

Infrared spectrum of crystalline and glassy borosilicates $M^1\text{BSi}_2\text{O}_6$

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Synthetic pollucite, $\text{CsAlSi}_2\text{O}_6$, has been considered as a radio-caesium host phase for various nuclear materials applications [1], but much less attention has been paid to the corresponding borosilicates $M^1\text{BSi}_2\text{O}_6$ ($M^1 = \text{caesium, rubidium, potassium}$), which are known to have a pollucite-type structure [2-6]. The caesium compound is known to suffer a substantial weight loss when heated above 850°C [2], but the matter has not been investigated further. We present here a study, by infrared spectroscopy, of the crystalline and glassy compounds, and of their thermal stability.

All compounds are synthesized by conventional solid state reaction techniques. The stoichiometric quantities of $M^1_2\text{CO}_3$, H_3BO_3 and SiO_3 are well ground and mixed, and progressively heated in covered platinum crucibles up to a fixed temperature of 800°C (250°C for the thallium compound). The mixtures are reground and reheated until a pure, well-crystallized phase is obtained, as deduced from X-ray diffraction and infrared spectroscopy. This result is generally obtained after two days, but the heating and grinding cycle is repeated for a total of five days. The glass is obtained by melting the pure compound at 1200°C for 1 min, followed by rapid quenching. In these conditions, no significant weight loss is observed, and the glass is fully transparent. The infrared spectra were recorded with a Beckman 4250 spectrometer (1500 to 250 cm^{-1}) and a Polytec FIR 30 interferometer (350 to 20 cm^{-1}), KBr or polythene disks being used in the appropriate regions. Some spectra were also run in nujol to check the lack of ionic exchange between the KBr and the sample.

In addition to the known borosilicates $M^1\text{BSi}_2\text{O}_6$ with $M^1 = \text{potassium, rubidium, caesium}$, we have also synthesized TlBSi_2O_6 by reaction at relatively low temperature (520°C , five days). Its X-ray powder diagram is very similar to that of RbBSi_2O_6 ; all the peaks are indexed by a cubic cell with $a = 1.2775$ (3) nm, almost identical to that of RbBSi_2O_6 : $a = 1.278$ [3] or 1.2775 nm (this work). This is in agreement with the similarity of the ionic radii: 0.170 and 0.172 nm for Tl^+ and Rb^+ respectively, in twelve-fold coordination [7]. The compound is still stable at 600°C , but is decomposed at 700°C . We were unable to obtain the corresponding glass.

The spectra are essentially characterized by three prominent absorption regions near 1000 , 500 and 100 cm^{-1} (Fig. 1) and by some broadness of the bands: this broadness is due to the statistical distribution of boron and silicon on the tetrahedral sites of the lattice. The strong, high-frequency bands are clearly due to the antisymmetric stretching vibrations of the BO_4 and SiO_4 tetrahedra. The study of ^{10}B - ^{11}B isotopic species

of CsBSi_2O_6 shows a frequency shift of 10 cm^{-1} for the strongest band at 1037 cm^{-1} , and of 26 cm^{-1} for the band at 886 cm^{-1} . This latter shift is almost the same as that already observed for the antisymmetric stretching modes of BO_4 tetrahedra in sinhalite MgAlBO_4 [8] and in Fe_3BO_6 (unpublished results from this laboratory). Thus, the 886 cm^{-1} band is essentially a stretching vibration of the BO_4 tetrahedra. This assignment is further supported by the disappearance of this band in the infrared spectrum of pollucite $\text{CsAlSi}_2\text{O}_6$.

The existence of a stretching vibration specifically due to the BO_4 tetrahedra was not obvious: because of the statistical distribution and the similar stretching frequencies of BO_4 and SiO_4 groups, a full mixing of these vibrations was possible. Such a mixing does indeed exist for the 1037 cm^{-1} band, as indicated by the 10 cm^{-1} ^{10}B - ^{11}B shift.

No significant ^{10}B - ^{11}B isotopic shift is observed for the remaining bands, but we have shown [8] that the BO_4 bending frequencies are hardly modified by the ^{10}B - ^{11}B replacement: the band near 490 cm^{-1} may be assigned to a bending vibration of either SiO_4 or $\text{SiO}_4 + \text{BO}_4$ tetrahedra.

