Lattice simulation studies of the ferroelastic phase transitions in (Na,K)AlSi_3O_8 and (Sr,Ca)Al_2Si_2O_8 feldspar solid solutions

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ABSTRACT

Lattice-energy minimization calculations have been performed on the feldspar systems (Ca,Sr)Al_2Si_2O_6 and disordered (Na,K)AlSi_3O_8 as functions of composition to simulate the ferroelastic phase transitions $I2/c-I1$ and $C2/m-C1$, respectively. In both cases the phase transition occurs as a function of composition and is driven by the vanishing of the quantity $C44 - C66$, without any of the individual elastic constants being strongly dependent on composition and without softening of an optic mode. In both cases, the strains ε_4 and ε_6 are proportional to each other for small values of strain, but nonlinear coupling becomes dominant when |ε_i| becomes larger than about 0.02. The results are consistent with experimental data and explain the nature of coupling of the displacive transition to Al-Si ordering in Al:Si 2:2 feldspars.

INTRODUCTION

Both the (Ca,Sr)AlSi_3O_6 "2:2" feldspars and the (Na,K)AlSi_3O_8 "1:3" feldspars undergo ferroelastic phase transitions as functions of composition at low temperature. The former display a generally ordered arrangement of Al and Si over the tetrahedral sites, although sometimes with varying degrees of Al-Si order, whereas the ferroelastic phase transition in the alkali feldspars occurs only when the Al and Si are disordered over the tetrahedral sites (equivalent to the monalbite–high-albite transition). The changes in space group are $I2/c-I1$ and $C2/m-C1$, respectively. In both cases, if the transition is a proper ferroelastic the stability condition that is broken at the symmetry change is $C_{44} - C_{66} > 0$ (Cowley 1976). However, with such ferroelastic phase transitions the question always arises as to whether or not the elastic instability is precipitated by softening of an optic phonon (necessarily at zero wave vector) rather than acoustic softening. Recent theoretical work with the rigid-unit mode model (Hammonds et al. 1996), applied to the feldspar structure, suggests that there is not an optic instability but that there is considerable softening of the acoustic modes, leading to the possibility that the observed structural phase transitions in these feldspars are due to intrinsic elastic instabilities. It is important to test these predictions, not least because of their implications for the thermodynamic modeling of these phase transitions: If the transition is a proper ferroelastic the spontaneous strain is the order parameter and the excess free energy may be written in terms of this strain explicitly, rather than in terms of some unknown coupled order parameter. It is also of interest to enquire as to how the stability condition $C_{44} - C_{66} > 0$ is broken. This may result from softening of either of the individual elastic constants $C_{44}$ or $C_{66}$, or else the combination $C_{44}C_{66} - C_{46}^2$ might be naturally soft and therefore extremely sensitive to changes in temperature and chemical composition without any of the individual elastic constants softening on their own. Again, this issue has implications for the thermodynamic modeling of the phase transition because different models predict different elastic behavior.

Although there is a large body of information on the crystallographic details of these phase transitions, there is none on the elastic constants. This reflects the experimental difficulty in obtaining good elastic data on well-characterized feldspar crystals as a function of composition or temperature. An alternative to experiment is the use of lattice simulation methods with reliable interatomic potentials. Here we present the results of a study of these phase transitions using static lattice-energy minimization and lattice dynamics calculations using empirical interatomic potentials. We chose to work with a model that simulates complete Al-Si disorder in the alkali feldspars because, in these feldspars, the ordering process results in the same symmetry change as the ferroelastic phase transition. For the alkaline-earth feldspars we calculated the solid solution at varying degrees of Al-Si order and ascertained the relationship between the zone-center ferroelastic instability and the zone-boundary Al-Si ordering process.

The details of the lattice-energy minimization and lattice dynamics calculations have been described in several studies (Price et al. 1987; Catlow 1988; Dove 1989; Winkler et al. 1991; Patel et al. 1991). We used the THBREL and THBPHON programs, which in several ways are particularly suited for the simulation of silicates. The pair interactions between atoms were modeled using the standard Coulomb and Buckingham potentials.