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INFLUENCE OF NEODYMIUM DOPING ON DIELECTRIC PROPERTIES OF FERROELECTRIC KVO₃ AND LiVO₃

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ABSTRACT

The dielectric properties of pure and doped with different concentrations of Nd_2O_3 ferroelectric KVO₃ and LiVO₃, have been studied by using a digital LCR meter VLCR-7 at fixed frequency (1KHz) in the region of their phase transition. The dielectric constant shows a sharp peak at the phase transition in all the compositions. The dielectric constant is found to increase significantly, when dopant concentration is increased up to 0.5 mol % Nd₂O₃, however decreases for higher concentrations. The curie temperature of all the samples decreases with increase in Nd concentration.

Materials Index : Potassium, lithium, carbonates, neodymium, oxides.

Introduction

The effect of impurities on ferroelectric properties of alkali metal meta vanadates have practically not been studied so far, thus recently a great deal of interest in these materials is to ascertain the effect of doping on the ferroelectric properties.

The most commonly measured, small signal electrical property is dielectric permitivity (6), also often refered to as the dielectric constant. The dielectric constant in ferroelectric materials is rarely constant, but varies with applied field, temperature and other parameters.

Studies on the Raman Scattering of lithium, sodium and potassium meta vanadates (1) show that sodium and lithium vanadate are monoclinic, while potassium vanadate is orthorhombic. Crystallographic studies on LiVO₃ and KVO₃ were reported (2,3) and concluded that LiVO₃ is monoclinic with space group C_2/c , while KVO₃ is orthorhombic with space group Pbcm. The structural systematics of C_2/c alkali metal meta vanadates were characterized by $(VO_3)\varpi$ chains formed by vertex

sharing VO₄ tetrahydra, which are closely related to the silicate pyroxenes (4). Dielectric dispersion over a wide range of frequency dielectric and pyroelectric properties for sodium vanadate at different temperatures were reported in the literature (5,6). Dielectric properties of NaVO₃, KVO₃, LiVO₃ and RbVO₃ and their solid solutions were also studied (7,8).

The diffuse phase transition of a rare earth ions (Nd³⁺, Pr³⁺) doped SBN was studied (9) by measuring spontaneous polarization (P_s) and the dielectric constant (€). the temperature dependence of ε_{eff} and tand for BaTiO₃ ceramics with varying concentrations of Nd and Mn were reported (10).

In this paper an attempt has been made to understand the effect of neodymium oxide doping on the dielectric constant with variation of temperature of ferroelectric potassium vanadate and lithium vanadate at a fixed frequency (1 KHz).

Experimental

Preparation

Polycrystalline alkali metal meta vanadates were prepared by usual ceramic technique (1). Which were grown from a stoichiometric of AR grade alkali metal carbonates and vanadium pentoxide according to reaction.

$$X_2 CO_3 + V_2 O_5 = 2XVO_3 + CO_2 \uparrow$$

(X = K, Li). The alkali metal carbonate used was preheated at $473^{\circ}K$ for 2 h. before weighing, in order to minimize the moisture. The dried powder was then weighed and blended throughly with V_2O_5 . This mixture was slowly heated in platinum crucible to a temperature range $973-1023^{\circ}K$ depending on the composition to melt the mass. The molten mass was held at this temperature for about 5h. inside globar furnace and then cooled to room temperature.

The Nd additive used was a specpure Nd₂O₃ of purity 99.9% (John Baker Inc; Colorado, USA). The samples were prepared by weighing Nd₂O₃ in different percentage from 0.05 to 5 mol % in KVO₃ and LiVO₃. Every batch was subsequently dry mixed and then mixed wet with ethyl alcohol in an agate mortar. After the alcohol completely evaporated the batches were heated in platinum crucible to a temperature range 1173-1223°K depending on the composition to melt the mass. The molten mass was held at this temperature for about 5h. inside globar furnace and cooled to room temperature. The samples were then ground to pass a 120 mesh sieve. X-ray powder diffractometer traces for undoped and doped ferroelectric KVO₃ and LiVO₃ ceramics were obtained using Philips X-ray powder diffractometer with CuK_K radiations to confirm structures of prepared samples.

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The pellets were pressed at 7.6 x $10^7 {\rm Kgm}^{-2}$ pressure using hydraulic press, in the form of discs (diameter 1 cm and about 0.1cm thick) and were sintered on platinum foil at 773°K for 3 h. inside a globar furnace. The two opposite faces of each pellet were polished and silvered with air-drying silver paste to achieve good electrical contacts.

Apparatus and Measurements

The dielectric measurements were carried out by using a digital LCR meter VLCR-7 based on the principle of 'comparison of capacities'. The capacities of the materials, in the pellet form, were determined at different temperatures by keeping the pellet holder in a globar furnace and using temperature controller. The dielectric constant was calculated from capacitacne measurement data at different temperatures.

