ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 353–355

Journal of ALLOYS AND COMPOUNDS

Optical crystal field study of Sm_2O_3 (C- and B-type)

J.-F. Martel[a,*], S. Jandl[a], A.M. Lejus[b], B. Viana[b], D. Vivien[b]

[a]*Centre de Recherche en Physique du Solide, Département de Physique, Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada*
[b]*Laboratoire de Chimie Appliquée de l'État Solide, ENSCP, 11 rue P.M. Curie, 75231 Paris Cédex 05, France*

Abstract

Raman scattering, absorption and photoluminescence measurements were performed on B-type (single crystals and polycrystalline powders) and C-type (polycrystalline powders) Sm_2O_3 as a function of temperature. A Raman active crystal field excitation has been observed in the C-type and Sm^{3+} ion crystal-field levels $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, $^6H_{11/2}$, $^4G_{5/2}$ have been detected in both types. © 1998 Elsevier Science S.A.

Keywords: Samarium; Crystal field; Optical spectroscopies

---

1. Introduction

The electronic energy states of the 4f (RE) compounds have become a subject of growing interest because of their diverse transport, magnetic and optical properties [1–3]. Optical spectroscopies: Raman scattering, absorption and photoluminescence measurements provide a powerful tool to probe local electric and magnetic properties as reported recently for the $(RE)_2CuO_4$-type high T_c superconductors [4,5]. While transport and magnetic properties of the samarium sesquioxides Sm_2O_3 are well know, crystal field (CF) excitations of their Sm^{3+} ions in these compounds have been less studied.

Sm_2O_3 crystallizes in five different polymorphic modifications [6] which are labeled: A, H (hexagonal), B (monoclinic) and C, X (cubic). Our study focuses on the B- and C-type structures. Sm_2O_3 crystallizes essentially in these two phases that are stable at room temperature. The purpose of this paper is to detect and to compare B- and C-type phonons and CF excitations and to correlate them with the Sm^{3+} ion site symmetry. B-type single crystals of Sm_2O_3 (C^3_{2h} space group with three equally occupied Sm^{3+} site of symmetry C_s) grown by the Verneuil process [7] and C-type (bixbyite) pellets of Sm_2O_3 (T^7_h space group with two different site symmetries and occupation rates: $S_6(1/4)$ and $C_2(3/4)$ were used in Raman scattering, absorption and photoluminescence measurements. Because of the C-type hygroscopic character, the pellets were heated at 900°C for 4 days and, in order to measure their optical transmission, they were mixed with 95% KBr powder. They were also reheated at 1100°C for 24 h so that the C-type→B-type phase transition could be realized.

2. Experimental

Temperature-dependent Raman active phonon and luminescence CF spectra (20–300 K), of 1 cm^{-1} resolution in the 50–1200- and 9000–21 000-cm^{-1} ranges, respectively, were obtained using the 514.5-, 488-, and 476.5-nm (Ar) and the 647.1-nm (Kr) laser lines with a double monochromator and conventional photon counting system. Temperature-dependent transmission CF spectra (4.2–300 K), of 1 cm^{-1} resolution in the 350–21 000-cm^{-1} range, were obtained using a Bomem DA3 Fourier interferometer and various beamsplitters (KBr, CaF2, Quartz) and detectors (Ge:Cu, InSb, Si).

3. Results and discussion

Raman active phonons spectra of both structures (Fig. 1a–c) confirm previous published results [8,9]. Moreover, 19 of the 22 and 18 of the 21 Raman active modes, predicted by group theory for the C- and B-type, are observed, respectively (Fig. 1a,b). Transition from C- to B-type structure (around 850°C), following heat treatment,

---

[*] Corresponding author.

