Effect of Fe_2O_3 addition on the ferroelectricity of sodium and lithium vanadates

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Abstract. Spontaneous polarization and coercivity of sodium and lithium vanadates were found to be remarkably dependent on the solid solutions formed between the respective vanadates and Fe_2O_3 . The decreasing trend in P_s and the depression of T_c observed for increasing concentrations of the offvalent impurity were attributable to the formation of defective grain boundary layers of low electric polarization.

Keywords. Spontaneous polarization; hysteresis behaviour; transition temperature; sodium vanadate; lithium vanadate.

1. Introduction

Sodium and lithium vanadates have been found to have a monoclinic structure (Feigelson *et al* 1972). Sawada and Nomura (1951) studied the ferroelectric properties of sodium vanadate below its transition temperature of 380°C . Shaik *et al* (1978) reported the phase transition of sodium vanadates from their thermal expansion studies. Khan *et al* (1983) studied dielectric and pyroelectric properties of sodium and lithium vanadates. While pure materials have been extensively studied, doped materials have not received so much attention. The present work deals with the investigation of the effects of impurities on spontaneous polarization and coercive field of sodium and lithium vanadates.

2. Materials preparation

A stoichiometric mixture of corresponding carbonate, M_2^+CO_3 (where $\text{M}^+ = \text{Na}$ or Li) and vanadium pentoxide was heated up to a temperature of 800°C and maintained for about 5 h in a platinum crucible. Experimental samples were then prepared by mixing the vanadate with weighed amounts of high purity Fe_2O_3 (Fluka) in different proportions so that Fe_2O_3 were 0.1, 0.5, 1.0 and 2.0 mol% respectively in the samples. These samples were heated to about 900°C and kept inside a global furnace for 4 h. These were then cooled to room temperature. Pellets of these samples were then compressed into discs of about 1 mm thickness using a hydraulic press with a pressure of 5 tons. These samples were sintered on a metal foil for 4 h at 600°C in a furnace. These were subsequently cooled, polished and both faces were coated with silver paste for good electrical contacts.

3. Experimental

The experimental set-up for the study of hysteresis properties consisted of a furnace

which could be maintained at different temperatures electronically (accuracy being $\pm 1.0^\circ\text{C}$) inside which the samples were placed. The hysteresis curves were obtained on the oscilloscope (Phillips, PM 3206) screen using a hysteresis curve tracer designed in our laboratory with the underlying principle as proposed by Ishikawa *et al* (1983). This method had the advantage of obtaining complete hysteresis loop of a ferroelectric material by applying a sinusoidal field for only two cycles. Limited application of the field protected the specimen from temperature rise and made it possible to carry out precise measurements in the vicinity of the transition temperature of the specimen. Using additional circuits, one can also obtain the hysteresis curves on an X-Y plotter. Locally available low-cost microcomputer kit (Vinytics Peripherals, Bangalore) was used in the present work. The necessary hardware and software were fabricated and developed in our laboratory. The overall circuit used is shown in figure 1 and we were able to trace the hysteresis curves for the samples at different temperatures. The disappearance of the hysteresis loop was an indication of phase transition. The values of P_s (and E_c) were measured on the screen at different temperatures from the traces of the curves by suitable calibration (Madhusudana Rao 1990).

4. Results and discussion

Figures 2 and 3 bring out clearly the variation of spontaneous polarization P_s with temperature and Fe_2O_3 addition. P_s was found to decrease with increase of temperature and dropped to zero at the transition temperature of the sample. The coercive field E_c also showed a similar behaviour. There was also a decrease in the P_s value as the concentration of the additive increased. P_s and T_c values of pure materials were found to agree with those in the literature. Both the vanadates showed decreased values of T_c as the concentration of the additive increased. These observations were consistent with the results obtained by Nishioka *et al* (1956) for BaTiO_3 doped with Fe_2O_3 . But Yamaji *et al* (1977) found no noticeable change in

Figure 1. Block diagram of the experimental set-up.

Figure 2. Variation of P_s with temperature and Fe_2O_3 concentration for the system $\text{NaVO}_3 + \text{Fe}_2\text{O}_3$.

Figure 3. Variation of P_s with temperature and Fe_2O_3 concentration for the system $\text{LiVO}_3 + \text{Fe}_2\text{O}_3$.

T_c for the case of Dy-doped BaTiO₃. Issa *et al* (1984) reported an increase of $\epsilon_{\max}$ up to a certain concentration for BaTiO₃ doped with Gd₂O₃. Bonsack (1971) obtained a depression in the permittivity values for BaTiO₃ doped with additions such as MgO, NiO and ZnO and interpreted this decrease as due to reduced grain size. Goswami (1968) found that when there was a decrease in grain size, the proportion of the boundary phase increased. He attributed the decrease in permittivity with decreasing grain size of BaTiO₃ ceramics to the lower permittivity of grain boundary from the reflectance measurements. Issa *et al* (1984) concluded from their studies that the formation of defective grain boundary layers at the boundary of the grain was responsible for the depression of $\epsilon_{\max}$. These large boundary layers with lattice distortion were assumed to be compositionally different from the interior of the grain. A similar conclusion was arrived at by Knauer (1979) for BaTiO₃ doped with Fe₂O₃.

From the above results, it is reasonable to assume that the decrease in spontaneous polarization values consequent on decrease of permittivity values of the doped samples of NaVO₃ and LiVO₃ is due to the formation of defective grain boundary layers.

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