

Electrical conductivity of the ferroelectric sodium vanadate, potassium vanadate, lithium vanadate and their solid solutions

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Abstract. The d.c. electrical conductivity of sodium vanadate, potassium vanadate, lithium vanadate and their solid solutions sodium-potassium vanadate, sodium-lithium vanadate were measured by a two-probe method in the temperature range covering their transition points. These materials show sharp change in conductivity at their phase transition temperatures. In sodium, potassium and lithium vanadates an exponential increase in d.c. conductivity is observed in ferroelectric region while discontinuities are observed above the transition temperatures. The activation energy in paraelectric state of the solid solutions is found to be higher than in ferroelectric state. In solid solutions the activation energy depends upon sodium vanadate concentration.

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

1. Introduction

Grawford (1959) reported that almost all ferroelectric materials which possess a high Curie temperature lose their piezoelectric properties at temperatures considerably below their Curie points. Guruvich and Rez (1960) showed that the loss of piezoelectric properties of these materials was due to the increase in electrical conductivity at high temperatures. Electrical transport studies on heavy rare-earth tungstates were reported by Verma and Lal (1981) who showed that they are mixed ionic-electronic conductors. Lal *et al* (1982) reported the electrical transport in heavy rare-earth iron garnets. Kanchan Gaur and Lal (1985, 1986) reported the electrical transport in light and heavy rare-earth vanadates.

The present paper reports the variation of d.c. electrical conductivity with temperature of sodium vanadate (NaVO_3), potassium vanadate (KVO_3), lithium vanadate (LiVO_3) and their solid solutions, sodium-potassium vanadate ($\text{Na}_x\text{-K}_{1-x}\text{VO}_3$) and sodium-lithium vanadate ($\text{Na}_x\text{-Li}_{1-x}\text{VO}_3$).

2. Experimental

Crystalline solids of sodium vanadate, potassium vanadate and lithium vanadate were prepared from a stoichiometric mixture of M_2^+CO_3 ($\text{M}^+ = \text{Na, K and Li}$) and vanadium pentoxide (V_2O_5). This mixture was heated in a platinum crucible at 750°C for 4 hr inside a globar furnace and then cooled to room temperature. The solid solutions of $(\text{Na}_x\text{-K}_{1-x})\text{VO}_3$ and $(\text{Na}_x\text{-Li}_{1-x})\text{VO}_3$ were prepared from their respective vanadates by firing in the platinum crucible at 900°C for 3 hr and then

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allowed to furnace cool. The samples formed were confirmed by scanning them on X-ray diffractometer. The sample pellets were prepared in the form of discs (diameter 1 cm and thickness about 1 mm) by applying a 5 ton pressure using a hydraulic press. These pellets were sintered on a platinum foil at 500°C for 3 hr. The two sides of these sintered pellets were coated with a thin layer of silver paste for good electrical contact.

The experimental set-up consisted of a globar furnace, a digital DC microvoltmeter (VMV 15) with a Pico-ammeter adaptor, a transistorized power supply unit to provide d.c. electric field and a temperature controller arrangement. Current through the pellets was measured as a function of applied d.c. electric field at a constant temperature and the current density J was plotted against the applied electric field E . Three such plots are shown in figure 1. The current density J varies linearly with E up to the critical field and then the variation becomes nonlinear. For further study of d.c. conductivity the value of d.c. electric field is chosen (10 V) to fall within the critical field. The d.c. conductivity measurements were based on the d.c. resistivity data obtained by the two-probe method. A d.c. voltage of 10 V was applied across the pellet holder in series with Pico-ammeter. The pellet holder was heated slowly in the furnace and d.c. resistivity measurements were taken in the temperature regions covering the transition points of the samples. The resistivity data were used to calculate the d.c. conductivity.

