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THERMAL PROPERTIES OF SODIUM ACETYLACETONATE

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Sodium acetylacetonate was prepared by the interaction of acetyl acetone with sodium hydroxide. The thermal conductivity, phonon velocity, mean free path, Yong's modulus, and the thermal expansion coefficient were studied. The thermal conductivity of the material decreases with increasing temperature due to the thermal lattice scattering of phonons. The velocity of phonons is also decreased due to the perturbation of thermal phonons. The linear thermal expansion coefficient increases with temperature due to the weakness of the attractive forces between the small Na^+ cations and bulkier acetylacetonate anions in the lattice.

Keywords: dielectric constant, organometallic compound, sodium acetylacetonate, thermal conductivity

Introduction

The temperature dependence of the dielectric constant of sodium acetylacetonate was studied earlier by Sawaby [1]. He showed that this material undergoes an irreversible structural change at about 70°C from an orthorhombic phase to a triclinic structure. The maximum dielectric constant was about 35 at 10 MHz. The author tried to create a phenomenon of reversibility in this material by polarizing the preheated samples using a fairly high electric field. The polarized preheated sample of sodium acetylacetonate was found to be reversible and the hysteresis loops obtained on the cathode ray oscilloscope confirmed the existence of the ferroelectric properties in the material [2]. Little work has been done for measuring the thermal properties of Na(ac. ac.), thermal conductivity, thermal phonon velocity, mean free path, thermal expansion coefficient and Yong's modulus of Na(ac.ac.).

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The aim of the present investigations is to study the thermal properties of Na(ac. ac) as an organometallic compound. It is expected that the change in thermal properties will throw light on an important material that may have thermo-technological applications.

Experimental procedure

Thermal measurements

The apparatus used for the measurements is shown in Fig. 1. It consists of a sample holder held on three iron rods. The sample holder consists of a stainless steel bar which is fixed in the central axis of tubular stainless steel furnace working with a heater. The central steel bar, copper leads, thermocouple wires and heater connections are insulated from the holder base plate by a ceramic disc. Various wires and thermocouples are con-

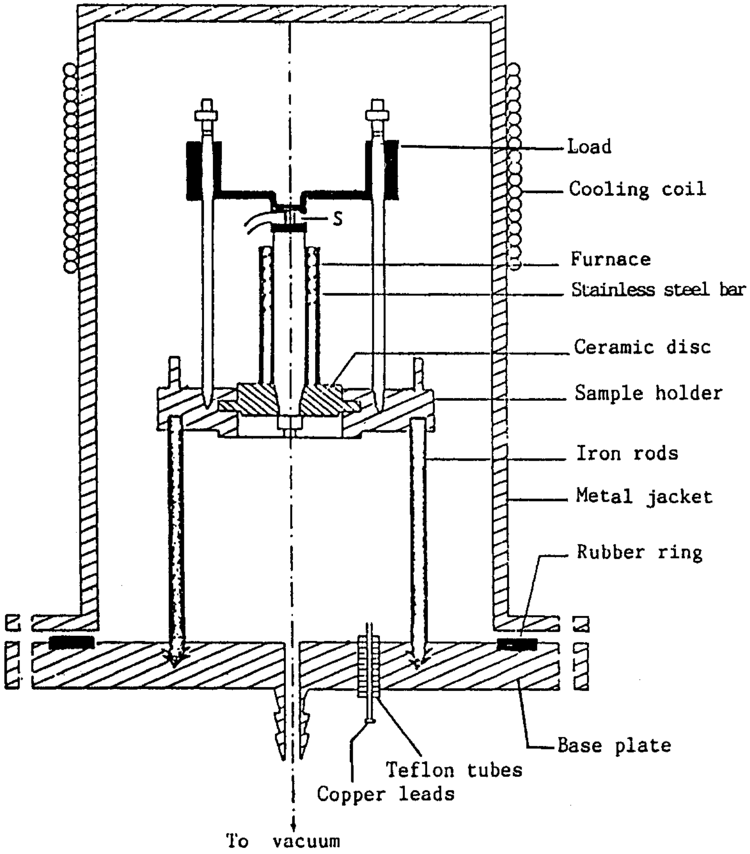

Fig. 1 Cross-section of the apparatus used for thermal measurements

nected to the outside by means of copper leads through teflon tubes. The sample S is slightly pressed by means of a small load placed on its top just to maintain good contact between the sample surfaces and the two copper electrodes. A metal jacket cooled with water through a copper coil placed around it, rests on an annular vacuum rubber ring fixed to the base plate.

