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# INVESTIGATION OF PYROELECTRIC CHARACTERISTICS OF $Al_2O_3$ DOPED $KVO_3$ AND $CsVO_3$

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**ABSTRACT**

The pyroelectric properties of undoped and aluminium-oxide doped potassium vanadate and cesium vanadate have been studied in the temperature range covering their transition points. The values of pyroelectric current and coefficient of undoped and $Al_2O_3$-doped $KVO_3$ and $CsVO_3$ show a sharp peak at their Curie temperature. These Curie temperatures are consistent with those investigated by dielectric-constant measurements and the hysteresis-loop method. The Curie temperatures of $KVO_3$ and $CsVO_3$ doped with $Al_2O_3$ decrease with increasing dopant concentrations.

**MATERIALS INDEX** : Aluminium, potassium, cesium, vanadates.

## INTRODUCTION

The pyroelectric effect is the change in polarization of a material when it undergoes a variation in its temperature (1). A dynamic method has been devised by Chynoweth to measure the pyroelectric effect in barium titanate (2). The temperature dependence of the pyroelectric current for a $NaNO_2$ crystal was observed by Sawada et al. (3). The pyroelectric current measurements and the effects of poling and of light illumination upon the pyroelectric current in SbSI were found by Imai et al. (4). Liu and Zook have studied how the ferroelectric properties of $PbTiO_3$ can be changed by the use of additives such as trivalent rare-earth ions (5). Lijima et al. observed the pyroelectric properties of La-modified $PbTiO_3$ thin films (6). Byer and Roundy introduced a direct method for measuring pyroelectric coefficients and applied it to a nano-second response-time detector $(Sr_xBa_{1-x})Nb_2O_6$ (7). The 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. (8). Similar properties of the ferroelectric ceramic $NaVO_3$ were reported by Khan et al. (9) and for triglycine sulphate polysterene composite by Mansingh and Sreenivas (10). Deb has investigated the pyroelectric characteristic of

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Ca-modified $PbTiO_3$ ceramics for improved IR detector performance (11). The pyroelectric properties of Fe-doped $LiVO_3$ were investigated by Chavan and Kashid (12). The pyroelectric properties of ferroelectric $NaVO_3$, $KVO_3$, $LiVO_3$ and their solid solutions were studied by Patil et al. (13). The low-temperature pyroelectric properties of modified TGS single crystals were studied by Zhang et al. (14). Kashid et al. studied the pyroelectric properties of Gd-doped $KVO_3$ and $LiVO_3$ (15).

This paper reports a study of the pyroelectricity of potassium vanadate and cesium vanadate doped with different molar concentrations (0.025 to 5 mol %) of aluminium oxide. These materials, being ferroelectric, exhibit interesting pyroelectric properties due to doping and have practical applications as pyroelectric detectors.

## EXPERIMENTAL

The $KVO_3$ and $CsVO_3$ ceramics used in this investigation were prepared by the usual ceramic technique (16). The crystalline solids of potassium vanadate and cesium vanadate were prepared from a stoichiometric mixture of $M_2CO_3$ (M = K,Cs) and $V_2O_5$; they were slowly heated in a globar furnace upto 750°C for 5 hr and cooled to room temperature. The modified vanadates were prepared by taking different molar concentrations of $Al_2O_3$ as an additive. Every batch was dry-mixed and then wet with ethyl alcohol in an agate mortar. After complete evaporation of alcohol, the batches were heated in a platinum crucible at 750°C for 5 hr. The formation of the compounds was confirmed by scanning them on an X-ray diffractometer using $CuK_\alpha$ radiation. The pellets of the samples were prepared in the form of a disc of 1 cm diameter and about 0.1 cm thick under $7.6\times10^7$ kg $m^{-2}$ pressure. To ensure good electrical contact, the two faces of each pellet were electroded with air-drying silver paste.

The experimental set-up (17) consists of a furnace, digital d.c. microvoltmeter (VMV15, Vasavi Electronics) with pico-ammeter adaptor, a digital multimeter and a temperature controller arrangement. The test samples were placed in a sample holder and heated slowly at the rate of 3°C/min inside the furnace. The pyroelectric current was measured for various temperatures and the corresponding time was noted to calculate the rate of heating.