3. Results and discussion

The variation of conductivity σ with temperature T can be represented by the general relation

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

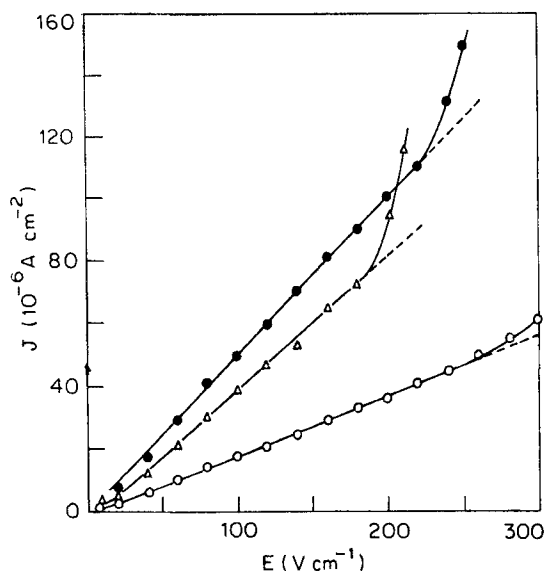


Figure 1. Variation of current density J with d.c. electric field E [—○— NaVO_3 ; $T=325^\circ\text{C}$. —●— $(\text{Na}_{0.5}-\text{K}_{0.5})\text{VO}_3$; $T=425^\circ\text{C}$; —△— $(\text{Na}_{0.5}-\text{Li}_{0.5})\text{VO}_3$; $T=425^\circ\text{C}$].

where ΔE is the activation energy, σ_0 the constant and K the Boltzmann constant. The variation of $\log \sigma$ with $1/T$ for NaVO_3 , KVO_3 and LiVO_3 is shown in figure 2 while figures 3 and 4 show such variations for solid solutions $(\text{Na}_x\text{-K}_{1-x})\text{VO}_3$ and $(\text{Na}_x\text{-Li}_{1-x})\text{VO}_3$ respectively. To determine whether the conductivity is ionic, electronic or mixed, the variation of d.c. conductivity with time is studied at a constant temperature using electrodes which block ionic conduction. For pure ionic conduction, conductivity decreases with time and tends to zero after a long time while for a pure electronic conductor, the conductivity is independent of time. In the case of mixed conduction, conductivity first decreases with time and then remains constant at some finite value. The variation of $\log \sigma$ with $\log t$ is shown in figure 5 for NaVO_3 , $(\text{Na}_{0.5}\text{-K}_{0.5})\text{VO}_3$ and $(\text{Na}_{0.5}\text{-Li}_{0.5})\text{VO}_3$.

It is clear from figure 2 that for NaVO_3 , KVO_3 and LiVO_3 an exponential increase in d.c. conductivity is observed only up to transition temperature (T_c) and thereafter there are discontinuities. The nature of conductivity below the transition temperature is ionic. In figures 3 and 4 the conductivity increases exponentially and a sharp change in conductivity is observed at the transition temperatures (T_c) of the respective solid solutions. These transition temperatures (T_c) are ferroelectric Curie temperatures of the respective samples which we have investigated by the hysteresis loop method and the dielectric constant measurements. For solid solutions $(\text{Na}_x\text{-K}_{1-x})\text{VO}_3$ and $(\text{Na}_x\text{-Li}_{1-x})\text{VO}_3$ the graphical variation of $\log \sigma$ with $\log t$ shows that the conductivity below T_c is of mixed type (partially ionic and electronic) (figure 5) and

