ionized and the electrons released from these will be trapped by either the impurity ions (e.g. R^{3+}) or anion vacancies. Therefore, following X-ray irradiation, the formation of F-centres, O^- ions, neutral oxygen atoms and R^{2+} ions are evident. The probability of the electrons being captured by R^{3+} ions or anion vacancies will be determined by the ratio of their concentrations. As the glow emission was the same colour for all peaks, it can be concluded that a single recombination site for the trapped electrons exists and that this may be attributed to either an O^- ion or a neutral oxygen atom. The growth curves of the three peaks (Fig. 2) shows that the 340°C peak saturates earlier than the other two peaks. This may be attributed to the substitutional impurities present as it is well established that the glow peak caused by substitutional impurities in ionic solids saturates earlier than other glow peaks and it is quite reasonable to assume that minute traces of impurities such as Fe and Cr occupy substitutional positions in the Al_2O_3 lattice. This result agrees with that reported by Maruyama *et al.* [13]. The first two glow peaks (at 192 and 240°C) must, therefore, be due to the recombinations of electrons, trapped at various energy levels of anion vacancies, with the O^- ion or neutral oxygen atom. Further work is in progress to identify the kind of F-centres responsible for the first two glow peaks and will be communicated shortly.

Acknowledgements

The author wishes to express his gratitude to Professors P. R. Dhar and H. N. Bose for providing facilities in this work. He is also thankful to S. Govenda for valuable discussions.

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Received 11 December 1974
and accepted 12 February 1975

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Dielectric behaviour and morphology of polyvinylidene fluoride

Polyvinylidene fluoride (PVDF) exists in three crystalline forms [1] and previous work [2-9] has shown the existence of three relaxations α, β and γ. The α relaxation (occurring at the highest temperature for a fixed frequency) has been shown to be associated with crystalline regions [7-9], the β with amorphous regions and the γ with local motion in amorphous regions. Yano [7] found that the magnitude of the α relaxation loss peak and the relaxation times increased with increasing lamellar thickness (although only a narrow range from about 160 to 220 Å was quoted) and assigned this relaxation to chain motion within the lamellae. However, the magnitude of the α relaxation for specimens preferentially oriented with their chain axes perpendicular to the applied field was found (surprisingly) to be lower than that for isotropic specimens. Since the dipole moment of PVDF is approximately perpendicular to the chain axis, such specimens would be expected to give a greater relaxation magnitude than an isotropic one if chain motion occurs within the lamellae [10, 11]. Kakutani [8] found a possible anisotropy in the size of the α loss peaks for an oriented specimen as compared with an isotropic one, but the data were complicated by a change in crystalline form from α to β on drawing and by lack of resolution of the α peak. Previous work [11, 12] of ours on polychlorotrifluoroethylene (PCTFE) has shown that the α relaxation arose mainly in the interior of the lamellae with little contribution from chain folds. We have extended this work to study the effects of orientation on the α (and β) relaxation in PVDF and have also made

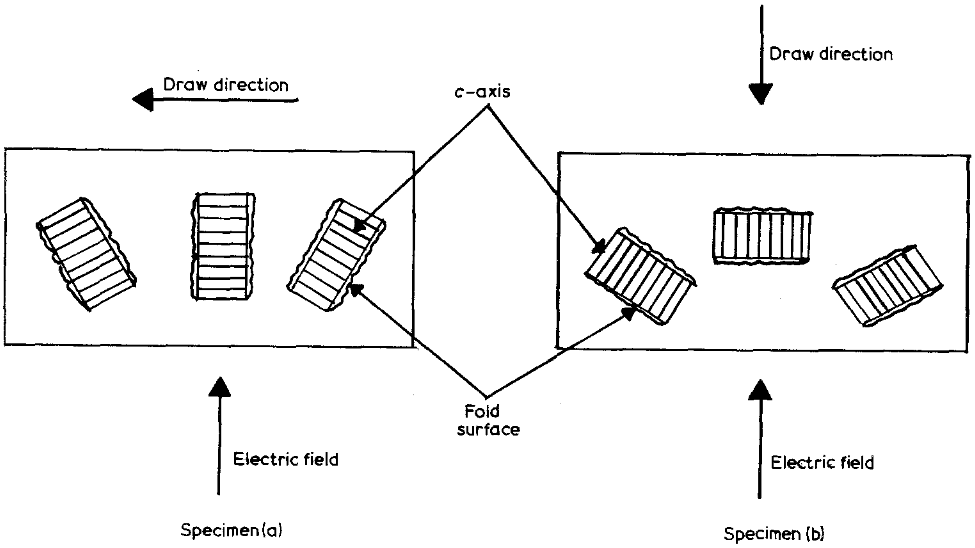

Figure 1 Relationship between the draw directions of PVDF specimens a and b and the applied electric field.

attempts to vary the lamellar thickness of the samples by conventional techniques.