The degree of vacuum was ≈ 10^{-3} mm Hg, and the heat leak due to convection was practically negligible.

The thermal conductivity K was measured at different temperatures. This was achieved by controlling the furnace heater to maintain constant temperature at the lower surface of the sample and then the temperature gradient was measured.

Yong's modulus measurements

The Yong's modulus of sodium acetylacetonate material was measured using an R.L.C. bridge, type (TESLA BM 591). The capacitance of the sample was measured (in the range 63–163 pF at 1 KHz and 1 V) at different temperatures (from room temperature up to 125°C) under applied stress (543 dyne/cm^2).

Results and discussion

Temperature dependence of thermal conductivity (K)

The coefficient of thermal conductivity of the sample was estimated using the formula

$$Q=\frac{IV}{J}=KA\frac{\mathrm{d}T}{\mathrm{d}X}$$

where Q is the quantity of heat per unit time transferred through the sample of thickness dX, J the Joule's coefficient, I, V, $\frac{\mathrm{d}T}{\mathrm{d}X}$, A are the current in amperes, voltage across the heater in volts, temperature gradient $\left(\frac{\text{degree}}{\text{m}}\right)$ and sample area (m^2) respectively.

The heat transport through lattice vibrations (phonons) is mainly important for insulators and semiconductors. The thermal conductivity of sodium acetylacetonate crystals has contributions from two components, lattice vibration (phonons), and the carriers (electrons).

$$K = K_{\mathrm{ph}} + K_{\mathrm{e}}$$

If we consider the heat conduction by carriers, the temperature gradient will cause a carrier concentration gradient, this results in a diffusion current which transports heat energy. At temperatures lower than the Debye temperature, the inelastic scattering processes become important thus a strongly affecting the thermal conductivity. In this range there is a sharp drop in phonon concentration with falling temperature, leading to a sharp increase in their mean free path, so K becomes proportional to T^3. But at temperatures higher than the Debye temperature, the scattering processes must be responsible for the thermal resistance and the elastic scattering is dominant since the phonon contribution to the thermal conductivity is relatively small compared with the electron contribution.

