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Characterization and dielectric properties of almandine-pyrope garnet

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Abstract. Some garnets collected from the Kothagudem area of Khammam district in Andhra Pradesh were characterized by chemical analysis. The results show the garnets to be of almandine ($Fe_3^{+2}\,Al_2Si_3O_{12}$)-pyrope ($Mg_3Al_2Si_3O_{12}$) group. Dielectric constant (ε) and dielectric loss ($\tan\delta$) were measured as a function of frequency and temperature in the frequency range of 100 Hz to 100 KHz and from room temperature to 400°C. The room temperature measurement was extended to 10 MHz. AC conductivity was calculated from the data on ε and $\tan\delta$. DC conductivity was also measured.

Keywords. Almandine-pyrope garnet; dielectric properties; conductivity; polarization additivity.

1. Introduction

Garnets are found to exist as natural minerals with chemical composition $X_3Al_2Si_3O_{12}$ where X represents Ca, Fe^{+2}, Mg, Mn, etc. The corresponding garnets are grossular, almandine, pyrope, spessartine etc. respectively. The garnets corresponding to any one member composition is rare. They are found to form isomorphous series with varying proportion of members. They are divided into two series namely, pyralspite (pyrope, almandine and spessartine) and ugrandite (uvarovite, grossular and andradite). Combination of members within the series is common but that of two series is rare. The garnets for our study were collected from the Kothagudem area of Khammam District in Andhra Pradesh.

The garnets are hard and lack cleavage. Their hardness is comparable with that of diamond and hence they find use as abrasives. Transparent and good quality garnets are used as gem stones and they have a wide variety of physical properties. Sriramdas (1957), Reddy and Bhimasenachar (1964) and Babuska *et al* (1978) earlier reported their elastic properties. Reports on structural analysis, thermal expansion, elastic constants and spectral studies are also available (Deer *et al* 1982). A literature survey however indicated that studies on electrical properties are meagre with only one report on the resistivity of pyrope (Tolland 1973). The dielectric properties of almandine-pyrope garnet have also not been studied. The present study concentrates on the following aspects: (i) characterization of samples by chemical analysis, (ii) systematic measurement of dielectric constant and loss ($\tan\delta$), (iii) AC and DC conductivity and (iv) to test the applicability of polarization additivity rule by using the data on dielectric constant in conjunction with Clausius-Mosotti relation.

2. Experimental

The samples were characterized by chemical analysis using the technique of atomic absorption spectrophotometry and titrimetry. The major and trace elements were obtained by adopting the procedure of Shapiro (1975) as described by Balaram (1988).

The garnets were found to have cubic symmetry with no cleavage. The present garnets were of pink colour with reasonably large dimensions. The sample was cut with a diamond wheel cutter and polished. The final dimensions were $0{\cdot}62\ \text{cm}^2 \times 0{\cdot}25$ cm. For good electrical contact and to remove air gap the sample was coated with silver paint. Dielectric constant (ε) and loss ($\tan\delta$) were measured using a GR 1620A capacitance bridge in conjunction with a laboratory built three-terminal cell. The temperature was maintained stable within 1°K. The measurements were carried out from 100 Hz to 100 KHz in the temperature range from room temperature to 400°C. For frequency beyond 10 KHz an external oscillator (Agronic 72) was used. The room temperature measurement was extended to 10 MHz using a 4275A H/P LCR meter. The overall accuracy in the measurement of dielectric constant and loss was 1 and 5% respectively. The DC conductivity was measured using 610C Keithley electrometer in conjunction with a laboratory fabricated cell.

3. Polarization additivity

The concept of additivity of polarization implies that the molecular polarization of a substance can be expressed as the sum of polarization of simple entities constituting the molecule. The three pure end member garnets almandine, pyrope and spessartine may be represented as

$$X_3Al_2Si_3O_{12} = 3(XO) + 3(SiO_2) + Al_2O_3, \tag{1}$$

where X = Fe, Mg or Mn. The molar polarization and ε are related through Clausius-Mosotti relation (Smyth 1955)

$$P = \frac{\varepsilon - 1}{\varepsilon + 2}\frac{M}{D} = (4/3)\pi N_A \alpha \tag{2}$$

where M is the molecular weight, D, the density, α the polarizability and N_A, the Avagadro number. The total polarization of the compound on the left hand side of (1) may be obtained as the individual polarization of the right hand side entities. The polarization of the individual molecules was obtained from ε using (2). The additional parameters required were density and molecular weight. From the total polarization, the ε value of garnet was evaluated.

