

Lanthanum oxide doping effect on dc electrical conductivity of ferroelectrics sodium vanadate and rubidium vanadate

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Abstract. The temperature dependence of dc electrical conductivity was measured by two-probe technique in the vicinity of phase transition point for ferroelectrics sodium vanadate and rubidium vanadate doped with different concentrations of La_2O_3 . These materials show a sharp change in conductivity at their phase transition temperatures. The results were found to obey the conventional exponential law and the activation energies were calculated for ferroelectric and paraelectric states. It was found that activation energy in ferroelectric phase is smaller than in the paraelectric phase. The activation energy increases slowly with increase in doping concentration of La_2O_3 up to 0.1 mol%, however, it decreases with further increase in doping concentration, in both ferro and para states. The dc electrical conductivity below the Curie temperature is of mixed type (ionic-electronic) while it is electronic type above the Curie temperature.

Keywords. Ferroelectrics; conductivity; phase transition; activation energy.

1. Introduction

Electrical conductivity is one of the important electrical characteristics of dielectric materials required not only for practical applications but also for the interpretation of various physical phenomena.

It was reported by Grawford (1959) that almost all ferroelectric materials which possess high Curie temperature lose their piezoelectric properties at temperatures considerably below their Curie points. Guruvich and Rez (1960) showed that the increase in electrical conductivity of these materials at high temperatures was due to loss of piezoelectric properties. The structural aspects of alkali metal vanadates were reported by Feigelson *et al* (1972) and they have shown that NaVO_3 belongs to the monoclinic system with space group Cc at room temperature. The crystal chemistry of M^+VO_3 ($\text{M}^+ = \text{Li}, \text{Na}, \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$ and Tl) pyroxenes were studied by Hawthorne and Calvo (1977) who concluded that NaVO_3 is monoclinic with space group Cc while RbVO_3 is orthorhombic with space group Pbcm.

The electrical conductivity of the rare earth vanadate LnVO_3 ($\text{Ln} = \text{La} - \text{Lu}$ and Y) compound was studied by Sakai *et al* (1976). Verma and Lal (1981) reported that the heavy rare-earth tungstates are mixed (ionic-electronic) conductors. The electrical transport in light and heavy rare earth vanadates was studied by Gaur and Lal (1985, 1986).

The aim of present communication is to study the dependence of dc electrical conductivity of sodium vanadate and rubidium vanadate doped with different concentrations (0.025 to 3 mol%) of lanthanum oxide.

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2. Experimental

The NaVO_3 and RbVO_3 ceramics used in this investigation were prepared from a stoichiometric mixture of $\text{M}_2^+ \text{CO}_3$ ($\text{M}^+ = \text{Na, Rb}$) and vanadium pentoxide (V_2O_5) by the usual ceramic technique following the method adopted by Feigelson *et al* (1972). These stoichiometric mixtures were slowly heated in a platinum crucible inside a global furnace and fired at 750°C for 5 h and then cooled gradually to room temperature. The modified vanadates were prepared by taking different molar concentrations of La_2O_3 (99.9% purity) as an additive. Every batch was dry-mixed and then wet-mixed with ethyl alcohol in an agate mortar. After complete evaporation of alcohol, the batches were heated in a platinum crucible at 750°C for 5 h inside global furnace and cooled to room temperature. The ceramic samples were then ground to pass 120 mesh sieve. Crystallinity was confirmed with X-ray diffraction.

Sample pellets were prepared in the form of disc of 1 cm diameter and about 0.2 cm thickness by applying $7.6 \times 10^7 \text{ kg/m}^2$ pressure using a hydraulic press. The pellets were sintered on a platinum foil at 500°C for 4 h. The two opposite faces of each pellet were polished and silvered with air-drying silver paste to achieve good electrical contact.

