Study of ferroelastic behavior and microstructure in polycrystalline LaCoO$_3$ using Transmission Electron Microscopy

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LaCoO$_3$ is a ferroelastic perovskite-type oxide. It has been shown to undergo creep at room temperature. LaCoO$_3$ responds to stress by changing its domain structure, resulting in formation of spontaneous strain. The microstructure of a sample of polycrystalline LaCoO$_3$ with history of stress was investigated using Transmission Electron Microscopy (TEM). It was compared to an unstrained sample to determine what changes are produced. TEM analysis has shown an increase in defect density as well as the appearance of atomic scale ordering. The causes of the observed ordering and their relation to ferroelastic behavior are explored.

Introduction

Lanthanum Cobaltite, LaCoO$_3$, has been studied for its potential use in solid oxide fuel cells, oxygen separation membranes, reduction catalysts, and oxygen sensors[1-8]. At higher temperatures it exhibits ionic-electronic conductivity[9]. Additionally, changes in its magnetic susceptibility around 80K and 500K suggest corresponding spin state transitions, the nature of which has been investigated in numerous studies[10-18]. More recently, and to a lesser extent, the mechanical properties of LaCoO$_3$ have been studied[19,20]. Understanding of its mechanical properties will be essential for the development of practical applications for the material. For example, when LaCoO$_3$ based ceramics are to be used as solid electrolytes and membranes, cracking caused by thermal instabilities could seriously compromise the membranes[20].

LaCoO$_3$ is a perovskite type oxide, which has general form ABO$_3$. The ideal perovskite structure is cubic. However, due to differences in the ionic radius of La and Co a slight distortion results making LaCoO$_3$ rhombohedral. Its nearly cubic structure, however, allows it to be thought of and indexed as a pseudo-cubic. Fig. 1 shows a pseudo-cubic reprentation of a unit cell. The pseudo-cubic lattice backbone is made of Lanthanum. The Co centered in each cell as well as the O centered on the each face of the cube make up the CoO$_6$ octahedra.

Of particular interest, it has been reported that LaCoO$_3$ undergoes room temperature creep[21]. Typically, ceramics undergo creep—the continuous deformation of a solid under stress with time—only at temperatures at least as high as about half their melting point[22] (the melting point of LaCoO$_3$ is about 1800° C). The ability of LaCoO$_3$ to undergo room temperature creep is indicative of its ferroelastic behavior. The application of stress in LaCoO$_3$ as with other ferroelastic materials results in a hysteresis loop in the stress-strain behavior. By comparison, so-called "paraelastic" materials exhibit a linear stress-strain behavior. Furthermore in ferroelastic materials application of strain can result in spontaneous strain, which remains in the material after all external stress is removed. This is the result of the reorientation of ferroelastic domains induced by stress. A recent study modeled the creep behavior of LaCoO$_3$ during the loading and unloading of stress, incorporating the locally consumable nature of domains[21].

In room temperature $LaCoO_3$ a large number of domains are present in the form of deformational crystallographic twins although monoclinic domains have also been reported[23]. Twins are a crystallographic shear deformation, whereby a crystal intergrowth leads to different crystal orientations on either side of the shear. However, twins share lattice points along the twin boundary. Under the application of stress one direction of the twin becomes unstable and collapse into the other when the critical stress is surpassed[20]. This process is what is referred to as domain switching. Potentially, appropriate stress levels could cause dramatic detwinning, even across grain boundaries, resulting in significant changes in microstructure.

The types of twins vary and include short parallel domains oriented at 180° to each other, wedge shaped twins, long lamellas, and herring bone structures[20] and are usually between 20 and 200nm in size. At lower temperatures pure $LaCoO_3$ is in a rhombohedral phase allowing for deformation twinning, at higher temperatures (near its melting point) $LaCoO_3$ transitions to a high symmetry cubic phase where lack of twinning makes $LaCoO_3$ paraelastic[20]. Since stress can reorient domains permanently, one would expect the twin structure to alter dramatically after the application of an appropriate load. The nature of the response of $LaCoO_3$ to stress makes an investigation of the relation between its ferroelastic behavior and microstructure of particular interest. Understanding how strain is produced in its microstructure could shed light on its mechanical properties and perhaps be exploited to engineer a specific state or mechanical response for relevant application. On this note, one should consider that strain induced ferromagnetism has been demonstrated in $LaCoO_3$ thin films[24]. With more knowledge it is hopeful that the ferromagnetic and ferroelastic properties could be coupled, with potential for application such as in sensors where a predictable change in strain due to some stress could be detected via the corresponding change in ferromagnetic properties.

