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Pyroelectric properties of Gd-doped KVO_3 and $LiVO_3$

A P KASHID, V V PATIL† and S H CHAVAN*+
Department of Physics, Warana Mahavidyalaya, Warananagar, Kolhapur 416 113, India
†Department of Physics, Main Rajaram Junior College, Kolhapur 416 002, India
+Department of Physics, Shivaji University, Kolhapur 416 004, India

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Abstract. Pyroelectric properties of Gd-doped and undoped potassium vanadate and lithium vanadate investigated in the temperature range covering their transition points show sharp increase at Curie temperature for undoped and for 0·025, 0·05, 0·1 mol% Gd_2O_3-doped, but no remarkable peak at Curie temperature for 0·5, 1, 3 mol% Gd_2O_3-doped KVO_3 and $LiVO_3$. The Curie temperature of all the samples remains the same for various concentrations of Gd.

Keywords. Ferroelectricity; pyroelectricity; phase transition.

1. Introduction

The pyroelectric effect is the change in polarization of a material when it undergoes a variation in its temperature (Cady 1946). A static method for measuring the pyroelectric coefficient has been presented by Ackermann (1915), which can be used only at discrete temperatures. Chynoweth (1956) devised a dynamic method for the study of the pyroelectric effect in barium titanate. The pyroelectric current variation with temperature for a $NaNO_2$ crystal was observed by Sawada *et al* (1961). Lang and Steckel (1965) described a method for measuring the pyroelectric coefficients of a polar material over a broad temperature range. The technique is based on the observations of the capacitive charging of a pyroelectric sample by pyroelectric current generated during a continuous temperature change. The pyroelectric effect in barium titanate ceramic was studied by Lang *et al* (1969). Byer and Roundy (1972) introduced a direct method for measuring pyroelectric coefficients and application to a nanosecond response time detector $(Sr_x-Ba_{1-x})\,Nb_2O_6$. Dielectric and pyroelectric measurements were carried out for $Pb_3\,(VO_4)_2$ crystals in the lowest temperature phase (phase III) by Midorikawa *et al* (1980). Dielectric permittivity and pyroelectric coefficients of mixed crystals of TGS and TGFB were reported by Mathur *et al* (1981). Chaves *et al* (1982) measured pyroelectric current in the crystal of $SbSe_x\,S_{1-x}I$ by measuring the potential difference across a short-circuiting resistance while heating the sample at a uniform rate and studied the variation of pyroelectric coefficients with temperature. The dielectric and pyroelectric studies of ferroelectric ceramic $NaVO_3$ was reported by Khan *et al* (1983). Similar properties were studied by Mansingh and Sreenivas (1983) for a triglycine sulphate polystyrene composite. The pyroelectric properties of the ferroelectric single crystal series $(K_xNa_{1-x})\,0{\cdot}4\,(Sr_YBa_{1-Y})\,0{\cdot}8\,Nb_2O_6$ were reported by Yuhan *et al* (1984). Similar properties of poled samples of lead–barium titanate and lead–strontium titanate have been investigated by Jamadar *et al* (1987). The pyroelectric properties of ferroelectric $NaVO_3$, KVO_3, $LiVO_3$ and their solid solutions have been recently studied by Patil *et al* (1988).

*For correspondence.

Thermal properties of $BaTiO_3$ crystals doped with cobalt were studied by Peraza *et al* (1976). The effect of DY_2O_3 doping and sintering parameters on dielectric properties of $BaTiO_3$ ceramics were studied by Yamaji *et al* (1977). Kuroda and Kubota (1980) studied diffuse phase transition of a rare-earth ion doped (Ba_xSr_{1-x}) Nb_2O_6 by measuring the spontaneous polarization and dielectric constant. The dielectric constant of barium titanate, doped with ytterbium oxide at different concentrations, was investigated at different temperatures by Molokhia *et al* (1984). Similar properties for barium titanate doped with Gd_2O_3 at different concentrations were studied by Issa *et al* (1984). The effect of rare-earth ions (La^{3+}, Nd^{3+}, Gd^{3+} and Sm^{3+}) doping on ferroelectric properties of (Sr–Ba) Nb_2O_6 ceramics modified with Na^+ and K^+ was observed by Umakantham *et al* (1987), the dielectric and ferroelectric properties of modified ferroelectric $Ba_4Na_2Nb_{10}O_{30}$ ceramics doped with La^{3+} and Pr^{3+} were studied by Subba Rao *et al* (1987).

