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Infrared Study of Alkali Tri- and Hexavanadates as Formed from Their Melts

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Alkali tri- and/or hexavanadates, formed by slow cooling and rapid quenching from melts, were analized by ir spectrometry and X-ray diffractometry. The trivanadate (MV_3O_8) was confirmed to be formed from melts by these procedures in both Li and Na samples and the hexavanadate ($M_2V_6O_{16}$) in both Rb and Cs samples but neither tri- nor hexavanadate in the K sample. The frequencies of the V=O stretching bands of the tri- and hexavanadates were observed to shift toward the lower region of 1005–955 cm^{-1} relative to the corresponding band at 1022 cm^{-1} for pure V_2O_5. By connecting the band shifts with Bond-Strength–Bond-Length parameters of Brown–Shannon, the V=O bond lengths for LiV_3O_8, NaV_3O_8, $Rb_2V_6O_{16}$, and $Cs_2V_6O_{16}$ were exactly evaluated. Based on the relative intensities of the bands, furthermore, the local structures in the sequences of the VO_4, VO_6, and V_2O_8 polyhedral units for the alkali vanadates were favorably discussed.

Introduction

In ir spectrum of pure V_2O_5 crystal a sharp band appeared at 1022 cm^{-1}, which has been assigned to the V=O stretching vibration (*1, 2*). The frequencies of the V=O stretching band of Cs trivanadate was previously found to shift to 1000 and 965 cm^{-1}, the intensity ratio of which was 1:2, relative to the corresponding band at 1022 cm^{-1} for V_2O_5 (*3*). The band shifts were suggested to be caused by the changes in the sequences of the VO_6 polyhedral unit accompanied by a regular insertion of Cs ion into the interlattice of V_2O_5 on the formation of CsV_3O_8. By connecting the band shifts with the Bond-Strength–Bond-Length parameters proposed by Brown and Shannon (*4*), the changes in the bond length of the V=O group were successfully evaluated (*3*), that is, it was made clear that there were two kinds of bond lengths in CsV_3O_8 (1.581 and 1.605 Å) and the intensity ratio was 1:2, which were reversely correspond to those given by the X-ay diffraction analysis.

This method serves to combine the band shift with the Bond-Strength–Bond-Length parameters and should be considered valuable for the evaluation of the characteristic bond length and for discussion on the local structures for similar inorganic materials as vanadate. Thus, in order to make the ir spectrometry extensive as an auxiliary means for the X-ray diffractometry, the application of the method for the estimation of the V=O bond length and the discussion on the local and detailed structures of alkali tri- and hexavanadates formed from the melts, was repeated for this paper.

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Experimental

Materials and procedures. Alkali tri- and/or hexavanadates were prepared from reacting mixtures of NH_4VO_3 or V_2O_5 with alkali carbonate, weighed exactly as the atomic ratios of alkali to vanadium became 1 : 3, as follows. (1) Four grams of NH_4VO_3 (Kanto Chem. Co. Ltd., guaranteed grade) was immersed into aqueous solutions of alkali carbonate (M_2CO_3, M = Li–Cs, Kanto Chem. Co. Ltd., guaranteed grade). They were dried at 110°C, decomposed in a quartz tubing (outer diameter, o.d. = 12 mm) open to air at 400°C for 12 hr, and further reacted fully at 600°C for 62 hr. Afterward the tubing was quenched in ice-water. The samples will be designated as *M–I* (*M* = Li–Cs) below. (2) Three grams of V_2O_5 (Kanto Chem. Co. Ltd., guaranteed grade) were mixed well with M_2CO_3 in an agate mortar and then were reacted in a quartz tubing (o.d. = 12 mm) open to air at 530°C for 14 hr. After further heat treatment at 590°C for 8 hr they were cooled naturally by standing in the furnace. Since only the Li sample had not melted under such heat treatment, it was heated again at 620°C for 9 hr. The samples will be designated as *M*–II (*M* = Li–Cs) below. (3) Four grams of NH_4VO_3 were mixed well with M_2CO_3 in an agate mortar and then reacted in a quartz tubing (o.d. = 12 mm) open to air at 620°C for 72 hr. After the reaction they were quenched in ice-water. The samples will be designated as *M*–III (*M* = Li–Cs) below.

