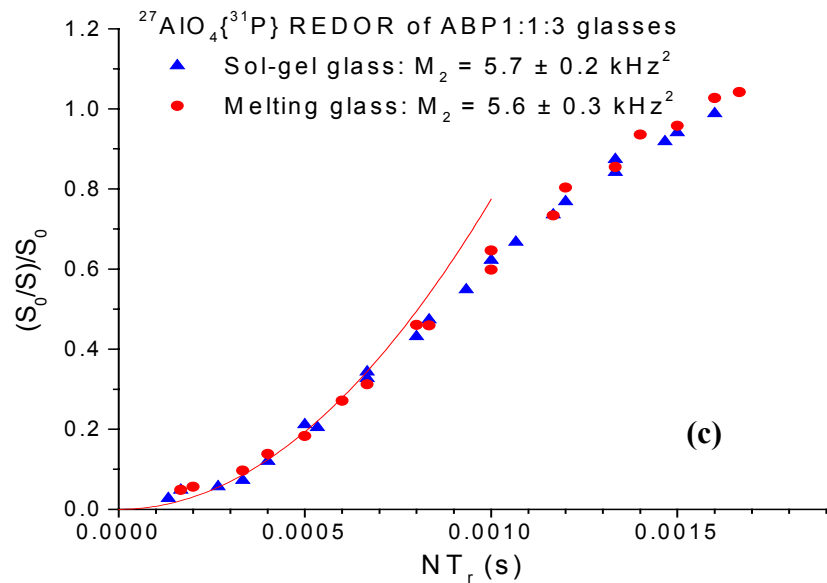
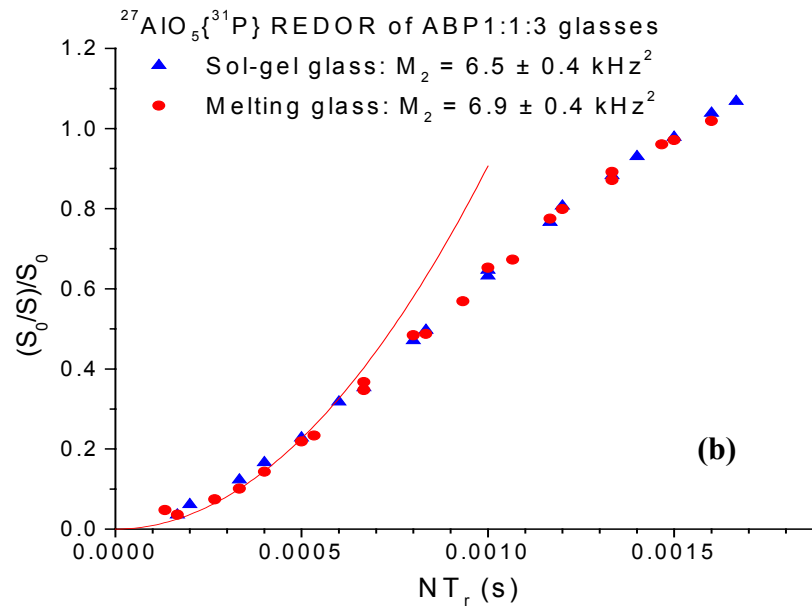
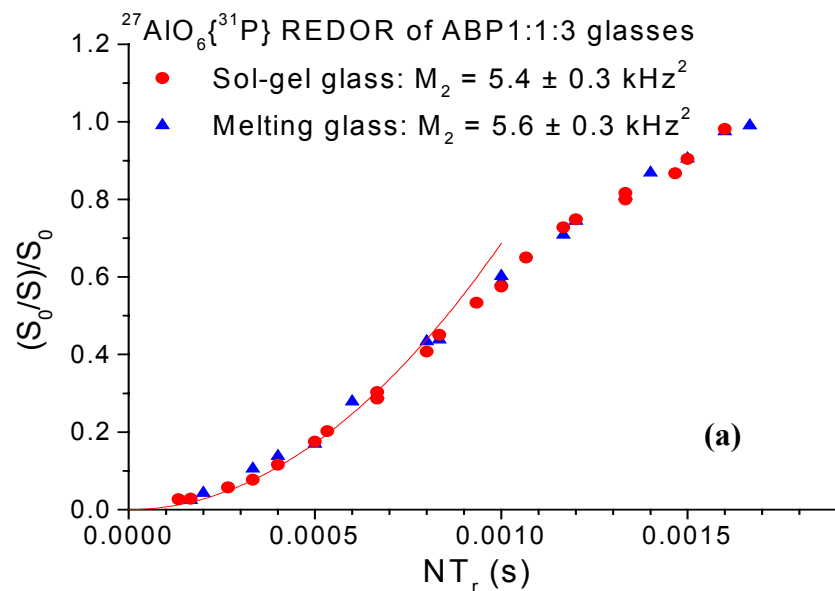


**Figure S1.** Experimental and simulated and  $^{11}\text{B}\{^{31}\text{P}\}$  REDOR dephasing curve of crystalline  $\text{BPO}_4$  model compound. The measurement was carried out at the spin rates of 8, 9, 10, 12 and 15 kHz, whereas the simulation was carried out at the spin rates of 8, 9, 10, 12, 15 and 25 kHz. For the simulation, the program SIMPSON was employed based on the tetrahedral  $\text{B}(\text{OP})_4$  environment. The maximum time step (max dt) over which the Hamiltonian is approximated to be time-independent was set to  $1 \mu\text{s}$ . A powder averaging scheme containing 320 REPULSION angles (alpha and beta) and 36 gamma angles was chosen.



**Figure S2.** Site resolved <sup>27</sup>Al{<sup>31</sup>P} REDOR of aluminum borophosphate glasses with composition Al/B/P 1:1:3, prepared via the sol-gel route and melt-cooling method. **a)** AlO<sub>6</sub> unit; **b)** AlO<sub>5</sub> unit; **c)** AlO<sub>4</sub> unit.