INTRODUCTION

Grain boundaries are thought to have an effect on the rheological performance of rocks in geological systems, and are major sites for both chemical reactions (Ahn and Buseck 1998; Loffler and Moder 2001) and phase transitions (Posfai and Buseck 1998; Hulsmans et al. 1999; Penn and Banfield 1999). And grain boundaries also offer the fastest path for fluid infiltration, which is a key process in metamorphic and economic geology (Whitney et al. 1996; Watson 1999). The performance of the grain boundary as a reaction site and a fluid path depends strongly on the nanometric structures of the boundary (Leeuw et al. 2000).

Nanostructures of grain boundaries have been investigated using high-resolution transmission electron microscopy (TEM) (Posfai and Buseck 1998; Ahn and Buseck 1998; Hulsmans et al. 1999; Penn and Banfield 1999) and atomic force microscopy (AFM) (Eggleston 1999; Schaufuss et al. 2000). These methods allow direct observation of the arrangement of atoms and chemical compositions at the nanometer scale, as well as the rearrangement of atoms caused by phase changes. In contrast, spatial resolution of optical spectroscopy, which has been used to study chemical structures (Libowitzky and Rossman 1997) and semiconducting band structures (Karall et al. 2000; Xu and Schoonen 2000; Sidike et al. 2000) of minerals, has been restricted to the micrometer scale due to the diffraction limit of light. Recently developed near-field optical technology has achieved subwavelength spatial resolution (Pohl and Courjon 1993; Ohtsu 1995; Saiki and Narita 2002). Combining near-field technology with conventional spectroscopy, optical spectroscopic analysis with submicrometer spatial resolution has been reported for semiconductor photoluminescence (Grober et al. 1994; Saiki et al. 1998; Kaneta et al. 2001), Raman spectroscopy (Narita et al. 1998), and infrared spectroscopy (Narita and Kimura 2002).

In this article, we use near-field spectroscopy to characterize the grain boundary of optically active Cr\textsuperscript{3+}-doped polycrystalline Al\textsubscript{2}O\textsubscript{3} (ruby) with submicrometer spatial resolution. In addition to the mineralogical interest, this Cr\textsuperscript{3+}-doped polycrystalline Al\textsubscript{2}O\textsubscript{3} is important as a potential solid-state lasing material. Currently, single crystals are mainly used for this application. However, these are difficult to fabricate and it is difficult to dope them with large concentrations of optically active elements. To avoid these limitations, polycrystalline ceramics have been proposed for use in lasers (Ikeseu et al. 1996). For this reason, optical characterization of grain boundaries is necessary.

EXPERIMENTAL METHODS

Sample preparation

\(\alpha\)-Al\textsubscript{2}O\textsubscript{3} powder (purity: 99.99\%) with a grain diameter of approximately 0.4–0.6 \(\mu\)m was used as the matrix (base) material (Murotani et al. 2000). Cr\textsubscript{2}O\textsubscript{3} powder (purity: higher than 99.0\%) with a grain diameter of approximately 3 \(\mu\)m was used as the doping material. After mixing the powders with a ball-mill for eight hours, a powder compact was made using a cold isostatic press (CIP). During the operation of the CIP, glycerin was used as a hydraulic fluid and a pressure of 0.54 GPa was applied for one minute followed by compression at 0.49 GPa for five minutes. The powder compact was sintered under a near vacuum (10\(^{-1}\) Pa) at 1800 °C for two hours to obtain a single-phase specimen in which Cr\textsubscript{2}O\textsubscript{3} was incorporated homogeneously into the Al\textsubscript{2}O\textsubscript{3}. The sample was polished to an optical grade in order to observe surface topography. The Cr concentration of the sample was determined by atomic absorption to be 0.66 wt%. The crystal structure of the sample was characterized by powder X-ray diffraction. For the annealing study, samples were annealed in an argon atmosphere at 1700 °C for 2, 12, or 72 hours, followed by slow cooling to room