Measurements. The ir spectra of the samples *M*–I–*M*–III were recorded in the frequency range from 650 to 1200 cm^{-1} by the normal KBr disk method. The spectrometer used was JASCO Model DS-402 G. The X-ray powder diffraction was also checked on all samples. The X-ray diffractometer used was Rigaku Denki Model GF-Rad-γA; Cu*K*α radiation (at 40 kV, 120 mA) and an Ni filter were used.

Results

Infrared spectra of the samples *M*–I are shown in Fig. 1, in which the spectrum of pure V_2O_5 is given with a dotted line for comparison. The sharp 1022-cm^{-1} band has been assigned to the stretching of the V=O group and the rather broad band at 815 cm^{-1} to the V—O—V stretching in pure V_2O_5 crystal (*1*, *2*). The sharp 999- and 966-cm^{-1} bands in the sample Cs–I has previously been assigned to the V=O stretching, which are subjected to shift from the value at 1022 cm^{-1} in pure V_2O_5 accompanied with the formation of CsV_3O_8 (*3*). Based on this standpoint, the lines at 1005 and 971 cm^{-1} in Rb–I and those at 996, 973, and 957 cm^{-1} in Na–I can be assigned to the V=O stretching bands. In the sample Li–I the splittings among the three lines are not

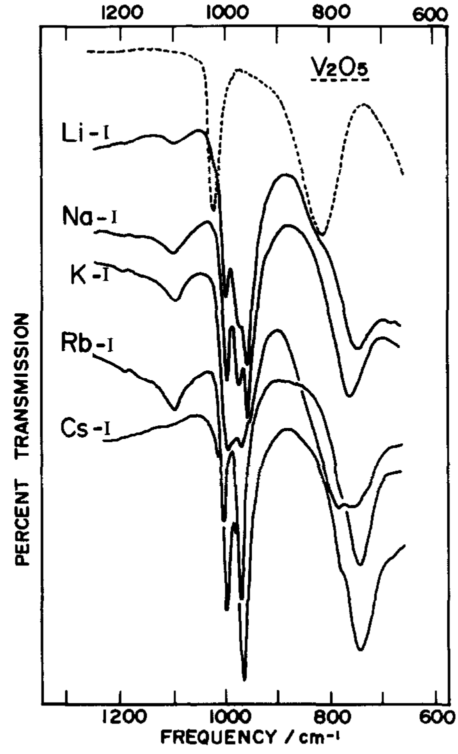

FIG. 1. Infrared spectra of the Li–Cs–I samples in the region of 650–1200 cm^{-1}.

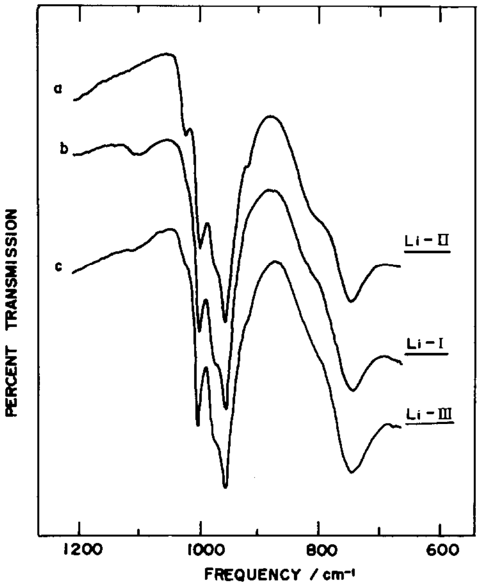

FIG. 2. Infrared spectra of the samples Li–I–III in the region of 650–1200 cm^{-1}.

so good while in the K–I those are too poor to be considered as the spectrum from an unified compound. The samples K–II and III did also not show clear splittings similar with the sample K–I. Infrared spectra of the samples Rb–II and III and Cs–II and III were completely consistent with the samples Rb–I and Cs–I, respectively.

In the samples L–I–III and Na–I–III only minor differences were seen among those band shapes with each other, respectively, as shown in Figs. 2 and 3. In the sample Li–II a shoulder band appeared at 1022 cm^{-1}, which suggests a small amount of V_2O_5 remained without reacting. In the samples Na–II and III a shoulder band appeared at 920 cm^{-1}, which seemed to be caused from some other phase mixed. In the spectra with such a shoulder band, in fact, the separations among the 996-, 973-, and 957-cm^{-1} bands tends to become poor, especially in the sample Na–II, which was prepared by the slow-cooling method.