## RESULTS AND DISCUSSION

The measurements of pyroelectric current and coefficients for the materials $KVO_3$ and $CsVO_3$ doped with $Al_2O_3$ obey the equation given by Chynoweth (2):

$$i = A\,(dPs/dT)\,(dT/dt) \qquad \ldots \quad [1]$$

where, 'i' is the pyroelectric current, 'A' the electroded area of the pellet, 'Ps' the spontaneous polarization, 'dT/dt' the rate of heating and 'dPs/dT', the pyroelectric coefficient. The temperature dependence of the

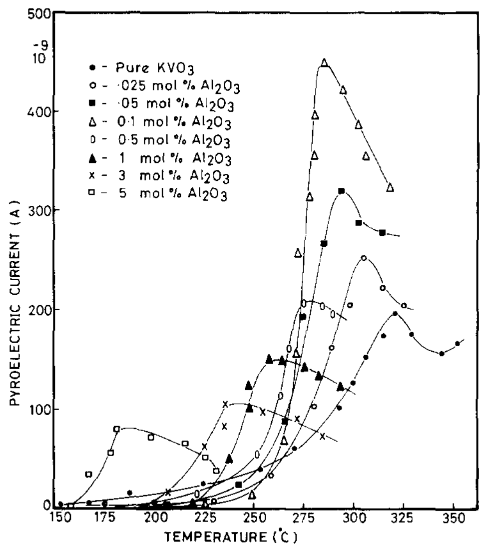


FIG.1
Variation of pyroelectric current with temperature for $Al_2O_3$ doped $KVO_3$.

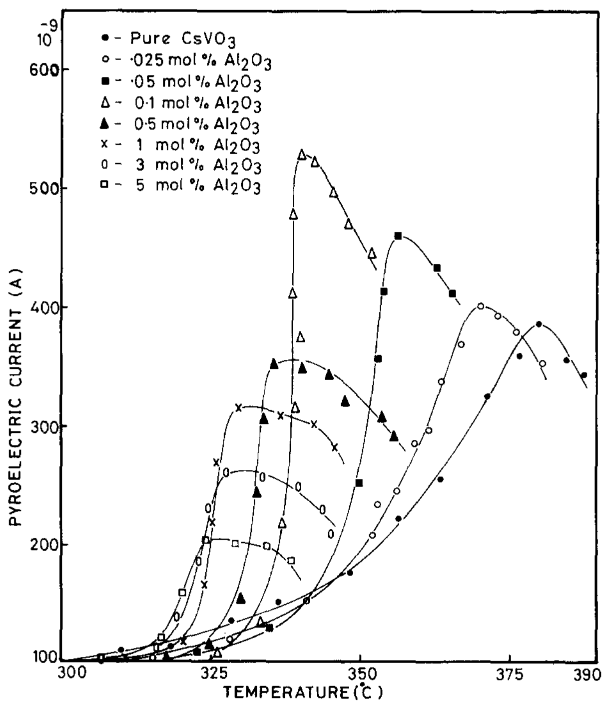


FIG.2
Variation of pyroelectric current with temperature for $Al_2O_3$ doped $CsVO_3$.

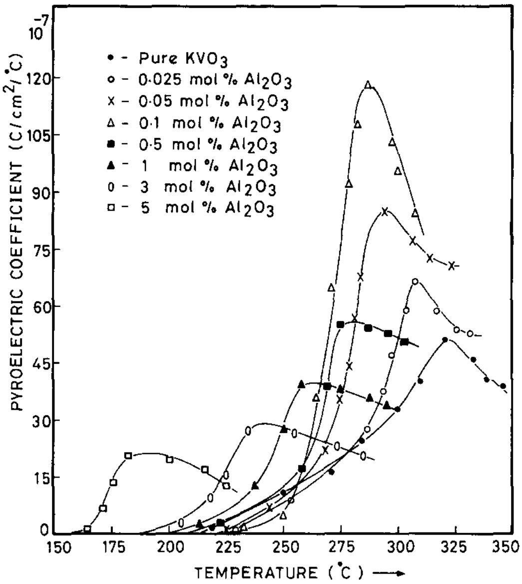


FIG.3

Variation of pyroelectric coefficient with temperature for $Al_2O_3$ doped $KVO_3$.

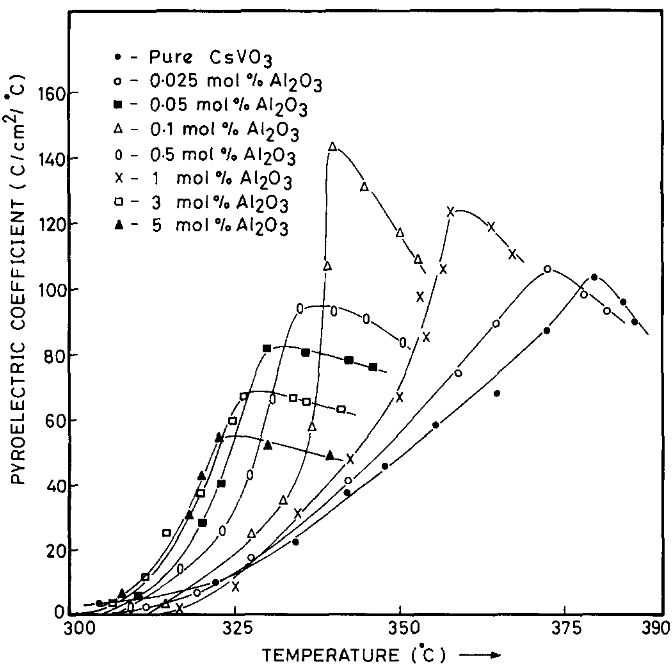


FIG.4

Variation of pyroelectric coefficient with temperature for $Al_2O_3$ doped $CsVO_3$.

