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The Study of Ferroelectric Behaviour and Phase Transition of Sodium Nitrite

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ABSTRACT

Sodium Nitrite is an example of crystal that were found to be ferroelectric a number of years after the discovery of their phase transitions. A change from a non-centrosymmetric to a centric structure is known to occur in NaNO₂ at approximately 160 °C. This transition was discovered to be a ferroelectric in 1958. Above the Curie point, the structure is orthorhombic with lattice constants at 205 °C and space group Immm. The dielectric constant \in_b exhibits

a sharp anomaly at the Curie point and obeys the Curie-Weiss law. The transition is obviously one of the first order. The spontaneous polarization is rather large, namely of the same order as that of KNO₃. At 143 °C, $P_s = 6.4 \times 10^{-6}$ C/cm², and the 50 c/s coercive field $E_c = 2.3$ kV/cm. The coercive field is is so large, at room temperature that hysteresis loops cannot be obtained with fields of the order of 25 kV/cm. Above the Curie point, these ions may oscillate along the [010] axis about positions which can be described in terms of the centrosymmetrical space group Immm, but there are also indications that this centric symmetry may be the result of random disorder.

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Introduction

The electric dipole moment $\iiint \rho(\mathbf{r})\mathbf{r} d\mathbf{x} d\mathbf{y} d\mathbf{z}$ of the nuclear and electronic charge distribution $\rho(r)$ of (nonconducting) crystals does not vanish for ten of the thirty-two crystal classes. Crystals with non-vanishing dipole moment are called polar. Generally the dipole moment of a polar crystal does not manifest itself since it is compensated by electrical charge carriers that have reached the surface by internal or external conduction during the growth of the crystal. However, the dipole moment has a temperature coefficient that originates from anharmonicity of the lattice vibrations. When such a polar crystal is heated or cooled, the external or internal conduction often cannot yield enough current to compensate for the change of the dipole moment, and the crystal acts as an electric dipole. For this reason polar crystals are called pyroelectrics[1]. The ferroelectrics are a subgroup of the pyroelectrics. Their outstanding property is the reversibility of the permanent polarization by an electric field. This reversibility is a consequence of the fact that the polar structure of a ferroelectric is a slightly distorted non polar structure. The reversal of the permanent polarization gives rise to a nonlinear dielectric behavior. The relation between the net macroscopic polarization of a ferroelectric crystal and the externally applied electric field is given by a hysteresis loop. In general, a ferroelectric crystal consists of domains. These are regions of homogeneous polarization that differs only in the direction of the polarization. Using the language of the mineralogist the domain formation may be called "twinning." The reversal of the net macroscopic dipole moment of a ferroelectric crystal occurs through nucleation and growth of domains that are favorably oriented with respect to the applied electric field.

Since the polar structure (of a domain) may be derived from a non polar structure by a slight strain, the free energy of the non polar state can closely approach the free energy of the polar state. In fact, in most cases a temperature exists, the Curie temperature, at which these free energies are equal, and at which the crystal undergoes a phase transition from a non polar state into a polar state. Therefore, the polarization is called spontaneous polarization. As a rule the low temperature phase is the polar phase. The phase transition can be of the first order or of a higher (generally second) order. In neither instance does it arise from the crossing of two entirely different free energy functions. It may rather be regarded as a transition from one "branch" (polarization=0) into another branch (polarization $\neq 0$) of the same free energy function. The transition temperatures that have been observed range from about 10°K to several hundred °K, and the order of magnitude of the spontaneous polarization ranges from 10⁻⁷clb/cm⁻² to 10⁻⁴ clb/cm⁻². In "normal" dielectrics, such as alkali halides fields between 10^5 volts/cm and 10^8 volts/cm would have to be applied to achieve such polarizations. At the transition point the dielectric susceptibility generally exhibits a peak and in the unpolarized phase it follows a Curie-Weiss law. Similar anomalous behavior is found in the piezoelectric, elastic and electrooptic properties. The observed transition entropies range from about 0.1 calmole⁻ ¹deg⁻¹ to about 4 calmole⁻¹deg⁻¹. For a long time it was thought that the existence of a Curie point is a necessary characteristic of ferroelectric crystals; however, recently a ferroelectric has been discovered which undergoes a higher than second order transition and has no Curie point [2].

