

Ferroelectricity and Phase Transitions in Disodium Hydrogen Orthophosphate

S. YADAVA[†], B.K. PANDEY*, S.P. DUBEY and J.P. SETH
Department of Applied Sciences, M.M.M. Engineering College
Gorakhpur-273 010, India
Fax: (91)(551)2273958; Tel: (91)(551)2273910, 2273958
E-mail: bkp11@rediffmail.com

The variation of dielectric constant *versus* temperature of disodium hydrogen orthophosphate has been studied from room temperature upto near melting point. It has been found that there are three transition temperatures in the heating cycle at the temperatures 46, 55 and 74 °C. The first two transition temperatures possess a small change in their high dielectric constant values, where as at 74 °C, the dielectric constant attains a tremendous value of 50,900. The cooling cycle shows a broad transition temperature, nearby 56 °C. The results have been explained on the basis of activated polarization process and structural imbalance due to the elimination of water molecules at low temperature (nearly 46 to 55 °C). The occurrence of broad peak in cooling cycle is explained on the basis of relaxor systems which are generally due to heterovalent disorder.

Key Words: Ferroelectricity, Phase Transitions, Disodium hydrogen orthophosphate.

INTRODUCTION

Ferroelectric materials are often dielectrics which can show one or more than one transitions. For most applications of ferroelectric materials, the dielectric constant and dielectric loss are important practical parameters. The studies of the dielectric properties¹ provide a great deal of information for understanding the molecular structure and the mechanism of electric polarization in ferroelectric materials. From physical point of view, ferroelectric crystals are those crystals which possess one or more ferroelectric phases. The 'ferroelectric phase' is a particular state exhibiting spontaneous polarization which can be reoriented by an external field. A reversal of polarization is considered as a special case of the polarization reorientation².

[†]Department of Physics, S.H.S Government Degree College, Dhanapur, Chandauli-232 105, India.

In general, uniform alignment of electric dipoles occurs only in certain regions of a crystal, while in other regions of the crystal spontaneous polarization may be in reverse direction. Such regions with uniform polarization are called ferroelectric domains. The interface between two domains is called the domain wall. The ferroelectric domains were first demonstrated in a study of spontaneous birefringence^{3,4}.

The characteristic of ferroelectrics is concerned the temperature of phase transition is one of the important parameters which is also known as Curie point. It is observed that the ferroelectric structure of a crystal is created by a small distortion of the paraelectric structure such that the crystal symmetry in the ferroelectric phase is always lower than that in the paraelectric phase⁵. If there are two or more ferroelectric phases in crystal, the Curie point only specifies the temperature at which a paraelectric-ferroelectric phase transition occurs. For example the Curie point of BaTiO₃ is 120 °C, however there are three ferroelectric phases in it below 120 °C⁶. It is also observed that in some ferroelectric crystals the dielectric response has a broad peak as a function of temperature, such crystals are also termed as relaxor systems. The origin of this behaviour is still controversial but is most likely due to heterovalent disorder⁷.

The present study on temperature dependent dielectric constant of pure disodium hydrogen orthophosphate shows high value of dielectric constant in ferroelectric phase which is due to high polarization. This compound has more than one transition temperatures, perhaps due to heterovalent disorder. The temperature dependence of dielectric constant has been explained on the basis of activated polarization process and the occurrence of broad peak has been explained on the basis of relaxor systems.

EXPERIMENTAL

The compound has been procured from E. Merck (India), Mumbai. The sample was grinded into the fine powder in a agate mortar, avoiding direct sunlight and preferably the most of the sample preparation was done at night. The pellets were prepared with compression machine (Flextural Testing Machine CAT No.AIM-313, S.No.91070 AIMIL Associated, India), having pressure range 0-10 tonne wt/cm². A suitable die was used having rectangular cross-sectional area of the piston = 2.33 cm².

