CRYSTAL STRUCTURE DETERMINATIONS OF THREE-LAYER AURIVILLIUS CERAMICS USING A NEW PARALLEL BEAM X-RAY POWDER DIFFRACTOMETER

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ABSTRACT

A new high-resolution parallel beam X-ray powder diffractometer incorporating multilayer X-ray optics in the incident and diffracted beams was constructed and used to refine the crystal structures of several three-layer Aurivillius ceramics using the Rietveld method. The intent of this study was to determine the feasibility of parallel beam data in a research environment. These results were compared to those previously obtained using a typical divergent beam diffractometer. In general, the refinement results were similar for both systems. However, the high-resolution data displayed statistically slightly larger \( a \) lattice parameters, and larger \( A \)-site Bond Valence Sum (BVS) values. The high-resolution data had much-improved signal to noise ratio and higher resolution.

INTRODUCTION

The Aurivillius structure materials [1] have been shown to be excellent ferroelectrics and ionic conductors. In order to improve upon the material properties, the crystal structure must be understood. However, most crystal structure models of the Aurivillius ceramics have been lacking in terms of the potential for site mixing among cations. Site mixing in these materials was discovered by Hervoches and Lightfoot [2] in the three-layer Aurivillius ceramics and by Blake and Falconer [3] for the two-layer phases. Since the stability of the Aurivillius structure is governed in large part by the lattice strain, site mixing is expected to play a role in determining structural stability. Bond Valence Sum (BVS) [4] calculations have been shown to indicate structural strains. For example, a BVS greater than the formal cation charge indicate an overbonded condition where the bonds are in compression. BVS values less than the ideal value indicate bond tension. The crystal structures of several three-layer Aurivillius ceramics were refined using the Rietveld method from powder X-ray diffraction data using a conventional divergent beam X-ray diffractometer. After construction of a new high-resolution X-ray diffractometer, the same structure refinements were performed in order to compare the differences between the two instruments.

EXPERIMENTAL PROCEDURE

Powder samples were prepared via solid-state synthesis. Precursor powders were pressed into pellets and fired in a powder bed according to the following schedule: twice at 750°C for 5 hrs, four times at 1050°C for 20hrs with intermediate regrindings.
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Diffraction measurements were taken on two instruments. A conventional diverging beam Siemens D500 diffractometer operated at 40kV and 30mA, using fixed 1° divergence slits, was used to measure the samples loaded in side-drifted sample holders. The measurements were taken from 2-100°2θ with a step size of 0.02°2θ and a count time of 10 seconds. Diffraction scans were also taken on the high-resolution parallel beam instrument. This instrument uses Cu Kα radiation with an Osmic Max-flux® multilayer parabolic optic on the incident side, a side-drifted sample holder, and an Osmic flat multilayer optic on the receiving side. The measurements were taken at 40kV and 35mA from 2-100°2θ with a step size of 0.02°2θ and a count time of 15 seconds.

The diffraction scans were refined using the GSAS [5] Rietveld code with the EXPGUI header [6]. The structure is shown schematically in figure 1. Refining the site mixing between the Bi³⁺ and A-sites proved to be impossible without introducing a refinement constraint. Because it was necessary to allow for three atoms to fractionally occupy one site, a constraint was set up to ensure that the total site occupancy added to unity. In order to accomplish the three-atom mixing, a new fictive atom was created by splitting one atom into two atoms [7]. For example, if Bi³⁺ occupies 0.8 of the Bi-site, the fictive atom would take 0.4 from the Bi³⁺ and thus two Bi³⁺ atoms would exist on the same site with identical occupancies. In this manner a “third” constraint could be added without violating the GSAS code. One Bi³⁺ atom would interact with Sr²⁺ and the other Bi³⁺ would interact with a Ca²⁺, for example.

