

Investigations on thermoelectric power of lanthanum oxide doped ferroelectric sodium vanadate

D V PAWAR, T S MAGDUM, S P RASAL and S H CHAVAN*

Ferroelectrics Laboratory, Department of Physics, Shivaji University, Kolhapur 416 004, India

*For correspondence

MS received 11 January 1993; revised 19 June 1993

Abstract. The thermoelectric power of ferroelectric sodium vanadate doped with different concentrations of lanthanum oxide has been measured in the temperature range covering their transition temperatures. It has been observed that the thermoelectric power increases with temperature, attains maximum value and with further increase in the temperature decreases to zero, indicating Curie temperature of the respective samples; however, it changes the sign for higher temperature. The thermoelectric power of sodium vanadate increases to maximum with increase in doping concentration of lanthanum oxide from 0.025 to 0.1 mol%; however, it decreases for higher concentrations. Pure as well as lanthanum oxide doped sodium vanadate samples show *p*-type behaviour in the ferroelectric region and *n*-type behaviour in the paraelectric region.

Keywords. Ferroelectrics; thermoelectric power; Curie temperature.

PACS No. 77-90

1. Introduction

In recent years, considerable advances have been made in the investigations on various properties of the ferroelectrics sodium vanadate, potassium vanadate and lithium vanadate, but the effect of doping on these properties has practically not been studied so far. The structural aspects of alkali metal vanadates were reported by Feigelson *et al* [1] who showed that NaVO_3 belongs to the monoclinic system with space group *Cc* at room temperature. The crystal chemistry of $M^+ \text{VO}_3$ ($M^+ = \text{Li, Na, K, Cs, Rb, NH}_4, \text{Tl}$) pyroxenes was studied by Hawthorne and Calvo [2]. The structural features of NaVO_3 single crystals and the variations in lattice parameters in the temperature range from room temperature to 500°C were reported by Ramani *et al* [3] and Shaikh *et al* [4]. Dielectric dispersion over a wide range of frequency, dielectric and pyroelectric properties for sodium vanadate at different temperatures were also investigated [5, 6]. The pyroelectric properties of ferroelectric NaVO_3 , KVO_3 , LiVO_3 and their solid solutions were studied by Patil *et al* [7].

The thermoelectric effects are utilized in a thermoelectric circuit to produce useful heating, cooling and/or power generation. The studies on thermoelectric power gives useful information regarding the nature, the number and the effective mass of charge carriers in solids. The thermoelectric power or Seebeck coefficient is defined as the emf developed when a unit temperature difference exists between the points of measurements. Saburi [8] studied the variation of the thermoelectric power with temperature in the doped BaTiO_3 . Ternary and Cook [9] investigated the d.c. resistivity

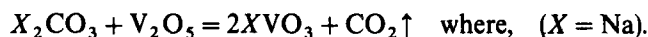
and thermoelectric power of rare-earth oxides doped BaTiO₃. Alder [10], Austin and Mott [11], Bosman and Daal [12] and Sumi [13] have studied the thermoelectric power and conduction mechanism in solids. The temperature variation of the thermoelectric power of KNbO₃ crystals doped with impurities was measured by Yanovskii [14]. Electrical conductivity and thermoelectric power of light and heavy rare earth vanadates were studied by Gaur and Lal [15, 16]. High temperature Seebeck coefficients on YBa₂Cu₃O_{7- δ} were carried out by Ramasesha *et al* [17].

The objective of the present communication is to study the effect of lanthanum oxide doping on the temperature dependence of thermoelectric power of ferroelectric sodium vanadate.

2. Experimental

2.1 Preparation

Polycrystalline alkali metal vanadate was prepared by the usual ceramic technique [1] which was grown from a stoichiometric mixture of AR grade alkali metal carbonate and vanadium pentoxide according to the reaction:



The alkali metal carbonate used was preheated at 200°C for 2 h before weighing, in order to minimize the moisture. The dried powder was then weighted and blended thoroughly with V₂O₅. This mixture was slowly heated in a platinum crucible inside a global furnace up to 750°C and this temperature was maintained for 5 h and then melted and the furnace cooled.

La₂O₃ (purity 99% Loba Chemie Indoaustranal Co., Bombay) was used as an additive. The samples were prepared by weighing La₂O₃ in different percentages from 0.025 to 3 mol % in NaVO₃. Every batch was subsequently dry-mixed and then mixed wet with ethyl alcohol in an agate mortar. After the alcohol was completely evaporated, the batches were heated in a platinum crucible at 750°C for 5 h inside a global furnace and then allowed to cool to room temperature. The prepared samples were then ground and passed through a 120 mesh sieve. The crystallinity was confirmed with X-ray diffraction. The pellets were pressed at 7.6×10^7 kg/cm² pressure, using hydraulic press, in discs of diameter 1 cm and thickness about 0.2 cm and were sintered on a platinum foil at 500° for 4 h in air inside a global furnace. The two major faces were polished and silvered with air-drying silver paste to have good electrical contact.

