

**Newnham R E & de Haan Y M.** Refinement of the  $\alpha$   $\text{Al}_2\text{O}_3$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  structures. *Z. Kristallogr.* 117:235-7, 1962.  
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Corundum-family oxides are important as lasers, refractories, conducting ceramics, magnetoelectrics, and gemstones. This paper describes the crystal structures of the sesquioxides of aluminum, titanium, vanadium, and chromium. Details concerning the bond lengths, bond angles, and the distorted nature of the metal-oxygen polyhedra are presented. [The SCJ® indicates that this paper has been cited in over 215 publications.]

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In 1958 I joined Arthur von Hippel's Laboratory for Insulation Research at the Massachusetts Institute of Technology as the resident crystallographer. Von Hippel was a scientist with very broad interests ranging from electric breakdown and ferroelectricity to molecular biology. He had a dream—a dream that many of us came to share—of engineering the atomic architecture of materials through an understanding of structure-property relations to optimize physical and chemical properties.

Under farsighted sponsorship by the Office of Naval Research, the Laboratory for Insulation Research brought together a team of engineers, physicists, ceramists, crystallographers, and chemists to study goal-directed problems in materials engineering. The laboratory, founded during World War II, served as a model for many of the materials research laboratories of today, although few, if any, have achieved similar levels of scientific integration and engineering relevance.

Many materials scientists tend to work on "fashionable" materials, and I am no exception. Last year it was quasicrystals, while this year many of us are making copper oxide superconductors.

Twenty-five years ago, in the early 1960s, solid-state lasers were the "hot topic." In the Laboratory for Insulation Research we were busy growing crystals of corundum, spinel, and chrysoberyl doped with chromium and other transition metal ions. Arthur Linz had just arrived from the National Lead Company to set up Verneuil burners for growing ruby crystals in oxyhydrogen flames. Rubies and sapphires

of many different colors were cut and polished for optical experiments, and we set about interpreting the absorption and fluorescent spectra in terms of crystal field theory.<sup>1</sup>

The chromium-doped aluminum oxide crystals ranged from pale pink to ruby red to deep green, depending on Cr content. When measured as a function of percent of transition metal, most of the absorption-band intensities were linearly proportional to the doping level—the normal crystal field spectra—but as the level increased, a number of new peaks appeared in the near-ultraviolet portion of the spectrum.<sup>2</sup> The intensities of these peaks were proportional to the square of the Cr content and were identified as pair spectra associated with neighboring Cr ions.

Interpretation of the spectra using the point charge model and crystal field splitting required a detailed knowledge of the crystal structure. The corundum structure had been determined by W.H. Bragg<sup>3</sup> 40 years earlier, but the coordinates of the atoms had never been accurately refined, so Yeb M. de Haan and I set about measuring X-ray diffraction intensities from Weissenberg films. Flame fusion crystals of  $\text{Al}_2\text{O}_3$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$ , and  $\text{Cr}_2\text{O}_3$  were used in the refinement. All four structures are isomorphous but differ slightly in bond lengths and in distortions of the oxygen octahedra.

In a later study<sup>4</sup> Simon C. Moss and I were able to show that chromium does not precisely replace aluminum in the ruby structure but occupies a position a few hundredths of an angstrom removed from the Al site. This fact proved crucial in interpreting the optical spectra of ruby.

The color changes and dichroism continued to interest us, and we went on to study alexandrite (Cr-doped  $\text{Al}_2\text{BeO}_5$ -family crystals).<sup>5</sup> A highly prized gemstone, alexandrite exhibits a fantastic color change from red to green. When viewed in incandescent light the crystals are reddish purple, but in daylight they turn grayish green. The tiny crystals we grew by flux fusion were too small for many experiments, but later work at Allied Corporation identified alexandrite as an excellent laser crystal.<sup>6</sup>

It seems likely that most of the citations to our crystal structure papers have to do with optical properties, but there are other reasons for interest in the transition metal oxides.  $\text{Ti}_2\text{O}_3$  and  $\text{V}_2\text{O}_3$  both show metal-semiconductor phase transitions, and  $\text{Cr}_2\text{O}_3$  was the first and best example of a magnetoelectric crystal. Magnetoelectricity—the linear relationship between magnetization and electric field—was another "hot topic" of the early 1960s.

I don't consider our structure refinement paper to be outstanding by any means, but it was a timely paper that appeared during a period of intense interest in corundum-family oxides.

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4. Moss S C & Newnham R E. The chromium position in ruby. *Z. Kristallogr.* 120:359-63, 1964.
5. Farrell E F & Newnham R E. Crystal field spectra of chrysoberyl, alexandrite, peridot and sinhalite. *Amer. Mineral.* 50:1972-81, 1965.
6. Powell R C, Lin X, Xu G, Quarles G J & Walling J C. Spectroscopic properties of alexandrite crystals. *Phys. Rev. B—Condensed Matter* 32:2788-97, 1985.