pyroelectric current for undoped and aluminium doped $KVO_3$ and $CsVO_3$ is shown in Figures 1 and 2, respectively. The pyroelectric coefficient calculated by using equation [1] are presented for the respective materials in Figures 3 and 4.

It is seen from Figures 1-4 that the materials show peak values of pyroelectric current and coefficient at their Curie temperatures. They increase with increasing dopant concentration and become a maximum at 0.1 mol % concentration; they decrease for higher concentrations. These Curie temperatures are consistent with those obtained by us using the hysteresis-loop method and dielectric-constant measurements. Samples with 0.025 to 0.1 mol % concentrations of $Al_2O_3$ exhibit a pronounced Curie peak, whereas those with 0.5 to 5 mol % concentrations have a broad, flat peak.

The addition of $Al_2O_3$ to $KVO_3$ and $CsVO_3$ causes a decrease in the Curie temperature, which is in agreement with the results obtained for $BaTiO_3$ doped with $Al_2O_3$ (18). The Curie temperatures of undoped $KVO_3$ and $CsVO_3$ are 318°C and 380°C, respectively, and are in good agreement with the values reported earlier (19,15).

TABLE I
Peak values of various parameters of $KVO_3$

| $Al_2O_3$ content (mol %) | Pyroelectric current ($10^{-9}$A) | Pyroelectric coefficient ($10^{-7}$C cm$^{-2}$ °C$^{-1}$) | Density (gm cm$^{-3}$) |
|---|---|---|---|
| 0(pure) | 198.0 | 50.5 | 2.48 |
| 0.025 | 250.3 | 66.3 | 2.74 |
| 0.050 | 318.1 | 84.3 | 2.85 |
| 0.100 | 448.4 | 118.8 | 2.91 |
| 0.500 | 210.2 | 55.7 | 2.87 |
| 1.000 | 150.7 | 39.8 | 2.86 |
| 3.000 | 110.1 | 29.2 | 2.84 |
| 5.000 | 80.2 | 21.2 | 2.83 |

TABLE II
Peak values of various parameters of $CsVO_3$

| $Al_2O_3$ content (mol %) | Pyroelectric current ($10^{-9}$A) | Pyroelectric coefficient ($10^{-7}$C cm$^{-2}$ °C$^{-1}$) | Density (gm cm$^{-3}$) |
|---|---|---|---|
| 0(pure) | 385.2 | 102.1 | 2.57 |
| 0.025 | 400.1 | 106.0 | 2.79 |
| 0.050 | 457.3 | 121.2 | 2.87 |
| 0.100 | 532.5 | 141.1 | 2.97 |
| 0.500 | 358.1 | 94.9 | 2.92 |
| 1.000 | 312.7 | 82.7 | 2.89 |
| 3.000 | 260.2 | 68.9 | 2.88 |
| 5.000 | 205.4 | 54.4 | 2.87 |

Table I summarizes the peak values of the pyroelectric current and pyroelectric coefficient together with the bulk densities for undoped $KVO_3$ and $KVO_3$ doped with different molar concentrations of $Al_2O_3$, while Table II summarizes those for undoped $CsVO_3$ and doped with different molar concentrations of $Al_2O_3$. Tables I and II reveal that the peak values of pyroelectric current and coefficients for $KVO_3$ and $CsVO_3$ ceramics containing 0.025 and 0.1 mol % $Al_2O_3$ increase with respect to the undoped ceramics, while they decrease for 0.5 to 5 mol % of $Al_2O_3$. The enhancement in pyroelectric effect on addition of 0.1 mol % $Al_2O_3$ in $KVO_3$ and $CsVO_3$ is correlated with an increase of density with the addition of 0.1 mol % $Al_2O_3$. The pyroelectric saturation states are attained at 0.1 mol % where the density is a maximum.

## CONCLUSIONS

The Curie temperature obtained by pyroelectric measurements for undoped and doped ferroelectric materials are in good agreement with those obtained by the hysteresis-loop method and dielectric-constant measurements. The Curie temperature of the samples decreases with increasing dopant concentration of $Al_2O_3$. The maximum peak value of pyroelectric current and pyroelectric coefficient is observed at 0.1 mol %, which corresponds to the composition of maximum density in each system.

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