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Dielectric and thermal properties of $LaAsO_4$

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Polycrystalline specimens of $LaAsO_4$ were prepared by metathesis reaction and characterized with the help of X-ray diffraction, SEM and differential thermal analysis. The dielectric constant (K), loss factor ($\tan \delta$) and conductivity (σ) of pressed pellets of $LaAsO_4$ were measured as a function of frequency in the range 10^2 to 10^4 Hz and in the temperature region 298 to 473 K. K increases with the temperature because of the increase in ionic and space charge polarizations. The plots of conductivity against temperature at different frequencies give an activation energy of 1.8 eV for the conduction intrinsic region. This moderately large value for the activation energy suggests that it is probably associated with the ions.

1. Introduction

Compounds of the general formula $RAsO_4$ (R = rare earth) are known to crystallize in two different structural forms. The compounds of the higher lanthanides crystallize in a monoclinic monazite structure, whereas the lower lanthanides crystallize in a tetragonal zircon-type structure [1, 2]. $LaAsO_4$ belongs to the higher lanthanide series, having a monoclinic space group $P2_1/n$ [3] at room temperature (298 K). Recently, ferroelectric properties in some monoclinic $RAsO_4$ (R = Pr and Nd) compounds have been reported in the temperature range 298 to 328 K [4]. Further, it has been suggested that other compounds of the series (i.e. $LaAsO_4$ and $CeAsO_4$) also possess these properties in the temperature region mentioned. Moreover, rare-earth phosphates were found to be potential host materials for nuclear waste isolation [5]. Therefore, because of the structural similarities with rare-earth phosphates, the centrosymmetric space group and the possibility of ferroelectric properties at room temperature stimulated us to carry out extensive studies on $LaAsO_4$. This paper presents the dielectric and thermal properties of $LaAsO_4$.

2. Experimental procedure

The starting materials were 99.99% pure La_2O_3 (Indian Rare-Earth Ltd, Kerala) and $(NH_4)_2HAsO_4$. La_2O_3 was dissolved in dilute hot HNO_3 and a stoichiometric amount of $(NH_4)_2HAsO_4$ was added to the solution. $LaAsO_4$ was formed by metathesis reaction. At this point, molten granular urea, $(NH_2)_2CO$, was added and the mixture was heated at 473 K until precipitation occurred. The dried powder was calcined at 1073 K, pressed and sintered at 1423 K in a platinum crucible for 12 h. The details of the preparation technique have been given elsewhere [6].

X-ray diffractograms were taken in a Jeol (JXR, Japan) X-ray diffractometer with Cu$K\alpha$ radiation. The line widths of the X-ray lines were monitored carefully and compared with the instrumental slit width and also with the results obtained for standard materials (e.g. silicon and CeO_2) in order to assess the chemical homogeneity and completion of reaction in the sample. The scanning electron micrographs (SEM) were taken using a Cambridge Stereoscan S-180.

The dielectric measurements were taken on a GEN-RAD 1620 AP capacitance measuring assembly (USA). The dielectric constant K and the loss factor $\tan \delta$ of the pellets were measured with an accuracy of 5% over the frequency range $f = 10^2$ to 10^4 Hz and in the temperature range T = 298 to 473 K. Silver paste was used as an electrode on either sides of the sample. The pellets were poled at 298 K using a d.c. field of $10\,kV\,cm^{-1}$ for 30 min. As the samples were found to be sensitive to moisture, proper care was taken to avoid this effect. Differential thermal analysis (DTA) and thermogravimetry (TG) were studied with the use of an MOM-Derivatograph, Model 874373 (Paulik–Paulik, Hungary) taking Al_2O_3 as a standard.

