

**$^{23}\text{Na}$  NMR study on ion dynamics in nonstoichiometric layer-type  
oxide  $\text{Na}_{0.67}\text{Co}_{0.33}\text{Ti}_{0.67}\text{O}_2$**

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Local structures and dynamics of the  $\text{Na}^+$  ions of newly synthesized nonstoichiometric layer-type oxide  $\text{Na}_{0.67}\text{Co}_{0.33}\text{Ti}_{0.67}\text{O}_2$  have been studied with  $^{23}\text{Na}$  ( $I = 3/2$ ) spin-lattice relaxation as well as line shape analysis. As temperature increases, the upfield shift of the  $^{23}\text{Na}$  resonance due to the paramagnetic interaction with Co(II) electron in  $e_g$  orbital was observed. The temperature dependence (298K- 475K) of static spectra shows a noticeable decrease in line width up to 360K and narrower but steady line widths above 360K manifest the motional narrowing. Three exponentially decaying components were observed and the kinetic parameters for the ionic motion were determined from relaxation measurement. The magnetic interaction between the unpaired electron of Co(II) metal and the sodium nucleus is responsible for the fastest relaxing pathway. The dominating relaxation mechanism of  $^{23}\text{Na}$  nuclei is closely related to sodium inter-dipolar interaction modulated by  $\text{Na}^+$  ion motion in the 2-dimensional channels perpendicular to the c-axis of which activation energy is observed as  $E_a = 157 \pm 3.71\text{meV}$ . Deconvolution of the spectra into three components reveals that the relative amounts of inequivalent  $\text{Na}^+$  sites agrees well with that from the relaxation study. From the temperature dependence of the relative populations of the sites, it could be concluded that the population of the sodium ions changes by the ion movement between the sites actively until 360K, and sodium ions come to reach their dynamic equilibrium between the two crystallographic sites at higher temperature. Our NMR study exhibits the existence of several inequivalent  $\text{Na}^+$  sites in  $\text{Na}_{0.67}\text{Co}_{0.33}\text{Ti}_{0.67}\text{O}_2$  and characteristic motional behaviors over the temperature range investigated.