Short Communication

Thermoelectric power measurement of lithium vanadate ceramics doped with chromium oxide

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Abstract

Thermoelectric power measurements of pure and chromium-oxide-doped lithium vanadate ceramics have been carried out in the temperature range that covers their phase transition. With increase in temperature, the thermoelectric power is found, in succession, to increase linearly to attain a maximum value, to decrease to zero (indicating the transition temperature of the given sample) and, finally, to change sign. The thermoelectric power of lithium vanadate increases with increase in the concentration of the chromium oxide dopant up to 0.1 mol%, and then decreases at higher concentrations. It is also observed that pure and chromium-doped $LiVO_3$ materials display p-type semiconductor behaviour in the ferroelectric state and n-type behaviour in the paraelectric state.

Keywords: Ferroelectric status; Doping; Thermoelectric power; Phase transition

1. Introduction

The thermoelectric power (TEP) provides useful information with respect to the nature, number and the effective mass of the charge carriers in solids. The TEP, or Seebeck coefficient, is defined as the e.m.f. developed when a unit temperature gradient exists between the points of measurement. The variation of the TEP with temperature in doped $BaTiO_3$ has been studied by Saburi [1]. Investigations on the d.c. resistivity and TEP of $BaTiO_3$ doped with rare earth oxides (Sm_2O_3, Gd_2O_3, HO_2O_3) have been made by Tennery and Cook [2]. In other work, Yanovskii [3] measured the temperature dependence of the TEP of $KNbO_3$ crystals doped with impurities. The electrical conductivity and TEP of light and heavy rare earth vanadates have been examined by Gaur and Lal [4]. Moekawa and Takagi [5] have reported the variation of the Seebeck coefficient for $Li_{1-x}Ti_{2-x}O_4$ with temperature. Finally, Ramasesha et al. [6] have measured the Seebeck coefficient of $YBa_2Cu_3O_7$ at high temperatures.

In the present investigation, an attempt has been made to study the temperature dependence of the TEP of $LiVO_3$, both undoped and doped with different concentrations of Cr_2O_3.

2. Experimental

Ceramic lithium vanadate was prepared from a stoichiometric mixture of lithium carbonate and vanadium pentoxide (V_2O_5) using the technique described by Feigelson and Martin [7], and Hawthorne and Calvo [8]. The mixture was heated slowly in a platinum crucible within a globar furnace, then fired at 750 °C for 5 h and, finally, cooled gradually to room temperature. The chromium-doped samples (0.025 to 5 mol%) were prepared by the same technique.

The samples were ground to a fine powder to pass a 120 mesh sieve. The crystalline structures of the samples were confirmed by X-ray diffraction using Cu $K\alpha$ radiation with NiF. Pellets were made from these samples (each in the form of disc with diameter 1 cm and thickness approximately 0.2 cm) by applying a 7.6×10^7 kg cm^{-2} pressure with a hydraulic press and then sintering at 450 °C. The two opposite faces of these sintered pellets were polished and silvered

with air-drying silver paste to achieve a good electrical contact.

The experimental system consisted of an electrically heated furnace, a temperature controller, a digital d.c. microvoltmeter (model VMV 15, Vasavi Electronics), a specially designed pellet holder, and a digital multimeter.

The TEP of these materials was measured by adjusting the thermal gradient ($\Delta T = 20$ °C) across the sample. The resulting thermo-e.m.f. (ΔE) across the pellet was measured by a digital d.c. microvoltmeter and thermoelectric power was determined by using the relation:

$$\text{thermoelectric power} = (S) = \text{TEP} = \Delta E / \Delta T \qquad (1)$$

