

Short Communication

Solid-state batteries with ferroelectric sodium vanadate doped with lanthanum oxide

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Abstract

The d.c. electric field effect on ferroelectric sodium vanadate, doped with different concentrations of lanthanum oxide, above the Curie temperature shows the formation of a solid-state battery. The voltage and current generated (measured between two electrodes placed in fused samples of the lanthanum-doped sodium vanadate) are recorded after applying and then removing a d.c. electric field of about 1 kV cm^{-1} at high temperature. The voltage and current both depend on the temperature as well as on the dopant concentration. A drastic change in both parameters is observed at the Curie temperature of the respective samples. The voltage decays with time, but the decay constant is quite large.

Keywords: Solid-state batteries; Sodium vanadate; Lanthanum oxide

1. Introduction

Solid-state batteries (SSBs) composed of ferroelectric materials have promising applications. Such batteries have been proposed as a result of experimental studies of the effect of an electric field on the ferroelectricity of KNO_3 crystals [1,2]. An electromotive force of about 1 V was observed between two electrodes placed in fused KNO_3 crystals after a d.c. electric field of about 1 kV cm^{-1} was applied to the material at high temperature and then removed [3]. It has been reported [4] that solid solutions of $\text{Li}_{1+x}\text{V}_2\text{O}_8$ can be used as cathodes for high-rate secondary lithium batteries. Extensive studies have also been made [5] of SSBs prepared from ferroelectric NaVO_3 , KVO_3 , LiVO_3 and their solid solutions [6]. Finally, SSBs using Al_2O_3 -doped potassium vanadate have also been reported [7].

The present communication presents studies on SSBs that are formed by the use of ferroelectric sodium vanadate doped with different concentrations (0.025 to 3 mol%) of lanthanum oxide.

2. Experimental

Polycrystalline solids of sodium vanadate were prepared from a stoichiometric mixture of Na_2CO_3 (99.9% pure) and V_2O_5 (99.9% pure), as reported by Feigelson et al. [8]. This mixture was slowly heated in a platinum crucible at 1023 K for 5 h and then slowly cooled to room temperature. The lanthanum additive used was lanthanum oxide (99.9% pure). The ceramics were prepared by taking lanthanum oxide in amounts that varied from 0.025 to 3 mol% in sodium vanadate. Each batch was dry mixed, and then mixed after wetting with ethyl alcohol in an agate mortar. After complete evaporation of the alcohol, the batches were heated in a platinum crucible at 1023 K for 5 h inside a furnace and then cooled gradually to room temperature. The composition of the prepared ceramics were confirmed by X-ray diffraction phase analysis. The pellets of the ceramics, in the form of discs of diameter 1 cm and thickness about 0.1 cm, were prepared by applying a pressure of $7.60 \times 10^7 \text{ kg m}^{-2}$ and sintering on platinum foil at 773 K for 4 h inside a furnace. The opposite faces of the pellets were polished and silvered with air-drying silver paste to achieve good electrical contacts.

The experimental setup consisted of a furnace, an electronically regulated power supply, a digital d.c.

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microvoltmeter (VMV 15) with a picoammeter adaptor, a digital multimeter, and a temperature-controller arrangement. A d.c. electric field of about 1 kV cm^{-1} was applied to the pellets (that were located in a holder with stainless-steel electrodes) at a temperature of 723 K for a short time. The pellets were fused and the d.c. electric field was removed. Immediately the generated voltage and current produced in the samples were measured while cooling the samples. A similar procedure was adopted to study the decay in the voltage at constant temperature.

3. Results and discussions

The temperature dependence of the voltage and current generated in the fused samples of NaVO_3 doped with different concentrations of La_2O_3 (0.025 to 3 mol%) are shown in Figs. 1 and 2, respectively. A sharp change was observed in both the voltage and the current at the Curie temperature of each sample. The values of Curie temperature of different samples are in good agreement with the ferroelectric Curie temperatures determined by the hysteresis-loop method and measurements of the dielectric constant. The observed Curie temperature 648 K for pure NaVO_3 is also in good agreement with the reported value [9,10].