The X-ray diffraction patterns for the samples *M*–I were shown in Fig. 4, in which the patterns of the corresponding compounds referred were added for comparison. In Li–I and Na–I the main lines are known to be almost consistent except for some of the minor lines with the references of Li– (*5*) and Na– (*6*) trivanadates (MV_3O_8), respectively, in which the samples were prepared from melts similar with the present. In Rb and Cs–I the *d*-values of the main lines are fairly consistent except for those with minor lines with the references of Rb- and Cs-hexavanadates (*8*), respectively, but the relative intensities differ rather largely with each other. In the paper referred, the samples were prepared from aqueous solutions, so that the crystalline habits might be expected to differ with those of the present samples prepared from the melts. In the case of K–I the lines do not correspond to potassium trivanadate (KV_3O_8) (*7*) and hexavanadate ($K_2V_6O_{16}$) (*8*) referred, but the rather strong lines at *d* = 4.7, 3.15, and 2.37 Å correspond well to those of $K_2V_8O_{21}$ (*9*) and the relatively

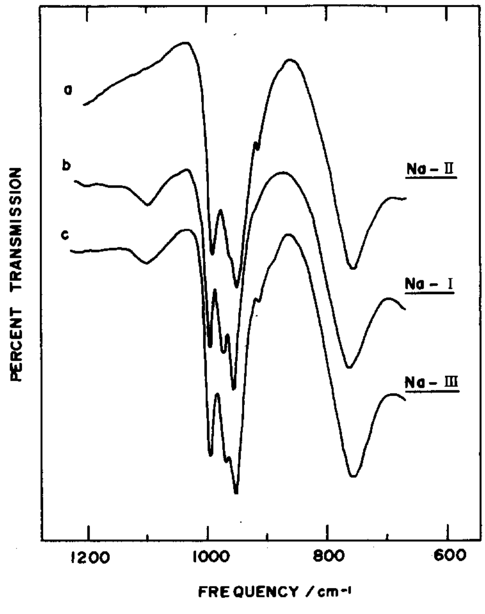

FIG. 3. Infrared spectra of the samples Na–I–III in the region of 650–1200 cm^{-1}.

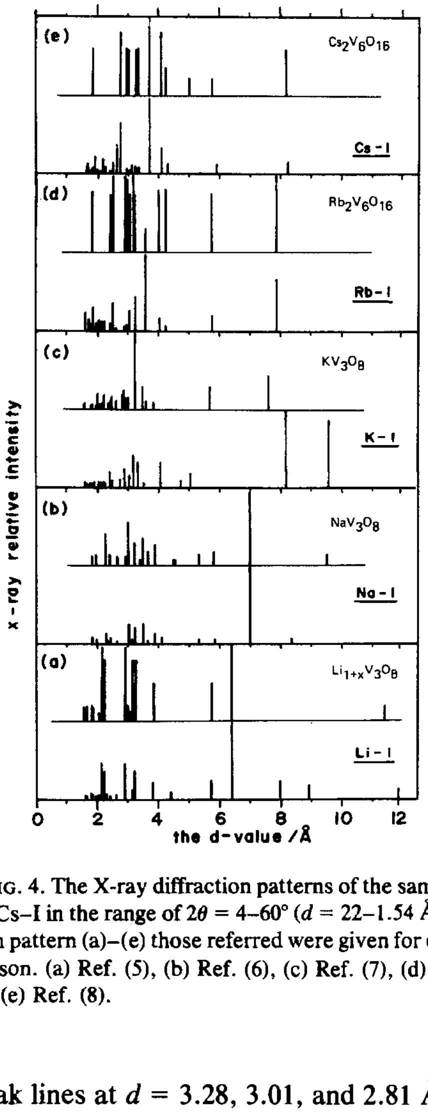

FIG. 4. The X-ray diffraction patterns of the samples Li–Cs–I in the range of $2\theta = 4$–$60°$ ($d = 22$–1.54 Å); in each pattern (a)–(e) those referred were given for comparison. (a) Ref. (5), (b) Ref. (6), (c) Ref. (7), (d) Ref. (8), (e) Ref. (8).

weak lines at $d = 3.28$, 3.01, and 2.81 Å to $K_3V_5O_{14}$ (*10*). With the highest line at $d = 8.2$ Å the corresponding *d*-value, however, could not be found in any of the ASTM-cards for K-vanadate and for something like the K–V–Si–O compound which might be formed by reacting with the vessel wall. In the X-ray diffraction lines of samples K–II and III any lines corresponding to tri- and hexavanadates were also not found. Therefore, only the K sample will be ruled out from discussion about the ir spectra as done below, and will be discussed in detail in another paper (*11*).

