

# Crystal structure, high-pressure, and high-temperature behavior of carbonates in the $\text{K}_2\text{Mg}(\text{CO}_3)_2\text{--Na}_2\text{Mg}(\text{CO}_3)_2$ join

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## ABSTRACT

Although alkali-alkali earth carbonates have not been reported from mantle-derived xenoliths, these carbonates may have a substantial role in mantle metasomatic processes through lowering melting temperatures. On the  $\text{Na}_2\text{Mg}(\text{CO}_3)_2\text{--K}_2\text{Mg}(\text{CO}_3)_2$  join only the Na-end-member eitelite ( $R\bar{3}$  space group), was reported in nature. The K-end-member ( $R\bar{3}m$ ) readily hydrates even at low temperatures, therefore, only baylissite,  $\text{K}_2\text{Mg}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$ , has been observed. Because of the role of (K,Na)Mg-double carbonates in mantle metasomatism, we performed high  $P$ - $T$  experiments on  $\text{K}_2\text{Mg}(\text{CO}_3)_2$ ,  $(\text{K}_{1.1}\text{Na}_{0.9})_2\text{Mg}(\text{CO}_3)_2$ , and  $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ . Structure refinements were done upon compression of single crystals from 0 to 9 GPa at ambient temperature employing synchrotron radiation. Fitting the compression data to the second-order Birch-Murnaghan EoS resulted in  $V_0 = 396.2(4)$ ,  $381.2(5)$ , and  $347.1(3)$  Å<sup>3</sup> and  $K_0 = 57.0(10)$ ,  $54.9(13)$ , and  $68.6(13)$  GPa for  $\text{K}_2\text{Mg}(\text{CO}_3)_2$ ,  $(\text{K}_{1.1}\text{Na}_{0.9})_2\text{Mg}(\text{CO}_3)_2$ , and  $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ , respectively. These compressibilities are lower than those of magnesite and dolomite. The KMg-double carbonate transforms into a monoclinic polymorph at 8.05 GPa; the high- $P$  phase is 1% denser than the low- $P$  polymorph. The NaMg-double carbonate has a phase transition at ~14 GPa, but poor recrystallization has prevented structure refinement. The parameters for a  $V$ - $T$  EoS were collected at 25–600 °C and ambient pressure and are  $\alpha_0 = 14.31(5) \times 10^{-5}$  K<sup>-1</sup> and  $16.73(11) \times 10^{-5}$  K<sup>-1</sup> for  $\text{K}_2\text{Mg}(\text{CO}_3)_2$  and  $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ , respectively. Moreover, fitting revealed an anisotropy of thermal expansion along the  $a$ - and  $c$ -axis:  $\alpha_0(a) = 2.84(6) \times 10^{-5}$  and  $4.78(5) \times 10^{-5}$  K<sup>-1</sup> and  $\alpha_0(c) = 10.47(11) \times 10^{-5}$  and  $8.72(5) \times 10^{-5}$  K<sup>-1</sup> for  $\text{K}_2\text{Mg}(\text{CO}_3)_2$  and  $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ , respectively.

**Keywords:** Alkali-alkali earth double carbonates, synchrotron, high pressure, phase transition