Experimental report

17/05/2024

Proposal:	**5-31-2948**	**Council:**	10/2022

Title: Crystal and magnetic structures ofthe high pressure double perovskite (Ca0.5Mn0.5)2MnTeO6

Research area: Materials

This proposal is a new proposal

Main proposer: **John Paul ATTFIELD**

Experimental team: Simon KLOSS
Kunlang JI
Yao YUAN

Local contacts: Clemens RITTER

Samples: (Ca0.5Mn0.5)2MnTeO6

Instrument	Requested days	Allocated days	From	To
D20	1	1	19/06/2023	20/06/2023

Abstract:

Perovskite oxides ABO3 have become one of the most interesting classes of materials because of their notable magnetic, electric and optical properties. We recently showed that CaMnMnWO6 can be prepared in both double double perovskite DDPv-CaMnMnWO6 and double perovskite DPv-(Ca0.5Mn0.5)2MnWO6 polymorphs with interesting difference of magnetic properties; DDPv-CaMnMnWO6 is ferrimagnetic with TC = 45 K but Ca/Mn disorder in DPv-(Ca0.5Mn0.5)2MnWO6 gives a spin glass below Tg = 8 K.

We are now investigating possible analogues and we have recently synthesised DPv-(Ca0.5Mn0.5)2MnTeO6 which has ~75 K and ~5 K magnetic anomalies. Powder neutron diffraction is needed to discover whether a spin ordered or glassy ground state is formed as well as for accurate structure refinement. We request 1 day of beamtime at D20 to study the small amount of high pressure sample available.

Experimental report

Proposal: 5-31-2948 **Council: 6/2023**

Title: $(Ca_{0.5}Mn_{0.5})_2MnTeO_6$ – An Anomalously Stable High-Pressure Double perovskite Double Perovskite

Research area: Materials

This proposal is new

Main proposer: John Paul ATTFIELD

Experimental team: Azizah ALMADHI

Kunlang JI

Sean D. INJAC

Local contacts: Clemens RITTER

Instrument	**Request days**	**allocated days**	**From**	**To**
D20	2	2	19/6	20/6

Samples: $CaMnMnTeO_6$

Abstract

Cation ordering at A or B sites of the ABO_3 perovskite structure gives $AA'B_2O_6$ or $A_2BB'O_6$ double perovskites (DPvs) and 1:1 cation ordering at both sites can give $AA'BB'O_6$ double double perovskites (DDPvs). During our high–P,T (HPHT) synthesis studies of Mn-based DPvs and DDPvs, we discovered an anomalous result – that CaMnMnTeO6 gave only a DPv $(Ca_{0.5}Mn_{0.5})_2MnTeO_6$ structure whereas CaMnMnReO6 (where Re is slightly smaller than Te) and CaMnMnWO6 (where W is slightly larger than Te) both gave DDPvs. We hypothesise that significant formation of Te^{4+} occurs under HPHT synthesis conditions - Te^{4+} is unusually large due to lone pair effects and so could favour the DPv structure. In situ XRD experiments on ID06-LVP are requested to observe the structure under HPHT synthesis conditions to test this hypothesis and to discover whether DDPv or intermediate structures are formed during synthesis

$(Ca_{0.5}Mn_{0.5})2MnTeO_6$ – An Anomalously Stable High-Pressure Double Perovskite

