Dielectric properties of $K_2Zn_2(SO_4)_3$ and $(NH_4)_2Mg_2(SO_4)_3$

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Abstract. Dielectric constant (ϵ), dielectric loss ($\tan \delta$) and conductivity (σ) for $K_2Zn_2(SO_4)_3$ and $(NH_4)_2Mg_2(SO_4)_3$ have been measured over the frequency range 100 Hz — 100 kHz and in temperature range 30°C — 400°C. The values of static dielectric constant at room temperature are 7.67 and 4.80 for $K_2Zn_2(SO_4)_3$ and $(NH_4)_2Mg_2(SO_4)_3$ respectively. The plots of $\log \sigma$ against reciprocal temperature at different frequencies of these samples merge into a straight line beyond 250°C and the activation energies calculated in this region are found to be 0.67 eV and 1.98 eV for $K_2Zn_2(SO_4)_3$ and $(NH_4)_2Mg_2(SO_4)_3$ respectively.

Keywords. Dielectric constant ; dielectric loss ; conductivity ; activation energy.

1. Introduction

Langbeinite-type crystals $K_2Zn_2(SO_4)_3$ and $(NH_4)_2Mg_2(SO_4)_3$ belong to the cubic system specified by the space group T^4-P_{213} . Hikita *et al* (1977a) have reported the dielectric and pyroelectric measurements on these substances in the low temperature region from -200°C to 20°C. These dielectric measurements pertain to a fixed frequency of 1kHz. Hikita *et al* (1977 a, b) have reported that $K_2Zn_2(SO_4)_3$ and $(NH_4)_2Mg_2(SO_4)_3$ show a phase transition at -137°C and -52°C respectively. Systematic measurements over a wide frequency range and at higher temperatures have not been made so far for these substances.

In this paper, we report measurements of dielectric constant and dielectric loss over a wide range of frequency and temperature.

2. Experimental

The dielectric measurements were taken using GR 1620A Capacitance Measuring Assembly with two terminal configuration in the frequency range 100 Hz to 10 kHz and using an external oscillator for the frequency range 10 kHz to 100 kHz. As single crystals of sufficient size were not available, die pressed pellets were prepared using powders of particle size $45\mu - 75\mu$. The samples were dried in

vacuum desiccator. The samples were of diameter 8.5 mm and thickness 0.95 mm and 0.81 mm for $\text{K}_2\text{Zn}_2(\text{SO}_4)_3$ and $(\text{NH}_4)_2\text{Mg}_2(\text{SO}_4)_3$ respectively. The measurements were done with a laboratory built sample holder in the temperature range $30^\circ\text{C} - 400^\circ\text{C}$. Temperature was measured using a copper constantan thermocouple.

3. Results and discussion

Several equations are available for correlating the powder value ϵ_p to the bulk value ϵ . We have used the following equation given by Looyenga (1965)

$$(\epsilon_p^{1/3} - 1) = \delta (\epsilon^{1/3} - 1),$$

where δ is the packing fraction.

The density values, calculated from lattice constants have been used to obtain the packing fraction. The values of density, given by Hikita *et al* (1977a) are to be multiplied by a factor of 1.67 (table 1).

Table 1. Input properties for evaluation of dielectric constant and experimental values of dielectric constants and activation energies.

Sample	Lattice constant a (Å)	Density	Packing fraction	Dielectric constant at 1 kHz		Static dielectric constant	Activation energy (eV)
				Hikita <i>et al</i> 1977a	Present work		
$\text{K}_2\text{Zn}_2(\text{SO}_4)_3$	9.90	3.42	0.44	13	10.26	7.67	0.67
$(\text{NH}_4)_2\text{Mg}_2(\text{SO}_4)_3$	9.98	2.05	0.70	5.7	5.7	4.80	1.98

Plots of dielectric constants and loss, as a function of frequency, are shown in figure 1. The value of dielectric constant for $\text{K}_2\text{Zn}_2(\text{SO}_4)_3$ at 100 Hz is 16.8 and it decreases continuously up to 7.67 at 10 kHz. Beyond this frequency, the dielectric constant value is frequency independent. In $(\text{NH}_4)_2\text{Mg}_2(\text{SO}_4)_3$, the value 9.84 at 100 Hz decreases up to a value of 4.80 at 10 kHz. Beyond this frequency, it remains constant. The value of ϵ at 1 kHz for $(\text{NH}_4)_2\text{Mg}_2(\text{SO}_4)_3$ agrees with the value of 5.7 reported by Hikita *et al* (1977a). But the value of ϵ for $\text{K}_2\text{Zn}_2(\text{SO}_4)_3$ at 1 kHz is lower than the value of ≈ 13 reported by Hikita *et al* (1977b). The static dielectric constants for both the langbeinites are less than the values reported by them. The value of $\tan \delta$ at 100 kHz is of the order of 10^{-5} for $\text{K}_2\text{Zn}_2(\text{SO}_4)_3$ and 10^{-3} for $(\text{NH}_4)_2\text{Mg}_2(\text{SO}_4)_3$.

Dielectric constant (ϵ) depends on electronic, ionic, dipole orientation and space charge polarization. Contributions due to electronic and ionic polarization are frequency independent, whereas dipole and space charge contributions are frequency dependent at low frequencies. The variation ceases at 10 kHz. The frequency independent value is taken as the static dielectric constant. The low loss for both the langbeinites at higher frequencies indicates that the samples have very low concentration of defects.

The variation of dielectric constant and loss with temperature, for both the langbeinites are shown in figure 2.

Figure 1. Variation of ϵ and $\tan \delta$ with frequency.

Figure 2. Variation of ϵ and $\tan \delta$ with temperature at 100 kHz.

The increase of dielectric constant takes place in two stages. ϵ increases slowly up to 140°C and more steeply at higher temperatures at all frequencies. The slow increase is due to the increase of ionic polarization (Smyth 1955) and the rapid increase is due to the space charge polarization due to thermally generated carriers.

The conductivity values have been calculated at different frequencies and temperatures using the relation $\sigma = \epsilon_0 \epsilon \omega \tan \delta$ (ϵ_0 is the vacuum dielectric constant and ω the frequency). These values are plotted against the reciprocal of temperature in figure 3. They are straight lines at higher temperatures and are frequency independent. In the low temperature region, the plots are frequency dependent due to the impurities in the samples (Brown 1967). The activation energy values obtained from straight line portion of the graph, in the temperature region 200°C — 300°C are 0.67 eV and 1.98 eV for $\text{K}_2\text{Zn}_2(\text{SO}_4)_3$ and $(\text{NH}_4)_2 \text{Mg}_2(\text{SO}_4)_3$ respectively.

Figure 3. Conductivity σ (mho-cm)⁻¹ against $(1/T)$ for (a) $\text{K}_2\text{Zn}_2(\text{SO}_4)_3$ and (b) $(\text{NH}_4)_2 \text{Mg}_2(\text{SO}_4)_3$ at different frequencies.

It is not possible to understand the nature of the charge carriers responsible for conduction and the difference in activation energy values for the two samples from the present measurements alone.

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