ESRF	**Experiment title:** **Phase separation and reduction of CaCu3Ti4O12**	**Experiment number**: HE-3614
Beamline: ID-31	**Date of experiment**: from: 05.05. 2011 to: 11.05.2011	**Date of report**: 08.09.2015
Shifts: 12	**Local contact(s)**: A. Hill	*Received at ESRF:*

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Report:

{This report is an abbreviated version of [W. Slawinski et al. Mater.Res.Express, 1 (2014) 016306.]}

$CaCu_3Ti_4O_{12}$ is a material which shows colossal dielectric constants ~10^4 over a wide range of temperatures and frequencies [1-3]. A dielectric anomaly is observed in $CaCu_3Ti_4O_{12}$: between 100 K and 200 K [1-3] the dielectric constant, ε, jumps up to values about 10^6 between 200K and 600K. At higher temperatures there are pronounced maxima of ε in the 650K – 1050 K region [4,5].

The crystal structure of $CaCu_3Ti_4O_{12}$ has been studied by SR powder diffraction at ID31. All observed Bragg peaks of $CaCu_3Ti_4O_{12}$ are asymmetric with additional broadening towards higher diffraction angles. Selected regions of the SR based X-ray diffraction patterns of CCTO_2 sample at RT around the positions of the cubic (4,0,0), (4,4,0) and (4,4,4) Bragg peaks are shown in Figure 1. This peak-shape asymmetry is most pronounced at high scattering angles. The measurement made in the same instrumental configuration with a NIST Si reference sample shows symmetric Bragg peaks, so it is clear that the observed shapes, shown in Figure 1, are due to the $CaCu_3Ti_4O_{12}$ sample morphology. A Williamson-Hall analysis was made fitting a single pseudo-Voigt function to the observed Bragg peaks (as shown in Fig. S1). The estimated crystallite size L ranges between 2000 Å and 3000 Å. The observed peak-shape asymmetry can be explained with several alternative models:

- Two cubic phase model, i.e. two phases with cubic symmetry, both described with the space group *Im-3*, having slightly different lattice constants.

or

- Single phase models using subgroups of *Im-3* including the orthorhombic, *Immm*, as well as monoclinic *C2/m* and *P2/c* space groups.

The proposed structural models were used in the analysis of SR based X-ray diffraction patterns by using the program FullProf (19) and the program Jana (20).

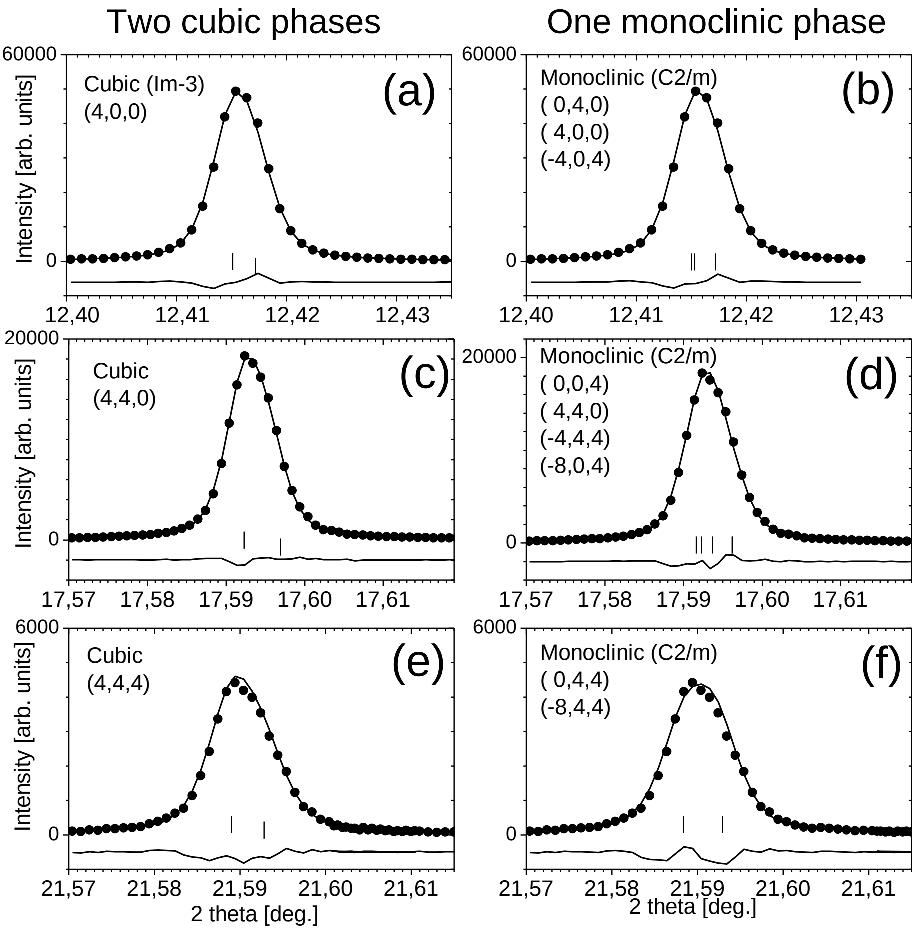

Figure 1. Parts of SR diffraction patterns of the $CaCu_3Ti_4O_{12}$ sample CCTO_1 (experimental data = solid symbols). The measurements were performed with $\lambda = 0.39996$ Å *at* RT. *Panels a,c,e present the refinement with the two-phase cubic model, space group Im-3 (solid line). Panels b,d,f present the refinement with the monoclinic model, space group C2/m (solid line). Ticks indicate the positions of the Bragg peaks due to both cubic phases (a,c,e) and the monoclinic phase (b,d,f). The bottom solid lines are difference curves. The corresponding* (hkl) *are listed.*

The best agreement is obtained with the two-phase cubic model. The single cubic phase model gives worse agreement as compared with the two-phase cubic one. None of the models based on the subgroups *C2/m, Immm* or *P2/c* gives better agreement than the two-phase cubic model. A discussion and the possible relation between the phase separation and the $CaCu_3Ti_4O_{12}$ dielectric properties are discussed in [6].

References

[1] Subramanian M A, Li D, Duan N, Reisner B A and Sleight A W 2000 *J. Solid State Chem.*, **151**, 323

[2] Homes C C, Vogt T, Shapiro S M, Wakimoto S and Ramirez A P 2001 *Science*, **293**, 673

[3] Ramirez A P, Subramanian M A, Gardel M, Blumberg G, Li D,Vogt T and Shapiro S M 2000 *Solid State Comm*, **115**, 217

[4] Zhang M N, Xu K B, Wang G J and Wang C C 2013 *Chinese Science Bulletin*, **58**,713

[5] Onodera A, Takesada M, Kawatani K and Hiramatsu S 2008 Japanese *J. of Appl. Phys.*, **47**, 7753

[6] Slawinski W, Przenioslo R, Wardecki D, Sosnowska I, Hill A, Fitch A and Bieringer M 2014 *Materials Research Express*, **1**, 016306.