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XRD studies on barium titanate ($BaTiO_3$)/polyvinylidene fluoride (PVDF) composites

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XRD studies were carried out on barium titanate ($BaTiO_3$)/polyvinylidene fluoride (PVDF) composites in the ranges 98° to 103° and 10° to 50°. The structures of PVDF/$BaTiO_3$ composites were affected significantly. In the composites, elimination and suppression of some of the peaks of PVDF and shifting of some of the peaks of $BaTiO_3$ was observed. The observed changes are attributed to the internal stresses.

1. Introduction

Polymer/ceramic composite materials have a wide range of applications because of their improved properties over the individual constituents. In addition, their properties can be tuned to requirement by changing the proportions of the constituents. Because this is an upcoming field, much work is needed to understand their behaviour thoroughly so that they can be effectively used for various applications.

Almost no work has been done in a systematic way on the XRD behaviour of any polymer/ceramic composite to see the structural variations. Yamazaki *et al.* [1] performed X-ray diffraction (XRD) studies on PVDF–$PbTiO_3$ composite to determine the effect of poling field on the composite. They observed that the peak height (0 0 2) of $PbTiO_3$ increases and the peak height (2 0 0) of $PbTiO_3$ decreases with increase in the poling field. They attributed this to the increase of polarization of $PbTiO_3$, by which the pyroelectric coefficient of the composite is increased [1].

No XRD work has been reported on $BaTiO_3$/PVDF composites. In our previous communication [2] the XRD studies on PVDF, $BaTiO_3$ and $BaTiO_3$/PVDF composite of 70% weight fraction of $BaTiO_3$ in the range 98° to 103° were discussed. Therefore in the present work, it was thought desirable to make a detailed study of how the structural variations take place in $BaTiO_3$/PVDF composites by changing the weight fraction of $BaTiO_3$ in the ranges 98° to 103° and 10° to 50°. This technique is useful, effective and important, changes in different forms of the constituents in $BaTiO_3$/PVDF composites can be observed.

2. Experimental procedure

The XRD studies were done in powder form using a Rigaku X-ray diffractometer, Japan. Its voltage and current ratings were 40 kV and 30 mA.

3. Results and discussion

Figs 1a to g show the XRD pattern of PVDF, 10%, 30%, 50%, 70%, 90% weight fractions of $BaTiO_3$ composites and $BaTiO_3$, respectively, in the range 98° to 103°. The scan speed was 1° min^{-1} and step/sampling was 0.01°. Smoothing was 7 and differential was 5. It is clear from Fig. 1a that there is no peak in PVDF. There is a (4 0 0) tetragonal peak at 101.16° with pseudocubic form (Fig. 1g) because of the ultra-fine particle size of $BaTiO_3$ (about 1 μm). This tetragonal peak with pseudocubic form is present in all compositions of the composites, but there is a maximum change at the (4 0 0) position in 90% weight fraction of $BaTiO_3$ composite at 100.98° (Fig. 1f). In fact this composition should be of general interest, but SEM studies have shown that the connectivity is poor [3] and this is greatly reflected in various properties such as low dielectric constant and low pyroelectric coefficient [4]. Therefore, in the present work, study was concentrated on 70% weight fraction of $BaTiO_3$ composite for which the (4 0 0) position is at 101.1° with a change in the pseudocubic form (Fig. 1e) from other compositions. Also this composition has a high pyroelectric coefficient and a high dielectric constant [4], with relatively good connectivity compared to other compositions studied in our previous work [3]. The change in the (4 0 0) position with pseudocubic form lies in between the values mentioned above for the remaining compositions. All these changes can be accompanied by the internal stresses developed in the composites which vary from composition to composition because of the change in interaction between PVDF and $BaTiO_3$. As the shift is maximum in 70% weight fraction after 90% weight fraction of $BaTiO_3$ composites, and also the connectivity is relatively good when compared to other compositions, this composition has an off-valency additive effect in addition to the ultra-fine particle-size effect [2, 5]. Because of the vicinity of the valency defect, the symmetry of the lattice is disturbed [5]. This is reflected in the appearance of disturbance in the composites, which is mainly due to internal stresses, which also vary from composition to composition as explained

