
Thermochemistry of the alkali feldspars: Calorimetric study of the entropy relations in the low albite–low microcline series

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ABSTRACT

New heat capacity data obtained on 12 samples of the low albite–low microcline series are presented. They were measured by relaxation and differential scanning calorimetry between 5 and 773 K. Two series, differing in their starting materials, were investigated, both of which were prepared via molten salt and solid-solid ion-exchange techniques in previous studies. The heat capacity of both series deviates positively from the ideal behavior leading to positive excess vibrational entropies of mixing, which can be described by a Margules mixing model yielding \( W_{\text{MgO}} = 8.60 \) and \( W_{\text{NaAl}} = 9.28 \) J/(mol·K). The heat capacity and the vibrational entropy obtained on these Al,Si ordered samples are compared with those described in the literature for disordered samples. The solvi of the Al,Si ordered and disordered alkali feldspar systems were calculated from the calorimetric data and compared to experimentally determined solvi. Large deviations are detected for the ordered system, whereas consistent results are found for the disordered system, provided Na,K clustering is taken into account.

Keywords: Low-temperature heat capacity, NaAlSiO₄, KAlSiO₄, enthalpy, mixing model, miscibility gap

INTRODUCTION

The heat capacity \( (C_P) \) of a solid solution has often been found to deviate from that of a mechanical mixture (ideal mixing) at low temperatures (∼100 K) giving rise to excess vibrational entropies. Al,Si disordered feldspars are characterized by positive excess vibrational entropies of up to 2.5 J/(mol·K) (Haselton et al. 1983). In high-structural state plagioclases, positive excess vibrational entropies of up to 2.8 J/(mol·K) were measured by Benisek et al. (2009), whereas an almost ideal vibrational behavior was found for the low-structural state plagioclases at 298.15 K (Benisek et al. 2013). The K–Ca feldspar binary, although derived from high-structural state plagioclases, is also characterized by a more or less ideal vibrational entropy-composition relation (Benisek et al. 2010a). On the other hand, strongly positive vibrational entropy behavior has been found in ternary series of high-structural state feldspars (Benisek et al. 2010b). Although the origin of these excess vibrational entropies is the heat capacity behavior at low temperatures, it has a strong influence on the stability of crystalline solutions at high temperatures, as worked out by Benisek et al. (2010c) for the ternary Na-K-Ca feldspar system.

In an attempt to explain the source of the excess vibrational entropy, first-principles studies proposed a “bond stiffness vs. bond length” interpretation (Van de Walle and Ceder 2002; Burton and van de Walle 2006). The latter study compared the MgO-CaO and NaCl-KCl solid solutions and found a similar size mismatch but different excess vibrational behavior, which was attributed to different bond stiffness relations. The Na-Cl bonds were significantly softened with increasing K content producing the positive excess vibrational entropy. Benisek and Dachs (2011, 2012) presented a relationship that allows to assess the excess vibrational entropy of a binary solid solution. It is based on the idea that the elastically stiffer end-member forces the softer one to fit to its size. Accordingly, the excess vibrational entropy was related to the difference between the end-member volumes \( (\Delta V) \) and to the difference between the end-member bulk moduli \( (\Delta K) \). The maximum deviation from ideal behavior \( (\Delta_{\text{max}} S^\text{exc}) \) can be obtained from the relation

\[
\Delta_{\text{max}} S^\text{exc} = (\Delta V + m\Delta K)f
\]

where \( m \) and \( f \) are fit parameters, determined by Benisek and Dachs (2012). \( \Delta V \) is defined to be positive, whereas \( \Delta K \) may be positive or negative depending on which end-member (larger or smaller) is elastically stiffer (i.e., \( \Delta V = V_A - V_B \) and \( \Delta K = K_A - K_B \), where end-member A is larger than B). The authors found that strongly negative \( \Delta K \) values are connected with negative excess vibrational entropies, whereas positive \( \Delta K \) values correlate with positive ones. Equation 1 could be successfully applied to different classes of materials, i.e., silicate solid solutions, binary alloys, and the NaCl-KCl binary (Benisek and Dachs 2011, 2012, 2013).

The alkali feldspars constitute a binary system consisting of the end-members NaAlSiO₄ (Ab) and KAlSiO₄ (Or). They represent a thoroughly investigated mineral group, for which many structural, calorimetric, and phase equilibrium data have been obtained. The calorimetric data set, however, lacks information on the behavior of the vibrational entropy across the Al,Si ordered system. This information is provided in this contribution to calculate the solvs and to compare it to the experimentally determined solvs. Due to the sluggish Al,Si (dis)ordering kinetics, the Al,Si ordering states of the samples that delineate the experimental solvs are not in equilibrium with temperature. Thus, solv determined from Al,Si disordered and ordered samples are metastable with respect to their Al,Si distribution, whereas...