Akhtenskite-nsutite phases: Polymorphic transformation, thermal behavior and magnetic properties

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Abstract:

Two different MnO$_2$ polymorphs, namely akhtenskite (ε-form) and nsutite (g-form) were obtained from the comproportionation reaction between Mn$^{2+}$ and MnO$_4^{-}$. The conditions that administer the transformation between both phases i.e. temperature, reflux time and concentration of reactants were explored. Other manganese oxide/hydroxide phases are obtained depending on variation of the pH of the medium or the solvent used in the reaction. Heat-treatment of both MnO$_2$ polymorphs was done under isothermal and non-isothermal conditions, various pathways were adopted in both cases. The results of TGA/DTA analysis showed also that g-MnO$_2$ is more stable than ε-MnO$_2$ and that ε-form contains much more excess mass over its surface (i.e. surface bound hydroxyl groups) than g-form. Surface area measurements revealed that the reaction temperature has pronounced effect not only on the product phase but also on its surface properties. Very high surface area of 345 cm$^2$/g was adopted by ε-MnO$_2$ and decreases with increasing of reaction time (239 m$^2$/g). SEM investigations showed that g-MnO$_2$ has a plate-like shape whilst ε-MnO$_2$ exhibits a sponge-like morphology. Magnetic properties of both oxides were explored using SQUID magnetometer under zero field cooled and field cooled conditions. Both phases showed a ferromagnetic spin ordering with Curie temperature as 45 K for g-form and 20 K for ε-form. The coercive force was found as 2500 and 2130 Oe, respectively. Remanent magnetization was 35 and 30 emu mol$^{-1}$ for g- and ε-MnO$_2$, respectively.

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