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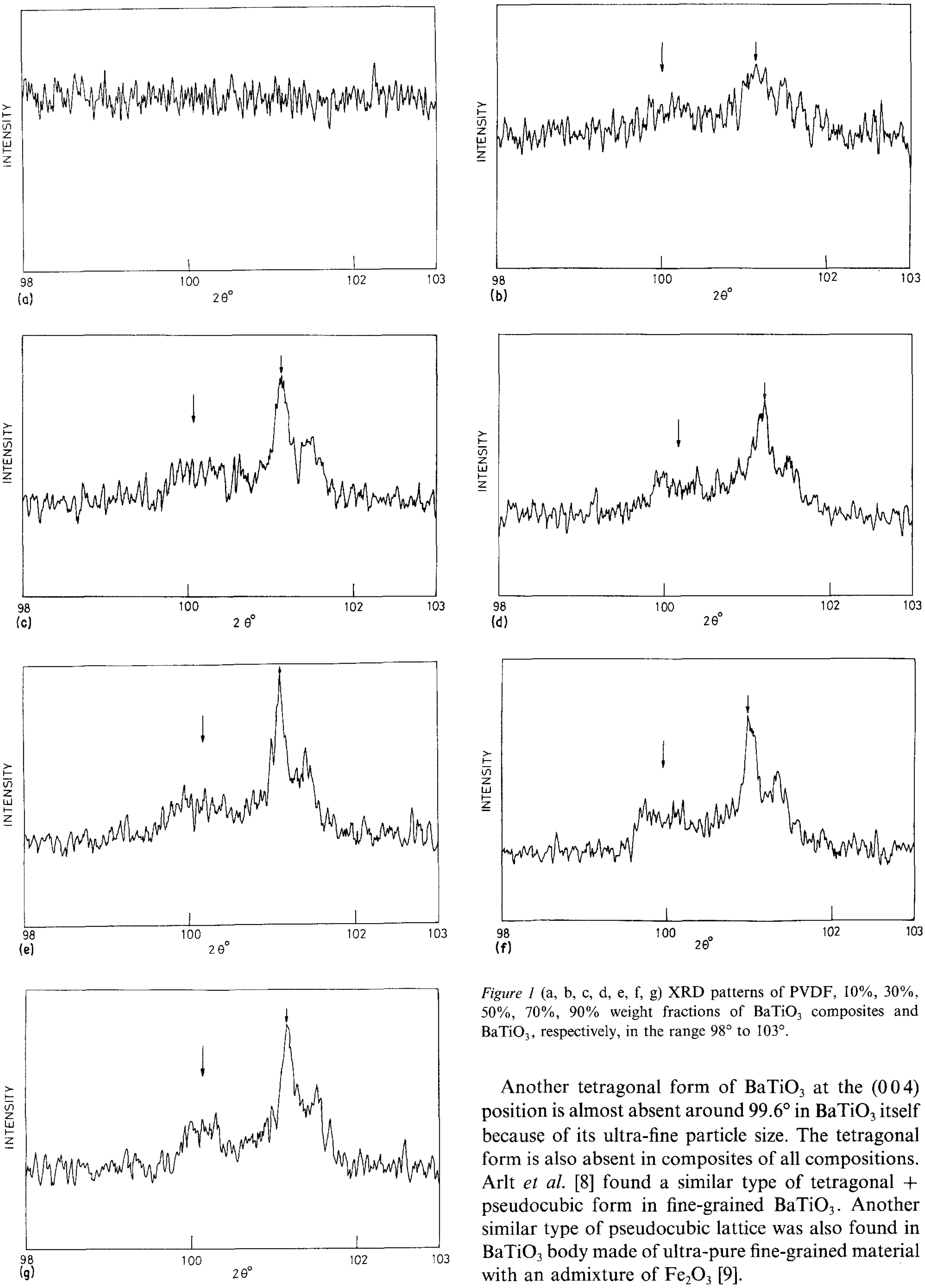

Figure 1 (a, b, c, d, e, f, g) XRD patterns of PVDF, 10%, 30%, 50%, 70%, 90% weight fractions of $BaTiO_3$ composites and $BaTiO_3$, respectively, in the range 98° to 103°.

above. The Curie peak is nearly washed out because of the combined effects of ultra-fine particle size and off-valency additive effects [5]. The absence of a Curie peak in 70% weight fraction of $BaTiO_3$ composite is also confirmed by the absence of any abrupt change in the dielectric, resistivity and hysteresis behaviour of the same composition [5–7], respectively.