PII: S0925-8388(98)00338-7

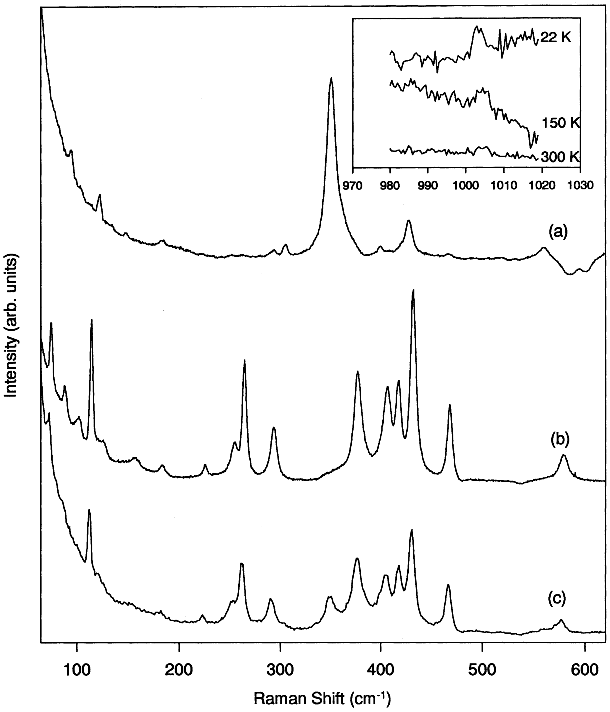

Fig. 1. Raman active phonon spectra of Sm_2O_3 excited with the 514.5-nm laser line for C-type polycrystalline powder (a), B-type single crystal (b) and B-type polycrystalline powder (c). Inset: Raman active CF excitation of the C-type at different temperatures.

is evidenced in Fig. 1c. Phonon widths in the B-type pellet and B-type single crystal are practically equal, thus indicating the absence of additional processes that limit the phonon lifetime in the pellet. A Raman active CF excitation around 1004 cm^{-1} is also observed (inset of Fig. 1) in the C-type but not in the B-type. Both argon and krypton laser lines were used to discriminate it from luminescence. It is associated with the S_6 site symmetry since CF excitations of ions in the C_2 site symmetry should be very close to the ones in the B-type due to their environment similarities. Such observation indicates that CF excitation Raman activity is not necessarily forbidden when the ion is located in a site with an inversion center of symmetry.

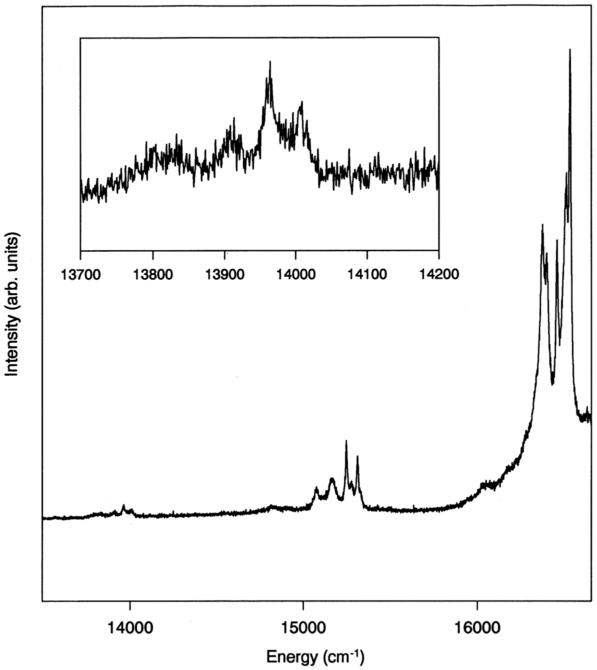

Fig. 2. Photoluminescence spectra of the B-type single crystal, at 22 K, excited with a 488-nm laser line. The 13 700–16 600-cm^{-1} range corresponds to transitions between $^4G_{5/2}$ and the first three excited multiplets. Inset: intensified $^4G_{5/2}\rightarrow{}^6H_{11/2}$ transition.