3. Results and discussion

Fig. 1 shows that the TEP increases with increasing temperature and attains a maximum value. It then decreases and becomes negative with further increase in temperature. The magnitude of the TEP for pure and Cr_2O_3-doped $LiVO_3$ becomes zero at a particular temperature. This corresponds to the Curie temperature of a given sample. The values are in good agreement with those determined in our laboratories by using the
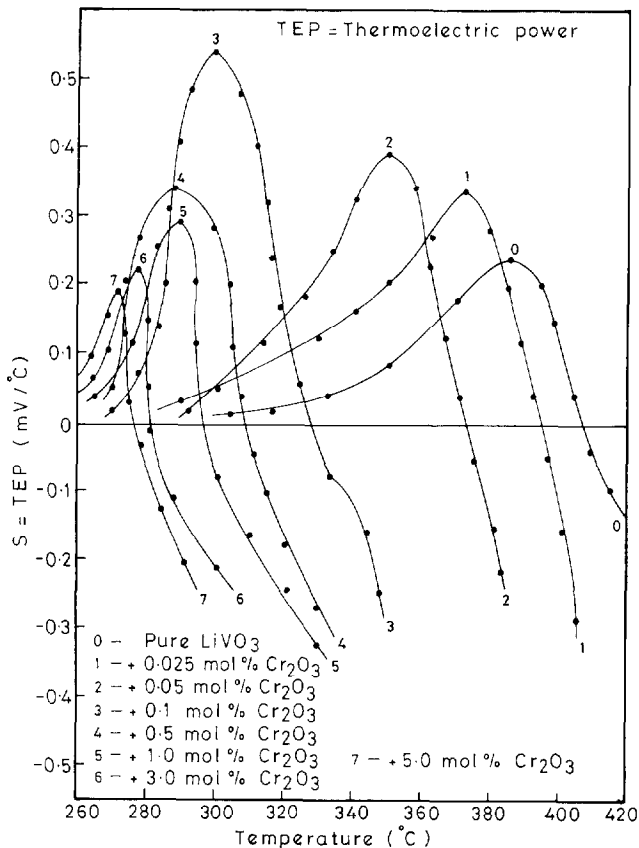

Fig. 1. Thermoelectric power vs. temperature for chromium-doped $LiVO_3$.

hysteresis-loop method and dielectric constant measurements.

It can be seen from Fig. 1 that the TEP increases to a maximum value with increasing the concentration of the Cr_2O_3 dopant from 0.025 to 0.1 mol%. At higher doping concentrations, however, it decreases. The rise in the TEP is attributed to a greater solid-state reaction that takes place in the material. This is due to an enhancement of the density of the lithium vanadate with increasing dopant concentration up to 0.1 mol%. The maximum densification at 0.1 mol% doping may represent the solubility limit of Cr_2O_3 in the $LiVO_3$ lattice.

The data presented in Fig. 1 also demonstrate that the TEP is positive in the ferroelectric region. This indicates that the majority of the charge carriers are positive charges or holes. In the paraelectric region, the TEP is negative as the majority of carriers are electrons. The sample becomes a p-type semiconductor in the ferroelectric region, while it is an n-type semiconductor in the paraelectric region.

The increase in TEP for these materials is due to the increasing mobility of the charge carriers. The latter increase exponentially with temperature. The increase in the mobility of the charge carriers with temperature in the ferrostate of the sample suggests a mechanism that involves poloron-hopping conduction. Similar results have been reported by Bosman and Van Daal [9] and Ansari et al. [10]. In the parastate, the TEP decreases. This observation is in accordance with the normal band conduction as explained by Methfessel and Mattis [11].

4. Conclusions

The TEP of $LiVO_3$ doped with different concentrations of Cr_2O_3 changes sign at the transition temperature, and matches the ferroelectric Curie temperature of the respective samples. The pure, as well as the doped materials, behave as a p-type semiconductor in ferroelectric state and an n-type semiconductor in the paraelectric region. The TEP increases as the dopant concentration is raised from 0.025 to 0.1 mol%, but decreases at higher concentrations. The ferroelectric Curie temperatures decrease with increasing concentration of Cr_2O_3 in the $LiVO_3$ lattice system. It is obvious, therefore, that such doping affects the thermoelectric properties of the host material.

References

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