The polishing of the pellets has been done to obtain smooth parallel surface to be used for electrode formation. Polishing of the crystal introduces electrical charges inside the material. These charges and strains are to be removed, which is done by the process of annealing of the sample. In this process the pellets are kept in a suitable furnace at nearly 2/3 of their melting points for sufficient times (generally 8-10 h). The most of the irreproducibility was removed by annealing and therefore this process was

necessarily done. The electrodes were formed using Acheson's colloidal graphite paint.

The sample holder loaded with pellet is kept into the furnace such that it lies near to the middle part of the furnace. A good quality thermometer, precisely calibrated is used to record the temperature. This thermometer is adjusted with the help of stand in such a way that it touches the metallic part of sample holder to record the exact temperature of sample.

The usual substitution method *i.e.* with and without the specimen in suitable sample holder is used⁸. The sample holder was directly fastened to the capacity measuring unit (Zenith M 92A).

RESULTS AND DISCUSSION

Disodium hydrogen orthophosphate has chemical formula $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ having molecular weight 177.99. The solid has refractive index 1.463 and specific gravity 2.66. The solid loses water of crystallization ($-2\text{H}_2\text{O}$) at temperature 95°C , therefore, the measurement has been done from room temperature upto *ca.* 80°C . The variation of dielectric constant vs. temperature plot (in heating cycle) has been shown in Fig. 1. It has three transition temperatures in heating cycle at the temperatures 46, 55 and 74°C . The dielectric constants of the compressed pellet as measured are given in the Table-1.

TABLE-1

Temperature ($^\circ\text{C}$)	Dielectric constant (ϵ)
46	31340
55	31510
74	50920

The electrode used is colloidal graphite paint. The first two transition temperatures possess a small change in their high dielectric constant values where as at 74°C , the dielectric constant attains tremendous value of 50,900 and afterwards it decreases sharply within a span of 6°C (upto 80°C) to the original value of nearly 30,000. The higher temperature records were not done to avoid damage to the sample⁹. Similar type of results has been found in thiourea¹⁰. The dielectric behaviour of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ exhibits a number of anomalies at lower temperature while ferroelectric phase transition appears at the temperature 74°C . Thus the 74°C has the prominent maxima. The anomaly of the dielectric constant in the lower temperature region would be expected, of course to consist in two peaks at the temperatures corresponding to the onset and vanishing of the spontaneous polarization¹¹. The fluctuation in the dielectric constant of sample in

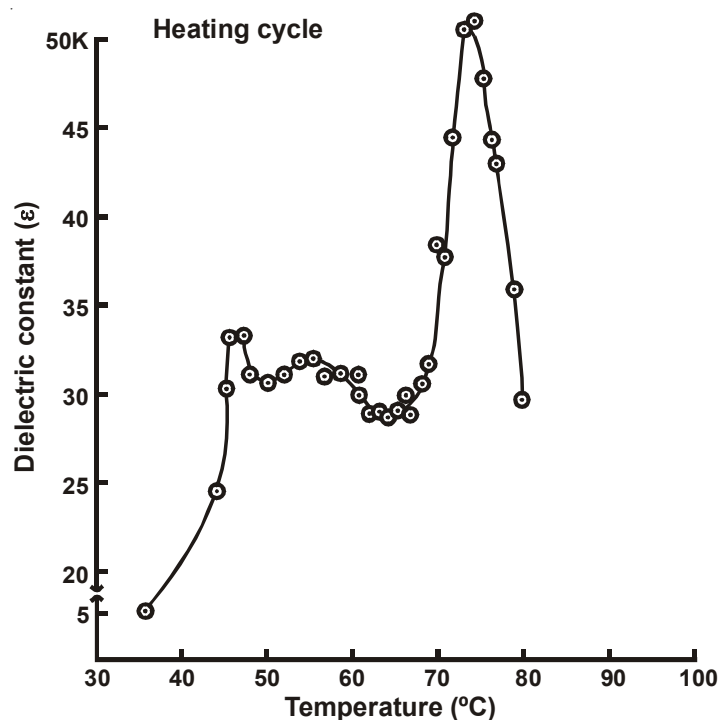


Fig. 1. Variation of dielectric constant of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ pellet with temperature, $p = 5 \text{ tonne}/2.33 \text{ cm}^2$

