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An Irreversible Phase Transformation in Sodium Acetyl-Acetonate Compound

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During the study of the temperature dependence of the dielectric constant, ϵ, and dielectric loss, tan δ, of some metal acetylacetonate compounds, anomalous behaviour in Na(acac) showed itself as a peak value in both ϵ and tan δ at a critical temperature T_c about 82°C. The measured values of ϵ and tan δ at any temperature were strictly reproducible as long as the test temperature did not exceed T_c. Above this value, a thermally activated decrease with time of the ϵ-values was observed. This behaviour implied the existance of some unidirectional transformation in the internal structure. Sudden cooling from above T_c caused a complete freezing of the reaction An isothermal annealing study made at higher temperatures showed that the process was activated by an energy of 1.34 eV and followed a second order rate reaction. X-ray analysis indicated that above 82°C Na(acac) transforms irreversibly from the orthorhombic ($a = 11.78$ *A*, $b = 10.42$ *A*, $c = 9.00$ *A*) to the triclinic ($a = 14$ *A*, $b = 13.17$ *A*, $c = 11.7$ *A*, $\alpha = 117° 15'$, $\beta = 96° 52'$, $\gamma = 92° 28'$) structure.

INTRODUCTION

Metal acetylacetonates, M(acac), are mostly used as catalysts and chemical activators. A lot of investigations[1] has been made to determine their structure, electrical and optical behaviour. However, the available data is still far from being complete. Infrared studies[2] showed that the metal-oxygen bond strength differed from one compound to another. Electrical polarization and micro-wave absorption of $Al(acac)_3$ in benzene solution showed[3] that the dielectric loss decreased with an increase of temperature and were dependent on frequency.

The aim of the present work is to study the dielectric properties in relation to structure of some metal aceylacetonate compounds, with special attention to Na(acac). This forms a part of a wide program for collecting more data and knowledge about the behaviour and the possible phenomena which these compounds might show aiming to find out the relationship between their structure and chemical activity.

EXPERIMENTAL

Metal (Na, Cu, Ni, Fe, Cr) acetylacetonates were locally prepared according to standard procedures given in the literature.[4] The degree of purity of the compounds was tested through the measurement of their melting points and infra-red spectra which agreed well with the reported values in the literature. The morphology of the crystals was tested by the electron microscope using the suspension method. A typical transmission electron micrograph of one fibre of Na(acac) compound is shown in figure 1. The fibre is thought to consist of a single planar array of fibrils about 150–200 Å width, parallel to each other in a band-form structure. The fibrils which lie perpendicular to the length of the fibre are held to the boundary by very fine threads less than 50 Å thick. The links between the fibrils and the external boundary were found to be weak and could be easily torn by the electron beam effects.

Samples in the powder form were compressed in a standard way into tablets having diameters of 1.22 cm and thickness 2 mm. A V.H.F. admittance bridge was used for measuring the dielectric constant and loss. An

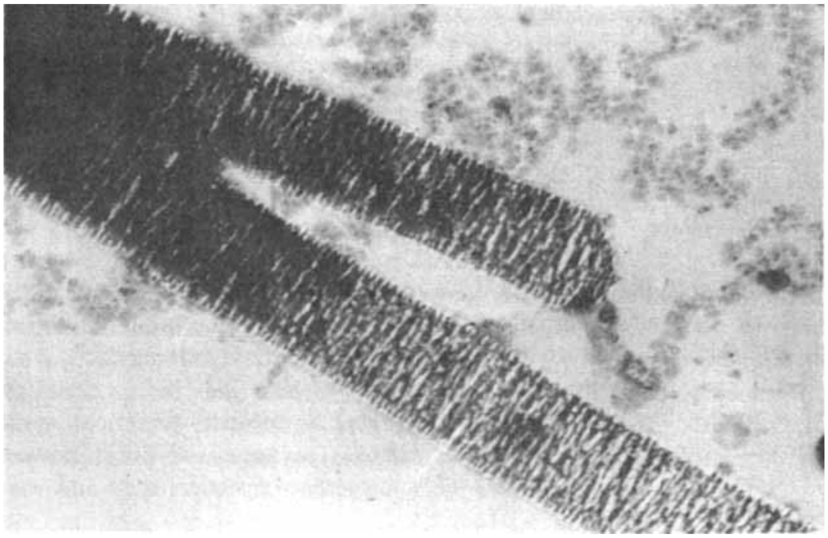

FIGURE 1 A typical transmission electron micrograph of Na(acac).

