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Pyroelectric properties of ferroelectric potassium-cesium vanadate and potassium-lithium vanadate

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Abstract. Measurements of pyroelectric currents and coefficients of poled sintered discs of ferroelectric solid solutions, potassium-cesium vanadate and potassium-lithium vanadate have been investigated in the temperature range covering their transition points. In these solid solutions, $K_xCs_{1-x}VO_3$ and $K_xLi_{1-x}VO_3$, pronounced peaks have been observed at the ferroelectric curie temperatures. The peak values of pyroelectric currents and coefficients change with change in potassium concentration in both the solid solutions.

Keywords. Ferroelectricity: pyroelectricity; phase transition; vanadate solid solutions.

1. Introduction

The pyroelectric effect has been known since ancient times. Initially the static method for the measurement of pyroelectric coefficient was introduced by Ackermann (1915). The pyroelectric effect as explained by Cady (1946) is the change in polarization of material when it undergoes a change in its temperature. Chynoweth (1956) devised a dynamic method for the measurement of pyroelectric effect in barium titanate. The direct method for measurement of pyroelectric coefficients of $Sr_xBa_{1-x}Nb_2O_6$ was introduced by Byer and Roundy (1972). $Pb_3(VO_4)_2$ crystals were studied for dielectric and pyroelectric measurements in the lowest phase (phase III) by Midorikawa *et al* (1980). Feigelson *et al* (1972) have studied structures of single crystalline $LiVO_3$, $NaVO_3$ and KVO_3 which were grown from their stoichiometric melts. $LiVO_3$ and KVO_3 are found to be monoclinic and orthorhombic respectively. Similar types of investigations have been carried out by Hawthorne and Calvo (1977) on the crystals of $M^+VO_3(M^+ = Li, Na, K, NH_4, Tl, Rb$ and Cs). They have reported that the structure of $LiVO_3$ is monoclinic while that of KVO_3 and $CsVO_3$ are orthorhombic. Khan *et al* (1983) studied the dielectric and pyroelectric effect of ferroelectric $NaVO_3$. Patil *et al* (1988) investigated the properties of ferroelectric $NaVO_3$, KVO_3 and $LiVO_3$ and their solid solutions. The pyroelectric properties of Gd-doped KVO_3 and $LiVO_3$ samples have been recently reported by Kashid *et al* (1989).

The aim of this paper is to report the variations in pyroelectric currents and coefficients with the temperatures in the poled sintered discs of the solid solutions, $K_xCs_{1-x}VO_3$ and $K_xLi_{1-x}VO_3$. These solid solutions being ferroelectric materials exhibit interesting pyroelectric properties and have a practical application as a pyroelectric detector which is of a special interest.

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2. Experimental

The stoichiometric mixture of $M_2^+ CO_3(M^+ = K, Cs, Li)$ and V_2O_5 was slowly heated at 750°C for 4 h in a platinum crucible inside a globar furnace to form the crystalline solids of potassium vanadate, cesium vanadate and lithium vanadate. Solid solutions, $K_xCs_{1-x}VO_3$ were prepared from a mixture of KVO_3 and $CsVO_3$ having molar proportions of $x = 0{\cdot}8 - 0{\cdot}2$ in the globar furnace at 780°C for 4 h and were allowed to cool to room temperature. Similarly, the solid solutions $K_xLi_{1-x}VO_3$ ($x = 0{\cdot}8 - 0{\cdot}2$) were prepared. The crystal structures of the samples have been confirmed by X-ray studies. The sintered pellets of the above solid solutions having thicknesses of about 1 mm and diameters of 1 cm were placed in a sample holder. The opposite faces of the pellets were coated with thin layers of silver paste for good electrical contact with the electrodes.

The experimental set-up consists of a furnace, electronically regulated power supply to provide a d.c. electric field, a digital d.c. micro-voltmeter (VMV 15), a pico-ammeter adaptor for VMV 15 and a digital multimeter. The test sample was polarized for 10 min at room temperature by a constant d.c. electric field of 250 V/cm. The test sample electrodes were short circuited for 20 min to eliminate the current due to the space charge before the pyroelectric measurements were made. This poled sample was slowly heated in a furnace at the rate of about 3°C/min and the pyroelectric current was measured with a digital d.c. micro-voltmeter connected to a pico-ammeter adaptor at various temperatures. The corresponding time was also noted for calculating the rate of heating. The pyroelectric coefficients were calculated by the direct method, as suggested by Byer and Roundy (1972), which is simpler than the dynamic method.

3. Results and discussion

Temperature variations of the pyroelectric current deduced by Chynoweth (1956) is given by

$$i = A\left(\frac{\mathrm{d}p_s}{\mathrm{d}T}\right)\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right), \tag{1}$$

where i is the pyroelectric current, A, the area of ceramic material, p_s the spontaneous polarization, $\mathrm{d}T/\mathrm{d}t$, the rate of heating and $\mathrm{d}p_s/\mathrm{d}T$, the pyroelectric coefficient.

The change of pyroelectric coefficients, calculated by (1) in accordance with the changes in temperatures for ferroelectric solid solutions of $K_xCs_{1-x}VO_3$ and $K_xLi_{1-x}VO_3$ are plotted in figures 1 and 2 and it is clear from the figures that the pyroelectric coefficients show a peak at 405, 405, 400 and 400°C for different molor proportions of $K_xCs_{1-x}VO_3$ and at 350, 360, 375 and 375°C for different molar proportions of $K_xLi_{1-x}VO_3$. The above temperatures indicate that the curie temperatures of the respective solid solutions are in good agreement with the values observed by the hysteresis loop method (Sawyer and Tower 1930).

