



Vibrational and ^{57}Fe -Mössbauer spectra of $\text{LaFeGe}_2\text{O}_7$ and $\text{NdFeGe}_2\text{O}_7$

E.J. Baran^{a,*}, R.C. Mercader^b, C. Cascales^c

^aCentro de Química Inorgánica (CEQUINOR/CONICET, UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. Correo 962, 1900 La Plata, Argentina

^bDepartamento de Física and Instituto IFLP (CONICET), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina

^cInstituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain

Received 31 March 2004; accepted 6 July 2004

Abstract

The infrared, Raman and ^{57}Fe -Mössbauer spectra of $\text{LaFeGe}_2\text{O}_7$ and $\text{NdFeGe}_2\text{O}_7$ were recorded and analysed on the basis of their structural characteristics. Some comparisons with the stoichiometrically related materials containing the heavier lanthanides are made, showing that it is possible to differentiate spectroscopically both groups of materials. The Mössbauer parameters clearly reflect the small structural differences in the FeO_5 -polyhedra present in these compounds.

© 2004 Published by Elsevier Ltd.

Keywords: A. Inorganic compounds; C. Infrared spectroscopy; C. Mössbauer spectroscopy; C. Raman spectroscopy

1. Introduction

Mixed metal germanates of composition $\text{LnFe}^{\text{III}}\text{Ge}_2\text{O}_7$ (Ln = trivalent lanthanide) belong to two different structural types, depending on the size of the lanthanide cation. Materials with the larger lanthanides (La–Gd) adopt the monoclinic $\text{NdAlGe}_2\text{O}_7$ structure type, space group $P2_1/c$, $Z=4$ [1–3]. The smaller lanthanides (Tb–Yb) and yttrium constitute a second isostructural series belonging to the monoclinic space group $P2_1/m$, with $Z=4$ [4].

In a previous paper we have reported the vibrational and ^{57}Fe -Mössbauer spectra of some members of this second series [5]. In order to complete the characterisation of this type of materials we have now performed a similar study for two members of the other group, namely $\text{LaFeGe}_2\text{O}_7$ and $\text{NdFeGe}_2\text{O}_7$.

The structure of these compounds is constituted by chains of edge-sharing flexed LnO_9 -tricapped trigonal prisms, which lie along the a axis, and are linked alternatively through an edge or a corner of isolated distorted FeO_5 trigonal bipyramids in the c direction. The intercalated digermanate groups, Ge_2O_7 , are found

along the [001] direction and present bent Ge–O–Ge bridges.

2. Experimental

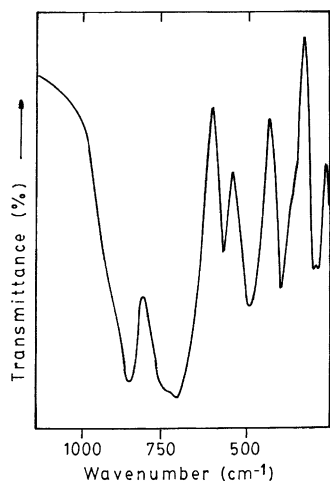
The two investigated compounds were obtained as polycrystalline powders, by standard solid state reactions of stoichiometric mixtures of Fe_2O_3 , Ln_2O_3 and GeO_2 , with this last oxide in a slight excess. Heating was performed in air, using zirconia crucibles, at temperatures about 1200 °C, during a period of 2 weeks with numerous intermediate regrinding. X-ray powder diagrams of the obtained samples confirmed that they were well crystallised and completely free from other phases.

The infrared spectra were recorded with a Bruker IFS 66 FTIR instrument, with the powdered samples dispersed in KBr. A total of 100 scans were accumulated. Raman spectra were obtained with the FRA 106 Raman accessory of the same instrument, using the 1064 nm line of a Nd:YAG solid state laser, for excitation.

Room temperature ^{57}Fe -Mössbauer spectra were taken in a conventional constant acceleration spectrometer of 512 channels with a 15 mCi nominal activity $^{57}\text{Co}/\text{Rh}$ source in transmission geometry. The absorbers were powdered

* Corresponding author. Tel./fax: +54-221-4259485.

E-mail address: baran@quimica.unlp.edu.ar (E.J. Baran).

Fig. 1. FTIR spectrum of NdFeGe₂O₇.

samples of about 15 mg cm² of both compounds. This absorber thickness gives the optimal signal-to-noise ratio, according to the criterion of Long et al. [6]. The spectral parameters were obtained by fitting the data to lines of Lorentzian shapes using a non-linear least-squares program. Isomer shifts are referred to an α -Fe foil at room temperature.

3. Results and discussion

Both materials present very similar IR and Raman patterns. As an example of these spectra, Fig. 1 shows the IR and Fig. 2 the Raman spectra of NdFeGe₂O₇. It is expected that in the higher energy region the vibrations of the Ge₂O₇-moieties essentially dominate the spectra, whereas motions related to the other two metal-oxygen-polyhedra should lie at lower energies.

