

## Electrical properties of SiO<sub>2</sub>-doped sodium metavanadate sintered discs

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**Abstract.** Impedance of sintered discs of 0.1, 0.25, 0.4 mol% of sodium metavanadate was measured in the frequency range 10 kHz–1 MHz and in the temperature region from room temperature (= 30°C) to 450°C. AC conductivity was calculated from the data. DC conductivity was measured in the temperature range 150–450°C. Debye type of relaxation effects were observed in the dielectric loss. The activation energy of the dipoles involved in relaxation was estimated. The activation energy for AC conduction in the temperature above 380°C was calculated. These values are larger than the activation energy of pure sodium metavanadate sample. The relaxation phenomenon observed is explained.

**Keywords.** Electrical properties; sodium metavanadate.

### 1. Introduction

ABO<sub>3</sub> type of materials generally crystallize in perovskite or illmenite structure, but sodium metavanadate is quite different (Sorum 1943). The space group of NaVO<sub>3</sub> is C<sub>2h</sub><sup>6</sup> at room temperature. Sawada and Nomura (1951) studied the dielectric properties of sodium metavanadate single crystals and found ferroelectric behaviour in them. Bahuguna Saradhi *et al* (1993) studied dielectric dispersion in a large frequency range and from room temperature to 450°C. They attributed the dielectric relaxation observed in the sintered discs of sodium metavanadate to defects. Dielectric measurements in vanadium-doped barium titanate were studied by Hanumaiah *et al* (1995). Dielectric hysteresis of ferroelectric potassium vanadate and lithium vanadate doped with Gd<sub>2</sub>O<sub>3</sub> was studied by Kashid *et al* (1989). The effect of impurities on spontaneous polarization and coercive field of sodium and lithium vanadates was studied by Gopalakrishnan and Seshamma (1991). Lanthanum oxide doping effect on DC electrical conductivity of ferroelectrics, sodium metavanadate and rubidium vanadate was studied by Pawar *et al* (1995). The ferroelectric behaviour of sodium vanadate niobate was reported by Pulvari (1965). Impedance measurements of pure NaVO<sub>3</sub> sintered disc were reported by us earlier (Bahuguna Saradhi *et al* 1993). In the present paper we report the results of electrical measurements on 0.1% silicon dioxide-doped sodium metavanadate sintered discs. In the

present paper we report the effect of SiO<sub>2</sub> doping in NaVO<sub>3</sub> on electrical measurements. The effect of impurity on the so-called ferroelectric phase transition and the spontaneous polarization through the study of dielectric, impedance and conductivity studies and a comparison of the results on pure and doped samples would give interesting information about the transition in this system of samples. The present paper reports the results.

### 2. Experimental

NaVO<sub>3</sub> compound was prepared by solid state reaction of Na<sub>2</sub>CO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> taken in stoichiometric proportions. The mixture was held at 750°C for 3 h and cooled to room temperature. The samples were doped by adding requisite composition of silicon dioxide. The compositions studied were 0.1, 0.25, 0.4 mol% of SiO<sub>2</sub> in NaVO<sub>3</sub>. Formation of NaVO<sub>3</sub> compound was confirmed by X-ray diffraction. The polycrystalline material was powdered and sieved (through 120 mesh). The powder was pressed into pellets of 10 mm diameter and 1 to 2 mm thickness at a pressure of 7 tons/cm<sup>2</sup>. The pressed discs were sintered at 500°C for 3 h for densification and slowly cooled to room temperature. The measured grain size was found to be 10 to 15 nm. Silver paint was applied to large area faces of the samples to serve as electrodes for impedance and conductivity measurements. Impedance was measured in the frequency range 10 kHz to 1 MHz and from room temperature (~ 30°C) to 450°C using a two-terminal sample holder and HP4192 A impedance analyser. DC

