Crystal structure of Cr-mullite

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ABSTRACT

A Rietveld refinement of Cr-doped mullite, Cr0.5Al3.92Si1.58O9.79, orthorhombic, space group Pbam [a = 7.56712(6) Å, b = 7.70909(6) Å, c = 2.90211(2) Å, V = 169.30 Å3] revealed Cr to reside predominantly in the octahedrally coordinated M1 site. The mean M1-O distance of 1.935 Å is that expected from Al1+ and Cr3+ molar fractions obtained from the chemical analysis and structure refinement. The small displacement factors of the T* and Oc* sites indicate deficiencies in the electron densities which could be compensated by assuming additional Cr atoms. The predominant Cr incorporation into the M1 site causes an expansion of the octahedral bonds which is directly related to the observed lengthening of the c edge. The strong expansion of the long and elastic octahedral M1-Od bond in Cr-doped mullite, which would affect the a and b edges, is partly absorbed by a shortening of tetrahedral bonds.

INTRODUCTION

Since the mineral mullite was first found in nature in the Isle of Mull in Scotland (Bowen and Greig 1924), it has been extensively studied due to its outstanding high-temperature properties. The composition of mullite refers to the general formula Al2Al2+2Si2–2O10–2, i.e., 3:2-mullite, where x denotes the number of oxygen vacancies. A range of ~0.20 < x < ~0.60 is frequently described in literature (e.g., Cameron 1977). Recent studies prove that under special synthesis conditions this composition range is not detected. We discuss here the results of X-ray Rietveld refinements and give new and contrasting information on site preference in mullite.

Comprehensive work on Cr-doped mullites has been mainly done by spectroscopic methods. This material gained some interest due to its luminescent properties of Cr3+ in glass ceramics to be used for laser technology (Andrews et al. 1986; Wojtowicz and Lempicki 1988). The site assignment of Cr in mullite is, however, still debated. Cr should be expected to reside preferably in the octahedral M1 site. This distribution of Cr over two octahedral sites has been confirmed by Ikeda et al. (1992) based on crystal-field spectroscopy. Also Nass et al. (1995) came to the same conclusion studying Cr-doped mullites by combined thermal analysis, quadrupole mass spectrometry, X-ray diffractometry, and electron microscopy. Piriou et al. (1996) and Bauchspiess et al. (1996) stated that Cr occupies both M1 and interstitial sites in Cr2O3-rich mullites. Rossouw and Miller (1999) investigated the same sample used here by incoherent channeling patterns (ICP) from characteristic X-ray emissions. They located Cr in the interstitial site at 0, 1/4, 0 which occurs at 1.93 Å from the next nearest M1 site, i.e., too close for simultaneous Al-Cr occupancy. It would imply that the M1 site is distorted, with vacancies equal to the number of Cr-atoms in the interstitial site which, however, was not detected. We discuss here the results of X-ray Rietveld refinements and give new and contrasting information on site preference in mullite.

EXPERIMENTAL METHODS

Sample preparation

The starting material was 52 wt% Al2O3 (V AW, 302), 38 wt% SiO2 (Ventron, 88316), and 10 wt% Cr2O3. The homogenized powder was pressed into pellets with 20 mm diameter and about 5 mm height. Calcination at 1650 °C for 10 days yielded mullite crystals up to 20 µm coexisting with a minor amount of silicate glass. The sample was treated with a HF/HCl acid mixture to dissolve the glass phase.

Chemical composition

Bulk chemical analysis performed by X-ray fluorescence analysis of the HF/HCl treated material yielded 61.9 wt% Al2O3, 27.8 wt% SiO2, and 10.3 wt% Cr2O3. Microprobe analyses of various crystals in this sample gave weight fractions slightly deviating from the bulk chemical analysis: 60.0 wt% Al2O3,