2.2 Apparatus and measurement

The experimental set-up consists of an electrically heated furnace, a digital d.c. microvoltmeter (VMV 15 Vasavi Electronics) a temperature controller arrangement, digital multimeter and a specially designed sample holder. A typical sample holder was designed in our laboratory for the measurement of thermoelectric power as shown in figure 1. The thermoelectric power of these samples was measured by producing a constant thermal gradient ($\Delta T = 25^\circ\text{C}$) across the sample pellets with the help of a small sub-heater, as shown in figure 1, attached to one of the hard electrodes of the sample holder. The ambient temperature was raised by the external heater. Silver electrodes were used for this measurement. The thermal gradient (ΔT)

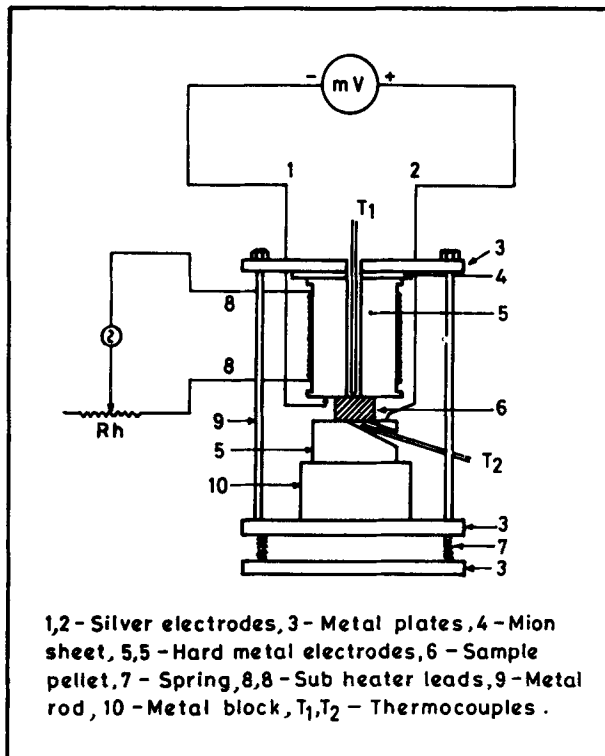


Figure 1. Typical sample holder for the measurement of thermoelectric power.

was measured using chromel–alumel thermocouples, T_1 and T_2 . The thermo emf (ΔE) developed across the sample pellet was recorded by the digital d.c. microvoltmeter after thermal stability was reached. The thermoelectric power (S) was computed using the relation $S = \Delta E / \Delta T$.

3. Results and discussion

The variation of thermoelectric power with temperature of pure sodium vanadate and that doped with lanthanum oxide in ferroelectric and paraelectric regions is presented in figure 2. From figure 2, it is clearly seen that the thermoelectric power increases with increasing temperature and attains a maximum value. These after it starts decreasing with increasing temperature and becomes negative with further increase in temperature. The magnitude of the thermoelectric power of sodium vanadate doped with different concentrations of lanthanum oxide becomes zero at a particular temperature, indicating the Curie temperature of the respective samples and are in good agreement with those investigated by us using hysteresis loop method and dielectric constant measurements. From figure 2, it is also obvious that the sign of thermoelectric power is positive in ferroelectric region of the samples, representing that the majority charge carriers are positive charges and hence, the sample shows p -type behaviour. The negative sign of the thermoelectric power in the paraelectric region of the sample shows that the majority charge carriers are electrons indicating n -type behaviour.