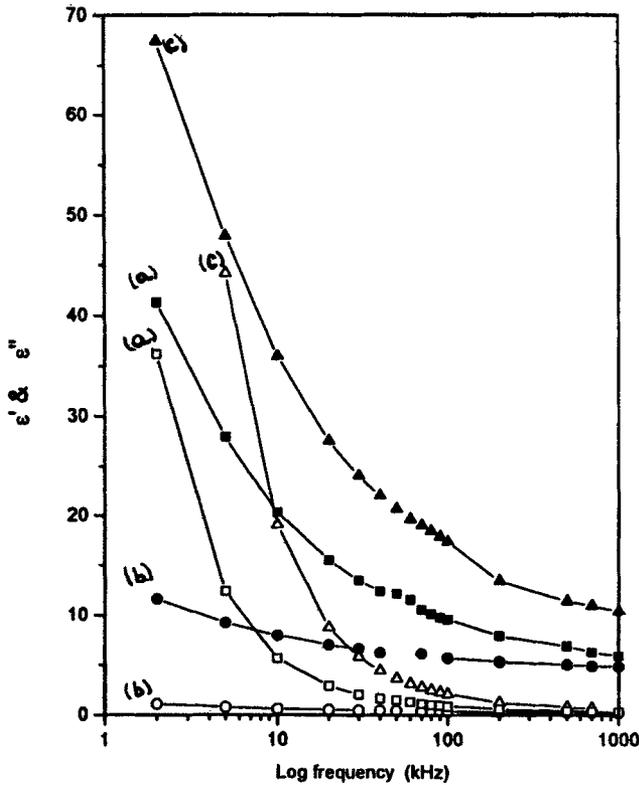
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conductivity was measured using a conventional two-probe set-up. The current in the sample was measured (Keithley 610 electrometer) keeping the sample at a set temperature and a DC bias of 100 V/cm.

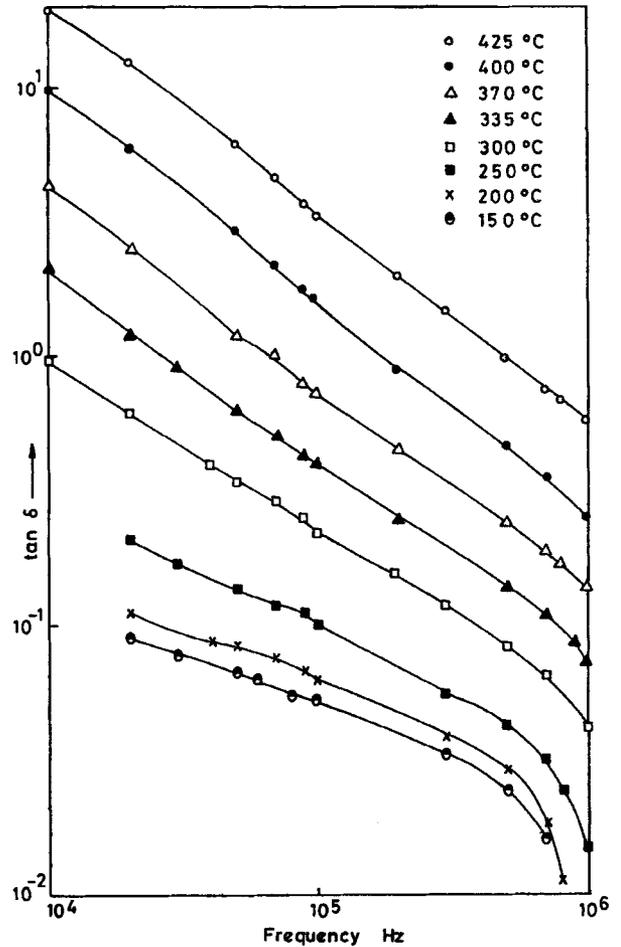
The error in the measurement of impedance was 0.01% and was dependent on the range of measurement (HP 4192A manual). DC conductivity measurements have an accuracy of 5%. Capacitance measurements have an accuracy of 2% (HP 4192A manual).

**3. Results and discussion**

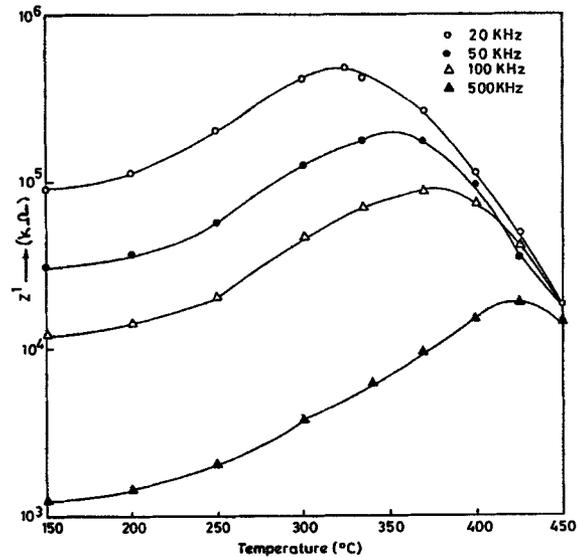
Figure 1 presents variation of real ( $\epsilon'$ ) and imaginary parts ( $\epsilon''$ ) of dielectric constant as a function of frequency at room temperature. The real part of dielectric constant ( $\epsilon'$ ) for these materials decreases with increase in frequency.  $\epsilon''$  values also showed similar behaviour. Values of  $\epsilon'$  and  $\epsilon''$  for doped  $\text{SiO}_2$  were less than pure sodium metavanadate at all frequencies. As in pure samples (Bahuguna Saradhi et al 1993) these materials also show a decrease of both  $\epsilon'$  and  $\epsilon''$  with increase in frequency. Temperature variation (figure not presented) of these properties does not show any obvious peaks as in the case of pure samples (Bahuguna Saradhi et al 1993), although small humps are