lower temperature (46 and 55 °C) range is perhaps due to the elimination of two molecules of water from the sample. Actually the elimination of water molecules from the crystal not only perturbs the physical measurements but also creates crystallographic defects, as observed in case of barium nitrate¹². After the elimination of water molecules the crystal have its ferroelectric phase transition at 74 °C, which can be interpreted in terms of Curie-Weiss law.

The cooling cycle (Fig. 2) shows a broad transition temperature nearby 56 °C where the dielectric constant decreases (from the value 20-30 K at 41-56 °C) to very low value at the temperature 70-80 °C. This fall is more or less of 1st order type. The probable polarization on set in the temperature range 60-70 °C is in accord with the first order character of this ferroelectric transition. The maxima at the Curie point are very flat, in the ferroelectric phase as observed in case of lithium thallium tartrate¹³. The dielectric constant at low temperature is mainly contributed by the resonance polarization¹⁴.

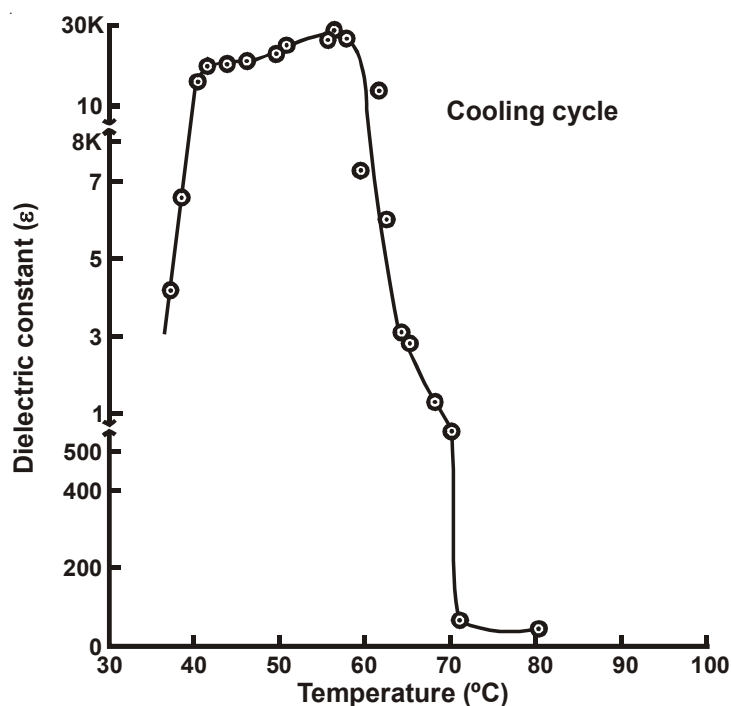


Fig. 2. Variation of dielectric constant of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ pellet with temperature, $p = 5 \text{ tonne}/2.33 \text{ cm}^2$

The cooling cycle, (Fig. 2) shows that at low temperature, distribution of relaxation times change into extremely broad because of the correlation among polar region, which leads the broad transition temperature¹⁵. The occurrence of broad peak in the selected sample can also be explained in terms of relaxor systems, which is generally due to heterovalent disorder⁷.

Conclusion

In this work, we have shown that the fluctuation in the dielectric constant of sample in lower temperature range (*ca.* 46 to 55 °C) is due to the elimination of water molecules from the sample. Actually the elimination of water molecules form the structural imbalance in the crystal, which is responsible for above said fluctuations. In the cooling cycle the occurrence of broad peak can be explain in terms of relaxor systems, which is generally due to heterovalent disorder.

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