The addition of La_2O_3 to NaVO_3 produces a noticeable shift in the Curie temperature to lower values,

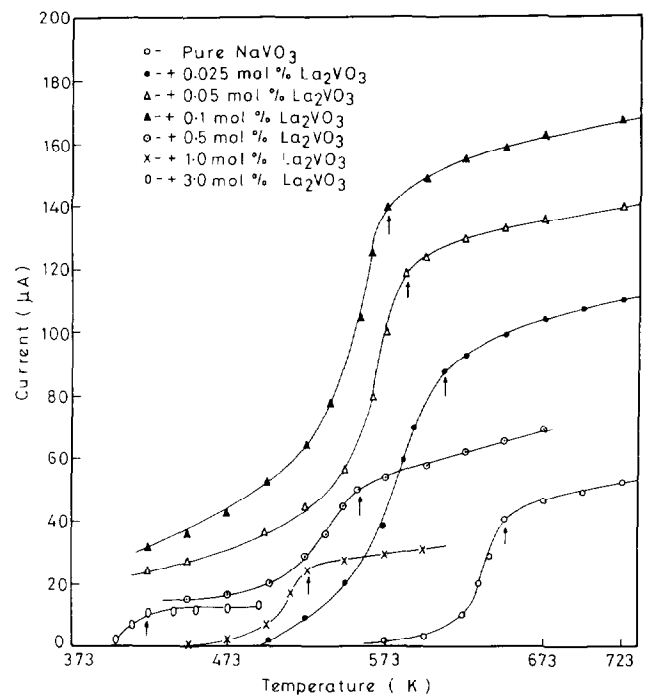


Fig. 2. Temperature dependence of current for NaVO_3 ceramics with different concentrations of La_2O_3 (mol%).

as reported by other investigators [11,12]. The data presented in Figs. 1 and 2 also reveal that both the voltage generated and the current produced in the formation of batteries that comprise NaVO_3 doped with La_2O_3 depend upon the doping concentration. High and steady values of voltage and current are observed in the para-electric state. The magnitudes of the voltage and current at the phase transition are found to increase when the dopant concentration is increased from 0.025 to 0.1 mol% La_2O_3 . There follows, however, a decrease in both parameters at higher concentrations.

The decay in voltage with time at a constant temperature of 723 K above the Curie temperature is shown in Fig. 3. The typical decay curve for NaVO_3 doped with 0.1 mol% La_2O_3 (when the electrodes are short-circuited) is presented in Fig. 4. The data in Fig. 3 reveal that the decay constant for each sample is quite large. It is clear from Fig. 4 that, even after the electrodes are short-circuited, the voltage gradually recovers to almost the value expected in the absence of short-circuiting (cf., equivalent curve in Fig. 3). From these observations, it is clear that some chemical reaction is taking place and a solid-state battery has been formed.

A plausible explanation for the generation of voltage and current during the formation of the battery is as follows. On applying a high d.c. electric field of about 1 kV cm^{-1} across the sample at high temperature for a short time, some parts of the sample become fused into alkali metal positive ions and negative radicals of vanadate, VO_3^- . The alkali metal positive ions become neutral by removing electrons from the cathode (i.e.,

