

VIBRATIONAL AND ELECTRONIC SPECTRA AND CRYSTAL STRUCTURE OF CUBIC  $\text{Na}_3\text{NbO}_4$

G. Blasse and G.P.M. van den Heuvel  
Solid State Chemistry Department, Physical Laboratory, State University,  
Sorbonnelaan 4, UTRECHT - The Netherlands.

(Received June 27, 1972 and in final form August 8, 1972; Refereed)

ABSTRACT

The infrared, Raman and luminescence spectra of cubic  $\text{Na}_3\text{NbO}_4$  are reported. From this we conclude that the structure is that of rocksalt with a more or less disordered distribution of the  $\text{Na}^+$  and  $\text{Nb}^{5+}$  ions among the cation sites.

Introduction

Recently Barker and Wood (1) have described a procedure to obtain the cubic modification of  $\text{Na}_3\text{NbO}_4$  and  $\text{Na}_3\text{TaO}_4$  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  $\text{NaTaO}_3$  and  $\text{NaNbO}_3$ , although the distances are shorter in the latter case (cubic parameter  $\sim 4.0$  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  $\text{Na}_3\text{NbO}_4$ .

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  $400\text{ cm}^{-1}$ ) contains four bands of about equal intensity at 850, 700, 525, and  $415\text{ cm}^{-1}$ . An identical spectrum has been observed for  $\text{K}_3\text{NbO}_4$  (3). The Raman spectrum consists of one broad band peaking at about  $800\text{ cm}^{-1}$  (halfwidth about  $50\text{ cm}^{-1}$ ). No other lines were observed, but they may have been drowned in the noise if they are as broad as the  $800\text{ cm}^{-1}$  band.

Electronic spectra. From the diffuse reflection spectrum of  $\text{Na}_3\text{NbO}_4$  the absorption edge is found at about 250 nm. Under short wavelength ultraviolet excitation  $\text{Na}_3\text{NbO}_4$  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  $\text{NaNbO}_3$  and  $\text{Na}_3\text{NbO}_4$  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  $\text{Na}_3\text{NbO}_4$  is at 250 nm, that of  $\text{NaNbO}_3$  at 320 nm (4);
- b.  $\text{NaNbO}_3$  does not show luminescence down to 77 K;
- c.  $\text{NaNbO}_3$  shows strong infrared absorption bands at 675 and  $375\text{ cm}^{-1}$  (5, 6), and a strong Raman line at about  $600\text{ cm}^{-1}$  (6).

Especially the latter point is important. It has been shown that corner-sharing niobate octahedra show strong Raman shifts around  $600\text{ cm}^{-1}$ , and infrared absorption in the regions around 650 and  $375\text{ cm}^{-1}$  (6). The vibrational spectra observed for  $\text{Na}_3\text{NbO}_4$  are not of this type. They indicate edge or face sharing of the niobate octahedra in view of the strong Raman shift at about  $800\text{ cm}^{-1}$ , and the strong infrared bands far above  $650\text{ cm}^{-1}$  (6).

From this we conclude that the structure proposal of Barker and Wood (1) is incorrect. The spectra of cubic  $\text{Na}_3\text{NbO}_4$  show a much stronger resemblance with those of  $\text{Li}_3\text{NbO}_4$  which has ordered rocksalt structure (7).

- a.  $\text{Li}_3\text{NbO}_4$  has its absorption edge at 240 nm (8),  $\text{Na}_3\text{NbO}_4$  at 250 nm;
- b.  $\text{Li}_3\text{NbO}_4$  shows efficient luminescence with an emission peaking at 375 nm

(8) ( $\text{Na}_3\text{NbO}_4$  at 390 nm). The Stokes shift is equal for both compounds; c.  $\text{Li}_3\text{NbO}_4$  shows no strong Raman lines in the  $600\text{ cm}^{-1}$  region, but in the  $800\text{ cm}^{-1}$  region (6). Further it shows infrared absorption bands at 860, 780, 685, 575, and  $450\text{ cm}^{-1}$  (6).

From this we conclude that the structure of the cubic modification of  $\text{Na}_3\text{NbO}_4$  is that of rocksalt with a more or less disordered distribution of the  $\text{Na}^+$  and  $\text{Nb}^{5+}$  ions among the cation sites in such a way that edge sharing of niobate octahedra prevails. In the structure of  $\text{Li}_3\text{NbO}_4$  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  $\text{Na}_3\text{NbO}_4$  ( $\text{Na}_3\text{TaO}_4$ ) 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.

#### References

1. M.G.Barker and D.J.Wood, J.Chem.Soc., Dalton Trans. 1972, 9.
2. A.F.Corsmit, H.E.Hoefdraad and G.Blasse, J.Inorg.Nucl.Chem., in press.
3. R.A.Nyquist and R.O.Kagel, Infrared spectra of inorganic compounds. New York, Academic Press, 1971. Spectrum nr. 315.
4. G.P.M.van den Heuvel, Unpublished.
5. J.T.Last, Phys.Rev. 105, 1740 (1957).
6. G.Blasse and G.P.M.van den Heuvel, Z.Physik.Chem. N.F. To be published.
7. G.Blasse, Z.Anorg.Allg.Chem. 326, 44 (1963); 331, 44 (1964); J.C.Grenier, C.Martin and A.Durif, Bull.Soc.Franç.Minéralog.Cristallogr. 87, 316 (1964).
8. G.Blasse and A.Brill, Z.Physik.Chem. N.F. 57, 187 (1968).
9. Y.Bouilland, Bull.Soc.Chim. France 1965, 519.