Controllable Ordering of the Fractional Double Perovskite $EuTa_2O_6$

Brenan Palazzolo[1], Tobias Schwaigert[2,3], Darrell Schlom[2,3]

[1]Clemson University Department of Physics and Astronomy, [2]Cornell University Department of Materials Science, [3]PARADIM

Abstract: Fractional double perovskites are novel structural derivatives of the conventional Perovskite aristotype. Due to the high amounts of vacancies, physical properties are dominated by the arrangement of defects. Here we demonstrate the Molecular-beam epitaxy growth of $EuTa_2O_6$ with controllable ordering of Europium vacancies. This works lays the foundation to explore the robustness of the proposed quasi 2D-electron gas behavior that is created by the displacement of Ta^{5+} towards vacancy layers, by systematically exploring the stability window of $EuTa_2O_6$ and its disordered parent structure $Eu_{0.5}TaO_3$. Structural characterizations were carried out with X-ray diffraction (XRD) and atomic force microscopy (AFM).

Introduction

Perovskites are a widely studied class of materials[1],[2] where their electronic properties are determined by the orbital character of the transition metal that resides in the B-site of the ABO_3 structure.

Distortions to perovskite structure have a significant impact of the physical properties. For example, in the double perovskite $LaBaMn_2O_6$ significant changes to the electrical properties can be observed. In a study on *a*-site ordering of $LaBaMn_2O_6$, and disordered counterpart $(La,Ba)MnO_3$, it was shown that the Curie temperature, T_C, was increased for the ordered structure (T_C = 335 K) opposed to the disordered structure (T_C = 270 K)[3].

In the structure $Eu_xTa_{2x}O_{6x}$ we define x = 0.5 to be the disordered structure and x = 1.0 to be the ordered structure. When ordering of our structure to $EuTa_2O_6$ occurs we see the formation of a quasi 2D-electron gas (quasi-2DEG) phase, opposed to that of $Eu_{0.5}TaO_3$ where the carriers can flow isotropically throughout the crystal structure.

In **Fig. 1**, the ordered structure, $EuTa_2O_6$, is shown on the left. Here, the vacant layer of Eu sites in the center causes the Ta atoms to shift closer to the O atom in the center of the unit cell, this antiferrodistortive displacement is known as a Second Order Jahn-Teller (SOJT) distortion[4]. This causes the splitting of the *d*-t_{2g} orbitals for the Ta atoms, resulting in the quasi-2DEG's formation (**Fig. 2)**. The strength of the SOJT is dependent on the ordering in the structure. In the ordered structure the bond between the center O and Ta atoms is shortened to 1.906 Å and the bond between the EuO layer has elongated to 2.054 Å from the disordered bond length of 1.980 Å. By systematic investigation of growth parameters, i.e., europium composition, tantalum composition, holding time, and the substrate temperature we gain insight to determine the level of contribution these parameters have to the ordering in the structure and subsequent electronic properties.

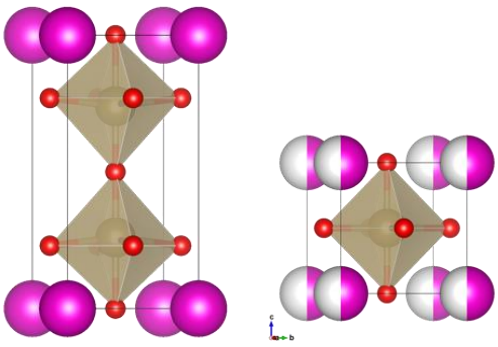

Figure 1: The ordered (left) and disordered (right) structures of $Eu_xTa_{2x}O_{6x}$. Eu atoms shown in pink, Ta polyhedral shown in gold, O atoms shown in red

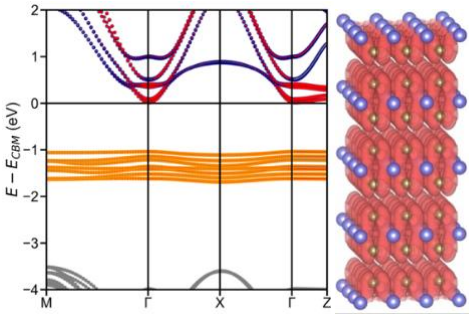

Figure 2: DFT calculation of $EuTa_2O_6$ band diagram (left). Between Γ and Z the red, Ta (d_{xy}), lines flatten suggesting no conduction in this plane. Empty space between red regions suggests quasi-2DEG formation in the charge density distribution (right).