4. Results and discussion

The chemical analysis of a typical sample given in table 1 shows that the mineral is of pyralspite group. In terms of the end members the composition is represented as $alm_{84.96}$-$pyr_{9.5}$-$spe_{0.87}$. Figure 1 shows the variation of dielectric constant with frequency at room temperature. The almost frequency-independent nature of variation shows that the sample is of high purity. The frequency-independent value taken as the static dielectric constant is equal to 11·70. Figure 2 shows the variation of loss with frequency. The loss at the highest frequency of measurement is of the order of 10^{-4}.

Figures 3 and 4 respectively show the variation of ε and $\tan\delta$ with temperature for different frequencies The variation is typical of ionic crystals with slow variation

Table 1. Chemical analysis.

Major elements (%)		Trace elements (ppm)	
SiO_2	42·32	Co	53
TiO_2	0·38	Cu	03
Al_2O_3	15·97	Ni	12
Fe_2O_3	1·7	Pb	70
FeO	30·40	Zn	75
MnO	0·33		
MgO	3·56		
CaO	1·79		
Na_2O	1·88		
K_2O	0·67		
P_2O_5	0·55		
Total	99·55		

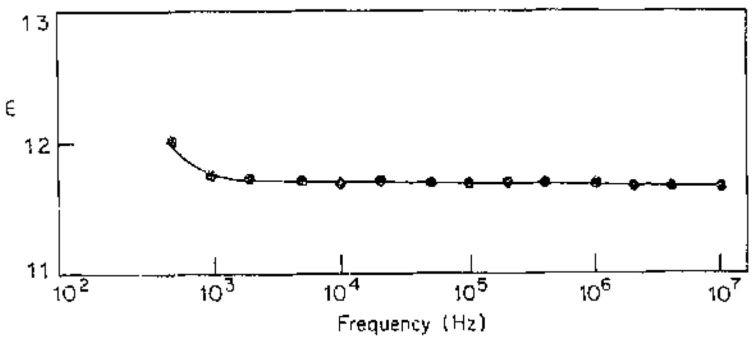

Figure 1. Variation of dielectric constant ε with frequency at room temperature.

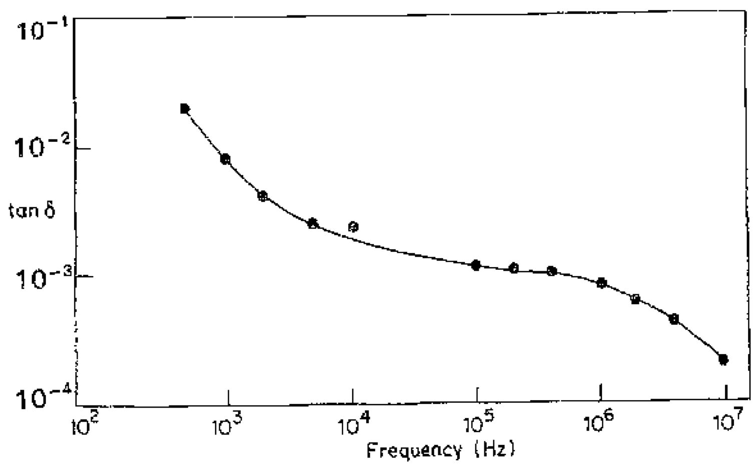

Figure 2. Variation of tan δ with frequency at room temperature.