Samples of oriented PVDF (Kynar 500 with a high average molecular weight and a melting point of 171°C) were obtained by crystallizing moulded dumb-bell specimens in silicone oil at 150°C for 3 days (4300 min) and drawing in an air oven at 169°C to a ratio of about 4:1. The specimens were then cooled to room temperature whilst held under extension. Wide-angle X-ray examination confirmed that the specimens remained in the α crystalline form with a reasonable degree of orientation. After cleaning with acetone, specimens were prepared as shown in Fig. 1, with the draw direction (a) perpendicular and (b) parallel to the applied field as described in a previous publication [9]. They were examined as a three-terminal guarded electrical arrangement placed in a shielded electrode assembly [11, 12] so that dielectric data could be obtained over a range of frequency (10^2 to 10^5 Hz) with a G.R. 1615 A Capacitance Bridge and also over a range of temperature -50 to $+150$°C, each temperature being held constant to $\pm$ 0.5°C. The results obtained are shown in Fig. 2, where loss factor ϵ'' is plotted against temperature, and show a marked anisotropy in both α and β relaxations. (The γ relaxation occurs on the low temperature side of the β relaxation and is not visible.) The data for the α relaxation have been corrected for conduction losses which would otherwise show up on the high temperature side of the α peak. The size of the loss peak and magnitude $\epsilon_s - \epsilon_\infty$ for the specimen a were appreciably greater than those for specimen b with the values of the peak heights for the isotropic specimen falling between for both α and β relaxations. Since the temperature of maximum loss $T_{\max}$ and the width of the loss curves are approximately the same for the isotropic and drawn samples and the activation energies for the drawn and undrawn polymers are the same within the limits

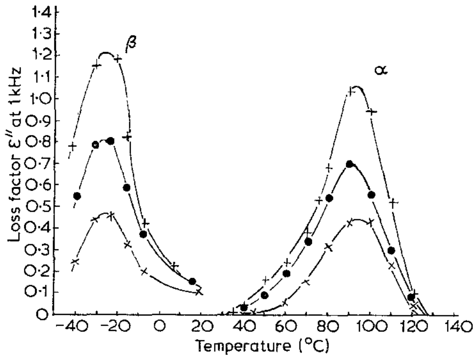

Figure 2 Plots of loss factor ϵ'' at 1 kHz against temperature for an isotropic specimen and for specimens a and b showing anisotropy in both α and β relaxations. (The α relaxation plot has been corrected for conduction losses which become appreciable on the high temperature side of the peak.) PVDF specimens. + Specimen a with draw direction perpendicular to the applied electric field; ● unoriented disc; × specimen b with draw direction parallel to the applied electric field. The crystallinity of all specimens was about 65% (from density measurements).

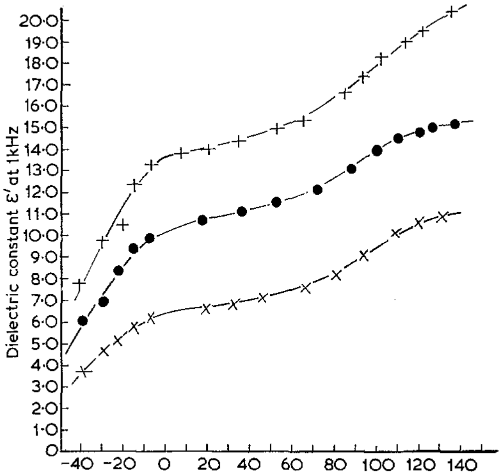

Figure 3 Plots of dielectric constant ϵ' at 1 kHz against temperature for an isotropic specimen and for specimens a and b showing anisotropy in both α and β relaxations. + Specimen a with draw direction perpendicular to the applied electric field; ● unoriented disc; × specimen b with draw direction parallel to the applied electric field. The crystallinity of all specimens was about 65%.