accuracy of 2% ± 0.5 pF could be maintained up to 100 MHz frequency. Experiments were performed at different temperatures using tablets of different densities and operating with different frequencies.

RESULTS AND DISCUSSION

The dielectric constant, ϵ, and dielectric loss, tan δ, of Na, Cu, Ni, Cr, and Fe acetylacetonate compounds were measured as a function of temperature. It was found that the values of ϵ for these compounds were generally small and ranged between 7 and 12 at room temperature. No significant temperature dependence was found for all these compounds except for the Na(acac) which showed an anomalous change with temperature as shown in figure 2. The dielectric constant for Na(acac) increased with temperature showing a peak value at about 82°C. Above this temperature, the ϵ-value decreased with increasing temperature approaching the starting value at about 180°C.

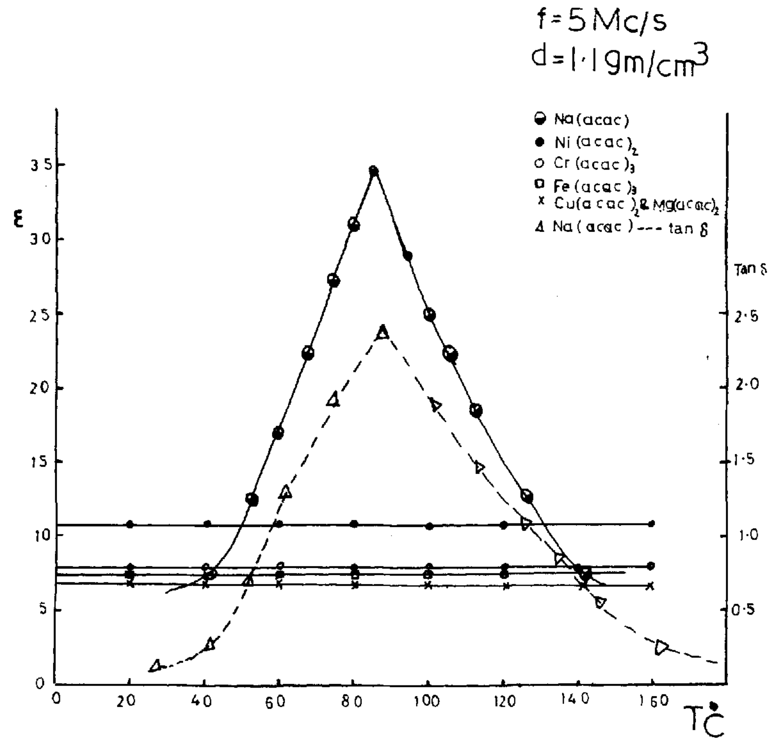

FIGURE 2 Temperature dependence of the dielectric constant and loss for some metal acetylacetonates.

It was also noticed that below 82°C the value of ϵ were strictly reproducible at any particular temperature, while above that temperature where the peak occurred the reproducibility of the ϵ-values was greatly impaired. This behaviour pointed towards the possible existence of some irreversible change in structure. The dielectric loss showed also a parallel behaviour. The increase of density of the material shifted the dielectric-temperature curve towards higher values of ϵ. The maximum density obtained under the present experimental conditions was 1.1 gm/cc. Samples having such density were taken as standard for the study of the dielectric constant in relation to other parameters.

Isothermal Annealing

The effect of isothermal annealing of Na(acac) compound at different temperatures on its dielectric behaviour was tested. Below a critical temperature $T_c = 82°C$ the dielectric constant was strictly time-independent (see figure 3). Above this temperature the value of ϵ decayed gradually with time. The rate of decrease depended on the annealing temperature.