**Figure 1.** Variation of real ( $\epsilon'$ ) and imaginary part of dielectric constant as a function of frequency at room temperature for (a) 0.1%, (b) 0.25%  $\text{SiO}_2$ -doped  $\text{NaVO}_3$ , (c) pure  $\text{NaVO}_3$  (closed symbols  $\epsilon'$ , open symbols  $\epsilon''$ ).



**Figure 2.** Loss tangent ( $\tan \delta$ ) as a function of frequency at different temperatures for 0.1%  $\text{SiO}_2$ -doped  $\text{NaVO}_3$ .



**Figure 3.** Variation of real part of impedance ( $Z'$ ) as a function of temperature at different frequencies for 0.1%  $\text{SiO}_2$ -doped  $\text{NaVO}_3$ .

observed at frequencies less than 100 kHz at temperatures below 370°C. Figure 2 shows frequency variation of  $\tan\delta$  for 0.1%  $\text{SiO}_2$ -doped sample on log scale at different temperatures. Below 300°C the loss parameter decreases rapidly with frequency from 500 kHz onwards. An important feature of these curves is the suppression of peaks observed in pure samples. There is an increase of  $\tan\delta$  with increase of temperature. Here again the broad peak around 380°C observed in pure samples is missing. All the doped samples showed similar behaviour. Below 300°C there is a linear variation of real part of impedance ( $Z'$ ) with frequency. Above 300°C,  $Z'$  tends to decrease with increase of temperature at lower frequencies. At higher frequencies  $Z'$  increases with increase of temperature. Variation of  $Z'$  with temperature shows a broad peak. The peak temperature decreases with decrease of frequency as shown in figure 3 for 0.1%  $\text{SiO}_2$ -doped samples. As in pure samples, the imaginary part of impedance ( $Z''$ ) versus frequency curves shows a peak in high temperature region beyond 300°C. This peak shifts to higher frequencies at higher temperature (figure 4). All other compositions show similar impedance vs temperature variation.

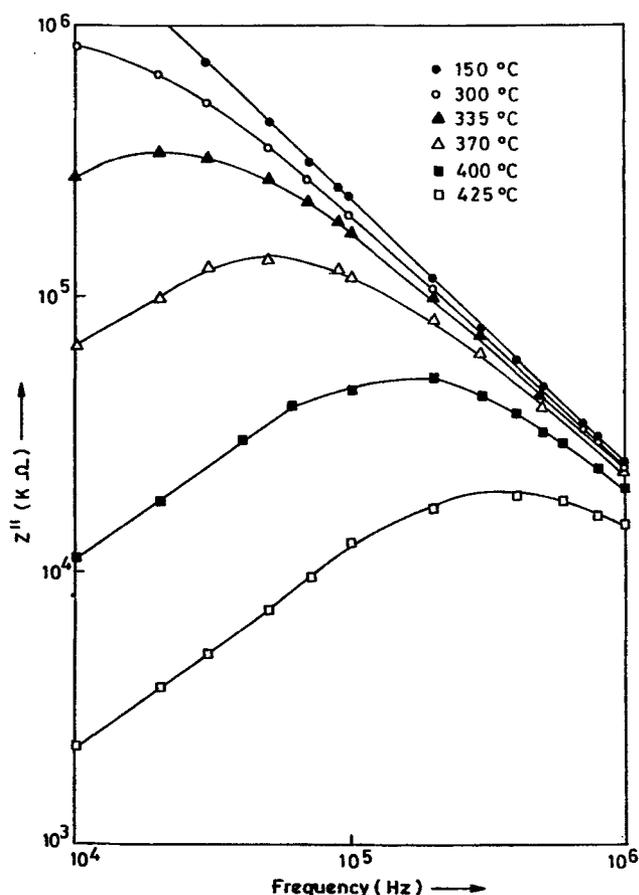


Figure 4. Variation of imaginary part of impedance ( $Z''$ ) as a function of frequency at different temperatures for 0.1%  $\text{SiO}_2$ -doped  $\text{NaVO}_3$ .