Azizah Almadhi, Kunlang Ji, Sean D. Injac, Clemens Ritter, and J. Paul Attfield

Transition metal oxides, and notably those with perovskite and related structures, have many outstanding physical and chemical properties leading to a variety of applications.[1,2] Cation ordering at *A* or *B* sites of the ABO_3 perovskite structure can produce many superstructure types such as $AA'B_2O_6$ and $A_2BB'O_6$ double perovskites (DPvs).[3] 1:1 cation ordering at both sites to give an $AA'BB'O_6$ double double perovskite (DDPv) is rarer but an extensive family of DDPvs has recently been discovered based on the high-pressure stabilization of Mn^{2+} at perovskite *A*-sites.[4] *B*-site manganites are well-known and much studied for magnetoresistance, charge-ordering, and other properties,[5] but high-pressure high-temperature synthesis allows Mn^{2+} to occupy *A*-sites while other magnetic or non-magnetic cations occupy *B*-sites to produce *A*-site manganites with multiple magnetic sublattices.[4] The HPHT $AMnMnB'O_6$ double double perovskite compositions are found to adopt double perovskite structures, written as $(A_{0.5}Mn_{0.5})_2MnB'O_6$ to show that the *A* and Mn^{2+} cations are disordered over perovskite A-sites while Mn/B' retain rock salt type long-range order such as $CaMnMnWO_6$ composition where a fully-ordered DDPv form was recovered from synthesis at 1000 ºC and 10 GPa, while the *A*-site disordered DPv polymorph $(Ca_{0.5}Mn_{0.5})_2MnWO_6$ resulted from treatment at 1600 ºC and 10 GPa[5]. The change from Ca/Mn order to disorder led to an interesting switch of magnetic properties as DDPv-$CaMnMnWO_6$, is ferrimagnetic below $T_C = 45$ K whereas DPv-$(Ca_{0.5}Mn_{0.5})_2MnWO_6$ is highly frustrated with a spin glass freezing temperature $T_g = 8$ K.

A new double perovskite $(Ca_{0.5}Mn_{0.5})_2MnTeO_6$ is obtained by HPHT treatment of the composition $CaMnMnTeO_6$ over the investigated ranges of temperature (550-1250 °C) and pressure (10-15 GPa), with no double double perovskite (DDPv) phase observed. Approximately 80 mg of sample combining several high pressure products in a 3 mm V-foil can be scanned in D20 using $\lambda = 1.54$ Å to provide a precise structural model and for magnetic structure determination. The data collected at 1.6, 45, and 300 K, revealed no magnetic diffraction peaks from DPv-$(Ca_{0.5}Mn_{0.5})_2MnTeO_6$ appear below the spin freezing transition at 5 K, although a diffuse feature is apparent at $2\theta \approx 15$-$30°$ in the 1.6 K profile and a small impurity magnetic peak appears at $2\theta = 25°$ between 300 and 45 K.

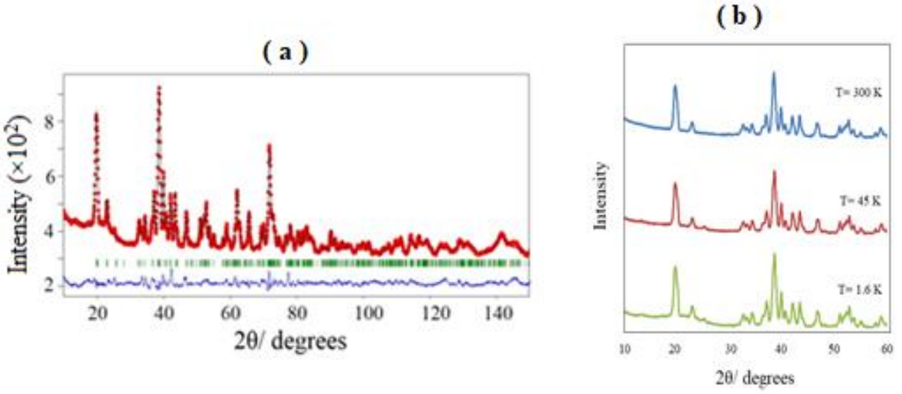

Fig. 1. (a) Rietveld fits against 1.6 K NPD data (b) Low angle NPD data at 1.6, 45, and 300 K

[1] Transition Metal Oxides: Structure, Properties, and Synthesis of Ceramic Oxides, Eds. C. N. R. Rao, B. Raveau, Wiley -VCH, **1998**.

[2] C. N. R. Rao, Perovskites, in Encyclopedia of Physical Science and Technology (Third Edition), Ed. R. A. Mayers, Academic Press**, 2001**.

[3] G. King, P. M. Woodward, *J. Mater. Chem*. **2010**, 20, 5785-5796.

[4] E. Solana-Madruga, A. M. Arévalo-López, *J. Solid State Chem*. **2022**, 315,123470.

[6] J. P. Attfield, *Angew. Chem. Int. Ed*. **2021**, 10, 1002, 8586.