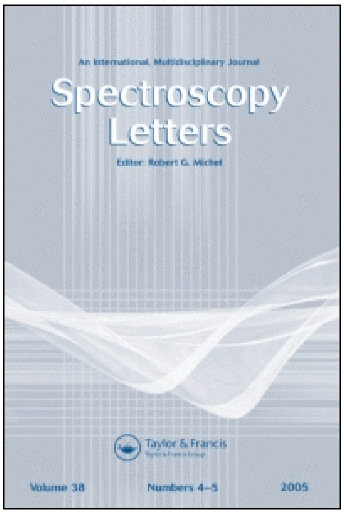

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A Raman Spectral Study of Lanthanide Oxybromides

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A RAMAN SPECTRAL STUDY OF LANTHANIDE OXYBROMIDES

Key Words: Raman spectrum, Band assignment, Lanthanide oxybromide

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ABSTRACT

The Raman active vibrational fundamentals of lanthanide oxybromides, LnOBr, where Ln = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, Yb and Lu, have been reported in solid phase and the observed data have been analyzed by comparison with those of the oxychlorides on the basis of the results of factor group analysis.

INTRODUCTION

Previously Basile *et al.*[1] have reported the infrared spectra of lanthanide oxychlorides and oxybromides, LnOCl and LnOBr, and assigned the observed bands taking into account the results of the factor group analysis and the wavenumber shifts of the fundamental vibrations. Using these infrared spectral data, Hase *et al.*[2] have shown that the fundamental wavenumber shifts from LnOCl to LnOBr can be easily explained in terms of the kinetic mass effects only. This fact indicates that the potential energy terms may be considered to be almost the same between LnOCl and LnOBr. Recently, the Raman active vibrational fundamentals have been studied for LnOCl and normal coordinate calculations have been carried out to confirm the vibrational assignment and to obtain the force constants.[3]

In this paper we report the Raman spectra of polycrystalline lanthanide oxybromides and the observed spectral data are discussed by comparison with those for LnOCl.

EXPERIMENTAL

LnOBr, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, were prepared using the method described in the literature[4] and the purities were examined by elemental analyses for Ln and Br. CeOBr and PmOBr are not treated in the present Raman study. The Raman spectra of the powder samples were recorded in the region 1000-80 cm^{-1} on a Jarrell-Ash Model 25-300 spectrometer. Most of the observed spectra showed the complicated fluorescence bands due to certain Ln^{+3} or impurity Ln^{+2} in addition to the Raman bands. Therefore, the Raman bands for LnOBr were found out by comparing the Raman spectra measured using the excitation lines of 476.5, 488.0 and 514.5 nm of an argon ion laser and of 647.1 nm of a krypton ion laser. For TbOBr and ErOBr these treatments were not effective and the Raman bands were not found out. The observed fundamentals are summarized in Table 1.

RESULTS AND DISCUSSION

The X-ray structural analysis showed that all the lanthanide oxybromides crystallize into a tetragonal PbFCl type lattice of space group $D_{4h}^{7} \equiv P4/nmm$ and the primitive unit cell contains two formula units.[5,6] Consequently, the structure of the reduced representation of the 15 normal modes of vibration is found to be

$$\Gamma = 2A_{1g} + 1B_{1g} + 3E_{g} + 2A_{2u} + 2E_{u},$$

in which the vibrations of A_{1g}, B_{1g} and E_g species are Raman active and those of A_{2u} and E_u species are infrared active.

According to the normal coordinate calculations for LnOCl,[3] the vibrational modes of two A_{1g} fundamentals are the coupling ones between the lanthanide site and halogen site translations and the band positions for LnOBr are expected below 200 cm^{-1}. Since it is well known that the totally symmetric vibrations are

TABLE 1

Observed Raman active fundamental wavenumbers (in cm^{-1}) for lanthanide oxybromides LnOBr

	$\nu_1(A_{1g})$	$\nu_2(A_{1g})$	$\nu_3(B_{1g})$	$\nu_4(E_g)$	$\nu_5(E_g)$	$\nu_6(E_g)$
La	128	110	330	430	182	(48)
Ce						
Pr	125	108	340	448	185	(48)
Nd	126	105	350	465	193	(48)
Pm						
Sm	125	105	350	497	195	(48)
Eu	125	104	355	500	215,195	(48)
Gd	124	104	373	522	220	(48)
Tb						
Dy	121	103	380	540	222	(45)
Ho	119	102	382	535	220	(45)
Er						
Tm	120	102	384	500	220	(44)
Yb	118	102	402,382	-	221	(43)
Lu	118	100	388	490	218	(43)

Values in parentheses were estimated from overtones (see text).

relatively intense in the Raman spectrum, the band at 128-118 cm^{-1} is assigned directly to A_{1g} fundamental. Two Raman bands are further observed in the wavenumber region below 200 cm^{-1}. The wavenumbers for these two weak intensity bands are 110-100 cm^{-1} and 96-85 cm^{-1}. As previously discussed on the infrared active fundamentals,[2] the potential energy terms for LnOCl and LnOBr can be considered to be almost the same and therefore the product rule[7] seems to be applicable to find out the remained A_{1g} fundamental. The calculated band position is about 115 cm^{-1} and the Raman band at 110-100 cm^{-1} is tentatively assigned to this A_{1g} fundamental.

Since the B_{1g} fundamental is the oxygen site translation, the band observed at 402-330 cm^{-1} is easily assigned by comparison with that for LnOCl at 384-335 cm^{-1}.

There are three Raman bands not assigned above. The band positions are 540-430 cm^{-1}, 222-182 cm^{-1} and 96-85 cm^{-1}. The two high wavenumber bands at 540-430 cm^{-1} and 222-182 cm^{-1} are comparable with the bands of LnOCl at 526-440 cm^{-1} and 236-190 cm^{-1}, respectively, and are assigned undoubtedly to E_g fundamentals. On the other hand, the band at 96-85 cm^{-1} is unreasonably high by comparing with the band at ~70 cm^{-1} for LnOCl. When the Teller-Redlich type product rule is also applied for E_g fundamentals, the band position of the last fundamental is expected at about 55 cm^{-1}. Here, the Raman band found at 96-85 cm^{-1} is assigned to the overtone of the lowest wavenumber band and the fundamental band can be estimated to be about 45 cm^{-1}.

Thus, the Raman spectral data of LnOBr could be analyzed completely and the effectiveness of the use of the product rule was also confirmed between the fundamentals of LnOCl and LnOBr.

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