The low frequency band exhibits a fairly regular relationship between the frequency and the square root of the mass of the monovalent cation M^1 (Fig. 2): it is thus assigned to a translational motion of this cation.

For a given M^1 cation, this band is also shifted towards lower frequencies when going from the boron to the aluminosilicate (88 and 65 cm^{-1} for CsB and $\text{CsAlSi}_2\text{O}_6$, respectively), thus suggesting an additional influence of the mass of the trivalent cation. This is contradicted by the fact that the frequency remains the same for the three compounds CsAl , CsGa and $\text{CsFeSi}_2\text{O}_6$. Thus, this frequency lowering is not due to a mass effect of the trivalent cation. It is probably related to the large unit-cell increase observed when going from the boron to the aluminium compound (1.300 and 1.368 nm, respectively [12]).

This unit-cell increase is much smaller when going from aluminium to gallium and iron compounds: according to literature data and to our own results, the following values have been observed: $\text{CsAlSi}_2\text{O}_6$, 1.365 to 1.368 nm [1, 2, 9, 10]; $\text{CsGaSi}_2\text{O}_6$, 1.372 to 1.373 nm [11]; $\text{CsFeSi}_2\text{O}_6$, 1.382 to 1.385 nm [2]; for this latter compound, the value of 1.366 nm quoted by Galli *et al.* [12] is very probably in error.

The crystal-to-glass transition is characterized by the following modifications in the infrared spectrum:

1. The appearance of new bands at about 1400 and 1300 cm^{-1} . Their assignment to the formation of BO_3 groups is straightforward; their fairly high frequency

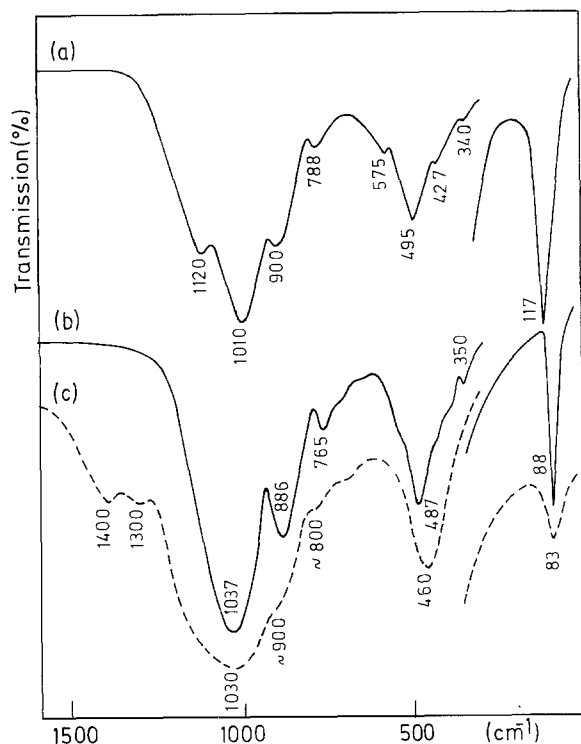


Figure 1 Typical infrared spectrum of $M^I \text{BSi}_2 \text{O}_6$ borosilicates. (a) M^I = potassium; (b) and (c) M^I = caesium, crystal and glass, respectively.

shows that the BO_3 groups are associated by bridging oxygen atoms, as in polyborates.

2. A correlative weakening of the 886 cm^{-1} band assigned to BO_4 tetrahedra, which is now reduced to a very weak shoulder. Thus, the crystal-to-glass transition is accompanied by the partial transformation of BO_4 into BO_3 groups. We have observed the same transformation in a series of borates or borocompounds whose crystal structure contains only BO_4 tetrahedra (PbB_4O_7 , SrB_4O_7 , $\text{Zn}_4\text{B}_6\text{O}_{13}$, PbBPO_5 , LiBGeO_4). This is in agreement with Zachariasen's rules;

3. The low frequency band corresponding to the M^I translation is still present. With respect to the crystal phase, its frequency is almost the same for M^I = caesium and rubidium, but very significantly higher for M^I = potassium. This could suggest that the coordination number of K^+ , which is twelve in the crystal phase, is reduced to a smaller average value in the glass, this reduction being allowed by the relatively moderate ionic radius of the K^+ cation.