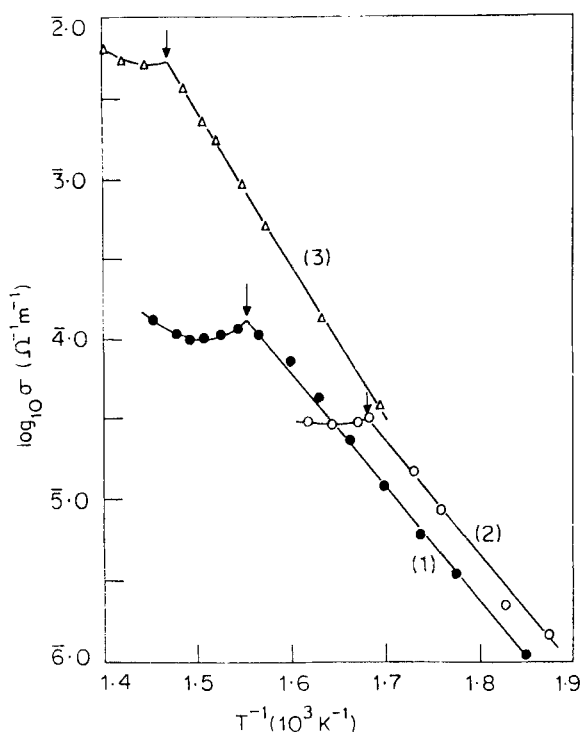


Figure 2. Variation of logarithmic conductivity σ with $1/T$ for 1. NaVO_3 , 2. KVO_3 and 3. LiVO_3 .

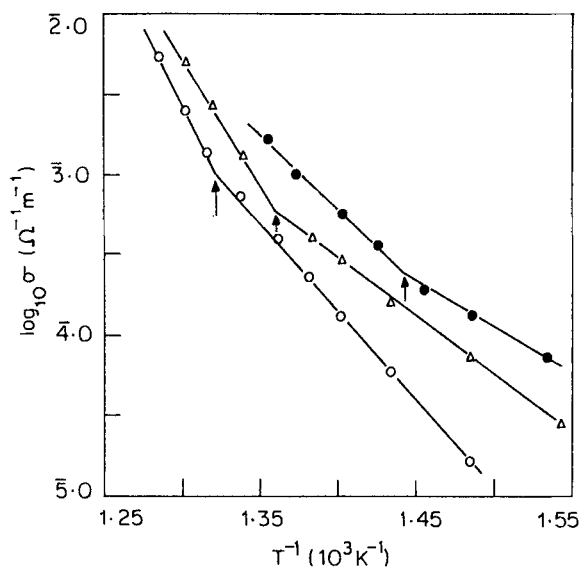


Figure 3. Variation of logarithmic conductivity σ with $1/T$ for $(\text{Na}_x - \text{K}_{1-x})\text{VO}_3$ [—●— $(\text{Na}_{0.75} - \text{K}_{0.25})\text{VO}_3$; —△— $(\text{Na}_{0.50} - \text{K}_{0.50})\text{VO}_3$; —○— $(\text{Na}_{0.25} - \text{K}_{0.75})\text{VO}_3$].

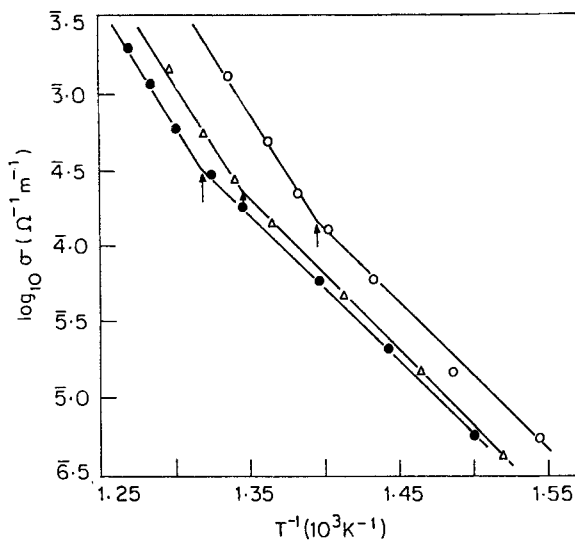


Figure 4. Variation of logarithmic conductivity σ with $1/T$ for $(\text{Na}_x - \text{Li}_{1-x})\text{VO}_3$ [—●— $(\text{Na}_{0.75} - \text{Li}_{0.25})\text{VO}_3$; —△— $(\text{Na}_{0.50} - \text{Li}_{0.50})\text{VO}_3$; —○— $(\text{Na}_{0.25} - \text{Li}_{0.75})\text{VO}_3$].

above T_c the electronic conduction dominates over the ionic conduction. The activation energies are evaluated from the slope of $\log \sigma$ against $1/T$ plot and their values are summarized in table 1.