3. Results and discussion

The crystallographic data obtained from the powder diagrams are a = 0.703(3) nm, b = 0.717(2) nm, c = 0.662(3) nm, β = 104.01(4)° and Z = 4. All the observed reflections satisfy the extinction rules of the space group $P2_1/n$. The densities calculated from X-ray line broadening using the Scherrer equation and by a pycnometric method using CCl_4 as the working

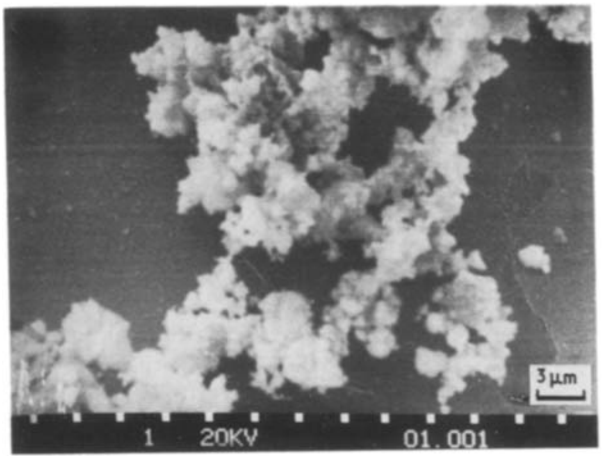

Figure 1 Scanning electron micrograph of urea-precipitated $LaAsO_4$ powder. Particles of spherical shape are in evidence.

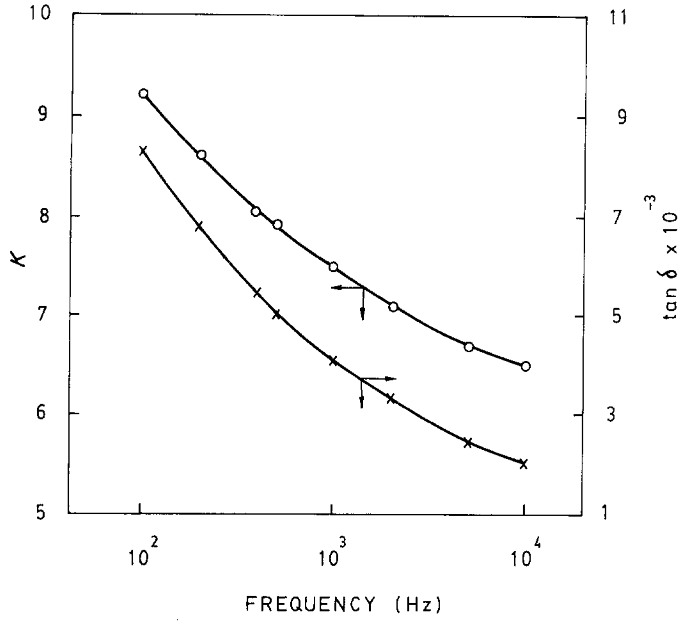

Figure 2 Variation of dielectric constant (K) and loss factor ($\tan \delta$) at 298 K with frequency for $LaAsO_4$.

liquid ($5.65\,g\,cm^{-3}$) are in good agreement and found to be more than 95% of the theoretical value. This may be due to the control of particle size by the addition of urea. The particles formed by precipitation in molten urea have a spherical shape. Fig. 1 shows an SEM micrograph of $LaAsO_4$ powder. These preliminary SEM data indicate that the grain size is affected substantially by the addition of urea. However, specific conclusions regarding the quantitative nature of grains cannot be drawn on the basis of the data presented here.

The variation of dielectric constant (K) and loss factor ($\tan \delta$) at room temperature (298 K) with frequency for this material is shown in Fig. 2. K is found to be frequency-dependent in the frequency range 10^2 to 10^4 Hz. K and $\tan \delta$ as a function of temperature for this solid are presented in Figs 3a and b, respectively. The dielectric constant and loss factor increase slowly with temperature. The loss is found to be frequency-dependent throughout the temperature range. The conductivity

$$\sigma = \frac{f K \tan \delta \times 10^{-12}}{1.8} \quad \Omega^{-1}\,cm^{-1}$$

has been calculated for the sample in the temperature and frequency ranges studied. As a typical example, a σ against $1/T$ graph is presented in Fig. 4. An intrinsic conductivity was observed in the high-temperature range. This trend indicates that intrinsic conductivity may also be observed at still higher temperatures. The activation energy for conduction calculated from the high-temperature region is 1.8 eV.