of experimental error, $\epsilon_S - \epsilon_\infty$ may be taken as proportional to ϵ''_m [10, 13]. The anisotropy of the β relaxation is similar to that observed by Yano [7] and Kakutani [8] and suggests a "lining up" of the PVDF chains towards parallelism in amorphous regions [14, 15] on drawing. The anisotropy of the α relaxation is in direct contrast to that found by Yano [7], but conforms with the behaviour expected for chain motion within the lamellae [11]. The pattern obtained in Fig. 2 has been checked using three separately oriented specimens a and b and has been found to be consistent. Similarly data in Fig. 3 showing the dielectric constant as a function of temperature in the region for both the α and β relaxations indicate the same anisotropy. By comparison with our previous arguments for PCTFE [11, 12] the data in Figs. 2 and 3 strongly suggest that the α relaxation arises mainly in the interior of the lamellae with little contribution from chain folds. This largely agrees with the conclusion of Nakagawa and Ishida [16, 17] from measurements on the relaxation magnitude in unoriented PVDF. However, this conclusion should be confirmed by making measurements on (isotropic) specimens with a wide range of lamellar thickness, as with PCTFE [12]. Attempts were made to thicken the lamellae of PVDF by annealing and by varying the temperature of crystallization. Specimens were crystallized for 3 days (4300 min) at different temperatures in the range 100 to 169°C (100, 120, 130, 140, 150, 160 165 and 169°C, the first specimen being quenched from the melt to 100°C and then allowing crystallization to proceed at 100°C). Specimens were also annealed at 169°C for various times up to 4×10^4 min (a) after being quenched in ice water from the melt and (b) after previous crystallization at 150°C for 3 days. The crystallinity of the samples crystallized at 150°C for 3 days was obtained from density measurements and was found to be about 65%. Small-angle X-ray measurements were made with a slit collimated Kratky camera. After desmearing, the data showed hardly any variation in lamellar thickness which remained at about 140 Å. Correspondingly, the parameters of the α and β relaxations (including peak height ϵ''_m and its position (T_{max} or f_{max})) were not visibly affected by the different thermal treatments. It is certainly worth commenting that these types of treatment are nearly always effective in varying lamellar thickness. Work is in progress to investigate this apparent lack of ability of the lamellae in PVDF specimens to thicken and to try to prepare samples with a wide range of lamellar thickness for dielectric studies.

Acknowledgement

The authors wish to thank the S.R.C. for financial support, through a joint research award.

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Received 15 January
and accepted 24 March 1975

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Nature of traps in CaS:Bi:Pd phosphors

Luminescence behaviour of alkaline earth sulphide phosphors activated with one or more impurity elements has been studied by many workers. Recently, studies on CaS phosphors co-activated with Bi^{3+} and various rare earth elements have been reported [1-3], and the effect of ferromagnetic impurity on the behaviour of CaS:Bi phosphors has been investigated by Zope and Walunjkar [4]. The thermoluminescence behaviour of CaS:Bi:Pd phosphors has also been studied and reported previously by the present authors [5]. However, these studies have been mainly devoted to the determination of trap depths and the spectral distribution of luminescence radiation and very little is known about the nature of traps in these phosphors. In this letter we report photo- and thermoluminescence studies carried out on CaS:Bi:Pd phosphors with a view to investigating the physical and chemical nature of traps responsible for the luminescence.

CaS:Bi:Pd phosphors containing varying concentrations of Bi and Pd were prepared by thermal reduction of purified gypsum, as described earlier [5]. Half the amount of the prepared samples was sulphurized in an atmosphere of H_2S at 900°C for $2\frac{1}{2}$ h. The samples studied are listed in Table I.

Fig. 1 shows typical decay curves for the sulphurized and unsulphurized samples. It is evident that the nature of the decay in both cases is similar, but the phosphorescence intensity in the case of sulphurized samples has decreased considerably. In the thermoluminescence study it is found that sulphurization does not give rise to new glow peaks and the peak position and shape of the glow curves also remain essentially unaltered. However, sulphurization has the effect of reducing the thermoluminescence intensity considerably (Fig. 2). These results indicate that sulphurization does not modify the mode of decay or the shape of the glow curves, but it certainly does cause a reduction of trapping levels responsible for photo- and thermoluminescence.

From decay and glow curves, the activation energies for sulphurized and unsulphurized samples were determined. The activation energies

TABLE I Experimental details and values of E for sulphurized samples

Sample no.	Concentration of Bi (wt %)	Concentration of Pd (wt %)	Values of E from "peeling off" of decay curves (eV)			Values of E from glow curves (eV)	
			Slowest exponential	Second exponential	Fastest exponential	First peak	Second peak
S4	0.00	0.001	0.63	0.52	0.48	0.66	—
S13	0.00	0.25	0.64	0.55	0.52	0.64	—
S17	0.005	0.00075	0.58	0.50	0.41	0.58	—
S31	0.01	0.00075	0.52	0.44	0.39	0.52	0.61
S45	0.05	0.00075	0.51	0.48	0.45	0.55	—
S57	0.1	0.00	0.55	0.46	0.42	0.55	0.73
S61	0.1	0.0025	0.53	0.47	0.43	0.57	—
S64	0.1	0.01	0.55	0.46	0.42	0.59	0.69
S66	0.1	0.05	0.56	0.45	0.41	0.58	—
S69	0.1	0.25	0.52	0.44	0.41	—	—