Results and discussion

The dielectric constant as a function of temperature for pure KVO₂ and LiVO₃ and these doped with different concentrations of Nd₂O₃ (0.05 to 5 mol %) are shown in figures 1 and 2 respectively.



Variation of dielectric constant with temperature for Nd_2O_3 doped KVO_3



FIG. 2 Variation of dielectric constant with temperature for Nd_2O_3 doped LiVO₃

Figures 1-2 show that the dielectric constant increases with temperature very slowly up to about 473° K and a comparatively faster rise beyond 473° K for undoped and doped KVO₃ and LiVO₃. The dielectric constant attained peak value at the transition temperature indicating the curie temperature of the sample; and then decreases for higher temperature according to Curie - Weiss law. The Curie - Weiss law was obeyed in all compositions in the para-region within 333°K. The peak values of dielectric constant are observed at 593°K and 682°K for KVO2 and LiVO2 respectively. These curie temperatures are in good agreement with those reported earlier (7).

The addition of Nd_2O_3 to KVO_3 and $LiVO_3$ shows noticeable in the curie temperature to lower temperature, in agreement shift the results obtained by previous investigators (9,10). These with curie temperatures are confirmed by the 'hysteresis loop method' using a modified form of Sawyer and Tower Circuit (11).

The peak values of dielectric constant, curie temperatures and their experimental densities for doped and undoped KVO_3 are summarized in table I, while those for doped and undoped $LiVO_3$ are summarized in table II.

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KVO3 AND LiVO3

TABLE I

Parameters discribing curie temperatures, dielectric constants (ε_{max}) and densities of pure and Nd-doped KVO3.

Nd ₂ O ₃ content	Curie Temp.	€ _{max}	Density
(mol ֆ)	(T° K)		(g cm ⁻³)
0	593	625	2.54
0.05	588	788	2.63
0.1	583	925	2.69
0.5	578	1140	2.75
1	571	695	2.64
3	561	450	2.53
5	551	360	2.48

TABLE II

Parameters discribing curie temperatures, dielectric constants (6 max) and densities of pure and Nd-doped LiVO₃.

Nd ₂ O ₃ content	Curie Temp.	e _{max}	Density
(mol %)	(T° K)		(g cm ⁻³)
0	682	835	2.74
0.05	675	960	2.82
0.1	668	1030	2.87
0.5	658	1250	2.93
1	651	878	2.85
3	643	672	2.78
5	635	480	2.76

Tables I - II reveal that the curie temperature decreases linearly with increase in concentration of Nd_2O_3 while the curie peaks of dielectric constant for doped 3.4 ceramics increase for lower doping concentrations up to 0.5 mol % Nd_2O_3 , however, decrease for higher concentrations with respect to undoped ceramics.

The enhancement in dielectric constant on addition of 0.5 mol % Nd₂O₃ in KVO₃ and LiVO₃ ceramics is attributed to a rather greater solid state interaction that takes place in the materials, which is indicated from the increase of density with the addition of Nd₂O₃. Doping with rare-earth ions (Nd³⁺) keeps the grain size small and thereby expedites densitifications. Thus the dielectric saturation states are atained at 0.5 mol % Nd₂O₃ addition. It may represent the solubility limit of Nd₂O₃ in KVO₃ and LiVO₃ lattices. Similar behaviours were observed for Fe₂O₃ doped PZT (12) and for Al doped BaTiO₃ ceramics (13).

The increase in dielectric constant at curie peak (6 $_{max}$) for lower doping concentrations 0.05, 0.1, 0.5 mol % Nd₂O₃, may depend on the type of solid solutions formed between Nd₂O₃ and KVO₃ and LiVO₃. In the present studies, the replacement of K-sites in KVO₃ or Li sites in LiVO₃ ceramics by Nd ions is most probable. As a result of the formation of these solid solutions, an increase in the polarization may be expected. This increase in polarization arises from those charge carriers which tend to become trapped and accumulate at lattice defects. It will produce an apparent increase in the dielectric constant.

Conclusions

The addition of Nd₂O₃ to KVO₃ and LiVO₃ shows noticeable shift in the curie temperature to lower temperature. The curie peaks of dielectric constant increase for 0.05, 0.1, 0.5 mol % Nd₂O₃ and then decreased for higher concentrations with respect to undoped ceramics. The dielectric saturation states are attained at 0.5 mol % Nd₂O₃ which indicates₃₊ good quality for ceramic dielectric. The doping of rare-earth ion (Nd) in KVO₃ and LiVO₃ plays an important role in modifying the dielectric and ferroelectric properties.

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