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Phase coexistence in $Sr_{0.70}Ca_{0.30}TiO_3$ studied through electron diffraction

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Abstract

A detailed structural study employing electron diffraction in selected area (SAD) and convergent beam electron diffraction (CBED) modes, followed by Rietveld analysis of the powder X-ray diffraction (XRD) data, has been carried out to identify the correct space group and to investigate the possible phase coexistence in $Sr_{0.70}Ca_{0.30}TiO_3$ (SCT30) ceramics. The occurrence of distinctly two types of wide-angle CBED patterns and the presence of mutually perpendicular A_2 type GM-lines in the forbidden reflections do show the coexistence of *Pnma* phase and a new orthorhombic phase with space group $P2_12_12$ in SCT30. The occurrence of $P2_12_12$ orthorhombic phase in SCT30 appears to be a result of distortion in addition with the rigid tilt of BO_6 octahedra. It so appears that the possibility of occurrence of $P2_12_12$ for distorted perovskite structures is yet to be theoretically investigated.

Keywords: $Sr_{0.70}Ca_{0.30}TiO_3$; $P2_12_12$ Space group; Phase coexistence; CBED

1. Introduction

The apparent simplicity of the perovskite structure belies the difficulties in identifying the correct structure of many of the distorted perovskite variants. The study of the evolution of crystallographic phases in perovskites, as a function of composition, temperature and pressure, is an area of continued interest. Most of these structural transitions involve rigid tilts, B-site cation displacement and chemical ordering at A and B sites of ABO_3 perovskite, and lead to a variety of structures [1–6]. The possible perovskite structures appearing due to rigid tilts of octahedra have been derived by Glazer [1,2]. These phases have been practically realized in a variety of perovskite systems. Out of these, $Sr_{1-x}Ca_xTiO_3$ (SCT) has been the subject of a number of studies, but the results still remain in dispute. The end members $CaTiO_3$ and $SrTiO_3$ occur in orthorhombic (*Pnma*) and cubic (*Pm*3*m*) structures, respectively, at room temperature.

It might be expected that the substitution of Ca for Sr in $Sr_{1-x}Ca_xTiO_3$ would produce the same structural sequence as obtained on heating $CaTiO_3$. McQuarrie [7] reported the occurrence of cubic, tetragonal and orthorhombic phases as a function of composition. Ball et al. [8] have proposed three phase boundaries corresponding to the crossovers from cubic (*Pm*3*m*) to tetragonal (*I*4/*mcm*) for $x > 0.05$, from tetragonal to orthorhombic (*Cmcm*) at $x > 0.35$ and from *Cmcm* to *Pnma* at $x > 0.55$. Granicher and Jakits [9] have reported that the *Cmcm* space group for the composition range $0.35 \leq x \leq 0.60$ corresponds to the ‘nearly cubic’ phase. Ceh et al. [10] proposed cubic to orthorhombic phase boundary at $x = 0.40$. Altogether a different sequence of structures have been proposed by Ranjan and Pandey [11] claiming that the structure is not tetragonal but orthorhombic in the composition range $0.12 \leq x \leq 0.40$. Earlier proposed [11] *Pnma* structure was later reanalyzed to be *Imma* based on improved data quality [12]. The assignment to *Imma* is based largely on the Rietveld refinement of lab XRD and neutron scattering data, which is supported by the observed asymmetry in the E_g lines and broad bands in Raman spectra [13]. There

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are very few reports on electron diffraction in these composition ranges. Ranjan et al. [14] using electron diffraction showed that the structure is cubic for $x < 0.06$, orthorhombic with different symmetry in the composition range of $0.09 < x \leq 1.0$ and either tetragonal or orthorhombic for $0.06 < x < 0.09$. Howard et al. [15,16] assigned the tetragonal space group $I4/mcm$ for the room temperature SCT30, whereas a recent report by Woodward et al. [17], based on electron diffraction studies, reports $P2_1/m$ structure for SCT30. In fact Woodward et al. [17] have given a new sequence of structures in the phase diagram. According to them the space groups are $Pm3m$ for $x = 0$, $I4/mcm$ for $x < 0.2$, $C2/m$ for $x = 0.2$, $P2_1/m$ for $0.2 < x < 0.6$ and $Pnma$ for $x > 0.6$. Ranjan et al. [14] have produced micro-diffraction patterns corresponding to all the three mutually orthogonal zones [100], [010], and [001]. However, we would like to emphasize that, practically it is not possible to get all three above zone patterns from the same grain due to mechanical limitation of the β-tilt of a double-tilt holder and hence there is possibility of mixing of patterns from different phases. Woodward et al. [17] have given a method in which one needs to collect patterns from different grains and decide based on the statistics of observing zone patterns with certain type of reflections. Howard et al. [16] in their recent report based on the analysis of SAD patterns have assigned $I4/mcm$ space group to SCT30. However, after digital enhancement, weak but clear presence of superlattice reflections were found, which are neither expected in any body centered lattice nor it will be produced by double diffraction in $Imma$ and $I4/mcm$ phases.

