

VIBRATIONAL AND ELECTRONIC SPECTRA AND CRYSTAL STRUCTURE OF CUBIC Na_3NbO_4

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ABSTRACT

The infrared, Raman and luminescence spectra of cubic Na_3NbO_4 are reported. From this we conclude that the structure is that of rocksalt with a more or less disordered distribution of the Na^+ and Nb^{5+} ions among the cation sites.

Introduction

Recently Barker and Wood (1) have described a procedure to obtain the cubic modification of Na_3NbO_4 and Na_3TaO_4 in a pure form. The lattice parameters were 4.61 Å. The structure was described as a superstructure of rocksalt with Ta (or Nb) on the corners of the unit cell and Na on the remaining cation sites. This means that the skeleton of the tantalate (niobate) octahedra is the same as in the perovskites NaTaO_3 and NaNbO_3 , although the distances are shorter in the latter case (cubic parameter ~ 4.0 Å, if distortions are neglected). In view of this analogy and in the course of our investigations on oxidic niobates it seemed interesting to study the vibrational and electronic spectra of the cubic modification of Na_3NbO_4 .

Experimental

The performance of the vibrational spectra has been described before (2). The luminescence spectra were measured on a Hitachi spectrofluorimeter MPF-2A. The diffuse reflection spectra were measured on a Perkin-Elmer spectrophotometer EPI-G3. The samples were prepared as described in ref. 1.

They were checked by X-ray diffraction. The powder pattern is that of rocksalt without any evidence of ordering reflections.

Results

Vibrational spectra. The infrared spectrum (down to 400 cm^{-1}) contains four bands of about equal intensity at 850, 700, 525, and 415 cm^{-1} . An identical spectrum has been observed for K_3NbO_4 (3). The Raman spectrum consists of one broad band peaking at about 800 cm^{-1} (halfwidth about 50 cm^{-1}). No other lines were observed, but they may have been drowned in the noise if they are as broad as the 800 cm^{-1} band.

Electronic spectra. From the diffuse reflection spectrum of Na_3NbO_4 the absorption edge is found at about 250 nm. Under short wavelength ultraviolet excitation Na_3NbO_4 shows a bright deep-blue luminescence at 77 K and at 300 K. The emission band peaks at 390 nm at 300 K. The excitation spectrum of this emission consists of a broad band peaking at 250 nm at 300 K and at 230 nm at 77 K.

Discussion

As mentioned above our aim was to compare the spectra of NaNbO_3 and Na_3NbO_4 in view of their structural resemblance as far as the niobate octahedra are concerned. This comparison shows a complete disagreement:

- a. the absorption edge of Na_3NbO_4 is at 250 nm, that of NaNbO_3 at 320 nm (4);
- b. NaNbO_3 does not show luminescence down to 77 K;
- c. NaNbO_3 shows strong infrared absorption bands at 675 and 375 cm^{-1} (5, 6), and a strong Raman line at about 600 cm^{-1} (6).

Especially the latter point is important. It has been shown that corner-sharing niobate octahedra show strong Raman shifts around 600 cm^{-1} , and infrared absorption in the regions around 650 and 375 cm^{-1} (6). The vibrational spectra observed for Na_3NbO_4 are not of this type. They indicate edge or face sharing of the niobate octahedra in view of the strong Raman shift at about 800 cm^{-1} , and the strong infrared bands far above 650 cm^{-1} (6).

From this we conclude that the structure proposal of Barker and Wood (1) is incorrect. The spectra of cubic Na_3NbO_4 show a much stronger resemblance with those of Li_3NbO_4 which has ordered rocksalt structure (7).

- a. Li_3NbO_4 has its absorption edge at 240 nm (8), Na_3NbO_4 at 250 nm;
- b. Li_3NbO_4 shows efficient luminescence with an emission peaking at 375 nm

(8) (Na_3NbO_4 at 390 nm). The Stokes shift is equal for both compounds; c. Li_3NbO_4 shows no strong Raman lines in the 600 cm^{-1} region, but in the 800 cm^{-1} region (6). Further it shows infrared absorption bands at 860, 780, 685, 575, and 450 cm^{-1} (6).

From this we conclude that the structure of the cubic modification of Na_3NbO_4 is that of rocksalt with a more or less disordered distribution of the Na^+ and Nb^{5+} ions among the cation sites in such a way that edge sharing of niobate octahedra prevails. In the structure of Li_3NbO_4 the niobate octahedra are connected by edge sharing only. Especially the broad Raman line is strong evidence for the disorder. The structure proposed by Barker and Wood is improbable anyway, because there are other superstructures in the rocksalt lattice with lower lattice energy (7). Perhaps the other Na_3NbO_4 (Na_3TaO_4) modifications described in the literature are the long-range ordered forms (1, 9) but it is difficult to obtain these completely pure.

These spectral data exclude a truly random distribution of Nb and Na, because in that case no first order Raman spectrum and only one infrared band is expected.

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