The proposed vibrational assignments are given in Table 1 and briefly discussed as follows:

- As expected for bent Ge–O–Ge bridges, both bridge vibrations are IR and Raman active [7–9] and they were assigned following the results of Tarte and co-workers,

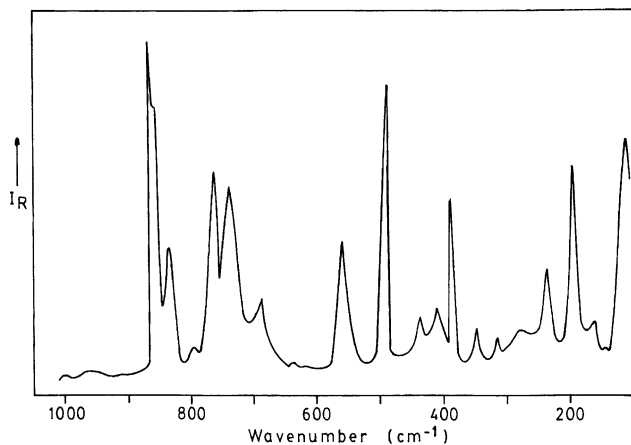
Fig. 2. Raman spectrum of NdFeGe₂O₇.

Table 1
Assignment of the IR and Raman spectra of LaFeGe₂O₇ and NdFeGe₂O₇ (band positions in cm⁻¹)

LaFeGe ₂ O ₇		NdFeGe ₂ O ₇		Assignment
IR	Raman	IR	Raman	
850 vs	867 vs, 852 vs	850 vs	872 vs, 861 sh	$\nu_{as}(\text{Ge-O-Ge})$
–	837 w	–	834 m	$\nu_s(\text{GeO}_3)$
750 sh,	760 vs, 734 s,	760 sh,	798 sh, 766 s,	$\nu_{as}(\text{GeO}_3)$
710 vs	708 m, 690 m	710 vs	735 s, 688 w	
563 m	548 m	571 m	553 m	$\nu_s(\text{Ge-O-Ge})$
488 s	468 sh, 483 vs	492 s	490 vs	$\delta_{as}(\text{GeO}_3)$
388 m,	435 w, 412 m,	397 s,	443 w, 417 w,	$\delta_s(\text{GeO}_3)$
359 w	385 s	372 sh	392 s	
	355 w, 320 m		350 w, 319 w	
291 m,	305 w, 275 m	304 m,	277 w	See text
280 sh		285 m		
	233vs, 201 vs,		237 m, 199 s,	
	190 s, 157 m		165 w	
	115 vs		118 vs	

vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

based on isotopic data [10,11]. Both vibrations are found at slightly lower energies than those measured for the series containing the heavier lanthanides [5] although the energy difference between the two vibrations is approximately the same, suggesting comparable bridge angles [9] in both series. The splitting observed for the $\nu_{as}(\text{Ge-O-Ge})$ vibration in the Raman spectrum is probably originated in correlation field effects. The deformational modes of the bridges are difficult to identify. They surely lie below 200 cm⁻¹ [7,9].

- The symmetric stretching vibration of the terminal GeO₃ groups is not observed in the IR spectra in which it, apparently, does not attain enough intensity. On the other hand, the antisymmetric mode appears splitted in a number of components, especially in the Raman spectrum. This is in agreement with the low site symmetry of the anion but also with the fact that the two GeO₃ units of the digermanate groups have different environments in the crystal lattice [1]. Besides, the present results confirm

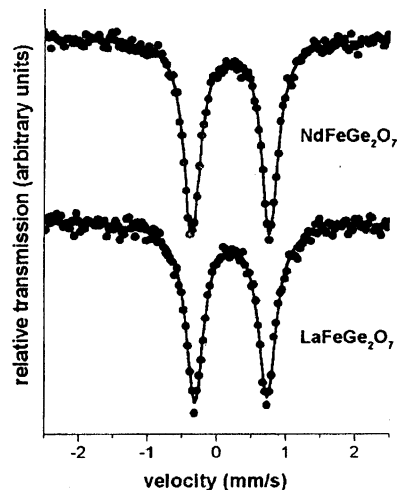
Fig. 3. ⁵⁷Fe-Mössbauer spectra of LaFeGe₂O₇ and NdFeGe₂O₇.

Table 2
Mössbauer parameters of the two investigated materials

Material	Δ (mm s ⁻¹)	δ (mm s ⁻¹)	Γ (mm s ⁻¹)
LaFeGe ₂ O ₇	1.05 ± 0.01	0.32 ± 0.01	0.31 ± 0.01
NdFeGe ₂ O ₇	1.13 ± 0.01	0.31 ± 0.01	0.29 ± 0.01

once again the fact that the symmetric stretching mode of these terminal groups lies higher than the antisymmetric one (cf. also Refs. [5,12]).