The dielectric constant at low frequencies depends on electronic, ionic and dipole orientations and on the

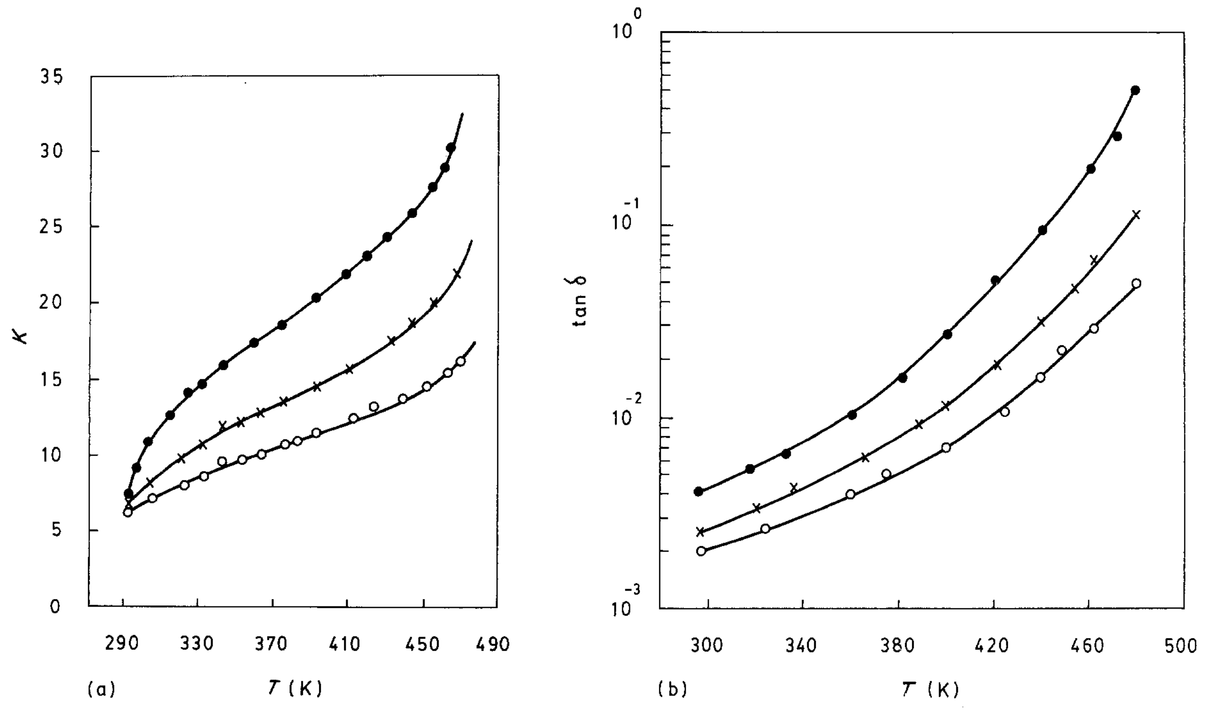

Figure 3 (a) Dielectric constant (K) and (b) loss factor ($\tan \delta$) as a function of temperature at different frequencies for $LaAsO_4$: (●) 1 kHz, (x) 5 kHz, (o) 10 kHz.

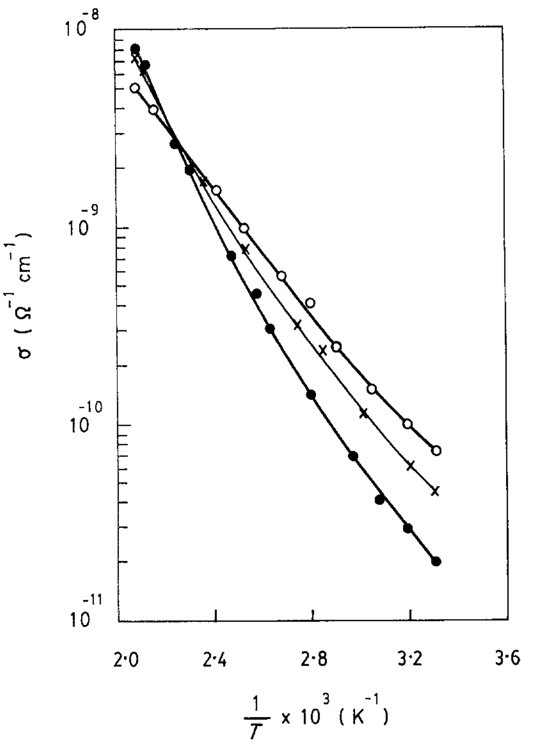

Figure 4 Conductivity (σ) as a function of temperature ($1/T$) at different frequencies for $LaAsO_4$: (●) 1 kHz, (x) 5 kHz, (○) 10 kHz.

space-charge polarization. At very low frequencies all four contributions may be active. The nature of the variation of dielectric constant with frequency indicates which contributions are present.