Figure 1 (right) shows the disordered compound $Eu_{0.5}TaO_3$ (Pm3m a = 3.926 Å). When in the ordered structure of $EuTa_2O_6$ a doubling of the unit cell along the c-axis occurs where the lattice constants are now a = b =3.926 Å, c = 7.929 Å. Due to the elongation of the *c*-axis the unit cell doubles splitting the reflections into two classes: (i) fundamental reflections (even-even-even) and (ii) ordering reflections (even-even-odd). The 001 and 002 peak was therefore used as an indicator for the emergance vacancy ordered planes shifting from 22.40° (002) in the disordered structure to 11.15° (001) once ordered. Intensity ratio analysis done from structure factor calculations by a software package, POMMES[5], allow us to determine the ordering of the europium sites in the structure by comparison to varied *a*-site ordered structures in VESTA.

Results

Methods

Growth of $EuTa_2O_6$ thin films were done using a modified Vecco Gen 10 molecular beam epitaxy (MBE). A molecular beam of TaO_2 was generated from crystallized Ta_2O_5 and Eu_2O_3 was evaporated from Eu metal.

Eu and Ta composition during growth was determined by the shutter time, which corresponds to the time interval required for deposition of one monolayer of atoms on the substrate surface, $SrTiO_3$. The sources were measured to have a flux, ~1.5×10^{13} atoms cm^{-2} s^{-1}, by quartz crystal microbalance (QCM). The shutter time is calculated from a calibration growth of Eu_2O_3 on YSZ and TaO_2 on R-plane Sapphire. From these growths x-ray reflectivity (XRR) is done on the sample and the thickness is gathered[6]. Slight variation in shutter time results in small alterations to the composition of the film.

Without variation of parameters, growth by shutter method results in the deposition of one atomic layer of Eu followed by two atomic layers of TaO_2. These growths were done at 800°C, 850°C, and 900°C for substrate temperature with a background pressure of 3×10^{-8} Torr.

Data was collected using X-ray diffraction (XRD) and atomic force microscopy (AFM).

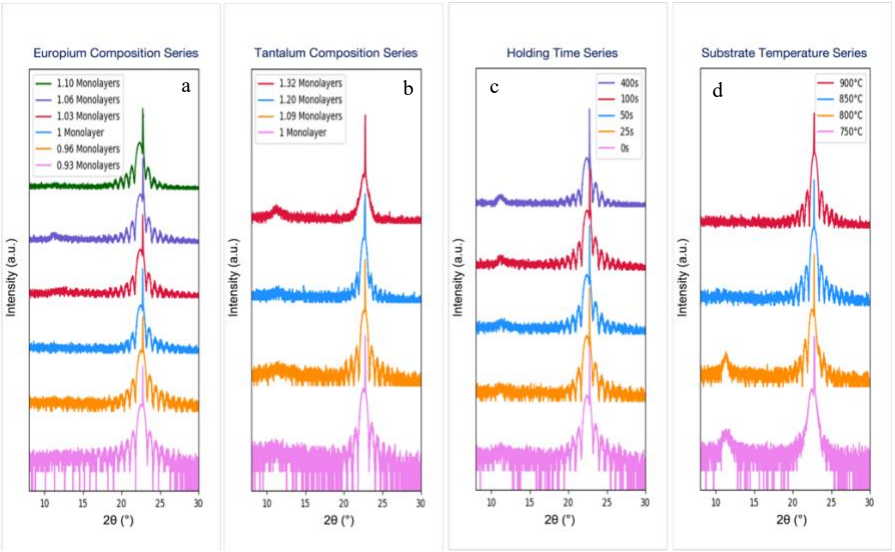

Figure 3: XRD scans of each series measurement. a) Europium composition series b) Tantalum composition series c) Holding time between unit cells series d) Substrate Temperature series

Table 1: AFM RMS Roughness values of series samples

Series	Conditions	RMS Roughness (pm)
Europium	0.93 Monolayer	198.2
	0.96 Monolayer	232.7
	1.00 Monolayer	240.7
	1.03 Monolayer	205.8
	1.06 Monolayer	113.7
	1.10 Monolayer	192.2
Tantalum	1.00 Monolayer	298.7
	1.09 Monolayer	173.4
	1.20 Monolayer	393.0
	1.32 Monolayer	794.4
Holding Time	0 seconds	180.1
	25 seconds	177.6
	50 seconds	190.9
	100 seconds	113.7
	400 seconds	236.4
Substrate Temperature	900 °C	307.4
	850 °C	115.7
	800 °C	285.2
	750 °C	526.0

Figure 3 shows the θ-2θ scans for various growth alterations of growth conditions. The series are varied independently from one another and do not build off the most optimal conditions of another series.

