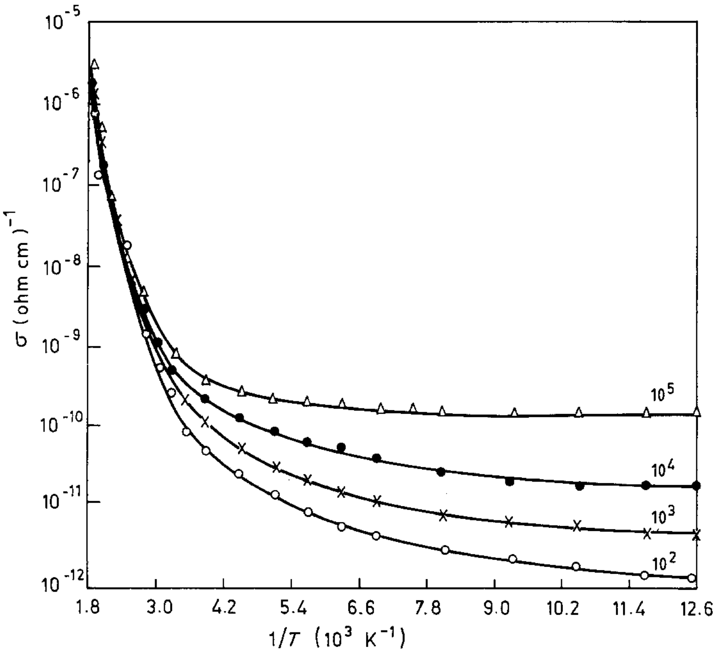

Figure 4 Log σ plotted against $1/T$ at different frequencies for $LaPO_4$ ceramic.

that the dielectric constant of $LaPO_4$ should not change considerably with increasing temperature. However, in the present measurements on this material, we notice a considerable increase of K with temperature, this increase being frequency dependent beyond −30° C. This behaviour can only be attributed to space-charge polarization due to lattice defects [8–10]. This conclusion seems to be supported by the fact that the dielectric loss at these high temperatures is large.

The conductivity graphs exhibit the usual extrinsic and intrinsic regions. The intrinsic conductivity region seems to be connected to the mobility of vacancies; the comparatively low activation energy (0.61 eV) suggests that the oxygen vacancies may be responsible for conduction in this region [11].

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Received 10 June
and accepted 20 August 1987