Experimental report

12/08/2021

Proposal: **5-21-1145** **Council:** 10/2019

Title: Nonconvergent cation ordering in spinel-structure $ZnGa_2O_4$ and $(Mg,Zn)Ga_2O_4$

Research area: Materials

This proposal is a new proposal

Main proposer: **Christian HIRSCHLE**

Experimental team: Clemens RITTER
Christian HIRSCHLE

Local contacts: Clemens RITTER

Samples: $ZnGa_2O_4$
$Mg_{0.33}Zn_{0.67}Ga_2O_4$

Instrument	Requested days	Allocated days	From	To
D2B	3	0		
D20	0	2	11/09/2020	13/09/2020

Abstract:

$ZnGa_2O_4$, $MgGa_2O_4$ and their solid solutions are transparent semiconducting oxides with spinel-type structure, which have many advantageous physicochemical properties for technological applications. In $MgGa_2O_4$, we found that the cation order on the two crystallographic sites becomes increasingly random after it is heated above a transition temperature T_c, below which the state of order cannot relax in laboratory timescales, which significantly affects its properties. In contrast to $MgGa_2O_4$, the thermoelastic properties of $ZnGa_2O_4$ suggest that the cations become increasingly ordered above T_c, which is very unusual and requires verification by an independent experimental approach. To investigate this issue and understand the properties of both $ZnGa_2O_4$ and a solid solution, $Mg_{0.33}Zn_{0.67}Ga_{2.00}O_4$, where there are no published data on the cation order as of yet, we plan to use neutron powder diffraction at several temperatures to determine the state of cation order in these materials. Laboratory X-ray techniques are insufficient to tackle this problem due to the extremely similar atomic form factors of Zn^{2+} and Ga^{3+}.

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Nonconvergent cation ordering in spinel-structure $ZnGa_2O_4$ and $(Mg,Zn)Ga_2O_4$

Proposers: Christian Hirschle, Jürgen Schreuer (Ruhr-University Bochum, Germany)
Local contact: Clemens Ritter
Instrument: D20
Allocated days: 2

In this experiment we originally intended to collect 6 neutron powder diffraction patterns of $Zn_{0.98}Ga_{2.02}O_4$ (ZGO) and $Zn_{0.67}Mg_{0.33}Ga_{2.00}O_4$ (ZMGO) each; one measurement at room temperature, 4 measurements at elevated temperatures and another one at room-temperature after the samples cooled down. We planned to perform Rietveld refinements on all the diffraction patterns to determine the cation distribution as a function of temperature.

Due to the COVID-19 pandemic, none of the proposers were physically present at ILL for the experiments; the measurements were performed by the local contact. Data were collected for ZGO at room-temperature (RT), 230 °C, 830 °C, 1030 °C and RT after heating (AH). Data for ZMGO were collected at RT, 230 °C, 780 °C, 880 °C, 780° C AH, 230 °C AH and RT AH. Measurement times were 2 h for measurements on ZGO, except for the measurement at 1030 °C, which only took 30 minutes. In the case of ZMGO, measurement times at RT and 230 °C were 2 hours; at 780 °C, 880 °C and 780 °C AH measurement times were 3 h. Data at 230 °C AH were collected twice, once with 2 h and once with 3 h of measurement time to gauge the influence of the measurement time. Data for RT AH were also collected twice, once for 2 h and once for 7 h. The samples were in a vacuum during the measurements and a neutron wavelength of about 1.065 Å was selected. Data were collected between 0.031 °2θ and 148.731 °2θ.

Unfortunately, both samples were turned out to be unstable in the vacuum at high temperatures, which led to the failure of the heating element during the ZGO measurement cycle. This is the reason for the shorter measurement time at 1030 °C and the comparatively decreased maximum temperatures in the measurement cycle on ZMGO. The sample holder also took damage during the high temperature measurements. The samples likely decomposed above 700 °C and lost oxygen, creating new phases. These new phases appeared as additional diffraction peaks in the measurements on ZGO starting at 830 °C and on ZMGO starting at 780 °C (Fig. 1).