In **Figure 3a**, the europium composition series is depicted with the 1.06 monolayers of europium being the most optimal composition for ordering while keeping good crystalline quality based on Laue fringes. **Figure 3b** shows the tantalum composition series where 1.09 monolayers has been determined to be most optimal for ordering. **Figure 3c** shows the holding time between unit cells series. The most optimal holding time was determined to be 100 seconds from this series. **Figure 3d** shows the substrate temperature series where the temperature is varied from 750°C to 900°C. The only scan that shows both Laue fringes and an ordering peak is 800°C, thus this was determined to be the substrate temperature that would lead to most ordering.

Table 1 shows the RMS roughness of each sample by AFM. The roughness values are lower for the most optimal conditions furthering the validity of these conditions for more ordering. In the substrate temperature series 850°C has shown to be an optimal condition for $Eu_{0.5}TaO_3$, which is shown with a low roughness value.

After the series measurements all optimal conditions were applied to one growth shown in **Fig. 4** by XRD.

This sample shows an intense ordering peak along with the desired Laue fringes. A dedicated software package (POMMES) was used to further investigate the degree of ordering[5]. Based on the intensity ratio calculations from POMMES it was deduced that there is 65% ± 4% occupancy of Europium in the outer layers of our unit cell, resulting in higher order of our crystal.

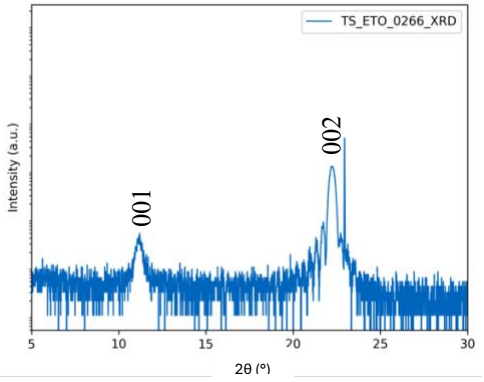

Figure 4: XRD data for a sample that applied the optimal conditions from the series measurements.

Conclusion

Modulation between the ordered structure, $EuTa_2O_6$, and the disordered structure, $Eu_{0.5}TaO_3$, is achievable. The systematic study of the growth window enables tuning of the degree of vacancy ordering. Further electronic measurements will investigate the effect of vacancy ordering on the anisotropy of electronic transport.

Acknowledgements

I would like to thank Ali Barooni, Benjamin Gregory, Paul Malinowski, and Dr. Kaveh Ahadi for collaboration on this project. This work is supported by the National Science Foundation under Cooperative Agreement No. DMR-2039380 and the PARADIM facility.

References

[1] A. Caiazzo, R. A. J. Janssen, *Adv. Energy Mater.* **2022**, *12*, 2202830.

[2] M. L. Medarde, *J. Phys.: Condens. Matter* **1997**, *9*, 1679.

[3] F. Millange, V. Caignaert, B. Domengès, B. Raveau, E. Suard, *Chem. Mater.* **1998**, *10*, 1974.

[4] O. Dowinton, D. Maryenko, R. V. Belosludov, B. Yang, M. S. Bahramy, *Adv. Funct. Mater.* **2023**, *33*, 2300995.

[5] S. Hasko, T. Schwaigert, A. Tenneti, *Stunion235/pommes: Pommes (peak-ordering measurement for multi-elemental systems)*, GitHub, **2025**. https://github.com/Stunion235/POMMES

[6] J. Sun, C. T. Parzyck, J. H. Lee, C. M. Brooks, L. F. Kourkoutis, X. Ke, R. Misra, J. Schubert, F. V. Hensling, M. R. Barone, Z. Wang, M. E. Holtz, N. J. Schreiber, Q. Song, H. Paik, T. Heeg, D. A. Muller, K. M. Shen, D. G. Schlom, *Phys. Rev. Mater.* **2022**, *6*, 033802.