A luminescence spectrum of the B-type single crystal excited with a 488-nm Ar laser line is shown in Fig. 2. This spectrum is obtained out of resonance and is identical to the one excited with the 514.5-nm Ar laser line. The frequency ranges 16 300–16 600, 15 000-15 400 and 13 700–14 200 cm^{-1} correspond to the $^4G_{5/2}\rightarrow{}^6H_{7/2}$, $^4G_{5/2}\rightarrow{}^6H_{9/2}$ and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ transitions, respectively. A strong luminescence is associated with the $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition and contrast with the $^4G_{5/2}\rightarrow{}^6H_{9/2}$ and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ oscillator strength weakness. Another transition $^4G_{5/2}\rightarrow{}^6H_{5/2}$, from the emitting level towards the ground state, is not observed since, at high Sm^{3+} concentration, reabsorption is the dominant process. In Fig. 3, the frequency range of the laser transition ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) in the B- and C-type is presented. While B-type luminescence is characterized by emission lines, C-type exhibits a broad band luminescence, of unknown origin, in which reabsorption dominates. The reabsorption occurs as dips in the broad emission feature.

In Fig. 4, absorption spectra in the frequency range of

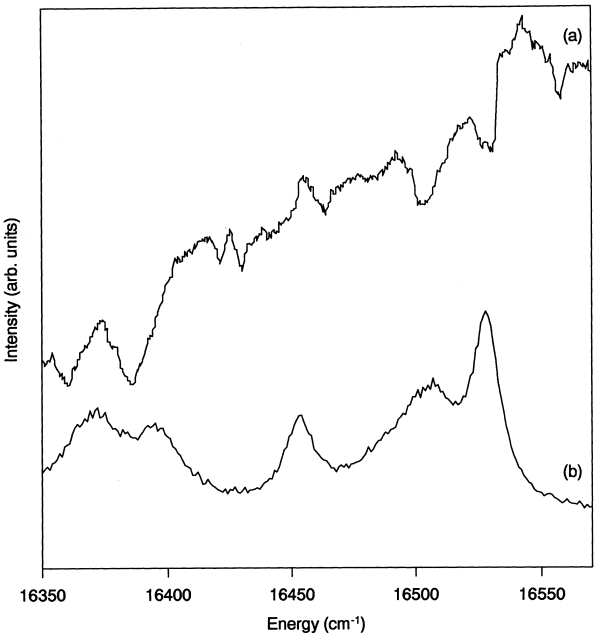

Fig. 3. Luminescence spectra of Sm_2O_3, at 22 K, excited with a 488-nm laser line in the 16 350–16 600-cm^{-1} range for C-type polycrystalline powder (a) and B-type polycrystalline powder (b).

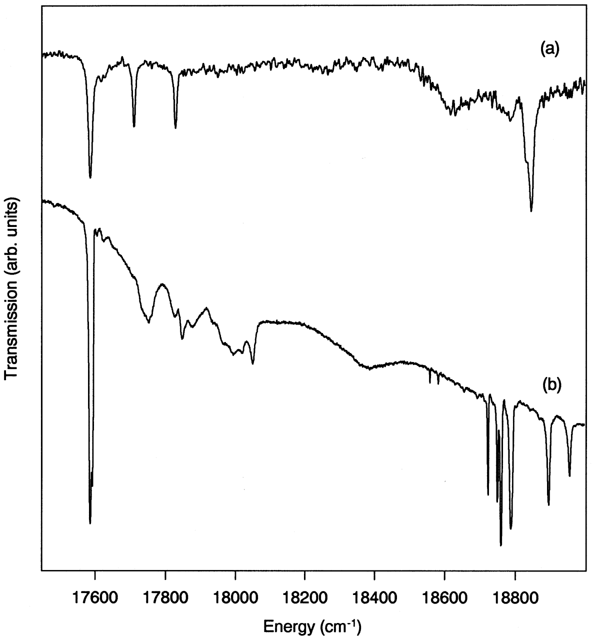

Fig. 4. Absorption spectra of Sm_2O_3 at 4.2 K for C-type polycrystalline powder (a) and B-type single crystal (b). The 17 500–19 000-cm^{-1} range corresponds to the $^4G_{5/2}$ and $^4F_{3/2}$ multiplets.

