



## $P2_1/c$ - $C2/c$ phase transition and mixing properties of the (Li,Na)FeGe<sub>2</sub>O<sub>6</sub> solid solution: A calorimetric and thermodynamic study



Edgar Dachs\*, Artur Benisek, Günther Redhammer

Fachbereich Chemie und Physik der Materialien, Abteilung Mineralogie, Universität Salzburg, Jakob-Haringerstrasse 2a, A-5020 Salzburg, Austria

### ARTICLE INFO

#### Article history:

Received 22 June 2017

Received in revised form 13 December 2017

Accepted 18 January 2018

Available online 31 January 2018

#### Keywords:

Calorimetry

Heat capacity

Standard state entropy and enthalpy of formation from the elements

$P2_1/c$ - $C2/c$  phase transition properties

(Li,Na)FeGe<sub>2</sub>O<sub>6</sub>

Thermodynamic mixing properties

### ABSTRACT

A calorimetric and thermodynamic study of the (Li<sub>1-x</sub>Na<sub>x</sub>)FeGe<sub>2</sub>O<sub>6</sub> solid solution with the pyroxene structure was undertaken. The molar heat capacity at constant pressure ( $C_{p,m}$ ) for compositions with  $x = (0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0)$  was measured using a Physical Properties Measurement System at temperatures from 2 K to 300 K and by differential scanning calorimetry between 282 and 870 K (these measurements were performed upon heating as well as upon cooling). Magnetic transitions below 20 K and structural  $P2_1/c \leftrightarrow C2/c$  phase transitions at higher temperatures were observed that decrease in temperature with increasing Na/(Na + Li). The  $P2_1/c \leftrightarrow C2/c$  transition showed a considerable temperature hysteresis that is largest for LiFeGe<sub>2</sub>O<sub>6</sub> (~30 K) and decreases with increasing Na/(Na + Li) in the pyroxene. The molar enthalpy and entropy changes associated with the  $P2_1/c \leftrightarrow C2/c$  phase transitions,  $\Delta H_{tr,m}$  and  $\Delta S_{tr,m}$ , were determined. They can be described by quadratic and linear functions across the solid solution. A linear correlation between  $\Delta H_{tr,m}$  and the square of the volume strain at the transition temperature was established. The  $P2_1/c \leftrightarrow C2/c$  phase transition of LiFeGe<sub>2</sub>O<sub>6</sub> is compared to that of  $\alpha$ - $\beta$  quartz, whose  $C_{p,m}$  was also measured. The molar enthalpy of order,  $\Delta H_{ord,m}$ , was calculated from the calorimetric data. It has a maximum of  $\Delta H_{ord,m} = (-11.6 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$  for the  $P2_1/c \leftrightarrow C2/c$  phase transition of LiFeGe<sub>2</sub>O<sub>6</sub>, which is in reasonable agreement with a maximum  $\Delta H_{ord,m} = -9.9 \text{ kJ} \cdot \text{mol}^{-1}$  calculated using density functional theory.  $\Delta H_{ord,m}$  vs.  $T$  behavior was described using a tricritical Landau model with an  $a$  parameter of  $a = (41.8 \pm 1.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . All properties associated with the  $P2_1/c \leftrightarrow C2/c$  phase transition in LiFeGe<sub>2</sub>O<sub>6</sub> can be calculated using this value.

The  $C_{p,m}$  behavior at  $T < 300$  K for each pyroxene composition was decomposed into molar vibrational ( $C_{vib,m}$ ) and molar magnetic ( $C_{mag,m}$ ) contributions by applying a single-parameter phonon dispersion model. The molar vibrational entropy at 298.15 K,  $S_{vib,m}^{298.15}$ , and the molar magnetic entropy,  $S_{mag,m}$ , were also calculated. Both quantities, together, give the molar calorimetric entropy at 298.15 K,  $S_{cal,m}^{298.15}$ . The term 'calorimetric' means that configurational contributions that are non-zero for solid solution compositions are excluded (for the endmember pyroxenes this corresponds to the molar third law entropy,  $S_m^0$ ). The behavior of  $S_{mag,m}$ ,  $S_{vib,m}^{298.15}$  and  $S_{cal,m}^{298.15}$  as function of Na/(Na + Li) in the pyroxene was described by applying Darkens' quadratic formalism (DQF) and a Margules model.  $S_{vib,m}^{298.15}$  as function of composition is ideal within error, whereas  $S_{mag,m}$  shows significant positive deviations from a linear combination of the end members. This leads to positive excess molar magnetic entropies of mixing that can be described by a symmetrical Margules parameter  $s_{mag,m} = (3.7 \pm 1.3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . Because solid solutions with Na/(Na + Li) > 0.4 have the  $P2_1/c \leftrightarrow C2/c$  phase transition below 298.15 K, this results in a discontinuity in  $S_{cal,m}^{298.15}$  behavior as function of composition at Na/(Na + Li) = 0.5. DQF was applied to model this behavior and the corresponding parameters were retrieved. The entropy of mixing behavior of the (Li,Na)FeGe<sub>2</sub>O<sub>6</sub> solid solution at 298.15 K is characterized by positive excess molar magnetic entropies of mixing onto which entropy changes due to the structural  $P2_1/c \leftrightarrow C2/c$  phase transitions are superimposed in the Na-rich part of the binary system.