The new phases interfered with the primary purpose of the measurements, that is evaluating the cation order via Rietveld refinements. Thus, only the data at RT and 230 °C could be quantitatively analyzed. The RT data were successfully evaluated and the results were published as part of a larger study [1].

References

[1] Hirschle, C., Schreuer, J., Galazka, Z. and Ritter, C. (2021). On the relation of structural disorder and thermoelastic properties in $ZnGa_2O_4$ and $Zn_{1-x}Mg_xGa_2O_4$ ($x \approx 0.33$). Journal of Alloys and Compounds 886, 161214.

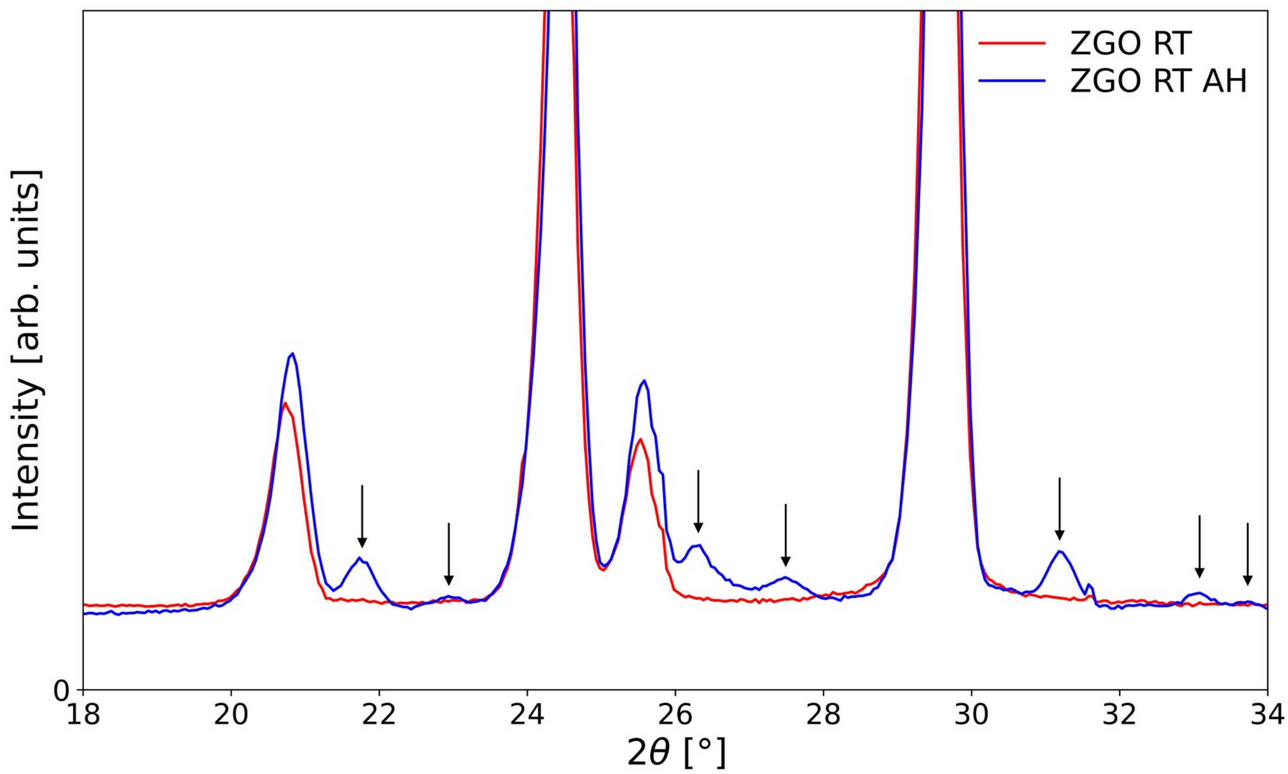

Figure 1: Parts of the diffraction pattern of ZGO at RT and ZGO at RT after heating. Black arrows mark peaks corresponding to secondary phases that appeared during heating in vacuum.