To study the temperature dependence of this decay, isothermal annealing runs were carried out at different selected temperatures. The results shown

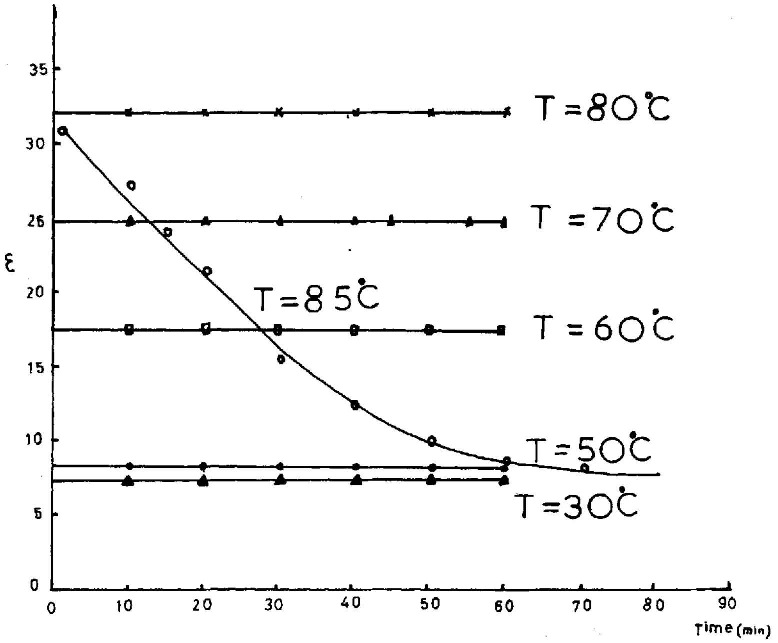

FIGURE 3 The effect of annealing on the dielectric constant of Na(acac).

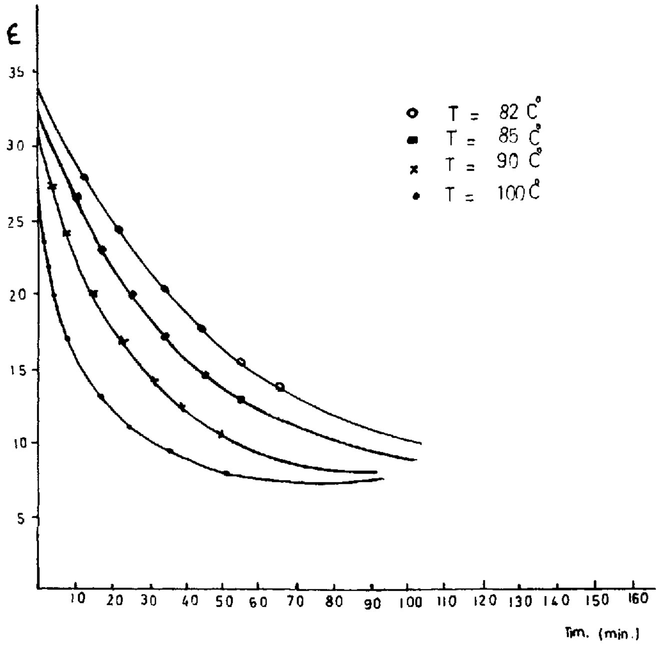

FIGURE 4 Isothermal annealing curves ($\epsilon - T$) above T_c.

in figure 4 implied that the observed decay in the dielectric constant of the sample might be attributed to some thermally activated change taking place above T_c. It will be here assumed to a first degree of approximation that the process in action is controlled by a chemical rate equation of the type:

$$t \exp(-E/kT) = \text{constant},$$

T being the absolute temperature, t the time of reaction, E the energy activating the process. The equivalent times and temperatures prescribing any particular degree of change were found by the cross-cut method from the isothermal annealing curves of figure 4.