Excess volumes of mixing for the (Li,Na)FeGe<sub>2</sub>O<sub>6</sub> solid solution were calculated from published data and DQF parameters were derived that allow volume as function of temperature and composition to be calculated.

The molar third law entropies at  $T = 298.15$  K are  $S_m^0 = (188.3 \pm 2) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  and  $S_m^0 = (203.1 \pm 2) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  and the molar enthalpies of formation from the elements at  $T = 298.15$  K are  $\Delta_f H_m^0 = (-1817.2 \pm 9) \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_f H_m^0 = (-1834.0 \pm 9) \text{ kJ} \cdot \text{mol}^{-1}$  for the end members LiFeGe<sub>2</sub>O<sub>6</sub> and NaFeGe<sub>2</sub>O<sub>6</sub>, respectively.  $\Delta_f H_m^0$  was calculated using density functional theory (DFT). Values for  $\Delta_f H_m^0$ ,  $S_m^0$ , and molar

\* Corresponding author.

E-mail address: [edgar.dachs@sbg.ac.at](mailto:edgar.dachs@sbg.ac.at) (E. Dachs).

volume, for the coefficients of  $C_{p,m}$  polynomials, for thermal expansion and for the bulk modulus of the end members were compiled and can be used, in combination with the derived volumetric and entropic mixing properties, for phase diagram calculations involving the (Li,Na)FeGe<sub>2</sub>O<sub>6</sub> solid solution.

© 2018 Elsevier Ltd.

## 1. Introduction

The pyroxene group includes important rock-forming members that occur over a wide variety of geological environments. Natural silicate pyroxenes can have orthorhombic or monoclinic symmetries depending on their chemistry and temperature and pressure of formation [1,2]. The crystallography of the pyroxenes has been studied intensely for decades due to phase transformations that are important for understanding planetary geochemistry and geophysical properties of the upper mantle. The first structure of a pyroxene was solved on diopside CaMgSi<sub>2</sub>O<sub>6</sub> and was determined to be monoclinic  $C2/c$  [3]. Subsequent investigations revealed structural polymorphism with archetype symmetries  $C2/c$ ,  $Pbca$ ,  $Pbcn$ ,  $P2_1/c$  and  $P2/n$ , as reviewed by [1]. A structural  $P2_1/c \leftrightarrow C2/c$  phase transition is frequently observed in natural and synthetic Ca-poor clinopyroxenes such as pigeonite [4–8]. This transition is also found at low temperatures (<273 K) especially in Li-pyroxenes [9–14].

The pyroxene structure is characterized by three main ‘building units’, infinite chains of corner-sharing tetrahedra, running parallel to the  $c$ -axis, zig-zag chains of edge-sharing octahedra also running parallel to  $c$  that interconnect the tetrahedral chains along the  $a$  and  $b$  directions. The interstitial space is filled by the 5–8-fold coordinated M2 site, where the coordination depends on the nature of the M2 cation (i.e., Li, Na, Ca), the temperature and pressure of crystallization and the crystallographic symmetry.

In the low-temperature  $P2_1/c$  structure there are two different tetrahedral chains, a strongly kinked B-chain and a straighter A-chain. The kinking angle of the former is given by the angle between the O3 oxygen atoms that bridge the TO<sub>4</sub> tetrahedra within a chain (O3–O3–O3 angle). In  $P2_1/c$  symmetry, the octahedral cations are coordinated by six crystallographically different oxygen atom positions, namely 3 from the A- and 3 from the B-chain. In the  $C2/c$  structure, the two tetrahedral chains become symmetrically equivalent and are almost stretched. Moreover, the geometry of the octahedra changes and – instead of six – there are only 3 different M–O bond lengths. Because the geometry of the tetrahedral chains changes, the M2 site is affected, and this is often connected with a change in oxygen coordination from 5 to 8. More detailed discussion of structural variations related to the  $P2_1/c \leftrightarrow C2/c$  phase transition can be found in the references cited above.