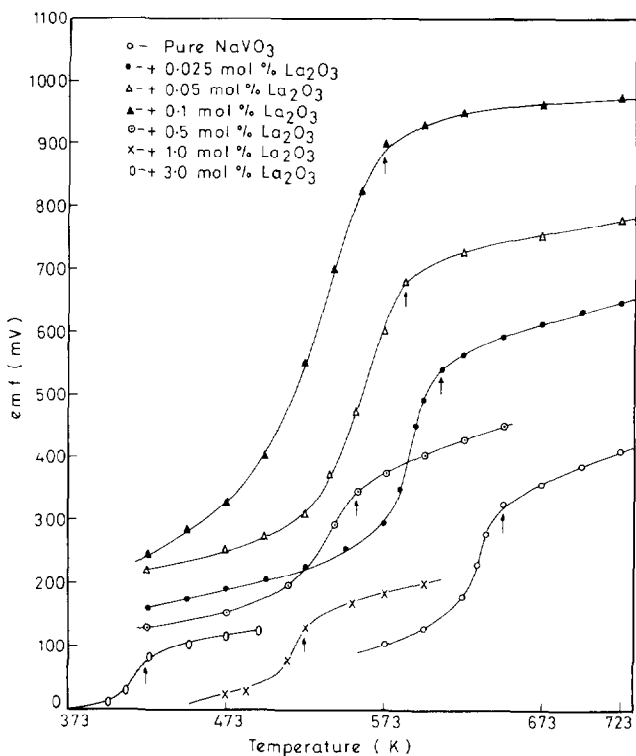


Fig. 1. Temperature dependence of potential for NaVO_3 ceramics with different concentrations of La_2O_3 (mol%).

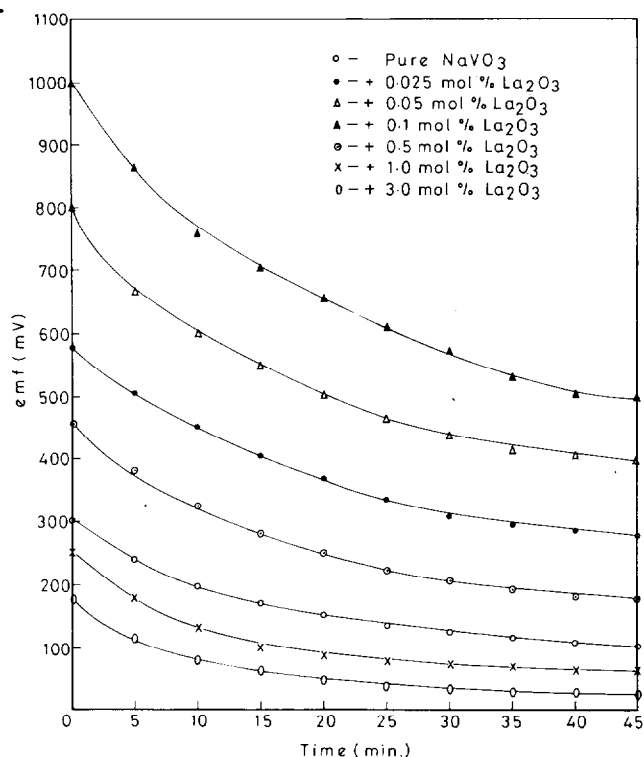


Fig. 3. Decay of potential for NaVO_3 ceramics with different concentrations of La_2O_3 (mol%) at 723 K.