Table 1 summarizes the observations of pyroelectric currents and pyroelectric

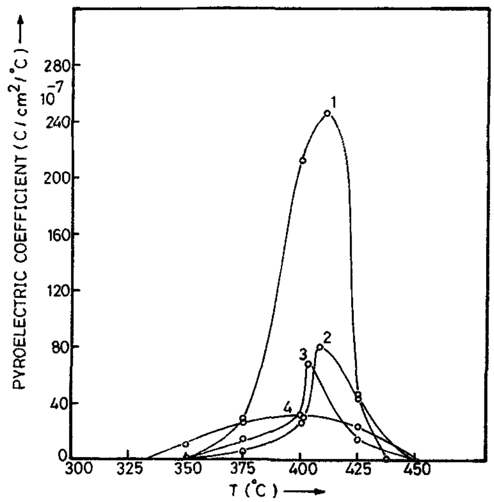

Figure 1. Variation of pyroelectric coefficient with temperature for solid solutions: (1) $K_{0.2}Cs_{0.8}VO_3$, (2) $K_{0.4}Cs_{0.6}VO_3$, (3) $K_{0.6}Cs_{0.4}VO_3$, and (4) $K_{0.8}Cs_{0.2}VO_3$.

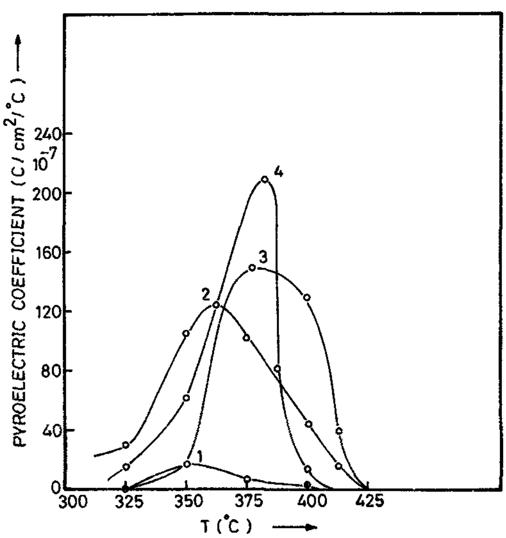

Figure 2. Variation of pyroelectric coefficient with temperature for solid solutions: (1) $K_{0.2}Li_{0.8}VO_3$ (2) $K_{0.4}Li_{0.6}VO_3$ (3) $K_{0.6}Li_{0.4}VO_3$ and (4) $K_{0.8}Li_{0.2}VO_3$.

coefficients at the curie temperatures of the vanadates and their solid solutions. The densities for the respective samples have also been mentioned in table 1.

Table 1 indicates that the pyroelectric current and coefficient decrease as the concentration of KVO_3 increases for potassium-cesium vanadate solid solutions and on the other hand, the pyroelectric current and coefficient increase as the concentration of KVO_3 increases for potassium-lithium vanadate solid solution.

Table 1. Peak values of various parameters KVO_3, $CsVO_3$, $LiVO_3$ and their solid solutions.

Material	Pyroelectric current (10^{-9}A)	Pyroelectric coefficient (10^{-7}C/cm^2°C)	Curie temp. (°C)	Curie temp. by hysteresis	Curie temp. by dielectric const. measurement	Density (g/cm^3)
KVO_3	50·2	7·71	315	314	315	2·31
$CsVO_3$	91·4	14·04	345	346	347	2·42
$LiVO_3$	415	63.77	405	405	404	2·24
$K_{.2}Cs_{.8}VO_3$	1732	266·17	405	406	407	2·33
$K_{.4}Cs_{.6}VO_3$	522	80·22	405	401	402	2·40
$K_{.6}Cs_{.4}VO_3$	447	68·69	400	394	396	2·40
$K_{.8}Cs_{.2}VO_3$	220	33·80	400	391	392	2·42
$K_{.2}Li_{.8}VO_3$	100	15·36	350	346	345	2·21
$K_{.4}Li_{.6}VO_3$	810	124·48	360	356	355	2·22
$K_{.6}Li_{.4}VO_3$	975	149·83	375	370	371	2.22
$K_{.8}Li_{.2}VO_3$	1348	207·16	375	377	376	2·20

4. Conclusions

(i) The ferroelectric curie temperatures 405, 405, 400 and 400°C for molar proportions of $K_xCs_{1-x}VO_3, x = 0{\cdot}2, 0{\cdot}4, 0{\cdot}6, 0{\cdot}8$ and that for $K_xLi_{1-x}VO_3$ for molar proportions $x = 0{\cdot}2$, 0·4, 0·6, 0·8 are 350, 360, 375 and 375°C respectively, which are in good agreement with the temperatures investigated by the hysteresis loop method.
(ii) The values of pyroelectric current and coefficient decrease with the increase in proportion of KVO_3 in solid solutions $K_xCs_{1-x}VO_3$ and these values increase with the increase in proportions of KVO_3 in solid solutions $K_xLi_{1-x}VO_3$.
(iii) These materials can be used as pyroelectric detectors.

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