Thus keeping in view the above-mentioned controversies we have carried out extensive structural study of SCT30, leading to the unequivocal identification of its space group. This is a composition, which has been studied by various groups through X-ray diffraction, neutron diffraction, electron diffraction and Raman scattering. We have studied the room-temperature crystal structure of SCT30 using TEM. We have followed the conventional way of determining symmetry elements and space groups (Tanaka [18], William and Carter [19], Gjϕnnes and Moodie, [20] and Morniroli and Steeds [21]). For this we have recorded selected area (SAD) and convergent beam electron diffraction (CBED) patterns from single domain. By its comparison with the simulated ones, we have discarded the possibility of some of the expected space groups. Our decisions are purely based on the absence or presence of certain reflections and diffraction features like superlattice spots and GM-lines in an otherwise properly processed diffraction patterns. Our diffraction studies show the coexistence of $Pnma$ with a new orthorhombic phase with space group $P2_12_12$. We emphasize that the possibility of $P2_12_12$ for a distorted perovskite structure has yet not been theoretically investigated.

2. Experimental

The SCT30 sample was prepared through solid-state reaction route using high purity (99.99%) powders of $SrCO_3$, $CaCO_3$ and TiO_2 [11,12]. The final sintered pellets were gently crushed to fine powder and subsequently annealed at 600 °C for ~10 h for removing residual strain present in the grains. Only the final heat-treated powder was used for the diffraction studies as described below. The powder was subjected to structural and phase purity characterizations using powder X-ray diffraction (XRD). The XRD was carried out using Cu Kα X-ray on a Rigaku make diffractometer working in Bragg–Brentano para-focusing geometry and mounted on a rotating anode X-ray generator operating at 15 kW output power. The composition of the synthesized sample was verified using EDAX. The complete absence of any contrast variation, appearing due to different effective-Z for different phases observed during backscattered SEM, confirmed the phase purity of the sample. EDAX revealed that the composition of SCT30 was the same within the typical error of EDAX to that of the intended one.

Transmission electron microscopy (TEM) was carried out employing Tecnai $G^2$20 TEM (FEI) operating at 200 kV, equipped with LaB_6 filament and a CCD camera (Mega view SIS). Sample for TEM observation was made by dispersing the annealed powders in methanol and drying a drop of the dispersion on a perforated carbon coated copper grid. TEM was performed in imaging, SAD, micro-diffraction and CBED modes. For TEM observations, a double-tilt holder ($\alpha = \pm 45°$ and $\beta = \pm 25°$) was used. Whenever necessarily required, the SAD patterns were recorded by tilting the required zone exactly along the beam direction. CBED patterns have been obtained using 10-μm condenser aperture with incident electron beam converging to an effective spot size of 50 nm on the specimen. The small spot size assures good spatial resolution and minimizes the likelihood of any significant thickness and orientation variations within the diffracting specimen volume. All SADs and low-angle CBEDs were recorded at camera lengths of 860 mm and wide-angle CBEDs were recorded at 265 mm. All the TEM photographs particularly SAD and CBED patterns, which have been presented here, are properly enhanced for clear visibility of even the weakest details like weak superlattice spots, HOLZ (Higher order Laue zone) rings and GM-lines. In general in a pristine diffraction pattern, these features may remain undetected otherwise. This was done using the "Analysis" software made available with the CCD camera. The decisions regarding the correct space group has been taken based on the systematic absence of reflections and presence of proper signatures of symmetry elements as indicated by the presence of GM-lines [18,19] appearing in kinematically forbidden reflections in CBED patterns. During TEM analysis, EDAX was also carried out and the composition was found to match with the intended one within the typical error of EDAX.

3. Results and discussions

Fig. 1a depicts Rietveld refined [22] X-ray diffraction patterns of SCT30 corresponding to different space groups. These patterns have been vertically enlarged to make some necessary details clear. Same fitting strategy was followed for each space group case. The five space groups under consideration differ