The experimental set-up consists of global furnace, a digital dc microvoltmeter (VMV 15) with picoammeter adaptor, a transistorized power supply unit to provide dc electrical field, digital multimeter and a temperature controller. To ensure that contacts between electrodes and pellet interfaces were ohmic, the current density (J)–electric field (E) characteristics for all samples at constant temperature were studied. The J – E characteristics are linear up to the electric field of 200 V/cm. Above this critical field, the increase of J with E becomes non-linear. The linear plot below 200 V/cm indicates the ohmic contact. In all measurements the electric field (100 V/cm) was maintained below the critical field (200 V/cm). The measurement of dc electrical conductivity was based on the dc resistivity data obtained by two-probe method. The pellet was slowly heated in a furnace by applying dc voltage of 100 V/cm in series with pico-ammeter. The dc electrical conductivity was obtained from resistivity data in the vicinity of phase transition points. To ensure whether conductivity is ionic, electronic or mixed (ionic-electronic), the variation of dc electrical conductivity with time at a constant temperature was studied both in the ferroelectric and paraelectric states.

3. Results and discussion

The results of the measurement of dc electrical conductivity in pure and doped NaVO_3 and RbVO_3 obey the well known equation

$$\sigma = \sigma_0 \exp(\Delta E/kT),$$

where ΔE is the activation energy, σ_0 a constant, σ the electrical conductivity at temperature T and k the Boltzmann constant. The variation of $\log \sigma$ with $1/T$ for pure NaVO_3 and doped with different concentrations of La_2O_3 (0.025, 0.05, 0.1, 0.5 m, 1 and 3 mol%) is shown in figure 1, while for pure RbVO_3 and doped La_2O_3 (0.025, 0.05, 0.1, 0.5, 1 and 3 mol%) is shown in figure 2. It is clear from figures 1 and 2 that the dc electrical conductivity increases exponentially with increasing temperature.

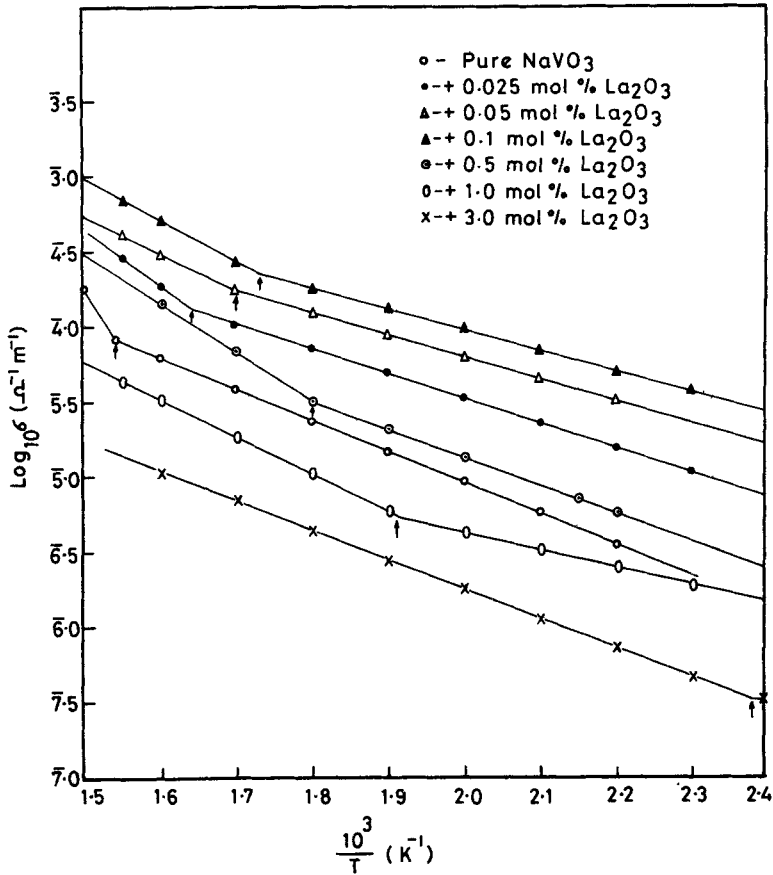


Figure 1. Variation of logarithmic conductivity (in $\Omega^{-1}\text{m}^{-1}$) with $1/T$ for pure and doped NaVO_3 .

A sharp change in conductivity is observed at the transition temperature (T_c). These transition temperatures (T_c) are ferroelectric Curie temperatures of respective samples, 648 K for NaVO_3 and 643 K for RbVO_3 which we have confirmed by hysteresis loop method (Sawyer and Tower 1930) and dielectric constant measurements. These temperatures are in good agreement with those reported previously (Patil *et al* 1989, 1990). The doping of La_2O_3 to NaVO_3 and RbVO_3 shows noticeable shift in the Curie temperature to lower temperature (figures 1 and 2) and is in good agreement with the results obtained by Gopala Krishnan and Seshamma (1991).