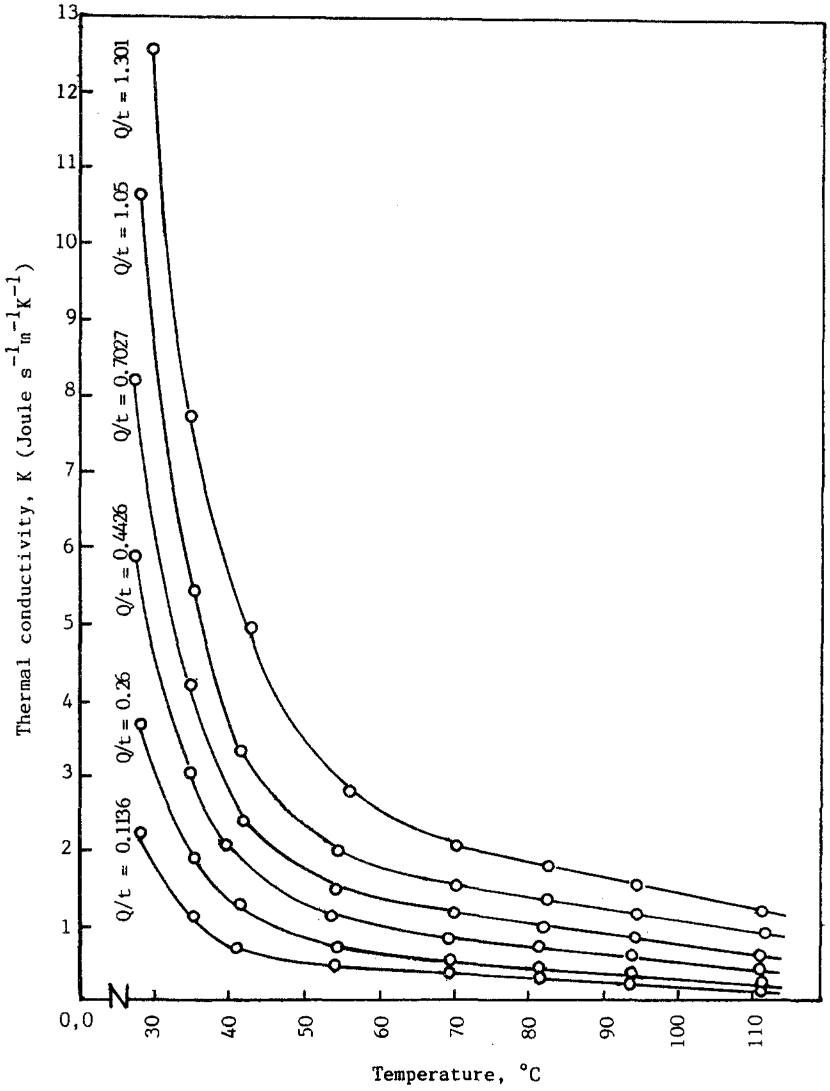

Fig. 2 Temperature dependence of thermal conductivity, K

The measured thermal conductivity is approximately equal to the contribution from electrons. In this range K is inversely proportional to the temperature ($K\alpha\, T^{-1}$).

The temperature dependence of K is shown in Fig. 2. A sharp drop of thermal conductivity with rising temperature can be observed up to the transition temperature. The concentration of phonons increases with rising temperature leading to a consequent increase in lattice vibrations. This increase of lattice vibration gives rise to lattice scattering causing a decrease in the mean free path which would result in a decrease of K. Above the transition temperature [3],the thermal conductivity is only slightly depending on the temperature. The increase in the rate of heating increases the thermal conductivity due to an increase in phonon density.

Temperature dependence of the mean free path (L)

The mean free path of thermal phonons in sodium acetylacetonate composition was estimated from the relationship [4]

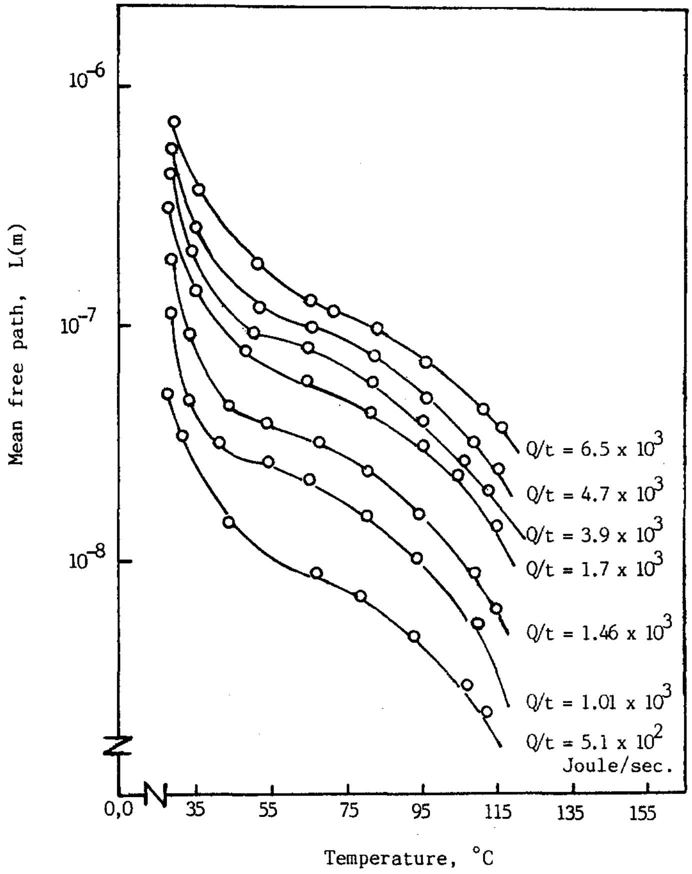

Fig. 3 Temperature dependence of mean free path, *L*

$$K = \frac{1}{3} LCV$$

where C, L, V are the specific heat at constant volume, phonon velocity, and mean free path, respectively.

Figure 3 shows the dependence of L on temperature. Below the transition temperature (70°C), a sharp decrease in the mean free path can be observed with the increase of temperature. The decrease in mean free path is due to lattice transformation from an orthorhombic to a triclinic structure [1]. This transformation results in a measurable increase in the concentration of lattice defects causing more lattice scattering which decreases the mean path (L) of the thermal phonons.

Above the transition temperature the decrease in the mean free path is easily understood in view of the marked increase in thermal vibration of lattice ions.