The activation energy E for this process was deduced by plotting the logarithm of time versus reciprocal of the corresponding absolute temperature. Figure 5 shows a parallel set of straight lines thus obtained. The slopes of these lines gave an average value for the activation energy amounting to 1.34 ev. The order of reaction was determined using Meechan and Brinkman's method[5] in which the isothermal annealing curves relating the time change of the physical property were analysed. It was presently found that the intermolecular reaction responsible for the observed change in ϵ followed a second order reaction.

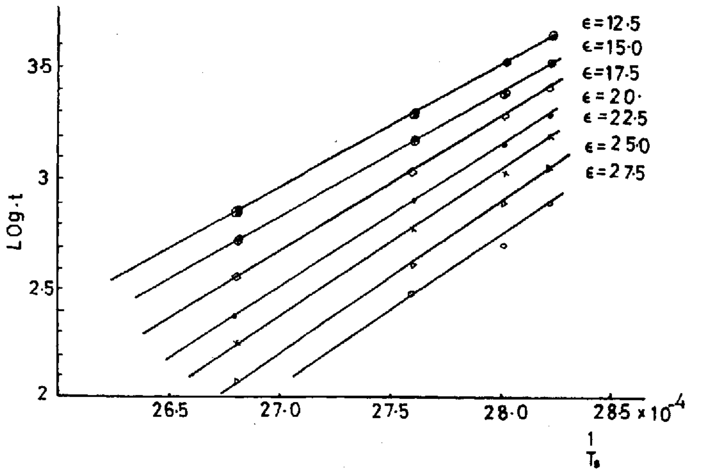

FIGURE 5 Equivalent time-temperature curves for the observed change.

Structure Analysis

As far as we are aware, the structures of the two forms of Na(acac) before and after the here observed transformation are not reported neither in the standard ASTM X-ray cards nor in the literature. Room temperature diffraction patterns were thus made on samples as prepared and on samples pre-heated at 90°C for one hour. Figures 6 and 7 typically represent the results obtained. Ito's method[6] was used to index the powder X-ray diffraction patterns. The reciprocal lattice method was used for analysis. The interplanar spacings, $d(hkl)$, and the corresponding Q values, $Q(hkl) = 1/d^2(hkl)$, were calculated and compared to observed values. Agreement between both results is shown in table I for the different lines shown in the chart pattern of the unheated Na(acac).

Table II shows a similar set of results for the pre-heated samples. The transformation of the reciprocal cell dimensions into direct cell dimensions showed that the as-prepared Na(acac) compound belongs to the orthorhombic system whose unit cell dimensions are: $a = 11.78\ A$, $b = 10.42\ A$, $c = 11.70\ A$, $\alpha = \beta = \gamma = 90°$. Pre-heating the sample at 90°C for one hour was found to transform the lattice structure to the triclinic system with a unit cell characterized by: $a = 14.00\ A$, $b = 13.17\ A$, $c = 11.70\ A$, $\alpha = 117°\ 15'$, $\beta = 96°\ 50'$, $\gamma = 92°\ 28'$.

Electron microscope diffraction patterns for the two structures were also tested. The patterns obtained for the unheated and pre-heated samples are shown in figures 8 and 9, respectively. The patterns were taken without using high electron beam intensities to avoid electron beam effects. Analysis of