Experimental

The compound has been procured from E. Merk (India), Mumbai. The chemical 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

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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 = 2.33cm².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 we did by the process of annealing of the sample.

In this process the pellets were kept in a suitable furnace at nearly 2/3 of their melting points for sufficient times (generally 8-10 hours). The most of the irreproducibility was removed by annealing and therefore this process was necessarily done. The electrodes were formed using colloidal silver paints. The sample holder loaded with pellet is kept into the furnace such that it lies very 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 used [3]. The sample holder was directly fastened to the capacity measuring unit (Zenith M 92A).

Results and Discussions

NaNO₂ represents a type of crystals that reveals like a miscellaneous ferroelectric after the discovery of their phase transitions. A change from a non-centrosymmetric to a centric structure was known to occur in NaNO₂ at approximately 160 °C [4]. This transition was discovered to be a ferroelectric by Sawada in 1958 [5]. Above the Curie point, the structure is orthorhombic with lattice constants (at 205 °C) [6]: a = 5.33 Å, b = 5.6 Å, c = 3.69 Å

and space group Immm. In the polar phase, the mirror symmetry perpendicular to [010] disappears, the space group becoming Im2m, and the lattice constants (at 25° C) a =5.390Å, b =5.578 Å, c = 3.570 Å

The ferroelectric axis is the b axis.

The dielectric constant \in_{b} exhibits a sharp anomaly at the Curie point (see Fig.1), and obeys the Curie-Weiss law, above this 5000°C

temperature, in the form $\epsilon_b = \frac{3000 \text{ C}}{\text{T} - 433^{\circ}\text{C}}$



Fig 1. Dielectric Constant of Sodium Nitrite measured along [010] and [101] as a function of temperature

The transition is obviously one of the first order. The spontaneous polarization is rather large, namely of the same order as that of KNO₃. At 143 °C, $P_8 = 6.4 \times 10^{-6} \text{ C/cm}^2$, and the 50 c/s coercive field $E_c = 2.3 \text{ kV/cm}$. The coercive field is strongly field and temperature dependent, and is so large, at room temperature, that hysteresis loops cannot be obtained with

fields of the order of 25 kV/cm [5]. X-ray structural investigations of NaNO₂ were carried out by Ziegler [7], Carpenter [8] and by Truter [9, 10]. The structure strongly suggests that the ferroelectric activity is probably the result of the favorable atomic configuration in the NO_2^- groups. The O-N-O bond is not linear, but rather forms an angle of approximately 115°, the N-O distances being equal to 1.24 A (see Fig. 2).



Fig 2. Schematic projection on (001) of the orthorhombic structure of Sodium Nitrite

Above the Curie point, these ions may oscillate along the [010] axis about positions which can be described in terms of the centrosymmetrical space group Immm , but there are also indications that this centric symmetry may be the result of random disorder [11]. A refinement of the polar structure was carried out via neutron diffraction by Kay and Frazer [11], with particular attention to the parameters of thermal vibrations. The usefulness of a neutron diffraction study, in this case, is provided by the fact that the neutron scattering lengths are independent of the scattering angle, and nitrogen appears as the "heaviest" atom in the structure, whereas in the case of X-rays (due to uncertainty in the electronic distribution of the NO_2^- groups) there is some question as to the proper X-ray scattering factors for nitrogen and oxygen, and, moreover, nitrogen is the "lightest" atom. The results of the neutron study are in excellent agreement with those obtained with X-rays, as far as positional parameters arc concerned, but indicate a measurable degree of thermal anisotropy only in the oxygen atoms.

The spontaneous polarization calculated on the basis of a strictly ionic structure (Na¹⁺, N³⁺, O²⁻) turns out to be 74 x 10⁻⁶ C/cm², which is about ten times larger than the experimental value. This, of course, is a confirmation of the highly covalent character of the nitrite group. Kay and Frazer computed the effective charges n_N and n_0 of nitrogen and oxygen, respectively that would provide agreement between the calculated and observed values of the spontaneous polarization [11]. The results: $n_N = 0.36$ and $n_0 = 0.32$, (assuming Na¹⁺), are qualitatively significant in showing that the effective charge of nitrogen is just as strongly negative as that of oxygen. This may suggest that the role played by the Na¹⁺ ions is to exert a strong counter-polarizing influence upon the nitrite groups [12].

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