AC conductivity calculated from impedance at different frequencies (figure 5) for 0.1%  $\text{SiO}_2$ -doped sample shows a strong frequency dependence of conductivity at low temperatures. However, at higher temperatures conductivity appears to be independent of frequency attaining intrinsic conductivity. In doped samples DC conductivity is at least one order lower than AC conductivity in general (figure 6). The DC conductivity of pure samples is slightly lower than 0.1%  $\text{SiO}_2$ -doped sample and higher than 0.4%  $\text{SiO}_2$ -doped sample at higher temperatures. At lower temperatures 0.1%  $\text{SiO}_2$ -doped samples show conductivity higher than 0.4%  $\text{SiO}_2$ -doped and pure samples. Pertinent dielectric properties of doped  $\text{NaVO}_3$  samples are summarized in table 1. The conductivities and activation energies of the samples are given in table 2.

The value of real part of dielectric constant for 0.1%  $\text{SiO}_2$ -doped samples decreases from 15.5 at 20 kHz to 5.8 at 1 MHz (figure 1). These values are smaller in comparison with pure samples. The loss tangent also has smaller values and lesser variation with increase of frequency (figure 2) as compared to pure samples. These indicate lesser space charge polarization and hence fewer defects in 0.1%-doped samples (Rao and Suryanarayana Rao 1971). Temperature variation of  $\tan\delta$  does not show pronounced peaks as in pure samples. The real part of impedance of 0.1%  $\text{SiO}_2$ -doped samples shows a hump at higher frequencies and at lower temperature. At higher temperatures and lower frequencies there is only slight variation of impedance. The real part of impedance shows

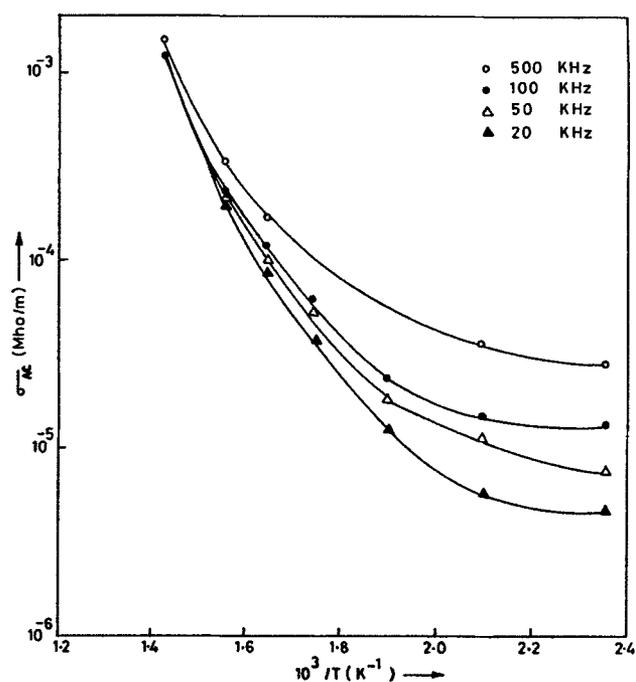
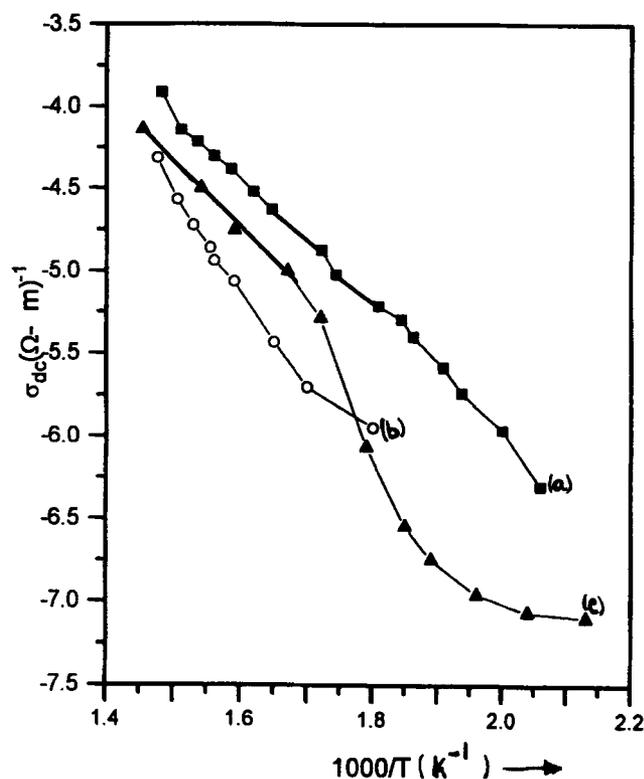