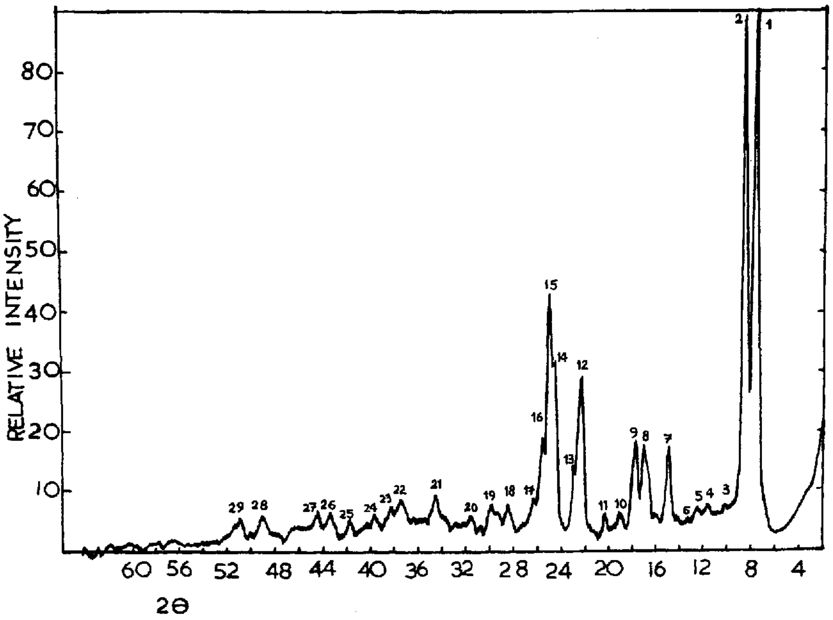

FIGURE 6 Chart diffraction pattern of the unheated Na(acac).

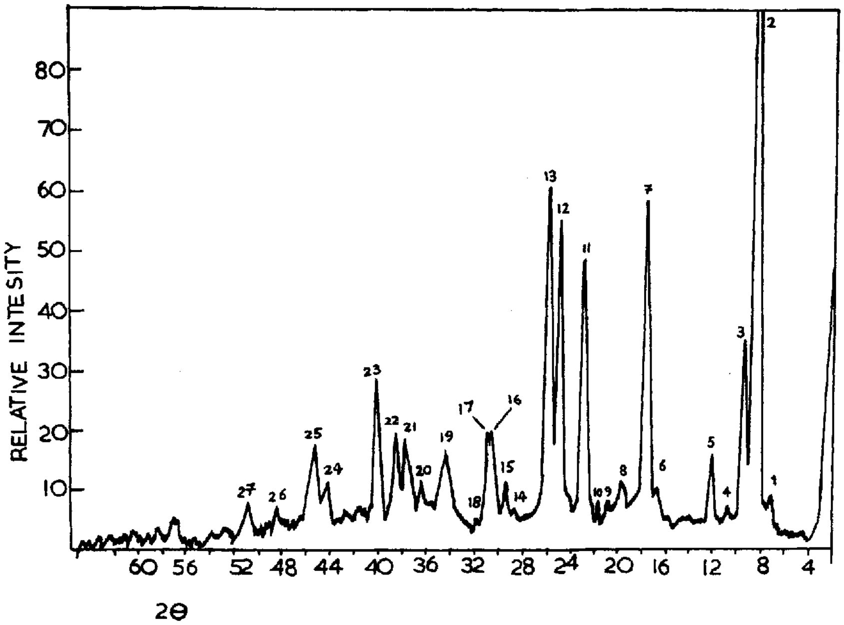

FIGURE 7 Chart diffraction pattern of the pre-heated Na(acac) above T_c.

TABLE I

Line	*Q*(obs.)	*Q*(calc.)	(hkl)
1	0.0076	0.0072	100
2	0.0092	0.0092	010
3	0.0130	0.0130	001
4	0.0169	0.0164	110
5	0.0199	0.0202	101
6	0.0226	0.0222	011
7	0.0286	0.0286	200
8	0.0368	0.0368	020
9	0.0403	0.0410	201
10	0.0459	0.0440	120
11	0.0528	0.0520	002
12	0.0636	0.0648	300
13	0.0670	0.0656	220
14	0.0770	0.0778	301
15	0.0796	0.0808	202
16	0.0834	0.0828	030
17	0.0877	0.0890	022
18	0.1015	0.1016	320
19	0.1122	0.1116	230
20	0.1250	0.1242	103
21	0.1491	0.1472	040
22	0.1725	0.1760	412
23	0.1814	0.1818	303
24	0.1944	0.1910	313
25	0.2165	0.2192	223
26	0.2316	0.2332	403
27	0.2408	0.2414	413
28	0.3012	0.2980	421
29	0.3100	0.3144	448

FIGURE 8 Electron diffraction pattern of the as prepared Na(acac).

