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A High-pressure Vibrational Spectroscopic study of Chromium Diphosphate and Iron Diphosphate up to 25 Gpa.

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The infrared and Raman spectra of chromium diphosphate ($\text{Cr}_2\text{P}_2\text{O}_7$) and iron diphosphate ($\text{Fe}_2\text{P}_2\text{O}_7$) have been studied under high pressures up to 25 GPa using diamond anvil cells and *in situ* Fourier Transform infrared spectroscopy (FTIR) and Raman spectroscopy. No prior high-pressure work exists on these two pyrophosphates, and the objective of our study was to explore the compounds' structural response to pressure by investigating the pressure-induced phase transitions occurring within each compound, and their reversibility during decompression. In particular, we examine how the P_2O_7 group responds to compression in order to evaluate whether polymerized phosphate tetrahedra might be stable under high-pressures. Our results constrain the pressure response of the symmetric and asymmetric bending and stretching modes of the phosphate groups between 600 to 800 cm^{-1} , and 950 to 1200 cm^{-1} , respectively. Chromium diphosphate compresses uniformly up to the highest pressure investigated with no phase transitions observed, and with normal pressure-induced increases in the frequencies of its normal modes. In contrast, iron diphosphate undergoes two phase transitions over the pressure-range of our experiment. In the first, the symmetric P-O-P stretching vibration splits at ~ 5 GPa, followed by the splitting of the initially single symmetric PO_4 stretching mode into four separate modes, and of the sole asymmetric PO_4 stretching mode into two distinct modes, both at ~ 9 GPa. Each of these changes indicate the presence of two separate P_2O_7 environments within a new, larger volume, unit cell, and the relative frequencies of the split vibrations are consistent with at least one of the P_2O_7 environments having a markedly narrowed P-O-P angle. Decompression data on the iron-rich compound show that the transitions are partially reversible; most of the P_2O_7 groups return close to their initial geometry. The rationale for the difference between the behaviors of the iron and chromium compounds is not entirely clear, but is likely associated with the smaller ionic radius of the divalent iron ion relative to divalent chromium: compression of the smaller iron-ion-bearing compound may require a

discontinuous decrease in the P-O-P angle at lower pressures than in the analogous chromium compound. Our results thus indicate that, at least at 300 K, the dimerized P_2O_7 group remains stable under compression, although its P-O-P angle may undergo discontinuous decreases under pressure.

I am applying for financial assistance to travel to the 2016 COMPRES Annual Conference in New Mexico, USA, and present my research on the structural behavior of diphosphates under high pressures. I am a senior physics undergraduate at the University of California, Santa Cruz, and have been involved in high-pressure geophysics research for the past year. I plan to apply to graduate programs in geophysics at the end of this year, and consider the COMPRES conference to be a very valuable opportunity to connect with faculty and students in the high-pressure research community. Attending COMPRES will expose me to the current research being done at other institutions, give me the opportunity to learn about the potential graduate school opportunities for graduating undergraduates like myself, and, most importantly, allow me to meet potential mentors personally. It is for these reasons that attending COMPRES is a crucial component to my successful transition into a rewarding graduate school program.