Table 1
Crystal field energy levels of Sm^{3+} in B- and C-type Sm_2O_3

	Energy level (cm^{-1})		
	B-type	C-type	
		C_2	S_6
$^6H_{7/2}$			1004
	1063	1058	
	1083		
	1096	1090	
			1126
	1139		
	1186	1183	
			1199
	1216		
	1254		
	1298	1304	
	1318		
			1334
	1431		
	1547		
	1629		
$^4G_{5/2}$	17 587		
	17 593	17 588	
			17 601
			17 702
			17 712
		17 731	
	17 824	17 828	
	17 848	17 841	
	17 875		
	17 994		
	18 020		
	18 049		

the $^4G_{5/2}$ (emitting level of the laser transition) and $^4F_{3/2}$ multiplets are presented for the B- and C-types. A direct correlation between the absorptions and their sites of origin is impossible when based only on the intensity. However, due to the environment similarities between one (considering Sm–O distance) of the C_s site symmetry (in the B-type) and the C_2 site symmetry (in the C-type), it is possible to distinguish two sets of levels in the C-type.

Associating luminescence with absorption at $T=4.2$ K allowed the determination of Sm^{3+} $^6H_{7/2}$, $^6H_{9/2}$, $^6H_{11/2}$ and $^4G_{5/2}$ CF levels in both polytypes. In Table 1, the energy levels of the $^6H_{5/2}$ and the $^4G_{5/2}$ multiplets are given with two different sets of levels presented for the cubic phase.

4. Conclusion

In conclusion, we have performed temperature-dependent Raman scattering, absorption and photoluminescence measurements on two polymorphic modifications (B- and C-type) of Sm_2O_3. Photoluminescence spectra demonstrate the strength of the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition, while light emission dominates in the B-type and strong re-absorption in the C-type. A Raman active CF excitation has also been observed around 1004 cm^{-1}, in the C-type, and associated with the S_6 site symmetry.

Acknowledgements

NATO exchange program NSERC and FCAR are acknowledged for their financial support.

References

[1] A.A. Kaminskii, Crystalline Lasers: Physical Processes and Operating Schemes, CRC Press, Boca Raton, FL, 1996.
[2] F.S. Ermeneux, C. Goutaudier, R. Moncorgé, M.T. Cohen-Adad, OSA TOPS Advanced Solid State Lasers 10 (1997) 476.
[3] N.C. Chang, J.B. Gruber, R.P. Leavitt, C.A. Morrison, J. Chem. Phys. 16 (1982) 3877.
[4] S. Jandl, P. Dufour, T. Strach, T. Ruf, M. Cardona, V. Nekvasil, C. Chen, B.M. Wanklyn, Phys. Rev. B 52 (1995) 15558.
[5] S. Jandl, P. Dufour, T. Strach, T. Ruf, M. Cardona, V. Nekvasil, C. Chen, B.M. Wanklyn, S. Piñol, Phys. Rev. B 53 (1996) 8632.
[6] A.M. Lejus, R. Collongues, in: E. Kaldis (Ed.), Current Topics in Materials Science, vol. 4, ch. 9, 1980.
[7] A.M. Lejus, J.-P. Connan, Rev. Int. Htes Temp. Réfract. II (1974) 215.
[8] W.B. White, V.G. Keramidas, Spectrochim. Acta 28A (1972) 501.
[9] J. Gouteron, D. Michel, A.M. Lejus, J. Zarembowitch, J. Solid State Chem. 38 (1981) 288.