TABLE II

Line	Q(obs.)	Q(calc.)	(hkl)
1	0.00665	0.0069	100
2	0.00926	0.0092	010
3	0.011557	0.0123	001
4	0.01490	0.0149	$1\bar{1}0$
5	0.01840	0.0184	110
6	0.03260	0.0320	011
7	0.03940	0.0394	020, $11\bar{2}$
8	0.04933	0.0493	002
9	0.05070	0.0507	$10\bar{2}$
10	0.06191	0.0619	102
11	0.0670	0.0665	$3\bar{1}0$
12	0.07890	0.0789	012
13	0.08340	0.0828	301
14	0.10430	0.1050	$2\bar{3}0$
15	0.10930	0.1093	103
16	0.11980	0.1219	$20\bar{3}$
17	0.12150	0.1219	$20\bar{3}$
18	0.12810	0.1280	022
19	0.14830	0.1480	303
20	0.16710	0.1688	231
21	0.1751	0.1746	$32\bar{3}$
22	0.1858	0.1833	$\bar{1}33$
23	0.1998	0.1986	303
24	0.2408	0.2410	232
25	0.2543	0.2562	223
26	0.2860	0.2844	332
27	0.3052	0.3022	133

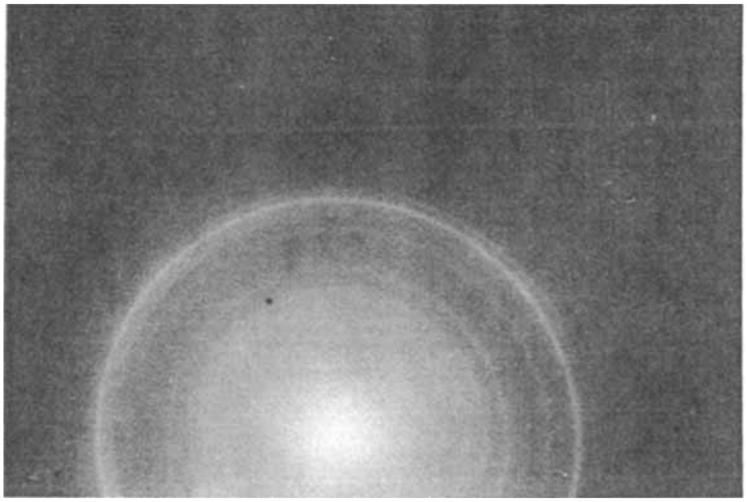

FIGURE 9 Electron diffraction pattern of pre-heated Na(acac) above T_c.

TABLE III

	Electron diffraction		X-ray diffraction	
No.	*d*	relative intensity	*d*	relative intensity
1	3.65	S	3.602	S
2	2.73	W	—	
3	2.44	W	2.408	W
4	2.14	S	2.149	V.W.
5	1.77	W	1.795	V.W.
6	1.51	V.W.		
7	1.40	V.W.		
8	1.26	V.W.		

these patterns yielded the interplanar distances listed in tables III and IV, with a parallel comparison of X-ray diffraction data. It could be noticed that low values of *d*-spacings as obtained from electron diffraction were not observed in the X-ray patterns. This might be attributed to the fact that the wave length of the electron beam is much smaller than that for the X-rays used.

As a conclusion, the previous study showed that the sodium acetylacetonate compound showed an anomalous behaviour in its dielectric properties at about 82°C where a phase change from the orthorhombic to the triclinic structure took place, the change being activated by an energy of 1.34 ev and followed a second order rate reaction.

TABLE IV

	Electron diffraction		X-ray diffraction	
No.	*d*	relative intensity	*d*	relative intensity
1	3.95	V.W.	4.01	V.W.
2	3.49	W	3.46	S
3	2.93	W	2.89	W
4	2.45	V.W.	2.44	V.W.
5	2.06	S	2.038	V.W.
6	1.85	W	2.038	V.W.
7	1.75	V.W.		
8	1.57	V.W.		
9	1.34	V.W.		
10	1.19	V.W.		

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