Another tetragonal form of $BaTiO_3$ at the (0 0 4) position is almost absent around 99.6° in $BaTiO_3$ itself because of its ultra-fine particle size. The tetragonal form is also absent in composites of all compositions. Arlt *et al.* [8] found a similar type of tetragonal + pseudocubic form in fine-grained $BaTiO_3$. Another similar type of pseudocubic lattice was also found in $BaTiO_3$ body made of ultra-pure fine-grained material with an admixture of Fe_2O_3 [9].

Figs 2a to g show the XRD pattern of PVDF, 10%, 30%, 50%, 70%, 90% weight fractions of $BaTiO_3$ composites and $BaTiO_3$ in the range 10° to 50°. The scan speed was 2° min^{-1} and step/sampling was 0.02°. Smoothing was 7 and differential was 5. It is clear from Fig. 2a that the peaks of PVDF at 18.34°, 19.9° and 26.5° decrease slowly and shift slightly as the weight fraction of $BaTiO_3$ increases in $BaTiO_3$/PVDF

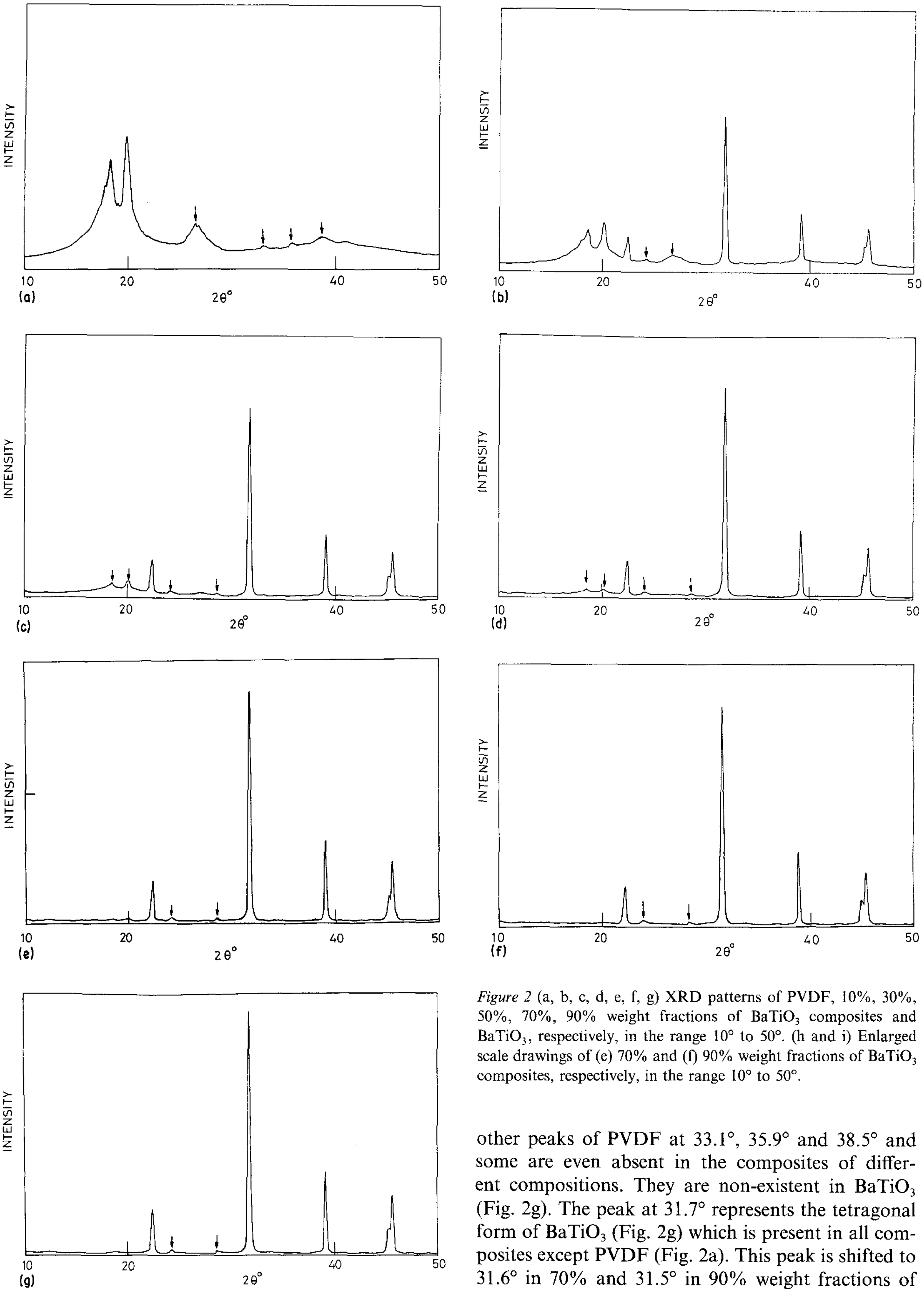

Figure 2 (a, b, c, d, e, f, g) XRD patterns of PVDF, 10%, 30%, 50%, 70%, 90% weight fractions of $BaTiO_3$ composites and $BaTiO_3$, respectively, in the range 10° to 50°. (h and i) Enlarged scale drawings of (e) 70% and (f) 90% weight fractions of $BaTiO_3$ composites, respectively, in the range 10° to 50°.

