Pressure-induced order–disorder transition in Gd_{1.5}Ce_{0.5}Ti_{2}O_{7} pyrochlore

Jingjing Niu, Xiang Wu, Haibin Zhang and Shan Qin

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Original submission: 1 June 2019
Revised submission: 9 August 2019
Final acceptance: 12 August 2019

Note: Reports are unedited and appear as submitted by the referee. The review history appears in chronological order.

Review History
RSOS-190842.R0 (Original submission)

Review form: Reviewer 1

Is the manuscript scientifically sound in its present form?
Yes

Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No
Recommendation?
Accept with minor revision (please list in comments)

Comments to the Author(s)
In this work, the authors report an experimental study on ordered pyrochlore structured Gd1.5Ce0.5Ti2O7 by synchrotron radiation X-ray diffraction and Raman spectroscopy. An order-disorder transition is observed, and the transition is controlled by cationic order-disorder modification.
This manuscript could be considered for acceptance after a minor revision.
1. To better understand the phase transition behavior, especially the isostructural transitions at lower pressures, the authors could perform some theoretical calculations if possible.
2. The grammatical mistakes and other errors in the manuscript should be carefully revised.

Review form: Reviewer 2 (Chengming Fang)

Is the manuscript scientifically sound in its present form?
Yes

Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Accept as is

Comments to the Author(s)
In the current manuscript Niu and co-workers performed high-pressure experiments for (Gd0.667Ce0.333)2Ti2O7, a pyrochlore. They observed a phase transition at about 45GPa. They also reported two iso-structural transitions at 6.5 GPa and 13 GPa. The topic is interesting for people working in the related fields. The experimental details were described well. The results might be of interest for some people. The measured data were analyzed in a clear way. The manuscript was written concisely. The text is in the scope of the Journal. Therefore I’d like to propose acceptance of this manuscript for publication in Royal Society Open Science.
Decision letter (RSOS-190842.R0)

30-Jul-2019

Dear Dr Niu:

Title: Pressure-Induced Order-Disorder Transition in Gd\(_{1.5}\)Ce\(_{0.5}\)Ti\(_2\)O\(_7\) Pyrochlore

Manuscript ID: RSOS-190842

Thank you for submitting the above manuscript to Royal Society Open Science. On behalf of the Editors and the Royal Society of Chemistry, I am pleased to inform you that your manuscript will be accepted for publication in Royal Society Open Science subject to minor revision in accordance with the referee suggestions. Please find the reviewers' comments at the end of this email.

The reviewers and handling editors have recommended publication, but also suggest some minor revisions to your manuscript. Therefore, I invite you to respond to the comments and revise your manuscript.

Because the schedule for publication is very tight, it is a condition of publication that you submit the revised version of your manuscript before 08-Aug-2019. Please note that the revision deadline will expire at 00.00am on this date. If you do not think you will be able to meet this date please let me know immediately.

To revise your manuscript, log into https://mc.manuscriptcentral.com/rsos and enter your Author Centre, where you will find your manuscript title listed under "Manuscripts with Decisions". Under "Actions," click on "Create a Revision." You will be unable to make your revisions on the originally submitted version of the manuscript. Instead, revise your manuscript and upload a new version through your Author Centre.

When submitting your revised manuscript, you will be able to respond to the comments made by the referees and upload a file "Response to Referees" in "Section 6 - File Upload". You can use this to document any changes you make to the original manuscript. In order to expedite the processing of the revised manuscript, please be as specific as possible in your response to the referees.

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4) Included the raw data to support the claims made in your paper. You can either include your data as electronic supplementary material or upload to a repository and include the relevant doi within your manuscript
5) All supplementary materials accompanying an accepted article will be treated as in their final form. Note that the Royal Society will neither edit nor typeset supplementary material and it will be hosted as provided. Please ensure that the supplementary material includes the paper details where possible (authors, article title, journal name).

Supplementary files will be published alongside the paper on the journal website and posted on
the online figshare repository (https://figshare.com). The heading and legend provided for each supplementary file during the submission process will be used to create the figshare page, so please ensure these are accurate and informative so that your files can be found in searches. Files on figshare will be made available approximately one week before the accompanying article so that the supplementary material can be attributed a unique DOI.

Once again, thank you for submitting your manuscript to Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry. I look forward to receiving your revision. If you have any questions at all, please do not hesitate to get in touch.

Best wishes,
Dr Laura Smith
Publishing Editor, Journals

Royal Society of Chemistry
Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF
Royal Society Open Science - Chemistry Editorial Office

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Mr Andrew Dunn.

RSC Associate Editor:
Comments to the Author:
(There are no comments.)

RSC Subject Editor:
Comments to the Author:
(There are no comments.)

Reviewer comments to Author:
Reviewer: 1
Comments to the Author(s)
In this work, the authors report an experimental study on ordered pyrochlore structured Gd1.5Ce0.5Ti2O7 by synchrotron radiation X-ray diffraction and Raman spectroscopy. An order-disorder transition is observed, and the transition is controlled by cationic order-disorder modification.
This manuscript could be considered for acceptance after a minor revision.
1. To better understand the phase transition behavior, especially the isostructural transitions at lower pressures, the authors could perform some theoretical calculations if possible.
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Reviewer: 2
Comments to the Author(s)
In the current manuscript Niu and co-workers performed high-pressure experiments for (Gd0.667Ce0.333)2Ti2O7, a pyrochlore. They observed a phase transition at about 45GPa. They
also reported two iso-structural transitions at 6.5 GPa and 13 GPa. The topic is interesting for people working in the related fields. The experimental details were described well. The results might be of interest for some people. The measured data were analyzed in a clear way. The manuscript was written concisely. The text is in the scope of the Journal. Therefore I’d like to propose acceptance of this manuscript for publication in Royal Society Open Science.

