

# Prediction of $^{29}\text{Si}$ MAS NMR spectra for tridymite modifications

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**Introduction:**  $^{29}\text{Si}$  MAS NMR measurements of the tridymite polymorphs have been reported for the MC and MX-1 polymorphs and for several high-temperature phases<sup>1-4</sup>. However, conflicting results have been reported for MX-1<sup>2,3</sup>. For MC, the measured spectra do not agree well with those predicted from the empirical equations<sup>5</sup>. For PO-10, there are no report and no prediction. Therefore, it is necessary to establish  $^{29}\text{Si}$  MAS NMR spectra of the tridymite polymorphs for phase identification and local structure study. Some of the tridymite polymorphs have so many Si sites that it is convenient to correlate the local structure with the chemical shifts and to check the empirical formulae proposed. In this study, the chemical shifts of MC, MX-1, and PO-10 polymorphs were calculated by first-principles calculations and compared with measured spectra, and the proposed empirical formulae for the correlation between local structure and chemical shift were also inspected.

**Calculation:** Firstly, crystal structures were optimized from observed ones using Quantum Espresso's pw-scf code. Using the optimized structure and electron densities, the NMR chemical shifts were calculated using the GIPAW method (gipaw code). For MC and PO-10, due to the large number of atoms (PO-10 contains 960 atoms in space group *F1*), the calculations were converted to a primitive lattice. In the case of MX-1, the average structure and a modulated structure model were used. In the case of tridymite polymorphs, the number of sites is large and their peaks overlap, making the decomposition of the peaks difficult. Therefore, a pseudo-spectrum was obtained by applying a Gaussian function to the chemical shift position of each Si site for easy comparison with the measured spectrum.

**Results and Discussion:** Predicted spectra are given in Fig. 1. For MC, there are several reports of measured spectra<sup>1-4</sup>, but there is no significant difference between them. The calculated MC spectrum is almost identical to the measured spectra, although there are some deviations of individual peaks, which is a great improvement from the empirically obtained spectra<sup>5</sup>. For MX-1, the spectra of Graetsch & Topalovic-Dierdorf<sup>2</sup> and Xiao et al.<sup>3</sup> differ significantly. The former can be interpreted as a significant contamination of peaks corresponding to the MC. The latter spectrum shows a simple spectrum with just two peaks close together, which corresponds to the one calculated from the average structure of MX-1, but is different from the spectrum predicted by the modulated structure model. There are no measured spectra for PO-10, so no comparison is possible at this time.

The relationship between local structure and  $^{29}\text{Si}$  MAS NMR chemical shifts in silicate crystals and glasses has been studied extensively<sup>1,5,6</sup>, and a number of empirical equations have been proposed and used to empirically predict chemical shifts from structure. In the present calculation, more than 100 Si sites were calculated (but the range is relatively narrow), which is useful to evaluate the empirical formulae. I plotted the correlation between the local structure and the chemical shift using the empirical formula proposed by Sherriff and Grundy<sup>6</sup>, and found a very good correlation, confirming the superiority of this empirical formula. The chemical shifts of PO-10 ride well on this correlation, and although we have not been able to compare it with the measured spectrum, we believe the calculated spectrum will reproduce the observed spectrum well. The identification of tridymite polymorphs using  $^{29}\text{Si}$  MAS NMR is now possible with confidence. The present results show that chemical shifts can be predicted practically by first-principles calculations (GIPAW method). However, as in the case of PO-10, where the unit cell contains many atoms, or in the case of applying the results to glass structure from MD simulations, first-principles calculations

are very time-consuming, and empirical formulas are still valid in such cases.

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