Discussions

Formations of Alkali Tri- and/or Hexavanadates from Melts

Kelmers tried to prepare anhydrous alkali hexavanadates from aqueous solutions (*8*). The $K_2V_6O_{16}$, $Rb_2V_6O_{16}$, and $Cs_2V_6O_{16}$ prepared were shown to have a monoclinic crystalline structure being isomorphous with each other and, furthermore, their lattice constants for the *a*-axis were linearly proportional to the ion size of alkali metal inserted into the interlattice. The crystalline feature, in fact, were confirmed for $K_2V_6O_{16}$ and $Cs_2V_6O_{16}$ by the detailed X-ray study of Evans and Block (*12*). Both Li and Na compounds were not formed by any of the procedures from aqueous solutions. On the other hand, Li- and Na-trivanadates have been easily prepared from the melts of the reacting mixtures of alkali carbonate or alkali metavanadate and V_2O_5 by many authors (*5, 6, 13, 14*). Conversely, K-trivanadate or K-hexavanadate were not seen in the phase diagrams for the K_2CO_3–V_2O_5 and K_2O–V_2O_5 systems of Holtzberg (*15*). Such compound also does not exist in the diagram for the KVO_3–V_2O_5 system of Kelmers (*16*) but only $K_2V_8O_{21}$ and $K_3V_5O_{14}$ as stable phases from melts. Existence of KV_3O_8 and/or $K_2V_6O_{16}$ phase[1] was also not shown in the samples K–I–III.

In Li–II weak diffraction lines appeared at $d = 4.38$ and 7.2 Å, which suggested the mixings of α–$Li_{0.04}V_2O_5$ (*17*) and β–$Li_{0.30}V_2O_5$ (*18*), respectively. In Na–II and III weak diffraction lines appeared at $d = 7.3$, 3.07, 2.17, and 1.67 Å, which suggested the mixing of $Na_{0.33}V_2O_5$ (*19*) or NaV_6O_{15} (*20*). Such mixings of the minor component were known to occur especially in the slow-cooling samples of Li and Na. On the other hand, with the Rb and Cs samples any dif-

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[1] The potassium vanadate, the atomic ratio of which was (K)/(V) = 0.33, was designated as trivanadate by Evans (*12*) and as hexavanadate by Kelmers (*16*).

TABLE I

THE V=O STRETCHING FREQUENCIES FOR THE SAMPLES Li–Cs–I AND THEIR RELATIVE INTENSITIES AND THE CORRESPONDING BOND LENGTHS EVALUATED BY CONNECTING THE BAND SHIFTS WITH BROWN–SHANNON'S PARAMETERS[a]

M-Vanadate	f (cm^{-1})	Relative intensity	The V=O bond length (Å)
Li–I	1000	1.0	1.599
	975	1.2	1.616
	957	1.9	1.629
Na–I	996	1.0	1.602
	973	1.0	1.618
	957	1.4	1.629
Rb–I	1005	1.0	1.596
	971	2.3	1.619
Cs–I	999	1.0	1.600
	966	2.1	1.622

[a] See text.

ferences between the samples prepared by slow cooling and by rapid quenching were not found, as already noted above. Therefore, it can be concluded that by the rapid quenching of the melt the trivanadate can be obtained in the Li and Na samples and hexavanadate in the Rb and Cs samples, whereas the mixture of $K_2V_8O_{21}$, $K_3V_5O_{14}$, and the unknown compound are obtained in the K sample.