Effect of temperature on the Yong's modulus (Y)

The Yong's modulus was estimated from the measurements of sample capacitance using the formula

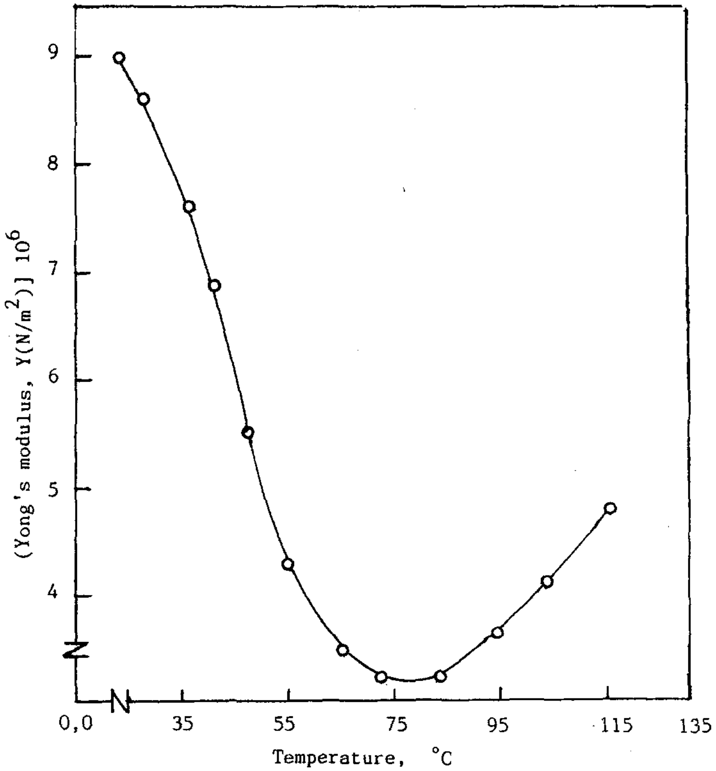

Fig. 4 Temperature dependence of Yong's modulus, Y

$$C_o d_o = C_s d_s$$

where C_o, d_o are the capacitance and thickness of the sample, respectively, at zero stress; C_s, d_s are those under stress.

The results are graphically presented in Fig. 4. Yong's modulus Y decreases with increasing temperature up to the transition temperature (70°C), then increases above this temperature. The increase in temperature weakens the bonds between the particles of Na(ac. ac). Bonds of lower rigidity correspond to lower Yong's modulus, hence the weakness of the bonds allows greater thermal vibration amplitude. At higher temperatures the bonds of higher rigidity correspond to higher Yong's modulus because the stronger rigidity allows lower thermal vibration amplitude in the lattice. The minimum value of Y is due to phase transition [1] leading to more weakness of ion rigidity.

Temperature dependence of phonon velocity (V)

The velocity of phonons (V) is given by the equation (5)

$$V = \left(\frac{Y}{\rho}\right)^{\frac{1}{2}}$$

where ρ is the sample density.