Author’s Response to Decision Letter for (RSOS-190842.R0)

See Appendix A.

Decision letter (RSOS-190842.R1)

12-Aug-2019

Dear Dr Niu:

Title: Pressure-Induced Order-Disorder Transition in Gd$_{1.5}$Ce$_{0.5}$Ti$_2$O$_7$ Pyrochlore
Manuscript ID: RSOS-190842.R1

It is a pleasure to accept your manuscript in its current form for publication in Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry.

The comments of the reviewer(s) who reviewed your manuscript are included at the end of this email.

Thank you for your fine contribution. On behalf of the Editors of Royal Society Open Science and the Royal Society of Chemistry, I look forward to your continued contributions to the Journal.

Yours sincerely,
Dr Laura Smith
Publishing Editor, Journals

Royal Society of Chemistry
Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF
Royal Society Open Science - Chemistry Editorial Office

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Mr Andrew Dunn.
RSC Associate Editor
Comments to the Author:
The manuscript can now be accepted as is.

Reviewer(s)' Comments to Author:
Dear editor and reviewers,

Thank you for your comments concerning our manuscript entitled “Pressure-Induced Order-Disorder Transition in Gd$_{1.5}$Ce$_{0.5}$Ti$_2$O$_7$ Pyrochlore”. Following the comments, we have made corrections in the new revision. Finally, on behalf of all the authors, I would like to express my gratitude to the editors and the two reviewers.

The point-by-point response:

Referee: 1

1. To better understand the phase transition behavior, especially the isostructural transitions at lower pressures, the authors could perform some theoretical calculations if possible.

Theoretical calculations to reveal the high pressure behavior mechanism of the Gd$_{1.5}$Ce$_{0.5}$Ti$_2$O$_7$ pyrochlore is a challenging topic. However, we are sorry to say that we don’t have enough resources to perform it. The reasons are following: First is the confusing magnetic structure. In Gd$_2$Ti$_2$O$_7$ pyrochlore, because of the topology of the crystal structure, the spins of the Gd$^{3+}$ are geometrically frustrated. The magnetic structure of Gd$_2$Ti$_2$O$_7$ is still a currently active research topic. What’s more, Ce$^{3+}$ replacing Gd$^{3+}$ will doubtfully effect the interaction of Gd$^{3+}$. So to determine the ground state magnetic structure of the Gd$_{1.5}$Ce$_{0.5}$Ti$_2$O$_7$ requires a lot of testing, and there is rarely experimental evidence can be consulted. Second, to perform the calculations on the Gd$_{1.5}$Ce$_{0.5}$Ti$_2$O$_7$ pyrochlore’s high pressure behavior, we lack enough computing resources. The crystal structure of the high pressure stable cotunnite-like phase is a highly disordered structure. Both cations and anions are randomly distributed on 4c positions in the cotunnite-like structures, and 1/8 of the anions are missing. In previous studies (Xiao et al, 2009, Xiao et al, 2010), the structure of the cotunnite-like phase is established by the special quasirandom structure approach by using the Monte-Carl simulated. Unfortunately, we don’t have enough source now. Besides, researchers believe that the similar isostructural transition in Sm$_2$Zr$_2$O$_7$ may be caused by the anion disorder (Zhang et al, 2007), and describing this anion disordered structure also requires a lot of computing resources. So it is hard for us to carry out theoretical calculations for better understand the high pressure behavior of the Gd$_{1.5}$Ce$_{0.5}$Ti$_2$O$_7$, but we have also found that it is an interesting and challenging topic worth carrying out. We will perform the theoretical research in the future.

Appendix A
References:
Xiao, H. Y., Fei Gao, and William J. Weber. "Ab initio investigation of phase stability of Y₂Ti₂O₇ and Y₂Zr₂O₇ under high pressure." Physical Review B 80.21 (2009): 212102.
Xiao, H.Y., et al. "Zirconate pyrochlores under high pressure." Physical Chemistry Chemical Physics 12.39 (2010): 12472-12477.
Zhang, F. X., et al. "Structural distortions and phase transformations in Sm₂Zr₂O₇ pyrochlore at high pressures." Chemical physics letters 441.4-6 (2007): 216-220.

2. The grammatical mistakes and other errors in the manuscript should be carefully revised.
They have been corrected.

P.S.
Jingjing Niu now works in Institute of Tibetan Plateau Research, Chinese Academy of Sciences. So his institution and e-mail address has been changed in the revised manuscript. This change has been agreed by the other co-authors.
We appreciate for Editors and Reviewers’ warm work earnestly, and hope that the correction will meet with approval.
Once again, thank you very much for your comments and suggestions.

Jingjing Niu
Institute of Tibetan Plateau Research, Chinese Academy of Sciences.
Beijing, 100101, P.R.China.