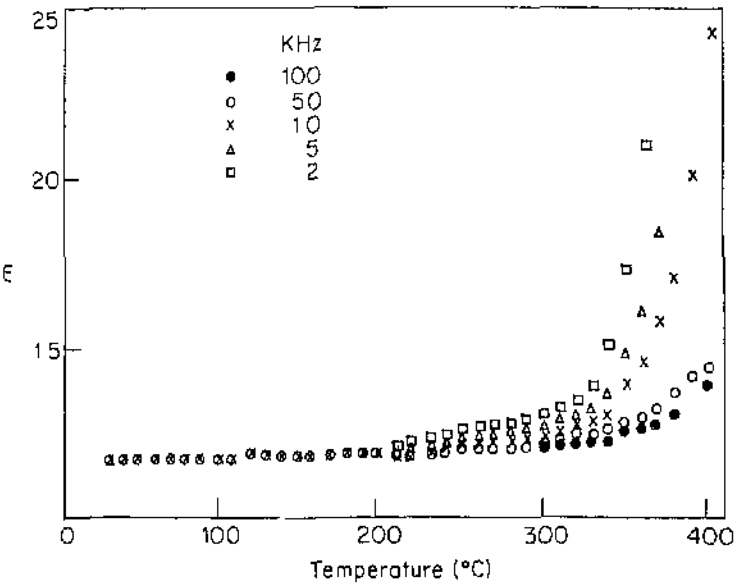

Figure 3. Variation of dielectric constant ε with temperature for different frequencies.

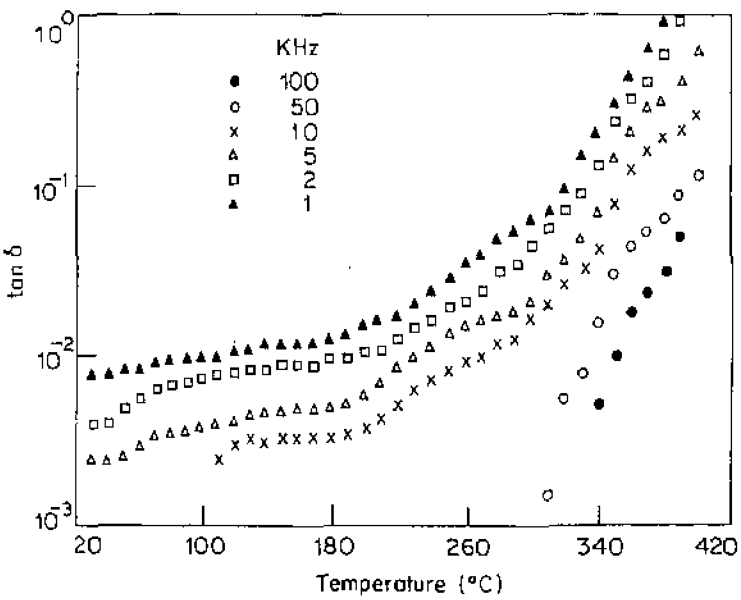

Figure 4. Variation of tan δ with temperature for different frequencies.

initially and faster frequency-dependent variation at higher temperatures. The results show that the effect of crystal imperfections and defects begin to show up beyond 200°C.

AC conductivity (σ_{AC}) was evaluated from ε and tan δ using the relation $\sigma = \varepsilon\varepsilon_0\omega \tan\delta$, where ε_0 is the vacuum dielectric constant and ω, the angular frequency. Figure 5 shows the variation of conductivity with reciprocal temperature for different frequencies. A slow increase in conductivity is observed up to a temperature of 160°C,