Even in single crystals, the contribution of space charge will depend on the purity and perfection of the crystals. Its influence is noticeable mainly in the low-frequency region. The dipole orientation effect can be exhibited by materials up to 10^{12} Hz. Ionic and electronic polarizations always exist below 10^{13} Hz.

Pressed samples generally contain voids, grain boundaries and other defects. The presence of voids decreases the dielectric constant [7]; however, when the density of the sample approaches the single-crystal value, this effect is practically eliminated. Moreover, pressed samples develop considerable space charge polarization due to defects [8], contributing to an increase in the dielectric constant and loss particularly at low frequencies. The density of $LaAsO_4$ samples has been controlled by addition of urea and the density is very near to the theoretical value (i.e. that of a single crystal). This has been shown in our X-ray measurements. We may therefore ascribe the larger values of K and tan δ at low frequencies to space-charge polarization which arises at the grain boundaries. The space charge may arise from the charges present at the surface of the crystallites. However, the reduction of grain size because of the addition of sufficient urea is also partly responsible for a decrease in the loss tangent values at 10^4 Hz.

Temperature has a complicated influence on the dielectric constant. Generally, increasing the temperature of the sample decreases the electronic polarization. The increase in ionic separation due to increased temperature influences the ionic and electronic polarizations. The decrease in electronic dielectric constant for many solids is found to be less than 3% for a temperature change of about 673 K [9]. Similarly, it appears that the changes in ionic polarization are not very large. At high temperature K is frequency-dependent. The lattice defect concentration can only increase with temperature, making the space-charge polarization dominant; it hence increases with temperature. The changes in K with temperature are smaller at higher frequencies as this type of polarization decreases considerably at such frequencies.

Though it is not possible to speculate on the nature of the charge carriers responsible for conduction in these samples, the moderately large value for the activation energy for conduction in the intrinsic region suggests that it is probably associated with the ions.

Fig. 5 shows the DTA and TG curves of $LaAsO_4$. In the lower temperature region (298 to 373 K) of the TG curve there is a considerable change of percentage weight loss ($\sim$4%) in comparison to that at 1273 K ($\sim$7%). From this it may be concluded that due to dehydration the percentage weight loss is changing faster in the low-temperature region. This predicts the hygroscopic nature of the sample at room temperature. One endothermic peak was observed at 573 K in the DTA curve which was not visible in the TG curve. This peak may be due to the dehydration effect.

Finally, the absence of anomaly in the dielectric constant, loss factor, DTA and TGA of $LaAsO_4$

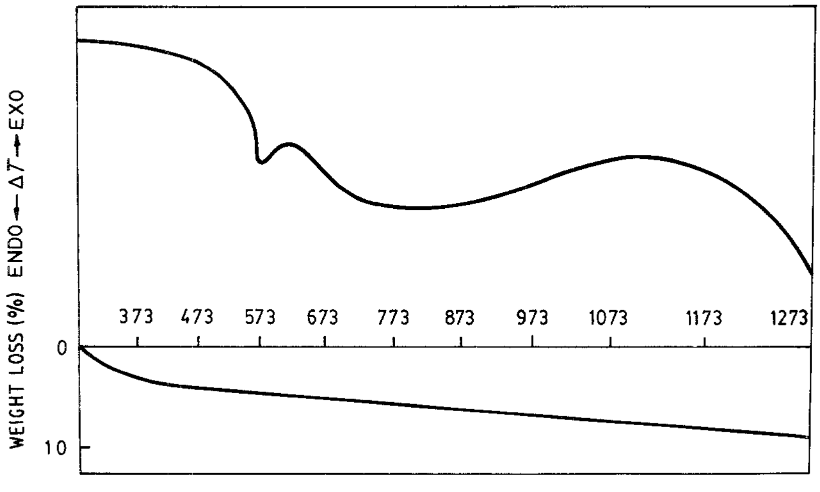

Figure 5 DTA (upper) and TG (lower) curves of $LaAsO_4$ in the temperature region 298 to 1273 K.

suggests that there may not be any ferroelectric phase transition in the temperature region 298 to 473 K.

Acknowledgements

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