The aim of this paper is to report the variations with temperature of pyroelectric current and coefficients of potassium vanadate and lithium vanadate both undoped and doped with different concentrations of Gd_2O_3. These materials, being ferroelectric, exhibit interesting pyroelectric properties due to doping and have practical applications as pyroelectric detectors.

2. Experimental

Crystalline solids of potassium vanadate and lithium vanadate grown from a stoichiometric mixture of $M_2^+CO_3$ ($M^+ = K$, Li) and V_2O_5 was slowly heated in a platinum crucible inside a globar furnace up to 750°C for 4 h and cooled to room temperature. Gd_2O_3 (purity 99·9%, John Baker Inc., Colorado, USA) was used as an additive. The samples were prepared by taking Gd_2O_3 in amounts varying from 0·025 to 3 mol% in KVO_3 and $LiVO_3$. Every batch was dry-mixed and then mixed after wetting with ethyl alcohol in an agate mortar. After the alcohol completely evaporated, the batches were calcined in a platinum crucible at 950°C for 5 h inside a globar furnace. The structures of the prepared samples were confirmed by scanning them on an X-ray diffractometer. The samples pressed at 5 t pressure into pellets 1 cm in diameter and about 1 mm thick, were sintered on platinum foil at 500°C for 3 h inside a globar furnace. To ensure good electrical contact, the two opposite surfaces of each pellet were silvered and placed in a sample holder.

The experimental set-up consisted of a furnace, a pico-ammeter adaptor connected to a digital d.c. microvoltmeter (VMV 15) and a digital voltmeter. Test samples were heated slowly at rates of about 3°C/min and the pyroelectric current was measured at various temperatures.

3. Results and discussion

The temperature variation of pyroelectric current deduced by Chynoweth (1956) is

$$i = A\left(\frac{dP_s}{dT}\right)\left(\frac{dT}{dt}\right), \tag{1}$$

where i is the pyroelectric current, A the area of ceramic material, P_s the spontaneous polarization, dT/dt the rate of heating and dP_s/dT the pyroelectric coefficient. The temperature dependence of pyroelectric current for undoped and Gd-doped KVO_3 and $LiVO_3$ is shown in figures 1 and 2 respectively. The pyroelectric coefficients calculated by using (1) are plotted for the respective materials in figures 3 and 4. It is clear from figures 1–4 that the materials show peak values of pyroelectric current and coefficients at the Curie temperature. Samples with concentrations of Gd_2O_3 from 0·025 to 0·1 mol% exhibit a pronounced Curie peak, whereas with 0·5 to 3 mol% concentrations it produced a broad, flat Curie peak. The former showed an increase with respect to undoped ceramics but the latter showed a decrease.

Addition of Gd_2O_3 to KVO_3 and $LiVO_3$ show no change in the Curie temperature, this agreeing with the results obtained for $BaTiO_3$ doped with rare earths (Lapluye *et al* 1960; Yamaji *et al* 1977; Issa *et al* 1984). The Curie temperatures of undoped KVO_3 and $LiVO_3$ are 320°C and 405°C, respectively and are in good agreement with those reported earlier (Patil *et al* 1988).

The peak value observations of pyroelectric current and coefficients at the Curie temperature and the bulk densities of the differently prepared samples for undoped KVO_3 and that doped with Gd_2O_3 are summarized in table 1, while those for undoped $LiVO_3$ and that doped with Gd_2O_3 are summarized in table 2.

Tables 1 and 2 show that the pyroelectric values at the Curie peak for KVO_3 and $LiVO_3$ ceramics containing from 0·025 to 0·1 mol% Gd_2O_3 increases with respect to undoped ceramics (figures 1–4). The enhancement in pyroelectric effect on addition of 0·1 mol% Gd_2O_3 in KVO_3 and $LiVO_3$ is attributed to a rather greater

Table 1. Peak values of various parameters of KVO_3.

Gd_2O_3 content (mol%)	Pyroelectric current (10^{-9} A)	Pyroelectric coefficient (10^{-7} C/cm/C°)	Density (g/cm^3)
0 (pure)	71·0	17·35	2·20
0·025	133·7	32·68	2·34
0·05	153·2	37·45	2·41
0·1	373·0	91·17	2·62
0·5	219·0	53·53	2·61
1	50·1	9·17	2·61
3	24·2	4·44	2·60

Table 2. Peak values of various parameters of $LiVO_3$.

