Si-Al ordering in leucite group minerals and ion-exchanged analogues: An MAS NMR study

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ABSTRACT

Two series of leucite group materials, with K, Rb, and Cs as extra-framework cations, have been synthesized by ion exchange from a natural well-ordered analcite and a natural disordered leucite. 29Si and 27Al MAS NMR data for the analcite-derived series provide complementary information on tetrahedral cation ordering. The ordering in terms of the number of Al next-nearest neighbors, Q4(nAl) (short-range order), does not change significantly during ion exchange, indicating that Al and Si remain essentially fixed in their original positions. In contrast, the ordering of Al over T1, T2, and T3 (long-range order) for the analcite-derived series changes dramatically with changing alkali cation; the Al occupancies for the three analcite-derived samples expressed as T1:T2:T3 are approximately 0.25:0.50:0.25 for KAlSi2O6, 0.40:0.20:0.40 for RbAlSi2O6, and 0.15:0.70:0.15 for CsAlSi2O6. During the ion exchange, at temperatures above the cubic-tetragonal phase transitions, only one symmetrically distinct T site is present. It is proposed that on cooling through the cubic-tetragonal phase transition the structure collapses around the non-framework cations to give the lowest energy Si-Al distribution over the three T sites irrespective of the original T-site ordering in the starting material. Our data suggest that the identity of the cation in the W site affects the orientation of the framework distortions associated with the cubic-tetragonal phase transition and leads to the possibility that a particular tetrahedral cation site can take on the characteristics of a T1, T2, or T3 site. The data and their interpretation have important implications for the mechanism of this type of structural phase transition.

INTRODUCTION

There has recently been considerable interest in the ordering behavior and structural phase transitions in leucite group minerals. As well as studies of natural KAISi2O6 leucite (e.g., Phillips et al. 1989; Hatch et al. 1990; Ito et al. 1991; Kohn et al. 1995; Baltisberger et al. 1996) there have been studies of leucite samples with Rb or Cs replacing K (Phillips and Kirkpatrick 1994; Palmer et al. 1997), leucite with Fe3+ replacing Al (e.g., Lange et al. 1986; Bell and Henderson 1994), and examples with divalent cations, such as Mg, Zn, Cd, Ni, and Mn, replacing Al (Kohn et al. 1991, 1994; Bell et al. 1994a, 1994b; Bell and Henderson 1996).

Kohn et al. (1995) studied the Si-Al ordering in two contrasting samples of leucite using MAS NMR. One sample was natural and the other was synthesized by ion exchange from an analcite with a small distribution of Al next-nearest neighbors (NNN). In the ion-exchange-derived specimen, the restricted range of NNN environments enabled a good estimate of the ordering pattern of Si and Al over the three T sites. The T2 sites contained 45–50% of the Al with the remainder distributed approximately equally between the T1 and T3 sites. It was found that the 29Si spectrum of the natural leucite sample could be fitted with a wide variety of Al distributions including either Al ordering onto T2 or with Al ordering onto T1 and T3. By analogy with the analcite-derived sample, and considering previous neutron and X-ray data, Al ordering onto T2 was preferred over alternative schemes.

The present paper represents an extension of the work of Kohn et al. (1995) in that Rb- and Cs-substituted analogues of the natural leucite and analcite samples were prepared and studied using MAS NMR. The NMR data complement the information on framework geometries recently reported by Palmer et al. (1997), but in addition the changes in short- and long-range order during ion exchanges probed by NMR provide a novel insight into the nature of the cubic-tetragonal phase transition.

EXPERIMENTAL METHODS

Samples

Two natural starting materials were used in this study: analcite M416 from Monteccio, Maggiore, Italy, and leucite from Alban Hills, Italy. These were converted into