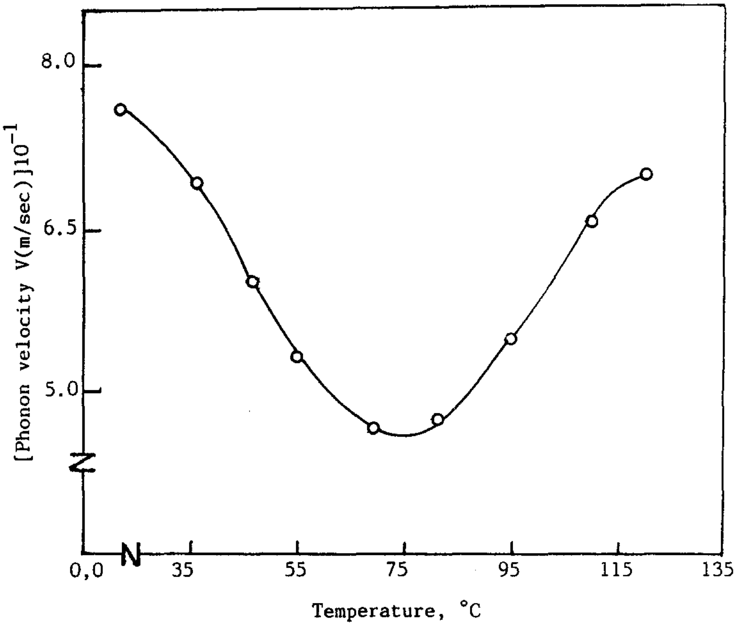

Fig. 5 Temperature dependence of phonon velocity, V

The temperature dependence of phonon velocity is shown in Fig. 5. It is noticed that V decreases with rise of temperature up to 70°C, then increases with further rise of temperature. The decrease in the velocity of thermal phonons is due to an increase in the lattice scattering of phonons inside the orthorhombic lattice. So, the rise of temperature enhances the lattice scattering near the transition temperature causing a minimum value of the phonon velocity around 70°C. The minimum value of V is attributed to the phase transition from orthorhombic to triclinic. This transition allows maximum lattice scattering of thermal phonons leading to minimum thermal velocity.

Thermal expansion coefficient α *vs. temperature*

The linear expansion coefficient α is determined by the equation

$$d_T = d_o\,(\,1 + \alpha\,\Delta T\,)$$

where d_T is the thickness of the sample at any temperature T.

Heating a body should result in an increase in the average distance between ions, consequently the body would expand. The variation of linear expansion coefficient α of Na(ac.ac) with temperature is shown in Fig. 6. The increase of α with rising temperature may be related to the increase in lattice vibrations leading to a weakening of the attractive forces between sodium ions in the compound. The weakness of attractive forces between the lattice ions tends to increase the linear expansion coefficient with tempera-

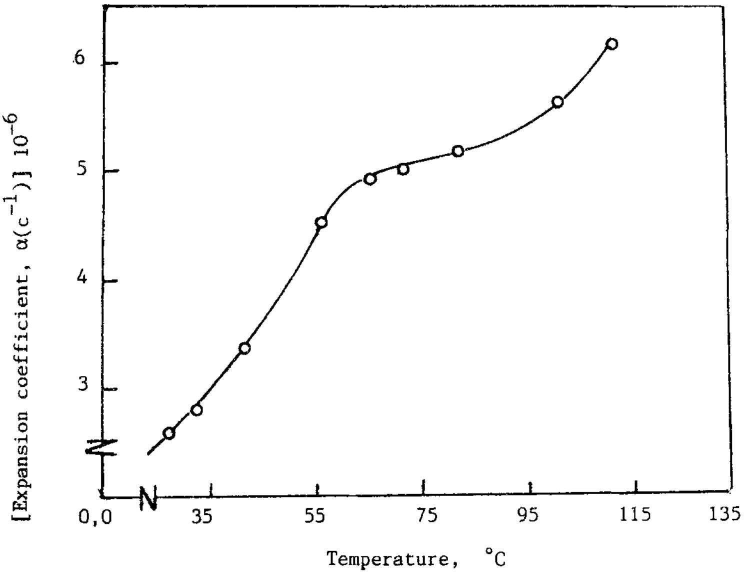

Fig. 6 Temperature dependence of thermal expansion coefficient, α

ture. The breaking of the curve is interpreted as being due to the transition of the crystal structure from orthorhombic to a triclinic phase [1].

Conclusion

Thermal studies on sodium acetylacetonate showed that the material undergoes a phase transition from orthorhombic to triclinic structure at 70°C. This transformation affects the thermal behaviour of the material (thermal conductivity, Yong's modulus, thermal phonon velocity and mean free path). The thermal phonon scattering and lattice scattering are responsible for the behaviour of the material at changing temperatures.

References

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Zusammenfassung — Natriumacetylacetonat wurde durch die Wechselwirkung zwischen Acetylaceton und Natriumhydroxid gewonnen. Es wurde die Wärmeleitfähigkeit, die Phononengeschwindigkeit, die mittlere freie Wegstrecke, das Elastizitätsmodul und der Wärmeausdehnungskoeffizient untersucht. Die Wärmeleitfähigkeit der Substanz nimmt wegen der thermischen Gitterstreuung der Phononen mit steigender Temparatur ab. Die Geschwindigkeit der Phononen nimmt auf Grund der Perturbierung der thermischen Phononen ebenfalls ab. Der lineare Wärmeausdehnungskoeffizient steigt mit zunehmender Temperatur an, was auf die schwachen Anziehungskräfte zwischen den kleinen Na^+ Ionen und den massigen Acetylacetonat-Anionen im Gitter zurückzuführen ist.