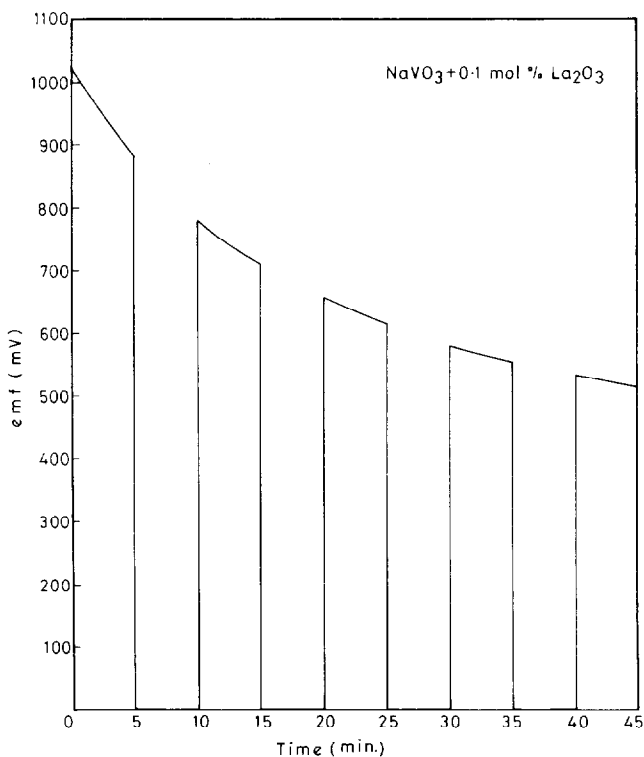


Fig. 4. Decay of potential for NaVO_3 doped with 0.1 mol% La_2O_3 at 723 K.

cathodic reduction). The negative vanadates become neutral by accepting electrons at anode (i.e., anodic oxidation). The neutral VO_3 radicals are unstable and therefore decompose into VO_2 and oxygen. The VO_2 remains as a residue while the oxygen is liberated at the anode. Thus, charging of the battery takes place. After short period of charging, when the d.c. electric field is removed, discharging of the battery takes place. Obviously, the chemical reaction during charging is reversed during the discharge process. In the latter, VO_2 and part of the oxygen combine by receiving electrons to form negative vanadate radicals VO_3^- . These radicals then react with positive alkali metal ions to form alkali metal vanadate.

Thus, in present study, the formation of a battery of NaVO_3 doped with different concentrations of La_2O_3 may be explained as follows. When a d.c. electric field of 1 kV cm^{-1} is applied across the samples of NaVO_3 doped with La_2O_3 at 723 K for a short time, part of the material is decomposed into $(\text{Na} + \text{La})$ and oxygen, and VO_2 remains as a residue. Oxygen is liberated at the positive terminal and $(\text{Na} + \text{La})$ radicals are deposited near the negative terminal. Therefore, by the process of oxidation/reduction, the following solid-state battery is formed:

steel, $(\text{Na} + \text{La})/\text{NaVO}_3: \text{La}/\text{VO}_2, \text{O}_2, \text{steel}$

The decay time required for the potential (E) to fall to the $(1/E)$ th value is calculated from the plots of voltage with time for different samples at constant temperature (Fig. 3) and are summarized in Table 1. The densities of samples with different doping concentrations, calculated at room temperature, are also given in Table 1. The results reveal that the decay time required for the potential to fall to its $(1/E)$ th value depends upon the dopant concentration in the sodium vanadate. The time increases for concentrations up to 0.1 mol% of La_2O_3 and then decreases for higher concentrations. The maximum values of the decay time and the density are attained at 0.1 mol% La_2O_3 .

Table 1
Decay time for the potential (E) to fall to its $(1/E)$ th value for different samples of NaVO_3 and their densities

La_2O_3 content (mol%)	Decay time (min)	Density at room temperature $10^{-3} \text{ kg m}^{-2}$
0.000 (pure)	330	2.50
0.025	735	2.59
0.050	773	2.66
0.100	799	2.72
0.500	431	2.70
1.000	178	2.67
3.000	134	2.62

4. Conclusions

1. The voltage and current generated by the solid-state battery increases with temperature and marked changes are observed at the Curie temperature.

2. Above the Curie temperature, the effect of a d.c. electric field on both pure and La_2O_3 -doped NaVO_3 shows the formation of a solid-state battery.

3. The addition of La_2O_3 to NaVO_3 causes a noticeable shift in the Curie temperature to lower values.

4. The voltage and current generated by the solid-state battery both depend upon the doping concentration. The values increase for samples containing 0.025, 0.05, 0.1 mol% of La_2O_3 and are maximum at 0.1 mol%. They then decrease at higher concentrations.

5. The voltage decays with time but the decay constant is quite large.

6. In general, ferroelectric materials show a sudden appearance of surface charge at the transition. In the present investigation, however, even when electrodes are short-circuited, the voltage gradually recovers almost to the same value as that expected without short-circuiting. This indicates the formation of a solid-state battery.

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