Gd_2O_3 content (mol%)	Pyroelectric current (10^{-9} amp)	Pyroelectric coefficient (10^{-7} c/cm/C°)	Density (g/cm^3)
0 (pure)	128·5	31·41	2·32
0·025	339·0	82·86	2·44
0·05	343·0	83·84	2·55
0·1	432·0	105·59	2·71
0·5	153·5	28·14	2·69
1	136·8	25·08	2·68
3	89·9	16·48	2·68

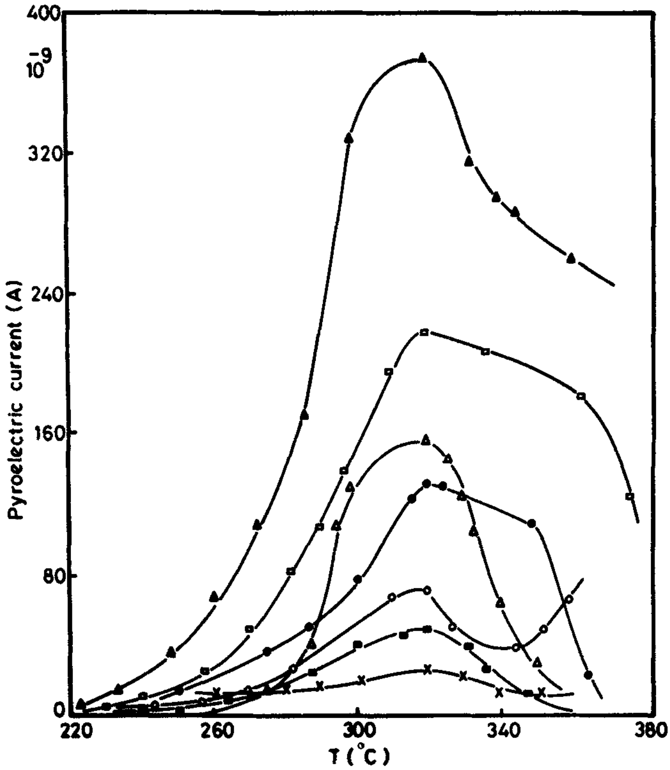

Figure 1. Variation of pyroelectric current with temperature for KVO_3 ceramics with different Gd_2O_3 additions (mol%): ○ 0, ● 0·025, △ 0·05, ▲ 0·1, □ 0·5, ■ 1 × 3.

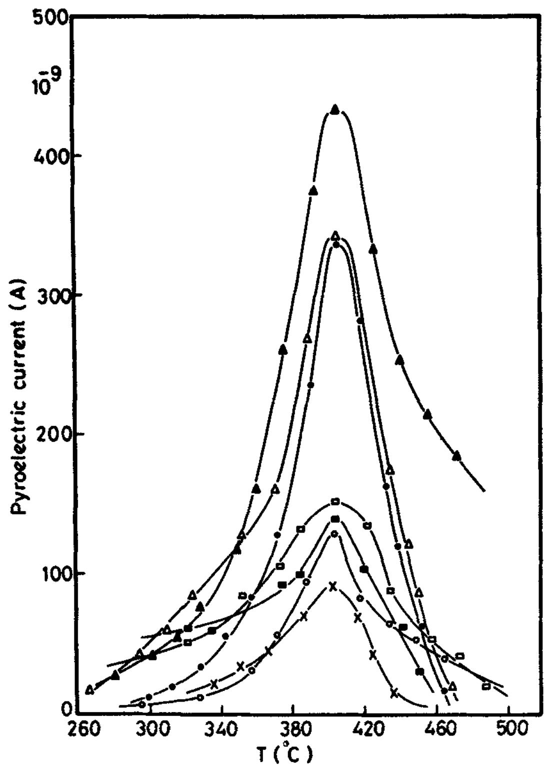

Figure 2. Variation of pyroelectric current with temperature for $LiVO_3$ ceramics with different Gd_2O_3 additions (mol%): ○ 0, ● 0·025, △ 0·05, ▲ 0·1, □ 0·5, ■ 1 × 3.