In the paraelectric state of the solid solutions the activation energy is higher than in ferroelectric state.

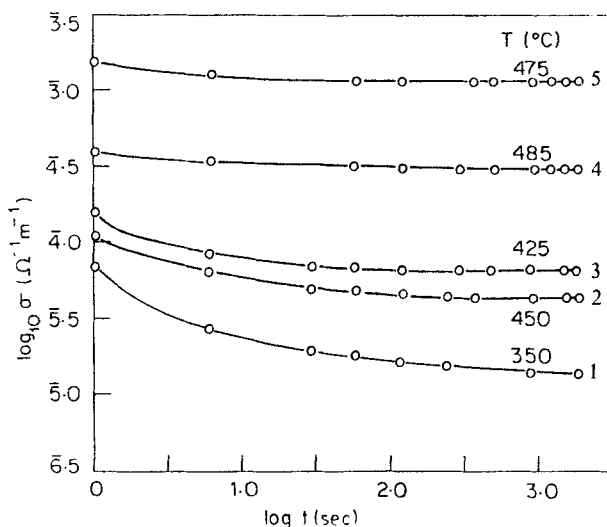


Figure 5. Variation of $\log \sigma$ with $\log t$ for 1. NaVO_3 , 3, 5. $(\text{Na}_{0.5}\text{K}_{0.5})\text{VO}_3$ and 2, 4 $(\text{Na}_{0.5}\text{Li}_{0.5})\text{VO}_3$.

Table 1. Activation energies and Curie temperatures of different samples.

Sample	Activation energy (eV)		Curie temperature ($^{\circ}\text{C}$)	Density of pellet (g cm^{-3})
	Ferro-state	Para-state		
NaVO_3	1.39	—	370	2.69
KVO_3	1.51	—	322	2.67
LiVO_3	1.92	—	407	2.81
$(\text{Na}_{0.75}\text{-K}_{0.25})\text{VO}_3$	1.12	1.85	420	2.48
$(\text{Na}_{0.50}\text{-K}_{0.50})\text{VO}_3$	1.38	2.69	462	2.61
$(\text{Na}_{0.25}\text{-K}_{0.75})\text{VO}_3$	2.14	3.96	483	2.23
$(\text{Na}_{0.75}\text{-Li}_{0.25})\text{VO}_3$	1.88	3.32	485	2.64
$(\text{Na}_{0.50}\text{-Li}_{0.50})\text{VO}_3$	1.98	3.12	470	2.56
$(\text{Na}_{0.25}\text{-Li}_{0.75})\text{VO}_3$	1.96	3.17	444	2.39

Experimental densities of the pellets of sodium vanadate, potassium vanadate and lithium vanadate relative to their crystal densities are 0.92, 0.93 and 0.92 respectively.

4. Conclusions

- (i) For NaVO_3 , KVO_3 and LiVO_3 , discontinuities are observed above the transition temperature and conductivity increases exponentially in ferroelectric region. The nature of electrical conductivity is ionic below the transition temperature.
- (ii) The electrical conductivity of all the materials shows a sharp change at the phase transition temperature, indicating the ferroelectric Curie temperatures of the respective materials.
- (iii) For solid solutions the nature of electrical conductivity below the transition temperatures is of mixed type (partially ionic and electronic) and above this temperature it is electronic.
- (iv) The activation energy of the solid solutions is higher in the paraelectric state than in the ferroelectric state and it depends upon the sodium vanadate concentration.

References

- Grawford A 1959 *Br. Commun. and Electron.* **6** 516
Guruvich V and Rez I 1960 *Sov. Phys. Solid State (Engl. Transl.)* **2** 624
Kanchan Gaur and Lal H 1985 *J. Mater. Sci.* **20** 3167
Kanchan Gaur and Lal H 1986 *J. Mater. Sci.* **21** 2289
Lal H, Verma B and Yadav V 1982 *J. Mater. Sci.* **17** 3317
Verma B and Lal H 1981 *Mater. Res. Bull.* **16** 1579