composites (Figs 2b to d). Finally these peaks are also present in 70% and 90% weight fractions of $BaTiO_3$ composites (Figs 2h, i, enlarged scale drawings of Figs 2e, f). However, they are not clearly evident as in other compositions of composites because their intensities are extremely low compared to other peaks in those compositions; the same is true in the case of other peaks of PVDF at 33.1°, 35.9° and 38.5° and some are even absent in the composites of different compositions. They are non-existent in $BaTiO_3$ (Fig. 2g). The peak at 31.7° represents the tetragonal form of $BaTiO_3$ (Fig. 2g) which is present in all composites except PVDF (Fig. 2a). This peak is shifted to 31.6° in 70% and 31.5° in 90% weight fractions of $BaTiO_3$ composites. Since maximum change has been observed in 90% weight fractions of $BaTiO_3$ composite, this composition should be generally interesting. However, SEM studies have shown that the connectivity is poor [3] and this is greatly reflected in various properties such as low dielectric constant and low pyroelectric coefficient [4]. Therefore, in the present work, study was concentrated on the 70%

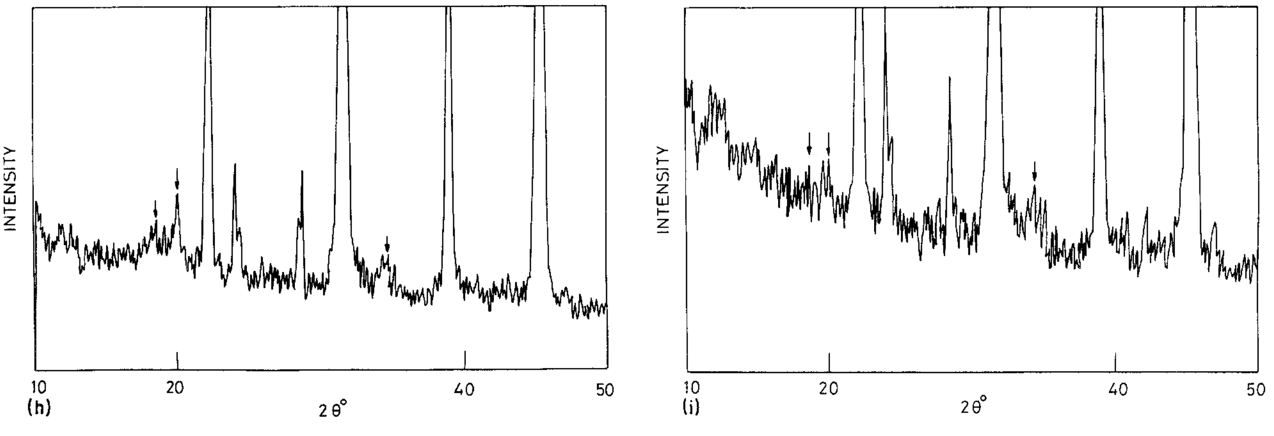

Figure 2 Continued.

weight fraction of $BaTiO_3$ composite, because this composition has a very high dielectric constant and a high pyroelectric coefficient compared with other compositions [4], and the connectivity is also relatively good [3]. The peak at 22.4° in $BaTiO_3$ (Fig. 2g) which is absent in PVDF has been shifted slightly in composites and is at 22.3° in 70% (Fig. 2e) and 22.2° in 90% weight fractions of $BaTiO_3$ composites (Fig. 2f). The peak at 24.18° in $BaTiO_3$ (Fig. 2g), which is absent in PVDF, has been shifted slightly in the composites and lies at 24° in 70% and 23.92° in 90% weight fractions of $BaTiO_3$ composites. The peak at 28.68° in the 30% weight fraction of $BaTiO_3$ composite (Fig. 2c) and which is present thereafter in the composites and also in $BaTiO_3$ has been shifted to 28.56° in 70% weight fraction of $BaTiO_3$. The peak at 39.14° in $BaTiO_3$ (Fig. 2g), which is absent in PVDF, has been shifted slightly in the composites and lies at 39.02° in 70% (Fig. 2e) and 38.92° in 90% weight fractions of $BaTiO_3$ composites (Fig. 2f).