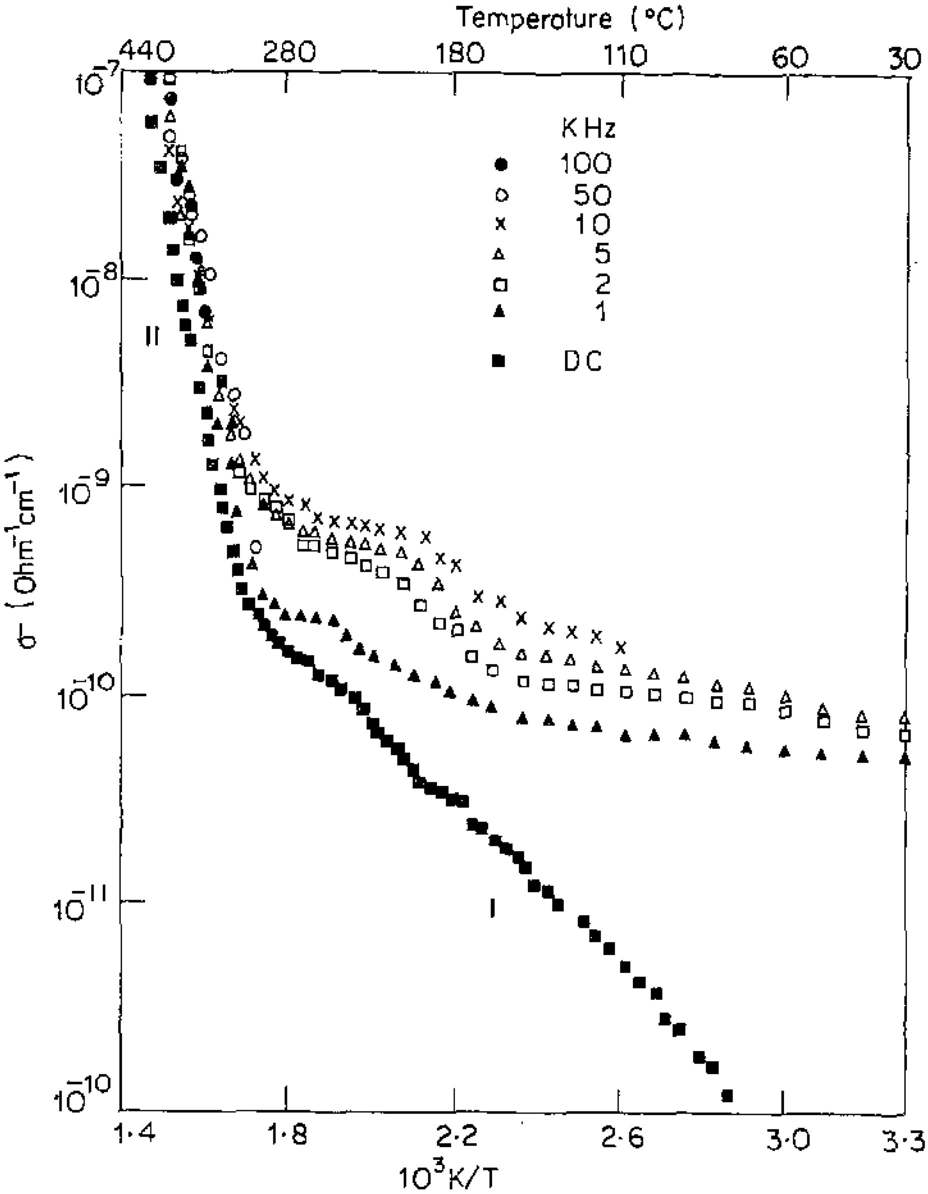

Figure 5. Variation of conductivity with reciprocal temperature for different frequencies.

peaks of low intensity are observed at certain frequencies between 180°C and 280°C, beyond 280°C the conductivity is almost frequency-independent. In the temperature range up to 315°C the DC conductivity shows a slow increase with temperature and throughout the AC conductivity is higher than DC conductivity. Beyond 315°C a frequency-independent steep rise both in AC and DC conductivity is observed.

The nature of variation of conductivity with temperature and the observation that $\sigma_{AC} > \sigma_{DC}$ shows the contribution from dielectric polarization to the loss is considerable at low temperatures. Conductivity observed beyond 315°C is due to

Table 2. Input data and calculated values of dielectric constant of pure mineral garnets.

Compound	Density ($g\,cm^{-3}$)	Dielectric constant (ε)	Reference
SiO_2	2·32	4·42	Young and Frederikse (1973)
Al_2O_3	3·965	9·34	Young and Frederikse (1973)
FeO	5·7	14·2	Young and Frederikse (1973)
MgO	3·58	9·65	Young and Frederikse (1973)
MnO	5·35	18·10	Chaudhury and Rao (1969)
$Fe_3Al_2Si_3O_{12}$ (Almandine)	4·318	12·52*	Deer *et al* (1982)
$Mg_3Al_2Si_3O_{12}$ (pyrope)	3·582	10·42*	Deer *et al* (1982)
$Mn_3Al_2Si_3O_{12}$ (spessartine)	4·190	13·16*	Deer *et al* (1982)

*Calculated values from additivity rule.

intrinsic conduction. The activation energy calculated from the slopes of the DC conductivity plot show values of 0·18 and 0·57 eV respectively in the two regions I and II.

Total polarization and the dielectric constant for garnet have been obtained as discussed earlier. The input data and the calculated values of dielectric constant for pure garnets are shown in table 2. For the garnet used in the present investigation, the ε value estimated from the values of pure garnets is 11·73 and is in good agreement with the observed value of 11·70. The polarization additivity concept is found to hold good for the garnets. The contribution from the spessartine component is only 0·87%. Hence, the crystal system may be taken as almandine-pyrope garnet.

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