Transport properties of $\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12}$ garnet

Citation for published version (APA):

Oversluizen, G., & Metselaar, R. (1983). Transport properties of $\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12}$ garnet. In R. Metselaar, H. J. M. Heijligers, & J. Schoonman (Eds.), *Proceedings of the 2nd European Conference on Solid State Chemistry in 1982 in Veldhoven (The Netherlands)* (pp. 353-356). (Studies in Inorganic Chemistry; Vol. 3). Elsevier Scientific Publishing Company. <https://doi.org/10.1007/s007750050244>

DOI:

[10.1007/s007750050244](https://doi.org/10.1007/s007750050244)

Document status and date:

Published: 01/01/1983

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

TRANSPORT PROPERTIES OF $\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12}$ GARNET

G. OVERSLUIZEN and R. METSELAAR

Laboratory of Physical Chemistry, Eindhoven University of Technology,
Eindhoven, The Netherlands

ABSTRACT

The results from dc conductivity and thermopower measurements on $\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12}$ single crystals are reported. The charge transport is shown to occur via thermally activated hopping of electrons situated at V^{4+} tetrahedral sites. The importance of correlation effects at higher concentrations is emphasized.

INTRODUCTION

Because of their technological importance ferrimagnetic iron garnets have been widely studied (ref.1). Many of the observed interesting physical properties, including photoinduced changes of the magnetic permeability are due to small amounts of Fe^{2+} ions present on the Fe^{3+} sublattices (ref.2). In this contribution the results of a study of the transport properties of $\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12}$ are reported. A number of V^{4+} centres, analogous to the Fe^{2+} centres in the iron garnets, were introduced by annealing the samples at low oxygen partial pressure.

RESULTS AND DISCUSSION

Single crystals have been grown from PbO and V_2O_5 fluxes. Polycrystalline specimens have been prepared by solid state reaction. The results discussed here refer to single crystals obtained from PbO fluxes. When annealed in air these crystals are transparent and no ESR signal is detected. After annealing at oxygen partial pressures $< 10^{-18}$ atm. at 700°C a double band in the optical absorption spectrum at $\sim 13 \times 10^3 \text{ cm}^{-1}$ and an ESR signal due to an $S = \frac{1}{2}$, $I = 7/2$ isotope in tetragonal symmetry are simultaneously observed. These features have been ascribed to V^{4+} ions at tetrahedral sites (ref.3). The intensity of the ESR signal decreases when the crystals are irradiated with light in the wavelength range corresponding to the double band; the decay time being of the order of several minutes. These observations suggest a light induced transport of the centre through the lattice. No photoconductivity could be detected however in the wavelength range mentioned. An actual study

of the charge transport mechanism is limited to temperatures above room temperature due to the high resistance of the samples. Important information in this respect may be obtained from the combined results of conductivity and thermoelectric power measurements. Because conductivity is determined by the product of the number of charge carriers and their mobility and the thermopower is solely dependent on the number of charge carriers, the mobility can be inferred from such measurements. Figs. 1a,b show schematically the observed behaviour of (dc) conductivity respectively thermopower as a function of inverse temperature for samples containing different concentrations of V^{4+} centres.

Fig. 1a. Conductivity vs inverse temp. b. reduced Seebeck-coefficient vs inverse temp. Increasing numbers correspond to increasing V^{4+} contents.

Inspection of the figures shows that the apparent activation energy corresponding to the slope of the conductivity curves, decreases with increasing concentrations while also at a fixed reduction degree changes occur as a function of temperature. At comparatively low concentrations the thermopower is little temperature dependent. At higher concentrations an increase of α (absolute magnitude) with temperature is observed. Both the conductivity and the thermopower curves tend to converge at higher temperatures. Some additional experiments indicate that measured conductivity and thermopower depend markedly on the thermal history of the samples. The above results clearly demonstrate that band like conduction, where the exponential temperature dependence of the conductivity is due to the generation of charge carriers must be ruled out, since in that case Fig. 1a should

consist of a number of vertically shifted parallel lines whose slope would be reproduced in Fig. 1b. On the other hand a description in terms of independent localized carriers would only account for the observation of temperature independent Seebeck-coefficients as in curves 3 and 4 (see below). Evidently correlation effects must be invoked to explain the above behaviour of conductivity and thermopower as a function of concentration and temperature. In materials where charge transport is attributed to independent localized carriers the thermopower has been shown to be related to the fraction of occupied transport sites by the well known Heikes formula

$$\alpha = \pm 198 \log \{(N-n)/n\} \quad (\mu V/K) \quad (1)$$

where n is the concentration of carriers and N is the concentration of available transport sites. (ref.4).

According to Chaikin et al (ref.5) the high temperature limit for the thermopower of a system of interacting localized carriers is governed entirely by the entropy change per added carrier. In this limit the calculation of this quantity is reduced to a combinatorial problem where the interactions are included by imposing constraints on the number of transport sites available. Essentially the same approach was followed by Goodenough (ref.6) who could successfully explain the thermopower data of vanadium spinels by assuming the formation of V_2 and V_4 clusters and applying the appropriate weighting factors in the determination of N .

A qualitative understanding of the thermopower data reported here may be attained in the same way by assuming an effective number of transport sites. This number increases with increasing temperature corresponding to an increasing Seebeck coefficient. At low temperatures and high concentrations the number of interactions large with respect to thermal energy increases so that eventually the situation $N_{\text{available}} < N_{V^{4+}}$ is attained, explaining the change of sign observed (curve 6). An attempt to interpret the conductivity data using the formula

$$\sigma = \{Nc(1-c)e^2 a^2 \nu / kT\} \exp (-E_H/kT) \quad (2)$$

where a is the smallest V-V separation, $\sim 3.8 \text{ \AA}$, E_H is the hopping energy determined from the slope of the conductivity curve, ν is the lattice vibrational frequency, c is the fraction of V^{4+} on tetrahedral sites calculated by setting $(1-c)/c = (N-n)/n$ with $N = [V_{\text{total}}]$ in Eq. (1) (i.e. neglecting interactions), and other symbols have their usual meaning, yields reasonable values for the vibrational frequency $\nu \sim 10^{13} \text{ s}^{-1}$, in case of curves 3 and 4. A similar calculation for curve 6 however results in $\nu \sim 10^7$ indicating that due to interactions, both the actual concentration of V^{4+} centres and the number of available transport sites must have considerably smaller values than calculated using $N = [V_{\text{total}}]$.

In fact quite probably a distribution of differently situated centres exists and a detailed knowledge of their respective concentrations and mobilities is required before a successful interpretation of the conductivity data $\sigma = \sum c_i \mu_i$ can be made. The existence of such a distribution is further sustained by the occurrence of inhomogeneously broadened ESR resonance lines and observations regarding the photoinduced ESR signal intensity reduction reported elsewhere (ref. 7).

REFERENCES

- 1 R. Metselaar and P.K. Larsen, in A. Paoletti (Ed.), Physics of Magnetic Garnets, North-Holland, New York, 1978, pp. 417-444.
- 2 R. Metselaar in Interaction of Radiation with Condensed Matter, Vol. II, IAEA, Vienna, 1977, pp. 159-221.
- 3 G. Oversluizen and R. Metselaar, accepted J. of Phys. C.
- 4 L.L. van Zandt and J.M. Honig, J. Appl. Phys., 52 (1981) 5625-5632.
- 5 P.M. Chaikin and G. Beni, Phys. Rev., B13 (1976) 647-651.
- 6 J.B. Goodenough, Mat. Res. Bull., 5 (1970) 621-630.
- 7 G. Oversluizen and R. Metselaar, to be published.