# Insights into the Structure of $Mn^{2+}$-dopped $K_2CO_3$-$MgCO_3$ Glass at High Pressure from Time-resolved Laser Fluorescence

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**Abstract**

The presence of carbonates in the mantle is supported by evidence from seismology, simulations, and natural samples. Deep carbonate melts exhibit extremely low viscosity and density, distinguishing them from silicate melts. High pressure experiments using $K_2CO_3$–$MgCO_3$ glass as an analogue for carbonate melts have suggested that pressure induces the formation of four fold coordinated carbon ($CO_3$ ($sp^2$-carbon) → $CO^{3+1}$ ($sp^3$-carbon)) above ~30–40 GPa, implying potentially large changes in the physical properties of the glass (and possibly the melt) [1-3]. The formation of the $CO_{3+1}$ configuration in the glass follows the strengthening of Coulombic attraction between $K^+$ and the oxygen atoms in distorted $CO_3^{2-}$ anions [2]. Because Mg is a cation with a stronger cation field strength than K (at 1 atm: ~3.86 $Å^{-2}$ for $Mg^{2+}$ vs ~0.53 $Å^{-2}$ for $K^+$), the pressure at which the $CO_{3+1}$ configuration forms may also depend on changes in the local electronic environment of Mg. For example, one may expect that an increase in the Mg coordination number (CN) by oxygen could slow structural changes within the $CO_3$ anion and thus shift the onset of the carbon $sp^2 \rightarrow sp^3$ transition to higher pressures. However, resolving variations in Mg–O and Mg site in the glass using conventional structural probes remains challenging.

Here we report on the structural characteristics of $Mn^{2+}$-doped $K_2CO_3$-$MgCO_3$ glass probed by time-resolved laser fluorescence spectroscopy in a diamond anvil cell up to 37 GPa. The identical formal charge and intermediate ionic radius of $Mn^{2+}$ allow it to serve as a proxy for common divalent cations (e.g., Mg, $Fe^{2+}$, Ca) in carbonates. The wavelength, intensity, and lifetime of the emission are sensitive to the $Mn^{2+}$ CN and site symmetry, and show a strong pressure dependence. To interpret pressure induced changes in $Mn^{2+}$ site, we performed reference measurements on $Mn^{2+}$-doped crystalline $CaCO_3$ and $MgCO_3$, whose high pressure behavior is well established. Our results show that upon compression the average Mn coordination increases from CN~6 at 1 atm to CN~7–8 at 13–14 GPa—well below the pressures reported for the carbon $sp^2 \rightarrow sp^3$ transition in the glass.

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