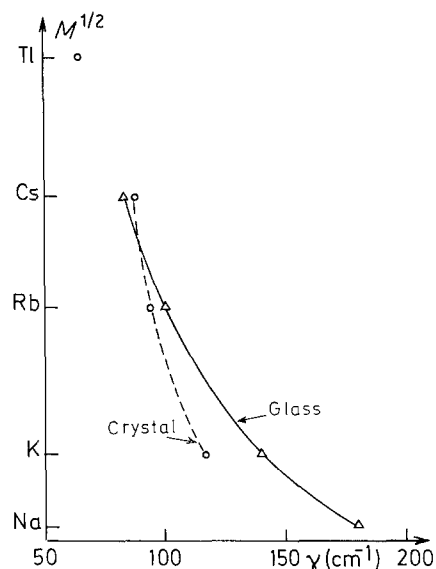


Figure 2 Relationship between the frequency of the far infrared band and the square root of the mass of the monovalent cation.

When heated above 850°C , CsBSi_2O_6 exhibits a substantial weight loss which, according to Richerson and Hummel, indicates that a certain amount of water was retained in the structure [2]. Our results agree with the existence of a weight loss, but not with the proposed interpretation. The experiments have been carried out as follows.

About 0.3 g $M^I \text{BSi}_2 \text{O}_6$ (M^I = potassium, rubidium, caesium) are weighed in covered platinum crucibles, and the crucibles are introduced in a furnace preheated at 950°C . The weight loss is then determined at regular intervals for a total of 8 days at 950°C , an additional 8 h at 1000°C and finally 1 day at 1100°C . The results are summarized in Table I, which gives the weight loss as a function of temperature and time. This loss is expressed, either in percentage of the initial weight, or in per cent of the loss corresponding to one $M^I \text{BO}_2$ molecule. The loss is the greater for the caesium compound, where it reaches eventually the theoretical value expected for the loss of CsBO_2 . The residue is pure cristobalite, as shown by X-ray diffractometry and infrared spectroscopy. The weight loss is smaller (for a given time) for rubidium and potassium compounds, but the existing results suggest that the final state would be the same (total loss of $M^I \text{BO}_2$) if the thermal treatment was resumed for a sufficient time.

It will be remembered that the corresponding

TABLE I Weight loss of $M^I \text{BSi}_2 \text{O}_6$ as a function of thermal treatment

	Weight loss						
	950° C					1000° C, 8 h	1100° C, 24 h
	8 h	24 h	72 h	144 h	192 h		
$\text{CsBSi}_2 \text{O}_6$ *	15.86	29.6	45.25	50.25	52.07	53.95	59.56
†	26.7	49.8	76.1	84.5	87.6	90.7	100.2
$\text{RbBSi}_2 \text{O}_6$ *	7.93	18.55	23.63	26.78	28.42	31.26	40.99
†	15.3	35.9	45.7	51.8	55.0	60.5	79.3
$\text{KBSi}_2 \text{O}_6$ *	3.15	5.62	11.86	16.08	19.60	‡	
†	7.8	13.8	29.2	39.6	48.3		

*Weight loss in per cent of the initial weight.

†Weight loss in per cent of the loss of one $M^I \text{BO}_2$ molecule.

‡Partial glass formation.

aluminium compounds $M^I AlSi_2O_6$ are stable at $1100^\circ C$. Thus, the thermal instability is primarily determined by the presence of boron, but it increases with increasing size of the monovalent cation M^I . This may be compared to the loss of B_2O_3 experienced during the high-temperature melting of borosilicate glasses.

The mechanism of the decomposition has not been investigated, but some preliminary results show that, at least for $CsBSi_2O_6$, intermediate, unidentified phases appear during the decomposition.

In conclusion, the essential features of the infrared spectrum of crystalline $M^I BSi_2O_6$ borosilicates are accounted for by the vibrations of a lattice of statistically distributed BO_4 and SiO_4 tetrahedra, and by the translational motion of the monovalent cation M^I . The spectral changes associated with the crystal-to-glass transition point to the partial transformation of BO_4 into BO_3 groups. These compounds are easily synthesized at moderate temperature, but their poor thermal stability is certainly a serious hindrance to practical applications.

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