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Electron spin relaxation of the PO_3^{2-} radical in ferroelectric betaine phosphite and in the proton glass betaine phosphate/betaine phosphite

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Abstract

Measurements of the electron spin–lattice relaxation time T_1 and the phase memory time T_M of the PO_3^{2-} radical in γ-irradiated betaine phosphite and betaine phosphate/betaine phosphite are presented. The temperature dependence of T_1 indicates the interaction of the electron spin with two groups of optical branches via Raman processes in both crystals. An additional relaxation path due to the interaction with two-level local tunneling states has been observed in the mixed crystal confirming glassy behaviour. The T_M temperature dependence reflects thermally activated local motional effects of the PO_3 group in both crystals.

1. Introduction

The molecular crystals betaine phosphite (BPI) $(CH_3)_3NCH_2COO^*H_3PO_3$ and betaine phosphate (BP) $(CH_3)_3NCH_2COO^*H_3PO_4$ belong to the well known family of betaine addition compounds that shows an impressive variety of ordered low-temperature phases [1,2]. Thus BPI transforms at $T_C=216$ K from an antiferrodistortive room temperature phase into a ferroelectric low-temperature phase [3,4] whereas BP exhibits below $T_C=86$ K antiferroelectric ordering [5]. The room temperature phase of BP is also antiferrodistortive. In solid solutions BP/BPI the competing antiferroelectric and ferroelectric interactions lead to a suppression of the long-range electric order. Proton glass behaviour has recently been observed [6] in mixed crystals of intermediate concentrations BP:BPI(40/60).

We showed in a previous paper [7] that PO_3^{2-} radicals can be formed by γ irradiation of BPI. The proton H14 is removed by γ irradiation from the H_3PO_3 group and one unpaired electron remains in this nonbonding phosphorus sp^3 orbital. In this Letter, we examine the electron spin relaxation of the paramagnetic PO_3^{2-} probe in a pure BPI single crystal and in a mixed single crystal BP:BPI(40/60) by means of electron spin echo (ESE) technique. Both the spin–lattice relaxation (SLR) time T_1 and the phase memory time T_M of the PO_3^{2-} centre have been investigated in the temperature range $4 \leqslant T \leqslant 300$ K. T_M is a measure of the spin–spin relaxation (SSR) time.

2. Experimental

The ESE measurements were carried out on a BRUKER ESP 380 FT-EPR spectrometer and on a homebuilt ESE spectrometer both working at X band

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