- In the frequency region below 500 cm⁻¹ the assignment is much more difficult because in this region one expects not only internal vibrations of the Ge₂O₇ groups but also motions related to the LnO₉- and FeO₅-polyhedra. Probably, most of the bands observed in this region are related to these polyhedra [5]. Notwithstanding, and based on intensity criteria, the two deformational modes of the GeO₃ groups have tentatively been assigned, although these vibrations are probably not longer 'pure' Ge₂O₇ modes. On the other hand, vibrations measured below 200 cm⁻¹ are essentially related to external (lattice) vibrations.

Finally, a comparison of the spectral data of both compounds shows that some of the bands are slightly displaced to higher wavenumbers as the unit cell dimensions decrease from La(III) to Nd(III). This is the usually expected trend for two isostructural compounds of this type, and is related to the reinforcement of the Ge–O bonds, which parallels the diminution of the unit cell dimensions (cf. also Refs. [5,13,14]).

The ⁵⁷Fe-Mössbauer spectra of LaFeGe₂O₇ and NdFeGe₂O₇ are shown in Fig. 3. The obtained data can be fitted to only one quadrupole split doublet. The results of these fittings are shown in Table 2.

Both materials exhibit almost identical isomer shifts belonging to the Fe(III) cations. The values observed for the quadrupole splittings are relatively large but are in agreement with the presence of the FeO₅ trigonal bipyramidal environment of the high-spin Fe(III) cations [15]. The somewhat higher Δ -value observed in the case of the neodymium compound suggests a slightly higher degree of distortion of the FeO₅ units in this case. This fact is in excellent agreement with the structural behaviour of this type of materials, in which the M^{III}O₅-polyhedra becomes increasingly distorted with the diminution of the Ln(III) size [1].

The isomer shifts of these materials are smaller and the quadrupole splittings larger than those measured previously for the similar compounds, containing the smaller lanthanide cations [5]. This behaviour is in agreement with the existence of different Fe(III) environments in both groups of materials, i.e. FeO₅-moieties in the present case, and FeO₆-units in the formerly investigated ones. It has been demonstrated that, for a given oxidation state and for identical ligands, a decrease of the iron coordination number leads to a decrease of the isomer shift [15]. On the other hand, the increase of

the quadrupole splitting may be related to the symmetry diminution in the case of the FeO₅-moieties.

4. Conclusions

The detailed analysis of the IR and Raman spectra of LaFeGe₂O₇ and NdFeGe₂O₇ are in excellent agreement with the structural characteristics of these isostructural materials. On the other hand, the results also show that it is possible to differentiate spectroscopically this group of materials, involving the larger lanthanides, from the other one, derived from the smaller lanthanides and belonging to a different structural type.

Also the Mössbauer parameters are in good agreement with the structural peculiarities related to the Fe(III) environment, which is slightly different in both investigated compounds. They also allow interesting comparisons of the behaviour of the FeO₅-polyhedra found in the present materials and that of the FeO₆-polyhedra which build up the structure of the previously investigated LnFeGe₂O₇ compounds, containing the smaller lanthanides.

Acknowledgements

This work was supported by the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina. E.J.B. and R.C.M. are members of the Research Career from this organisation.

References

- [1] A.A. Kaminski, B.V. Mill, A.V. Butashin, E.L. Belkoneva, K. Kurbanov, Phys. Status Solidi A 103 (1987) 575.
- [2] K. Jarchov, K.H. Klaska, H. Schenk-Strauss, Z. Kristallogr. 172 (1985) 159.
- [3] L. Bucio, C. Cascales, J.A. Alonso, I. Rasines, J. Phys. Condens. Matter 8 (1996) 2641.
- [4] C. Cascales, L. Bucio, E. Gutiérrez-Puebla, I. Rasines, Phys. Rev. B 57 (1998) 5240.
- [5] E.J. Baran, C. Cascales, R.C. Mercader, Spectrochim. Acta A 56 (2000) 1277.
- [6] G.J. Long, T.E. Cranshaw, G. Longworth, Mössbauer Effect Refer. Data J. 6 (1983) 42.
- [7] S.D. Ross, Inorganic Infrared and Raman Spectra, McGraw Hill, London, 1972.
- [8] B. Jezowska-Trzebiatowska, Pure Appl. Chem. 27 (1971) 89.
- [9] E.J. Baran, I.L. Botto, J.C. Pedregosa, P.J. Aymonino, Monatsh. Chem. 109 (1978) 41.
- [10] P. Tarte, M.J. Pottier, M.C. Procés, Spectrochim. Acta A 29 (1973) 1017.
- [11] M. Gabelica-Robert, P. Tarte, Spectrochim. Acta A 35 (1979) 649.
- [12] R. Sáez-Puche, M. Bijkerk, F. Fernández, E.J. Baran, I.L. Botto, J. Alloys Compd. 184 (1992) 25.
- [13] E.J. Baran, C.C. Wagner, A.E. Lavat, C. Cascales, J. Raman Spectrosc. 28 (1997) 927.
- [14] A.E. Lavat, E.J. Baran, R. Sáez-Puche, A. Salinas-Sánchez, M.J. Martín-Llorente, Vib. Spectrosc. 3 (1992) 291.
- [15] F. Menil, J. Phys. Chem. Solids 46 (1985) 763.