Figures 1 and 2 reveal that the magnitude of conductivity increases with increase of dopant content at low La_2O_3 concentrations (0.025, 0.05, 0.1 mol%) and exhibits a maximum at 0.1 mol% and then decreases for higher dopant concentrations from 0.5 to 3 mol% of La_2O_3 . The enhancement in dc electrical conductivity for addition of 0.1 mol% of La_2O_3 in NaVO_3 and RbVO_3 ceramics is attributed to a rather more solid state interaction that takes place in the materials. This might be due to the increase of density with addition of La_2O_3 up to 0.1 mol% (table 1). Doping with La^{3+} may keep the grain size small and thereby expedite densifications. It indicates

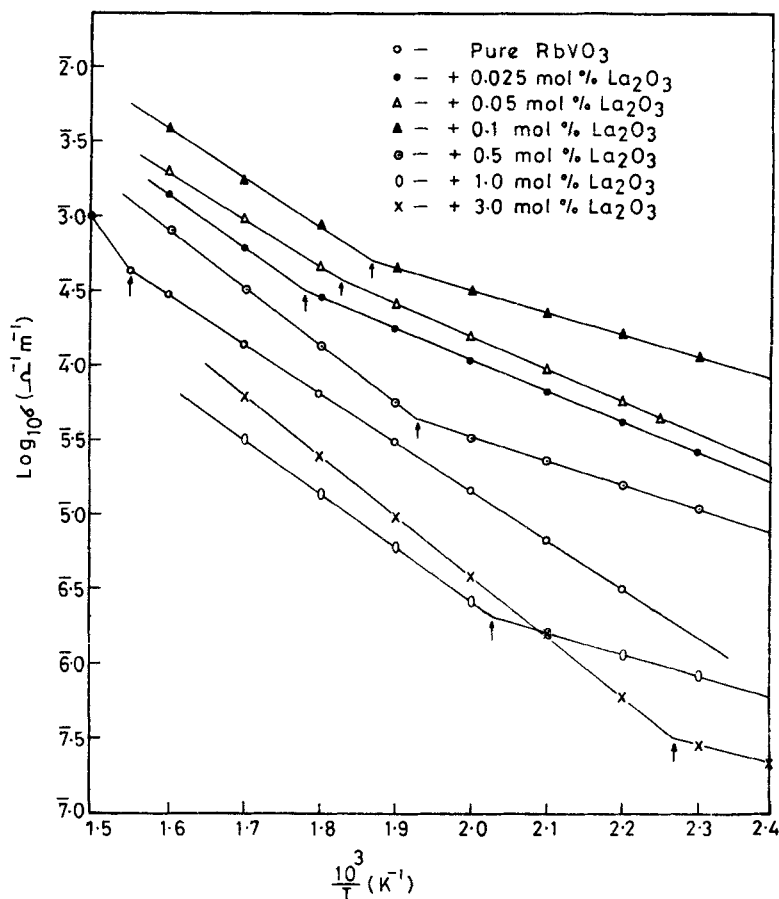


Figure 2. Variation of logarithmic conductivity (in $\Omega^{-1} \text{m}^{-1}$) with $1/T$ for pure and doped RbVO_3 .

that the 0.1 mol% doping may represent the solubility limit of La_2O_3 in NaVO_3 as well as RbVO_3 lattices. Similar results were reported by Weston *et al* (1969) for Fe_2O_3 doped PZT and by Tawfik *et al* (1978) for Al doped BaTiO_3 ceramics. Thus increase in conductivity for doping up to 0.1 mol% is because of the increasing concentration of cation vacancies in NaVO_3 and RbVO_3 . Here Na^+ and Rb^+ ions are considered solely mobile ions on account of their low equivalent weights compared to La^{3+} . The activation energies, both in ferroelectric and paraelectric states, and the experimental densities are summarized in table 1 for NaVO_3 and RbVO_3 ceramics doped with La_2O_3 . Table 1 reveals that the activation energy in paraelectric state is higher than in the ferroelectric state.

