ESRF	**Experiment title: Charge ordering and structural transitions in pseudoperovskite systems** $CaCu_xMn_{7-x}O_{12}$ **with (x=0.3) and (x=0.7)**	**Experiment number**: HE 1272
Beamline: BM – 01B	**Date of experiment**: 27/02-01/03/02 (6 shifts) and 15-17/05/02 (6 shifts)	**Date of report**: 12/08/2002
Shifts: 12	**Local contact(s)**: Wouter Van Beek	*Received at ESRF:*

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Report:

The SR diffraction measurements of $CaCu_{0.3}Mn_{6.7}O_{12}$ and $CaCu_{0.7}Mn_{6.3}O_{12}$ have been performed at at the BM-01B beamline in two series of measurements with the SR wave-lengths of 0.49949 and 0.79944 Å. The polycrystalline samples were mounted in a 0.5 mm diameter capillary in a cryostat operating between 10 K and RT.

Earlier structural studies [1,2] have shown that the undoped compound $CaMn_7O_{12}$ has a trigonal structure at RT (space group R-3). The structure of the fully Cu-doped compound $CaCu_3Mn_4O_{12}$ (i.e. x=3) is cubic at RT (space group Im-3) as reported by Chenavas et al. [3] and Zeng et al. [4]. According to Troyanchuk et al. [5] this family of compounds has a high temperature cubic phase and a low temperatute trigonal phase. The transition temperature decreases with increasing Cu content-x. For $CaMn_7O_{12}$ (x=0) it is about 440 K while for $CaCu_{0.3}Mn_{6.7}O_{12}$ (x=0.3) it is 310~K. For x > 0.4 it was suggested that the possible cubic-to-trigonal phase transition takes place below 100 K [5]. Recent structural studies by Zeng et al. [4] reported the cubic crystal structure described by the space group Im-3 in $CaCu_xMn_{7-x}O_{12}$ for Cu contents x > 0.5 at RT.

The SR and neutron powder diffraction data of $CaCu_{0.3}Mn_{6.7}O_{12}$ have been analyzed with the Rietveld method by using the program FullProf [6]. The diffraction pattern can be satisfactorily described with the cubic structure model (space group Im-3). The powder SR diffraction data of $CaCu_{0.3}Mn_{6.7}O_{12}$ measured at temperatures below RT has been analyzed

by assuming two different structural models. First the cubic structure described by the space group Im-3, and second by the rhombohedral structure described with the trigonal space group R-3, as described in [7]. The Rietveld refinements performed by assuming the cubic or the trigonal structure did not lead to relevant results. The reason of the difficulties of the structure determination is shown in Fig. 1a,b. One can see that the single cubic peaks at 300~K start to have side shoulders at lower temperatures. The 2-theta position of these side shoulders agree with the positions of the Bragg peaks due to the slightly distorted trigonal phase. The central part of the peaks which corresponds to the cubic phase do not disappear at low temperatures. It was therefore assumed that the observed SR diffraction patterns of $CaCu_{0.3}Mn_{6.7}O_{12}$ can be described as a sum of the contributions of a cubic and a trigonal phase. Another complication comes from the relatively large FWHM of the observed Bragg peaks, which is about 4 times larger than the instrumental FWHM (also shown in Fig. 1a,b).

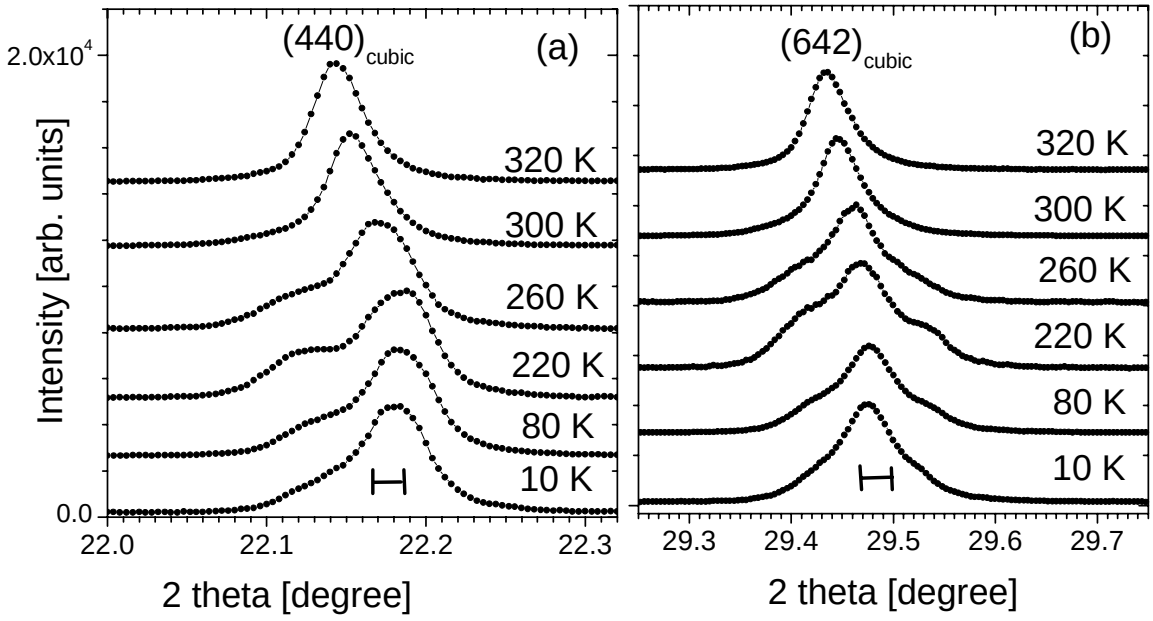

Fig. 1 Representative parts of the SR powder diffraction patterns of $CaCu_{0.3}Mn_{6.7}O_{12}$ around the (440) and (642) cubic Bragg peak positions are shown in (a) and (b), respectively. Solid circles represent measured data and the lines are shown to guide the eye. The patterns measured at different temperatures are shifted vertically for clarity. The short horizontal line indicates the instrumental FWHM estimated with a Si-NIST standard.

The present results can be interpreted in terms of a phase separation between the trigonal, low density, charge-ordered phase and the cubic, high density charge delocalized phase as it was already observed in the undoped $CaMn_7O_{12}$ compound [8].

The SR diffraction patterns of $CaCu_{0.7}Mn_{6.3}O_{12}$ have been analyzed by the Rietveld method by assuming the cubic structure described with the space group Im-3 in agreement with [4,7]. The resulting fits with a cubic structure agree well with the data at all the temperatures down to 10 K.

The present results have been presented at the International School and Symposium on Synchrotron Radiation in Natural Sciences, Jaszowiec, Poland, 17-22 June 2002. It is submitted for publication [9].

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