The V=O Stretching Frequencies in Alkali Tri- and Hexavanadates and Their V=O Bond Lengths and Local Structures

The frequencies of the V=O stretching band in the spectra shown in Fig. 1 were summarized in the second column of Table I. The values for the K–I were excluded from the table for the reason mentioned above. The peak intensities of the bands were estimated by procedures similar to those of previous papers (*2, 3*), and their relative intensities are given in the third column of Table I. With $Cs_2V_6O_{16}$ the V—O stretching frequency was already known to shift from 1022 to 1000 and 965 cm^{-1} in a previous paper (*3*). Moreover, the V=O bond lengths corresponding to the bands were evaluated as 1.581 and 1.605 Å by connecting the band shifts with the Bond-Strength–Bond-Length parameters of Brown–Shannon as follows: first, Eq. (1) was accepted as the bond strength:

$$S = S_0(R/R_0)^{-N}, \qquad (1)$$

where the values of $S_0 = 1.25$, $R_0 = 1.700$, and $N = 4.8$ were used (*4*); second, the stretching frequency for the V=O bond, f, was assumed to be proportional to $S^{1/2}$; and third, 1.567 Å was accepted as the standard of the V=O bond length, which was the mean value of those determined for V_2O_5 by Ketelaar (*21*), Bystrom *et al.* (*22*), and Bachmann *et al.* (*23*). In the present paper, however, 1.585 Å will be accepted as the standard for the reason that the value is reexamined exactly by Bachmann *et al.* (*23*) and thus can be regarded as the most accurate.[2] The V=O bond lengths evaluated by a similar procedure are given in the fourth column of Table I.

According to the crystalline structure determined by the X-ray analysis by Wadsly (*5*), $Li_{1+x}V_3O_8$ is monoclinic, the Li ion is placed into the octahedral site surrounded by the oxygen ions of VO_6 units, and three types of the V=O group are differentiated in the lattice, the bond lengths of which are 1.59, 1.60, and 1.64 Å and the intensity ratios are 1 : 1 : 1, respectively. The bond lengths are fairly consistent with those in Table I but the ratios differ rather largely. The intensity ratios similar to the Li–I (1 : 1.2 : 1.9) were seen in the other samples, Li–II (1 : 1.2 : 2.0) and Li–III (1 : 1.1 : 1.7). Wadsly also pointed out the existence of a type of tetrahedral site in the $Li_{1+x}V_3O_8$ crystalline and further suggested the possi-

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[2] The value was privately recommended by Dr. I. D. Brown.

bility that the Li ion might insert into the site because of its small size without giving any evidence for its occurrence by X-ray analysis (*5*). If the tetrahedral site was occupied by one Li ion, only one of the V=O groups should be affected as to change the bond length, while three types of the V=O groups were affected by the occupation of the octahedral site by one Li ion as mentioned above. The deviations of the intensity ratios of the bands (1 : 1.2 : 1.9) from the normal (1 : 1 : 1) could be caused by an irregular occupation of the octahedral site by the Li ions, for instance, it will be possible if a part of Li ion in the octahedral site is replaced in the tetrahedral site nearby.

In the case of NaV_3O_8 no accurate X-ray analysis has been done but the crystal structure can be well expected to be isomorphous with $Li_{1+x}V_3O_8$ because the characteristic bands of the Na–I are quite similar with those of the Li–I. Certainly the V=O bond lengths in Na–I and Li–I were almost the same but the intensity ratios differed rather largely as shown by the comparison of the third and fourth columns in Table I. The intensity ratios (1 : 1 : 1.4) in Na–I are more close to the normal (1 : 1 : 1) than Li–I. The ratios of the Na–II (1 : 1 : 1.3) and Na–III (1 : 1 : 1.4) samples are almost the same with that of Na–I. This is seemingly due to the fact that the ion size of Na is too large for the ion to be placed into the tetrahedral site without difficulty, while Li ion can be easily placed in the site. To interpret this rather large deviation from the normal intensity ratios, contamination effects from the other phase should be noted, but it would be only minor because of the small content as determined from the comparison of the X-ray diffraction patterns.