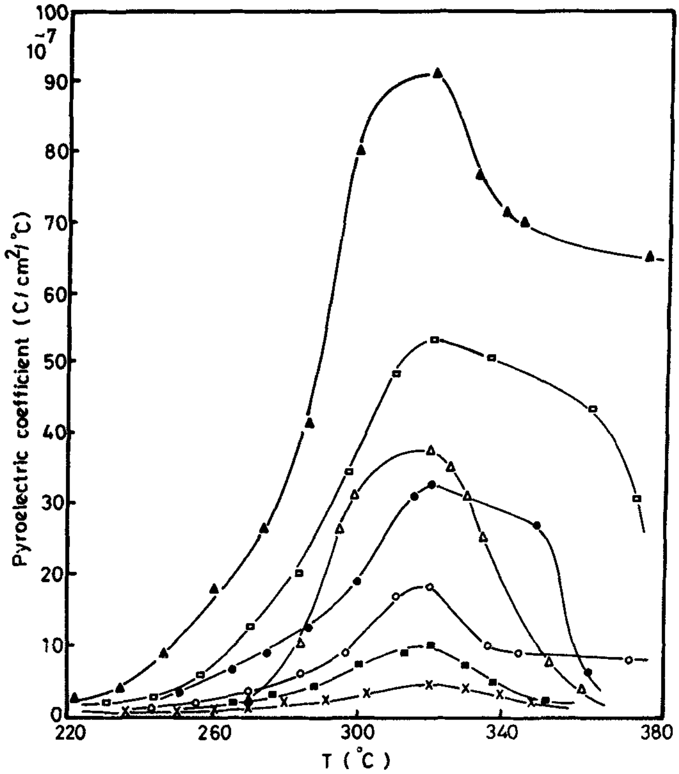

Figure 3. Variation of pyroelectric coefficient with temperature for KVO_3 ceramics with different Gd_2O_3 additions (mol%): ○ 0, ● 0·025, △ 0·05, ▲ 0·1, □ 0·5, ■ 1 × 3.

solid state interaction that takes place in the materials. This might be due to the pronounced increase of density with the addition of Gd_2O_3 up to 0·1 mol%. Doping with Gd keeps the grain size small and thereby expedites densifications. In this investigation the pyroelectric saturation states are attained at 0·1 mol% Gd_2O_3 addition. Thus 0·1 mol% doping may represent the solubility limit of Gd_2O_3 in KVO_3 as well as in $LiVO_3$ lattices.

4. Conclusions

(i) The ferroelectric Curie temperatures determined by pyroelectric measurements for undoped and doped materials are in good agreement with those obtained by the hysteresis loop method.

(ii) Curie temperatures of all the samples remain the same for various concentrations of Gd_2O_3.

(iii) The peak values of pyroelectric current and coefficients increase with increase of Gd_2O_3 concentrations up to 0·1 mol% and then decrease for higher concentrations.

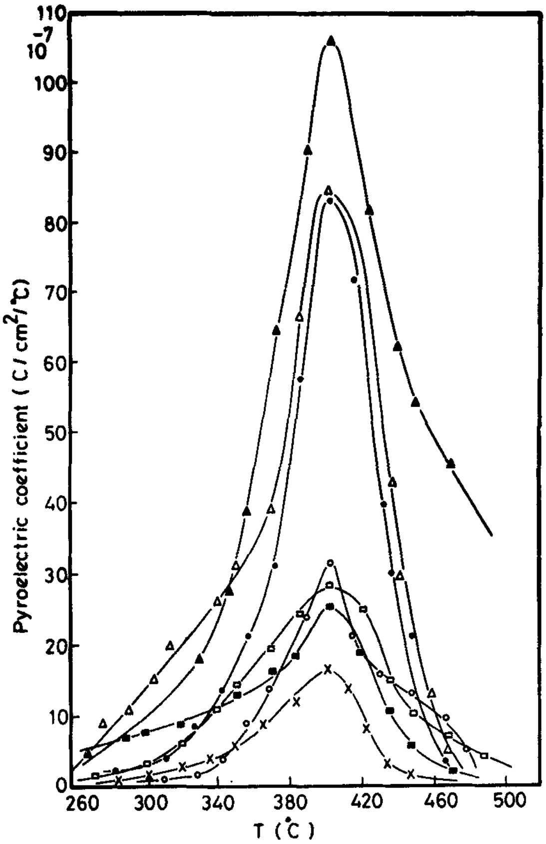

Figure 4. Variation of pyroelectric coefficient with temperature for $LiVO_3$ ceramics with different Gd_2O_3 additions (mol%): ○ 0, ● 0·025, △ 0·05, ▲ 0·1, □ 0·5, ■ 1, × 3.

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