Below  $T \sim 45$  K most of the transition-metal(TM)-bearing pyroxenes exhibit magnetic changes. The magnetic ground state is determined by an interaction between the TM with and between the M1 chains. Different pathways for magnetic super exchange are, thus, possible. This leads to a specific triangular configuration for the TM within and between neighboring M1 chains and may cause magnetic frustration. The distinct low-dimensional, quasi 1D character, and the discovery of multiferroic behavior by Jodlauk et al. [15] have attracted much interest in such “magnetic” pyroxenes. Most of them order magnetically in rather simple collinear structures [16–27], some however, among them NaFeGe<sub>2</sub>O<sub>6</sub>, show a more complex cycloidal and incommensurately modulated magnetic structure [28–30].

Due to their relevance in materials science, non-silicate analog compounds, in particular  $M^{2+}M^{2+}Ge_2O_6$  and  $M^+M^{3+}Ge_2O_6$  germanate pyroxenes, have been the focus of intensive systematic

study in order to understand structural variations with composition and temperature. Germanium analogue phases can serve as model systems in which structural phase transitions are shifted to lower pressures or higher temperatures compared to silicate pyroxene, as shown by the pioneering work of Ringwood and coworkers [31–33]. This approach has been adopted in recent studies on phase transitions of Ge-pyroxenes in the system LiFeGe<sub>2</sub>O<sub>6</sub>–NaFeGe<sub>2</sub>O<sub>6</sub> [10,14,26,34–36]. These pyroxenes show both structural  $P2_1/c \leftrightarrow C2/c$  and magnetic phase transitions. The structural phase transition temperature decreases from about 789 K in LiFeGe<sub>2</sub>O<sub>6</sub> to 109 K in Li<sub>0.3</sub>Na<sub>0.7</sub>FeGe<sub>2</sub>O<sub>6</sub> with increasing Na content and is not observed at any temperature for compositions with  $Na/(Na + Li) > 0.7$ . The system Li<sub>1-x</sub>Na<sub>x</sub>FeGe<sub>2</sub>O<sub>6</sub> is of special interest because here the magnetic ground state changes: For compositions with  $Na/(Na + Li) \leq 0.72$ , the magnetic structure can be described by a commensurate arrangement of magnetic spins with a propagation vector  $k$  ( $\frac{1}{2}, 0, 0$ ), an antiferromagnetic (AFM) coupling of spins within the M1 chains, and an alternating AFM and ferromagnetic (FM) interaction between the chains, depending on the nature of the tetrahedral chains (A and B). At higher Na contents of the  $C2/c$  phase, this commensurate spin structure evolves to a cycloidal, incommensurately modulated state. This cycloidal structure itself transforms to a spin density wave structure above 12 K, before these Na-rich pyroxenes transform to the paramagnetic state between 14 K and 15 K [37].

No study of the standard thermodynamic data or thermodynamic interpretations of phase transition behavior, neither structural nor magnetic, has been made, except for structural strain analysis [10]. In general, only few studies of clinopyroxene deal with a full thermodynamic interpretation of mixing properties and standard thermodynamic properties. Benisek et al. [38] and Etzel et al. [39] report on the thermodynamic mixing behavior of synthetic Ca-Tschermak–diopside pyroxene solid solutions, and only the work of Camara et al. [9] and Tribaudino et al. [7] attempt to interpret the  $P2_1/c \leftrightarrow C2/c$  phase transition in LiGaSi<sub>2</sub>O<sub>6</sub> and Ca-poor clinopyroxenes in terms of Landau theory, taking the intensity of C-forbidden Bragg peaks as the order parameter.

We investigate in this work i)  $P2_1/c \leftrightarrow C2/c$  phase-transition properties, ii) entropic and volumetric mixing properties and iii) the standard state entropies of the end members of the (Li,Na)FeGe<sub>2</sub>O<sub>6</sub> solid solution using low- and high-temperature heat capacity measurements. In addition, iv) the standard enthalpy of formation for LiFeGe<sub>2</sub>O<sub>6</sub> and NaFeGe<sub>2</sub>O<sub>6</sub> from the elements were computed using density functional theory. We apply Landau theory to model the  $P2_1/c \leftrightarrow C2/c$  phase transition in LiFeGe<sub>2</sub>O<sub>6</sub> and we derive its total enthalpy of order and compare it to the  $\alpha$ - $\beta$  quartz phase transition.

## 2. Methods

### 2.1. Sample synthesis and analytical techniques

The samples used for calorimetry along the (Li<sub>1-x</sub>Na<sub>x</sub>)FeGe<sub>2</sub>O<sub>6</sub> series were synthesized in the study of [14] applying a ceramic sintering route in steps of  $x = 0.05$ –0.1. The starting materials were prepared from Na<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and GeO<sub>2</sub> in the stoichiometry of the entire compounds (Table 1). The mixtures were intimately ground under ethanol to ensure good homogeneity,

Download English Version:

<https://daneshyari.com/en/article/6659804>

Download Persian Version:

<https://daneshyari.com/article/6659804>

[Daneshyari.com](https://daneshyari.com)