According to the X-ray crystalline structure for $Cs_2V_6O_{16}$ by Evans and Block, Cs ions were regularly placed into the sites which were between the zigzag infinite chains composed of the alternative strings of the single VO_4 group and the double V_2O_8 groups (*12*). Cs ion inserted can affect simultaneously the one V=O group in the VO_4 unit and the two V=O groups in the V_2O_8 unit. Therefore, two kinds of the V=O group can be expected to arise in $Cs_2V_6O_{16}$, the intensity ratio of which is 1 : 2, respectively. In fact, the bond lengths and the intensity ratio were obtained as 1.600 and 1.622 Å and 1 : 2, respectively, as shown in Table I. Thus, it was known that the bond lengths were quite consistent with each other, but the intensity ratio corresponded inversely to each other, although the inverse correspondence for the ratio was not pointed out in the previous paper (*3*). The inconsistency between the conclusions deduced from both X-ray and ir analyses will remain unclear for the present.

With $Rb_2V_6O_{16}$ the crystalline structure is isomorphous with $Cs_2V_6O_{16}$ (monoclinic) and only the *a*-axis becomes shorter than that of $Cs_2V_6O_{16}$ (*8*) in proportion to the ion size (r_{Rb}/r_{Cs}). The extents of the band shifts and thus the changes in the V=O bond length were smaller in Rb–I than Cs–I, which could also be understood to be an ion size effect. The intensity ratio of the two types of the V=O (1 : 2.3) was found to deviate a little from the normal (1 : 2.0). Since the similar ratios were obtained in the other samples Rb–II (1 : 2.2) and Rb–III (1 : 2.5), the deviation appears not to be a simple error in the experiment but rather to be caused by some statistical effect similar with the case of the Li and Na samples. However, the problem shall wait for future solving without further discussion.

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References

1. L. D. Frederickson, Jr. and D. M. Hansen, *Anal. Chem.* **35**, 818 (1961).
2. Y. Kera and K. Hirota, *J. Phys. Chem.* **73**, 3973 (1969).

3. Y. Kera, *Bull. Chem. Soc. Jpn.* **54,** 1693 (1981).
4. I. D. Brown and R. D. Shannon, *Acta Crystallogr. Sect. A* **29,** 266 (1973).
5. A. D. Wadsly, *Acta Crystallogr.* **8,** 695 (1955).
6. G. A. Kolta, I. F. Hewaidy, N. S. Felix, and N. N. Girgis, *Thermochem. Acta* **6,** 165 (1973).
7. ASTM-card No. 22-1247; *Nat. Bur. Stand.* (*U.S.*), *Monogr.* **25,** Sec. 8, 56 (1970).
8. A. D. Kelmers, *J. Inorg. Nucl. Chem.* **21,** 45 (1961).
9. A. Kato, I. Mochida, and T. Seiyama, *Anal. Chim. Acta* **54,** 168 (1971).
10. L. Zurkova, V. Sucha, C. Vargova, and J. Corba, *Coll. Czech. Chem. Commun.* **39,** 387 (1974).
11. Y. Kera, submitted for publication.
12. H. T. Evans, Jr. and S. Block, *Inorg. Chem.* **5,** 1808 (1966).
13. A. D. Wadsly, *Acta Crystallogr.* **10,** 261 (1957).
14. D. G. Wickham, *J. Inorg. Nucl. Chem.* **27,** 1939 (1965).
15. F. Holtzberg, A. Reisman, M. Berry, and M. Berkenblit, *J. Amer. Chem. Soc.* **78,** 1537 (1956).
16. A. D. Kelmers, *J. Inorg. Nucl. Chem.* **23,** 279 (1961).
17. ASTM-card No. 19-734; Hardy *et al.*, *Bull. Chim. Fr.* 2808 (1964).
18. ASTM-card No. 18-755; Hardy *et al.*, *Bull. Chim. Fr.* 1056 (1965).
19. ASTM-card No. 21-1175; Fotiev *et al.*, *Inorg. Mater.* **3,** 1138 (1967).
20. ASTM-card No. 19-1259; Siobodin *et al.*, *J. Appl. Chem. USSR* **38,** 799 (1965); ASTM-card No. 28-1172; Kolta *et al.*, *Thermochim. Acta* **6,** 165 (1973); ASTM-card No. 24-1155.
21. J. A. A. Ketelaar, *Z. Kristallogr.* **95,** 9 (1936).
22. A. Bystrom, K. A. Wilhelmi, and O. Broten, *Acta Chem. Scand.* **4,** 1119 (1950).
23. H. G. Bachmann, F. R. Ahmed, and W. A. Barnes, *Z. Kristallogr.* **115,** 110 (1961).