Figure 5. Variation of AC conductivity ( $\sigma_{AC}$ ) as a function of inverse of temperature at different frequencies for 0.1%  $\text{SiO}_2$ -doped  $\text{NaVO}_3$ .



**Figure 6.** Variation of DC conductivity ( $\sigma_{DC}$ ) as a function of inverse of temperature for (a) 0.1%, (b) 0.4%  $\text{SiO}_2$ -doped  $\text{NaVO}_3$  and (c) pure  $\text{NaVO}_3$ .

a broad peak which shifts towards lower temperatures at lower frequencies (figure 3). A strong frequency dependence of impedance and dielectric data of doped- $\text{NaVO}_3$  samples also indicates the presence of space charge polarization in these samples. The smaller measured values of impedance and dielectric parameters indicate that charges in doped samples get trapped in grain boundaries and dislocation (Rao and Smakula 1965). Further decrease in dielectric constant, impedance and conductivity with increase of impurity concentration seems to support this idea.

AC conductivity in doped samples attains its intrinsic value at lower temperature compared to pure samples. The activation energy of 0.1%  $\text{SiO}_2$ -doped samples at  $380^\circ\text{C}$  and 20 kHz is 1.20 eV. This value is larger than activation energy of pure sample (0.78 eV). This increase in activation energy for conduction may be due to redistribution of charges into larger agglomerations (Lidiard 1954). AC conductivity is higher than DC conductivity. Activation energy for DC conductivity for 0.1%  $\text{SiO}_2$ -doped samples is 0.79 eV and that of pure samples is 1.1 eV.

The cole-cole plots of these samples are also semicircles with centres below the real impedance axes (figure 7). Relaxation times of dipoles involved are calculated and plotted as function of inverse of temperature in figure 8. Activation energy of the dipole of this sample is 1.24 eV for 0.1%  $\text{SiO}_2$ -doped sample. The relaxation times of the dipoles in impure samples are in general smaller as against relaxation times in pure samples.

**Table 1.** Room temperature dielectric constant of  $\text{NaVO}_3$  samples.

Composition	20 kHz		100 kHz		1 MHz	
	$\epsilon'$	$\epsilon''$	$\epsilon'$	$\epsilon''$	$\epsilon'$	$\epsilon''$
Pure $\text{NaVO}_3$	28.4	3.7	10.1	0.82	6.2	0.29
0.1% Doped	15.5	2.9	9.4	0.86	5.9	0.28
0.25% Doped	7	0.5	5.7	0.34	4.8	0.21

$\epsilon'$  is real part of dielectric constant;  $\epsilon''$  is imaginary part of dielectric constant.

**Table 2a.** Summary of DC conductivity measured on  $\text{NaVO}_3$  samples ( $\text{mho}\cdot\text{m}^{-1}$ ).

Composition	300°C	350°C	400°C
Pure $\text{NaVO}_3$	$4 \times 10^{-6}$	$2.5 \times 10^{-5}$	$6 \times 10^{-5}$
0.1% Doped	$1 \times 10^{-5}$	$3.5 \times 10^{-5}$	$1.2 \times 10^{-4}$
0.4% Doped	$1.9 \times 10^{-6}$	$8.5 \times 10^{-6}$	$6.5 \times 10^{-5}$

**Table 2b.** Activation energy (eV) for dipole relaxation and AC/DC conductivities.

Composition	Activation energy of dipole (eV)	Activation energy for conduction (eV) above $380^\circ\text{C}$	
		$\sigma$ AC at 20 kHz	$\sigma$ DC
Pure $\text{NaVO}_3$	0.76	0.78	1.1
0.1% Doped	1.24	1.2	0.79