The Sr/Ca/Ba atoms occupying the Bi-site were not constrained to have the same position as the Bi ions. Bi³⁺ atoms have a stereochemical lone pair of electrons which repel the O4 layer of oxygen atoms. The alkaline earth atoms do not have a lone pair, and as a result may occupy a slightly different position than the Bi³⁺ cation. The Nb/Ti sites were constrained to occupy the same position. This constraint was also applied to the Sr/Ba/Ca/Bi cations on the A-site. Furthermore, the isotropic thermal parameters of the Bi-site, A-site, Nb-site and Ti-sites were all constrained to vary at the same rate. Oxygen anion thermal parameters were not refined.

An interesting check of the stability of the refinement is the occupancy of the Bi and A-sites. The occupancies were not constrained to add to unity, but the sum of the refined occupancies added to approximately unity.

RESULTS AND DISCUSSION

Diffraction scans taken with the parallel beam instrument demonstrated greater signal to noise ratio and improved resolution as seen in Figure 2. The results obtained from the parallel beam instrument were similar to those from the diverging beam system. In general, the weighted residual errors were slightly lower in the diverging beam refinements, typically around 9% compared to 14% in the parallel beam refinements. Chi-squared values were lower however in the parallel beam refinements. Si and LaB₆ standards were run with the new instrument and the calibration results compare favorably with accepted values.

Figure 3 shows the fraction of Bi³⁺ occupying the perovskite A-site in the Aurivillius structure versus the average cation radius of the Aurivillius A-site. As larger alkaline earth cations are substituted for the Aurivillius A-site, the fraction of Bi³⁺ moving to the Aurivillius A-site...
increases to reduce lattice strain. A similar effect is seen for the A-site cation moving to the Aurivillius Bi\textsuperscript{3+} site. Figure 3 depicts the effect for both the diverging beam and parallel beam experiments. Very little difference is noted between the two systems. The BVS of the Aurivillius A-site was larger in the parallel beam experiments. Figure 4 shows BVS versus average cation radius (ACR) for the A and Bi-sites for the diverging and parallel beam experiments. The Bi BVS tracks nicely, while the parallel beam A-site BVS is clearly larger. In order to explain this difference, the bond lengths were examined. The parallel beam refinements give smaller A-O5 bond lengths than the diverging beam refinements and as a result, the smaller bond lengths increase the BVS for the A-site. Figure 5 displays a schematic of “perovskite block” portion of the three-layer Aurivillius structure. The figure summarizes the differences noted in the parallel beam refinements. The A-site cations move slightly farther away from the center of the unit cell whereas the Nb atoms move slightly towards the center. This results in the Nb-O3 bond lengths being slightly smaller. It is not clear why these changes occur in the parallel beam refinements.

![Schematic of refined crystal structure for Bi\textsubscript{2}Sr\textsubscript{2}Nb\textsubscript{2}TiO\textsubscript{12}](image)

Figure 1. Schematic of refined crystal structure for Bi\textsubscript{2}Sr\textsubscript{2}Nb\textsubscript{2}TiO\textsubscript{12}.
Figure 2. Parallel beam diffraction pattern demonstrates improved signal to noise ratio.

Figure 3. Fraction Bi on A-site versus Average Cation Radius (ACR) for diverging beam and parallel beam refinements. Error bars are three sigma.
Figure 4. Bond Valence Sum (BVS) versus ACR for the Bi and A-sites for diverging beam and parallel beam refinements.

Figure 5. Schematic of the “perovskite block” section of the three-layer Aurivillius structure showing displacements of certain cations from the parallel beam refinements.
SUMMARY

A high-resolution parallel beam diffractometer using multilayer optics was constructed and used to measure several three-layer Aurivillius ceramics. Rietveld refinements were performed on data sets from a diverging beam diffractometer and the new parallel beam diffractometer. Comparisons indicate a good agreement with slight positional differences noted in the parallel beam data. As a result of the positional differences, the BVS of some atoms are larger in the parallel beam refinements. All positional, fractional and thermal parameters were refineable in the parallel beam system. The use of parallel beam diffraction data has been found to be acceptable for studying materials based problems.

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