Methods

In order to investigate the relationship between ferroelastic behavior and microstructure, two $LaCoO_3$ samples will be analyzed. One is a bar of polycrystalline $LaCoO_3$ with no history of strain. The other is a cylinder of polycrystalline $LaCoO_3$, to which 110 MPa of stress was applied biaxially for 8 hr. Strain data for that sample was collected at the time load was applied. From these bulk samples three TEM specimens were prepared. One was cut from the untreated bar of $LaCoO_3$. The other two, from the cylinder exposed to biaxial pressure. One of these was cut along the direction of applied pressure, the other normal to it. Specimens were cut with a diamond wheel saw to a size of about 1x2 mm with an initial thickness of ~600μm. The specimens were then attached to a mount with wax, which was placed into a Gatan Disk Grinder and the specimens were polished using the South Bay Polishing Wheel with Silicon Carbide paper of varying grain sizes until the sample was less than 100 μm in thickness. Diamond lapping films were used to finish polishing one side to about 80μm. Specimens were then flipped over and transferred onto a pyrex mount, which could be attached to a tripod polisher. The tripod polisher provided better control and allowed a polishing angle to be introduced to create a thickness gradient. Using diamond lapping films the specimens where thinned so that the minimal thickness was around 5μm.

Then, specimens were attached to a copper ring with an epoxy and cured for 24 hr. Specimens were then placed in acetone until wax was removed and they detached from the pyrex mount. Specimens were then washed in isopropanol for about 1 hr to clean surfaces. Then, the specimens (now supported by the copper ring) were firmly secured in a holder so that they could

be placed into a Fischione 1010 dual ion mill, where the surface of each specimen was bombarded with Argon ions in a at an angle of 15° and accelerating voltage of 3-4 kV until a small hole formed in the specimen. The region around the hole is thin enough to permit the transmission of electrons.

The different specimens were then analyzed using a JEOL 3010 Transmission electron microscope (TEM). This instrument uses a LaB_6 thermionic electron source and a 300kV accelerating voltage. It is equipped with a 1k by 1k slow scan Gatan CCD camera, and a Gatan digital acquisition system. The point resolution of the instrument is 2Å. Both low magnification (30,000X – 200,000X) and high magnification images (300,000X to 800,000X) obtained taken. In addition selected area diffraction patterns were obtained to determine lattice parameters and examine grain and twin boundaries. The Gatan Digital Micrograph software package will be used to analyze the diffraction patterns by measuring the distances from the central bright spot to each of the individual spots or rings. These distances can be used to calculate atomic and planar spacings in the crystal lattice. All images and electron diffraction patterns were taken along zone axes corresponding to the pseudo-cubic (001) orientation.

Results and Discussion

Reflection twins are observed in the untreated sample. This can be seen in diffraction patterns. Fig. 2 shows a diffraction pattern from a typical grain in the (001) orientation. The symmetry of the pattern implies the cubic orientation of the lattice. Slight splitting of the diffraction spots can be seen. The splitting is an indication of crystallographic twinning; the difference in orientation between twins gives rise to a different set of diffraction spots. The magnitude of splitting increases with distance from central spot. The slight nature of the splitting implies that the orientations are quite similar. This is because the twins formed in this orientation are a result of the very slight deformation of the lattice from cubic.

Figure 3 shows a region with no visible defects. The array of atoms that appears in the image is arranged symmetrically, demonstrating the cubic orientation of the lattice. The spacing along the (100) and (010) directions appear to equal.

Figure 4 shows a stacking fault in the untreated sample. In the image there is a shift in the arrangement of atoms along the region of contrast. Specifically, the positions of atoms shift by about half of a lattice spacing at the site of the defect. Note that the stacking fault occurs along the perpendicular (100) and (010) directions. The stacking faults, in general, formed closed loop structures and Fig. 4 shows just part of loop of the stacking fault. Furthermore, many of the stacking faults occur along regions that show up dark and express the strain associated with the stacking faults. Stacking faults in the untreated sample are rather common and have been reported before. They are expected to arise after sintering of the material as the bulk deals with thermal stresses. Although, they are the most common defect after reflection twinning, they are still relatively sparse.

The treated specimen also displayed stacking faults. The stacking faults observed in the treated specimen tended to be more extensive. It is possible that this difference is not characteristic of the two samples in general but, if significant, the result would not be surprising as applied stress could promote the creation and extension of the defect. Otherwise, the treated sample showed a higher overall defect density.