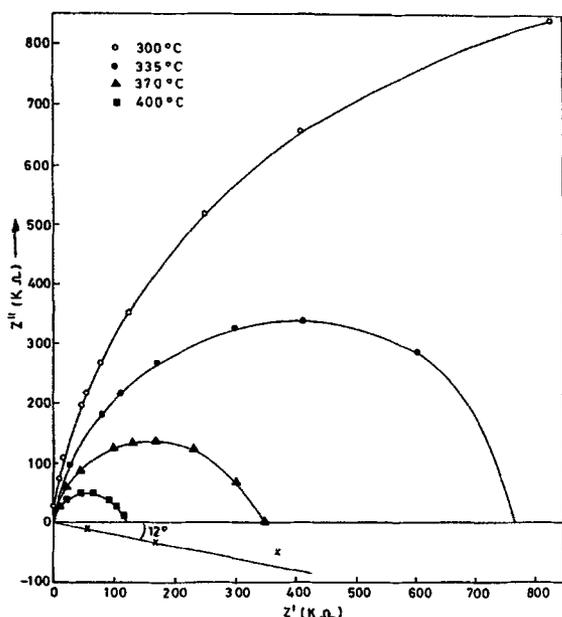


Figure 7. Cole-cole plots of impedance for 0.1% SiO<sub>2</sub>-doped NaVO<sub>3</sub> samples at different temperatures.

Cole-cole plot gives an average relaxation time ( $\tau$ ) of the dipole and varies with temperature.  $\log \tau$  vs  $10^3/T$  is a straight line in figure 8 indicating the approximate Debye behaviour. The depressed circles indicate deviation from Debye behaviour given by the angle of depression ( $12^\circ$ ), for 0.1% SiO<sub>2</sub>-doped sample. The semicircles also indicate multiple relaxations which are indicated by  $Z''$  versus temperature plots. The average activation energy for relaxation comes out to be 1.24 eV which is almost equal to activation energy associated with AC conduction. This indicates (Bunget and Popescu 1984) that the relaxation species are like conduction species.

#### 4. Conclusions

The measurements undertaken in the present study lead to the following conclusions: (i) Doped NaVO<sub>3</sub> samples show large values of  $Z$  and  $\epsilon$  and strong frequency dependence indicating space charge polarization, due to the presence of large concentration of charged defects. (ii) Lower values and smaller variations of impedance and dielectric parameter in comparison with pure samples seems to indicate the presence of lesser concentration of charged defects in doped samples than in pure samples. (iii) These samples show relaxations. The activation energy of dipoles responsible for relaxation is 1.24 eV for 0.1% SiO<sub>2</sub>-doped samples. (iv) Doped samples have smaller relaxation times and greater activation energies for dipoles. (v) The activation energy for AC conductivity at 380°C and 20 kHz is larger for doped samples compared to pure samples. Hence these results indicate clustering of charged defects in doped samples resulting in observed changes of the properties measured.

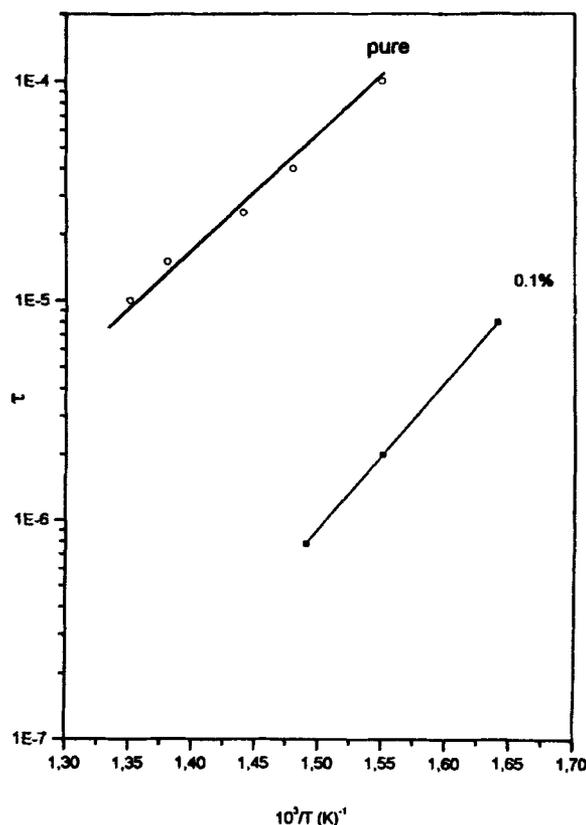


Figure 8.  $\log \tau$  versus  $10^3/T$  graph for pure and 0.1% SiO<sub>2</sub>-doped NaVO<sub>3</sub> samples.

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