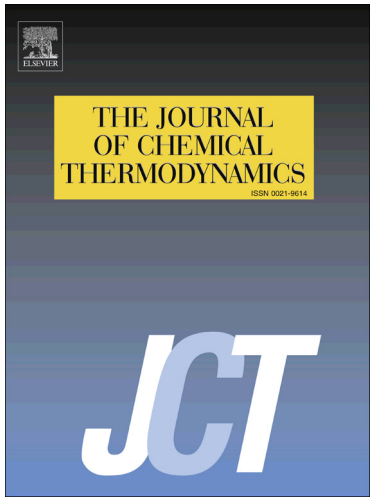

Synthesis, structure and thermodynamic properties of $Ba_5(MnO_4)_3Cl$ apatite

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Synthesis, structure and thermodynamic properties of $Ba_5(MnO_4)_3Cl$ apatite

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Abstract

The structure of $Ba_5(MnO_4)_3Cl$ is refined by the Rietveld method (space group $P6_3/m$). The heat capacities of $Ba_5(MnO_4)_3Cl$ apatite were measured by precision adiabatic vacuum calorimetry over the temperature range from T = (6 to 348) K. The experimental data were used to calculate standard thermodynamic functions, namely the heat capacity $Cp°(T)$, enthalpy $H°(T) - H°(0)$, entropy $S°(T) - S°(0)$ and Gibbs function $G°(T) - G°(0)$, for the range from (0 to 350) K.

Keywords: apatite; manganese (V); synthesis; crystal structure; heat capacity; thermodynamic functions

1. Introduction

Compounds with apatite structure form one of the well-known super group of natural minerals and synthetic inorganic compounds [1,2]. Such compounds and materials based on them are widely used in different areas of industry: from making of fertilizers to developing of new bioceramics and solid-oxide fuel cells [3-6]. One of the unique fields of apatites application is creating of new inorganic pigments [7-9].

Apatites may be described by following general formula $M_5(AO_4)_3L$, where M – mono-, di-, tris- and tetracharged cations; A – atoms, which can form tetrahedrons as coordination polyhedrons (Si, Ge; P,As,V, etc; S), but in rare cases triangles (As^{3+}) or octahedrons (Re, Os); L – halogens and other different negative-charged ions or groups of ions (CO_3^{2-}, O^{2-}, etc) [2].

Apatites with Mn^{+5} and Cr^{+5} in the A position usually used as a chemical basis of inorganic pigments due to their intensive green (or blue in some solid solutions) color [7-9]. There are only two individual apatites with $(MnO_4)^{3-}$ tetrahedral ion: $Ba_5(MnO_4)_3F$ and $Ba_5(MnO_4)_3Cl$ [10].

A limited number of phases for the M^{+5} is associated with a number of reasons. First, the existence of manganese in the oxidation state +5 is possible only in oxo-compounds in tetrahedral coordination. Secondly, the production of manganese in this oxidation state is possible only in an alkaline medium, which excludes disproportionation to more stable oxidation states (+2, +4, +6, +7). As is known, the first ionization potential of alkali and alkaline-earth

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