Crystal structures of Na and K aluminate mullites

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ABSTRACT

Mullite-type alkali aluminates (K$_{x}$Na$_{1-x}$)$_{2}$Al$_{2}$O$_{3}$ were synthesized from amorphous Al and alkali nitrates by sol-gel techniques. Rietveld refinements of six members of the solid solution series (y = 0.0, 0.2, ..., 1.0), together with Fourier syntheses and grid search analyses show that the Na and K atoms reside in the vacant Oc sites, with K at 1/2, 0, 1/2 and Na on a split site off the special position. The number of alkali atoms is restricted to 2/3 atoms per unit cell due to crystal chemical constraints. Consequently, unlike the aluminosilicate mullites, alkali mullites do not form a solid solution series with varying oxygen composition. All compounds studied here crystallize in space group Pbam with lattice constants ranging from $a = 7.6819(4)$ Å, $b = 7.6810(4)$ Å, $c = 2.9184(8)$ Å for the Na aluminate to $a = 7.6934(3)$ Å, $b = 7.6727(3)$ Å, $c = 2.93231(7)$ Å for the K aluminate mullite.

INTRODUCTION

The mullite-type structure family is characterized by AlO$_6$ octahedra that share edges to form chains running parallel to the crystallographic c axis. The chains are cross-linked by double chains of TO$_4$ tetrahedra with a random distribution of Al and Si atoms on the T site. Since some Si is substituted by Al, oxygen vacancies form to retain charge balance. The amount of Si $\rightarrow$ Al substitution and correlated oxygen vacancy formation is variable according to the general formula Al$_{1-x}$(Si$_{2-x}$,Al$_x$)$_2$O$_{10-x}$. The $x$ value ranges between approximately 0.2 and 0.5 (Burnham 1964a; Angel and Prewitt 1986). According to Burnham (1964b) the crystal structure of mullite fits any composition between sillimanite ($x = 0$) and $\alpha$-Al$_2$O$_3$ ($x = 1$). However, the aluminate end-member has not yet been observed, although mullite related phases with $x > 0.9$ have been described (Schneider et al. 1993; Fischer et al. 1994).

Mullite-type alkali aluminate phases were first synthesized by Perrotta and Young (1974) using sol-gel techniques. They observed the formation of mullite-type phases of good crystallinity after calcination above 950 °C. The compounds occur within a small temperature window; above 1000 °C the mullite-type phases decompose to form $\alpha$- and $\beta$-alumina. Elliot and Huggins (1975) crystallized mullite-type Na-aluminate by ashing filter paper soaked in aqueous salt solutions and heat above 800 °C. The resulting compound was designated as $\lambda$-Na$_2$O$\cdot$xAl$_2$O$_3$ with $x$ ranging between 3 and 12. Elliot and Huggins (1975) reported that the metastability of the $\lambda$-phase strongly depends on an intimate mixing of the reactants. The crystal structure of the Na-aluminate phase was discussed on the basis of the X-ray powder diffraction pattern that is similar to that of mullite. According to Elliot and Huggins (1975) the unit cell is orthorhombic with $a = b$, resulting in a pseudotetragonal metric. The alkali aluminate structure proposed by them corresponds to that of mullite with alkali ions occupying the Oc site at 0, 1/2, 1/2. It was mentioned that the substitution of Na by K leads to a better geometrical fit, since K has an ionic radius which is nearly identical to that of oxygen while Na is somewhat smaller. More recently, Mazza et al. (1992) published detailed data for mullite-type phases with compositions Na$_2$O $6$Al$_2$O$_3$ and K$_2$O $6$Al$_2$O$_3$, respectively. They confirmed the structural model given by Elliot and Huggins (1975). However, the alkali atom positions, the distribution of Al atoms in the aluminate tetrahedra, and the general compositions of the compounds seem to be doubtful because they do not agree with the crystal chemical constraints imposed by the local symmetry of the alkali and O atom positions as discussed in the results and discussion section. Possible synthesis routes for the alkali aluminates are oxalate coprecipitation or alkoxide and nitrate decomposition. It was confirmed that the mullite-type compounds transform to stable $\beta$-alumina above 1000 °C.

In the present study, we have synthesized Na and K aluminates with mullite-type structures to determine the alkali atom positions and to explain the chemical composition by crystal chemical considerations.

EXPERIMENTAL METHODS

Synthesis of aluminate compounds with mullite-type structure

The synthesis of the aluminate compounds was performed according to the method of Mazza et al. (1992). To begin with, a noncrystalline precursor was prepared that transformed into the crystalline phase after calcination at 950 °C. The noncrystalline precursor was synthesized by decomposition of Al- and alkaline nitrates. Beginning with a stoichiometric mixture of

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