Another pseudocubic form of (2 0 0) together with the (0 0 2) position is present in $BaTiO_3$ at 45.6° (Fig. 2g) because of the ultra-fine particle size, has been shifted slightly in composites and lies at 45.48° in 70% (Fig. 2e) and 45.38° in 90% weight fractions of $BaTiO_3$ composites (Fig. 2f). All these changes can be accompanied by internal stresses developed in the composites, which vary from composition to composition because of the change in interaction between PVDF and $BaTiO_3$. As the shifting is maximum in 70% weight fraction after 90% weight fraction of $BaTiO_3$ composites and also the connectivity is relatively good when compared to other compositions, this composition has an off-valency additive effect in addition to the ultra-fine particle size effect [2, 5]. Because of the vicinity of the valency defect, the symmetry of the lattice is disturbed [5]. It is this that is reflected in the appearance of the disturbance in the composites which is mainly due to the internal stresses, which also vary from composition to composition as explained above. The change in d values obtained by the variation of 2θ values in the different composites is small and appears only after the second decimal place of the value of d. From this it is clear that the change in d values, though not appreciable, cannot be neglected. The Curie peak is nearly washed out because of the combined effects of ultra-fine particle size and off-valency additive effects [5]. The absence of Curie peak is confirmed by no abrupt change being seen in the dielectric, resistivity and hysteresis behaviour of the same composition [5–7].

The pseudocubic (0 0 2) reflection was observed in the sintered semiconducting $BaTiO_3$ sample surfaces before and after the mechanical treatments by Amin and Shukla [10]. Das Gupta and Doughty [11, 12] observed the shifting and suppression of some of the peaks of PVDF after corona charging or annealing of PVDF. Bamji and Perlman [13, 14] also observed suppression of some of the peaks of PVDF after corona charging in PVDF. However, in the composites, the elimination and suppression of some of the peaks of PVDF and the shifting of some of the peaks of $BaTiO_3$ indicate how powerful the internal stresses are, because such a drastic change has been observed in composites not subjected to the external influences such as corona charging.

Therefore, the presence of internal stresses plays an interesting and important role in the composites, as is evident from the present studies, and hence they can never be neglected. They affected the structures of PVDF/$BaTiO_3$ composites significantly.

4. Conclusions

A maximum change in 2θ values of XRD studies of 70% after 90% weight fractions of $BaTiO_3$ composites has been observed. The structures of PVDF/$BaTiO_3$ composites were affected significantly as the weight fraction of $BaTiO_3$ varies in the composites. The presence of internal stresses plays a dominant role in effecting the observed changes in the composites.

References

1. H. YAMAZAKI and T. KITAYAMA, *Ferroelectrics* **33** (1981) 147.
2. C. MURALIDHAR and P. K. C. PILLAI, *J. Mater. Sci. Lett.* **6** (1987) 33.
3. G. MURALIDHAR and P. K. C. PILLAI, *J. Mater. Sci. Lett.* **6** (1987) 1243.
4. C. MURALIDHAR and P. K. C. PILLAI, *IEEE Trans. Electrical Insul.* **EI-21** (1986) 501.
5. *Idem, J. Mater. Sci. Lett.* **6** (1987) 346.
6. *Idem, ibid.* **6** (1987) 439.
7. *Idem, ibid.* **6** (1987) 349.
8. G. ARLT, D. HENNINGS and G. DEWITH, *J. Appl. Phys.* **58** (1985) 1619.
9. B. JAFFE, W. R. COOK and H. JAFFE, "Piezoelectric ceramics" (Academic, London, 1971) Ch. 5.

10. A. AMIN and V. SHUKLA, *J. Amer. Ceram. Soc.* **68** (1985) C-167.
11. D. K. DAS GUPTA and K. DOUGHTY, *IEEE Trans. Ind. Appl.* **IA-14** (1978) 448.
12. *Idem, Ferroelectrics* **60** (1984) 51.
13. S. S. BAMJI and M. M. PERLMAN, *J. Polym. Sci. Polym. Phys. Edn.* **19** (1981) 1365.
14. *Idem, ibid.* **18** (1980) 1945.

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