The contribution to electrical conductivity is due to migration of ions or electrons or both. To investigate the nature of electrical conductivity, one has to distinguish the principal charge carriers. It is well known that, the dc electrical conductivity in a pure ionic conductor decreases with time and tends to zero after a very long time. In case of pure electronic conductor, the conductivity is independent of time, while in mixed (ionic-electronic) conduction, the dc electrical conductivity first decreases

Table 1. Activation energies and densities of NaVO_3 and RbVO_3 .

La_2O_3 content (mol.%)	Activation energy (eV)		Ceramic density ($\times 10^3 \text{ kg/m}^{-3}$)
	Ferro	Para	
NaVO_3			
0.000	0.70	1.65	2.50
0.025	0.33	0.79	2.59
0.050	0.30	0.53	2.66
0.100	0.29	0.60	2.72
0.500	0.38	0.70	2.70
1.000	0.25	0.50	2.67
3.000	0.20	0.41	2.62
RbVO_3			
0.000	0.63	1.48	3.08
0.025	0.43	0.69	3.09
0.050	0.42	0.62	3.16
0.100	0.30	0.60	3.35
0.500	0.31	0.72	3.23
1.000	0.31	0.70	3.17
3.000	0.27	0.77	3.10

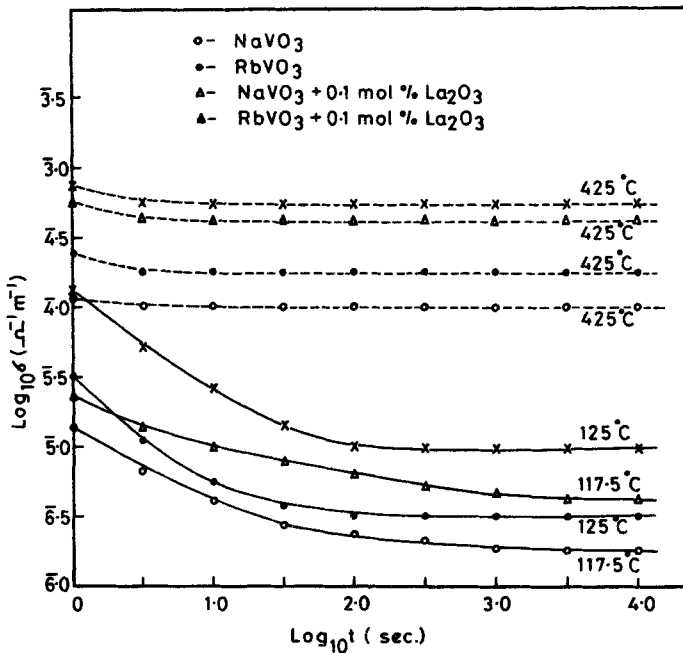


Figure 3. Variation of $\log \sigma$ with $\log t$ for NaVO_3 , RbVO_3 , $\text{NaVO}_3 + 0.1 \text{ mol}\% \text{ La}_2\text{O}_3$ and $\text{RbVO}_3 + 0.1 \text{ mol}\% \text{ La}_2\text{O}_3$.

with time and then acquires a constant value after a long time. Figure 3 represents the variation of $\log \sigma$ with $\log t$ at a constant temperature, both in ferroelectric and paraelectric states, for pure NaVO_3 and RbVO_3 and doped with 0.1 mol% La_2O_3 .

Figure 3 reveals that the dc electrical conductivity below transition temperature is of mixed type (ionic-electronic) while above transition temperature it is electronic. Similar type of conductivity behaviour was reported by Chavan and Kulkarni (1993) and Rasal *et al* (1993).

4. Conclusions

- (i) The dc electrical conductivity of all samples increases exponentially with increasing temperature, both in ferroelectric and paraelectric regions.
- (ii) A sharp change in electrical conductivity is observed at phase transition temperature, indicating the ferroelectric Curie temperature of respective samples.
- (iii) The addition of La_2O_3 to NaVO_3 and RbVO_3 shows noticeable shift in the Curie temperature to lower temperature.
- (iv) The activation energies of all the samples are higher in the paraelectric region than in the ferroelectric region.
- (v) The nature of electrical conductivity is of mixed type (ionic-electronic) in the ferroelectric region and electronic in the paraelectric region.

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