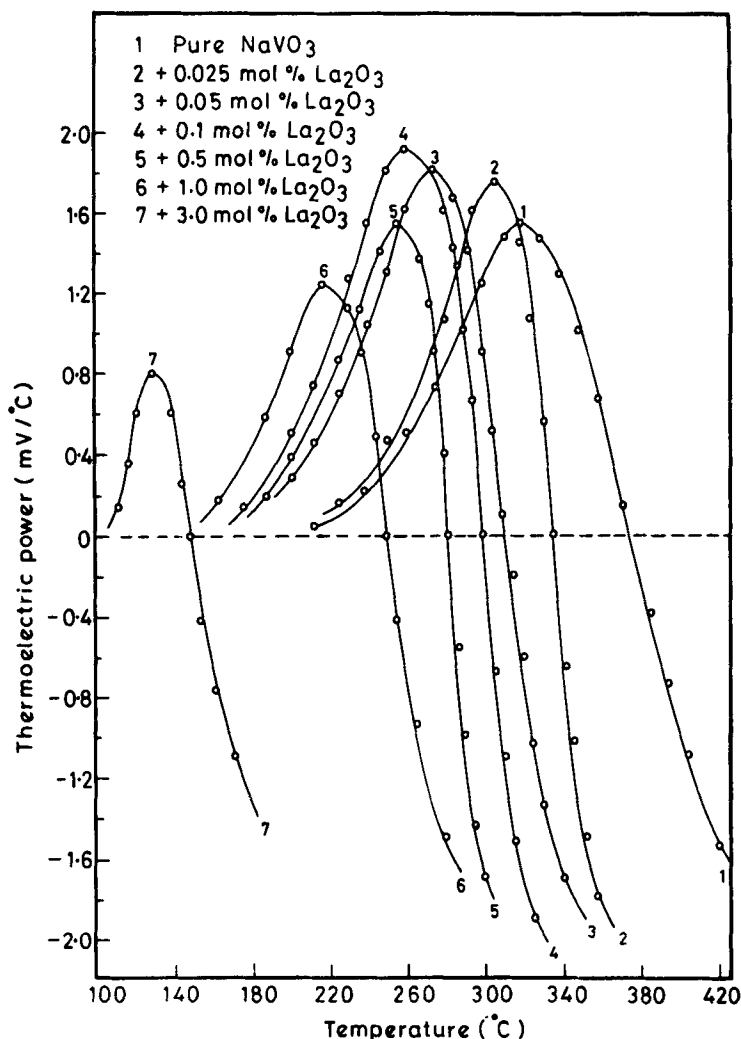


Figure 2. Variation of thermoelectric power with temperature for lanthanum oxide doped sodium vanadate.

The increase in thermoelectric power with increasing temperature of these samples in the ferroelectric region may be due to the increasing mobility of the charge carriers which increase exponentially with temperature. This increase in the mobility of charge carriers with temperature in ferroelectric region suggests a mechanism that deals with polaron hopping conduction. Similar results were also reported by Bosman and Daal [12] and Ansari *et al* [18]. In paraelectric region, the thermoelectric power decreases with increasing temperature, which is in the accordance with normal band conduction as explained by Methfessel and Mattis [19].

Figure 2 also shows that the thermoelectric power increases to maximum with increase in doping concentration of La₂O₃ from 0.025 to 0.1 mol%. However, for higher doping concentrations, it decreases. The increase in thermoelectric power is attributed to a rather more solid state interaction that takes place in the material. It is due to increase of density of NaVO₃ with increasing doping concentrations of La₂O₃ up to 0.1 mol%. The maximum densification at 0.1 mol% doping may represent

Thermoelectric power of ferroelectric NaVO_3

the solubility limit of La_2O_3 in NaVO_3 lattice. Similar behaviour was observed for Fe_2O_3 doped PZT [20] and for Al-doped BaTiO_3 ceramics [21].

4. Conclusions

The thermoelectric power of pure sodium vanadate and that doped with different concentrations of lanthanum oxide changes its sign at transition temperature, indicating the Curie temperature of the respective samples. The pure as well as doped materials show that the conduction mode is *p*-type in the ferroelectric region and *n*-type in the paraelectric region. The thermoelectric properties of sodium vanadate are affected due to addition of lanthanum oxide. The thermoelectric power increases for 0.025, 0.05 and 0.1 mol% concentrations of La_2O_3 ; it, however, decreases for higher doping concentrations.

References

- [1] R S Feigelson, G W Martin and B C Johnson, *J. Cryst. Growth* **13/14**, 686 (1972)
- [2] F C Hawthorne and C Calvo, *J. Solid State Chem.* **22**, 157 (1977)
- [3] K Ramani, A M Shaikh, B S Reddy and M A Viswamitra, *Ferroelectrics*, **9**, 49 (1975)
- [4] A M Shaikh, M A Viswamitra and P S Narayanan, *Ferroelectrics*, **22**, 311 (1978)
- [5] M Matsuda, *J. Phys. Soc. Jpn.*, **36**, 759 (1974)
- [6] A Khan, D Ghare and P Narayanan, *Bull. Mater. Sci.*, **5**, 133 (1983)
- [7] T A Patil, V M Jamadar and S H Chavan, *Indian J. Pure Appl. Phys.*, **26**, 456 (1988)
- [8] O Saburi, *J. Phys. Soc. Jpn.*, **14**, 1159 (1959)
- [9] V J Tennery and R L Cook, *J. Am. Ceram. Soc.* **14**, 187 (1961)
- [10] D Alder, *Solid State Phys.* **21**, 1 (1968)
- [11] I G Austin and N F Mott, *Adv. Phys.*, **18**, 41 (1969)
- [12] A J Bosman and H J Daal, *Adv. Phys.*, **19**, 1 (1970)
- [13] H Sumi, *J. Phys. Soc. Jpn.*, **33**, 327 (1972)
- [14] V K Yanovskii, *Phys. Status Solidi.* **A51**, 399 (1984)
- [15] K Gaur and H B Lal, *J. Mater. Sci.*, **20**, 3167 (1985)
- [16] K Gaur and H B Lal, *J. Mater. Sci.*, **21**, 2289 (1986)
- [17] S K Ramasesha, T Mathews and K T Jacob, *Mater. Res. Bull.*, **25**, 149 (1990)
- [18] T H Ansari, A K Pandit, M Prasad and R A Singh, *Indian J. Phys.*, **A63**, 784 (1989)
- [19] S Methfessel and D Mattis, *Handbook of Physics* Springer-Verlag, Heidelberg (1968) p. 389
- [20] T B Weston, A H Webster and N M McNamara, *J. Am. Ceram. Soc. (USA)* **52**, 253 (1969)
- [21] A Tawfik, M M A Sekina and M K El-Nimr, *Indian J. Phys.*, **A52**, 164 (1978)