Fig. 4 shows a high resolution of a region without apparent defects. The array of atoms that show up is very symmetrical, demonstrating the very close to cubic nature of the lattice. The lattice spacing in the [100] and [010] directions appear to be practically equal.

Fig. 5a is a high resolution image of defects in the sample. Bright lines running in the two perpendicular [100] and [010] directions are visible. The angle between these defects is nearly 90° and is indicative of the cubic structure in $LaCoO_3$. The lines are, in general, regularly spaced with three lattice spacings between each. However, there is some variation in the spacing along one direction with some spaced further apart. Also note that these features appear to be interwoven, with lines running in one direction in between lines running in the other. Fig. 5b is an SAD of the region in Fig. 5a. The defects seen in the image give rise to superstructure in the diffraction pattern. This is because the periodic nature of the bright lines gives rise to extra diffraction spots. Since, these lines are separated by three lattice spacings, the superlattice reflections in the diffraction pattern (which is a reciprocal space) show up at every third of the separation between the reflections due to the cubic lattice. In one direction the superlattice reflections are more spread out. This is a result of the lines in one of the directions not always being spaced equally. It is not clear what produces the defects in Fig. 5a. One explanation for this ordering is that strain causes distortion in the CoO_6 octahedra. The resulting asymmetry in the octahedral could produce electric or magnetic moments that, if possible to reorient, may lead to a ferroelectric or ferromagnetic material. Furthermore, it is possible that distortion of the octahedral under stress lead to oxygen vacancies, shifting the position of the cobalt in the lattice. The consequent changes in structure would cause ordering of the oxygen vacancies. Oxygen vacancies and their relation to distortion of structure in perovskite-type ceramics are well-known and have been studied considerably[25]. However, the creation of oxygen vacancies is normally observed at high temperatures. Another possibility is that the ordering seen corresponds to atomic scale monoclinic ferroelastic domains. These have been previously speculated in pure and doped LaCoO3 to explain similar ordering phenomenon which produced superstructure in diffraction patterns like that in Fig. 5b[23]. If so, the ordering is explained by the creation of a monoclinic phase which results in a unique type of domain. These monoclinic domains were shown to be ferroelastic. Furthermore, monoclinic domain walls do not move readily under the application of external stress like those of deformation twin domains and, therefore, their periodicity and the distance between them are fixed. This would mean that the ferroelastic behavior of LaCo3 is characterized by mechanisms of two different sets of domains: deformation twin domains that range from 20-200 nm and monoclinic domains on atomic scales (~ 1nm).

Conclusions

No transition from the ferroelastic rhombohedral phase to paraelastic cubic phase was observed. The sample subjected to strain had a noticeably higher defect density. It is not yet clear if the application of stress has caused a reduction in lattice dimensions. In addition, ordering was observed in both the [100] and [010] directions in the treated sample. The nature of the ordering is not well understood and there are a number of possible roots for this phenomenon. One possibility is that stress has produced distortion in the CoO6 octahedra and possibly oxygen vacancies as well. Ordering of this nature in perovskite-type oxides is already known. Alternatively, the ordering seen may actually be due to the presence of monoclinic domains. These have been previously speculated in another study of $LaCoO_3$. More investigation needs to be done to discern the nature of the observed ordering. Analytic STEM could be used to study the ordering through X-Ray Energy Dispersive Spectroscopy, Electron Energy Loss Spectroscopy as well as improved Z-contrast imaging. Also, if oxygen vacancies

are present they should align in the (110) orientation and observation along this zone axis could determine their presence. Further investigation on the effect of applied stress on grain size could be done using Scanning Electron Microscopy or X-Ray diffraction. Additionally, X-ray diffraction analysis could be used to determine any changes in lattice parameters. Also, a sample in the plane of the applied stress should be studied to see if the response of LaCoO3 to stress varies with its orientation to the direction of external stress.

Acknowledgements

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FIG.1: Diagram of $LaCoO_3$ unit cell in a pseudo-cubic representation

FIG 2: Diffraction Pattern of untreated sample showing splitting of spots, using 40 cm camera length

FIG 3: High magnification image of stacking fault in untreated sample

FIG 4: High magnification of a region without defects in treated sample

FIG 5: a) High magnifaction image of region with apparent ordering and b) a diffraction pattern of the same region using a 40cm camera length