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METASTABLE MODIFICATION OF SrB_2O_4

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During the course of heating the amorphous material prepared by the simultaneous hydrolysis of strontium methoxide and boron triethoxide, a new modification of SrB_2O_4, being metastable, was formed.

Crystalline SrB_2O_4 has been known only in the orthorhombic modification.[1,2] During the course of heating the amorphous material prepared by the simultaneous hydrolysis of strontium methoxide and boron triethoxide, a new modification of this compound, being metastable, was formed. On $SrSiO_3$, a metastable modification similar to SrB_2O_4, which is shown in the present study, has been reported by Roy et al.[3] as well as by the authors.[4,5]

Boron triethoxide used was the guaranteed purity one. Strontium methoxide was synthesized by heating 99.9% strontium metal in an excess amount of dehydrated methanol at 65 °C for 5 h. A mixture of boron and strontium alkoxides in the mole ratio of Sr^{2+}/B^{3+}=1:2 was poured into aqueous ammonia solution at 30 °C. The temperature was slowly raised up to 70 °C while being stirred. The resulting mixed powder was washed repeatedly with hot water and dried at 65 °C under reduced pressure. The average particle size of the mixed powder is ca. 550 Å.

Figure 1 shows a TG curve of the mixed powder in air. The weight loss of 16.7% up to 560 °C is attributed to the loss of ammonia, absorbed water, hydrated water, and organic residue from the parent alcohol. DTA was also performed. Two exothermic reactions were observed at 650-690 °C and 715-780 °C in the heating process. On the other hand, no peaks were detected in the cooling process. The specimens obtained in heating and cooling processes at a rate of 10 °C/min were identified by the high-temperature X-ray diffractometer using nickel filtered copper K_α. The recording of the powder pattern was done after keeping for 30 min at a desired temperature. The mixed powder as a raw material was amorphous, and no significant changes being observed up to 600 °C. At the top of the first sharp exothermic peak(at 670 °C), the

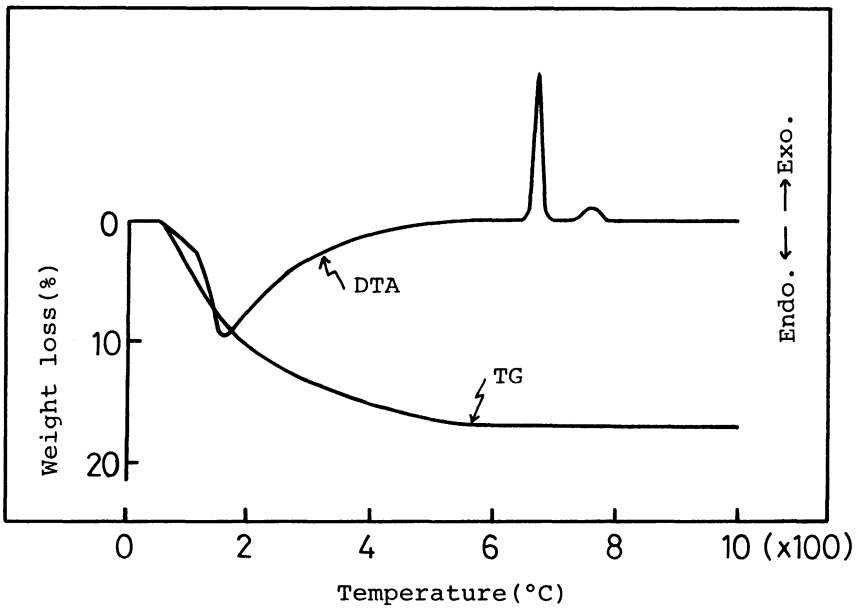

Fig. 1 TG and DTA curves of alkoxy-derived SrB_2O_4.
Sample weight:60 mg, Heating rate:10 °C/min.

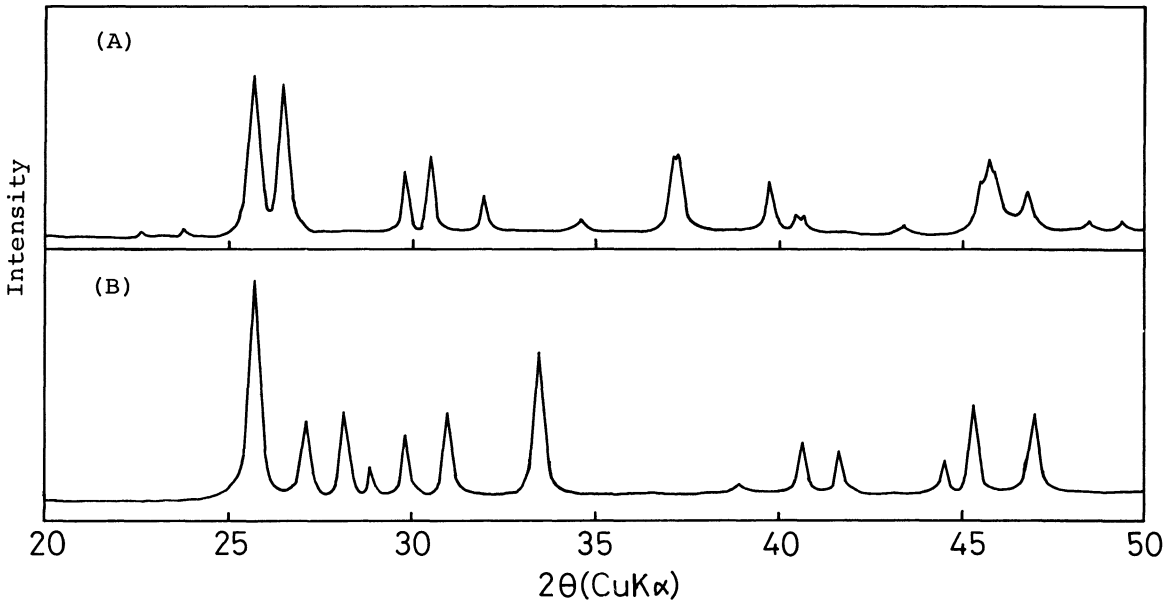

Fig. 2 X-ray diffraction patterns of metastable SrB_2O_4(A) and stable SrB_2O_4(B).

specimen showed an X-ray diffraction pattern of a hitherto undescribed new modification of SrB_2O_4(Fig. 2(A)). After the second exothermic peak(at 790 °C), the specimen gave the pattern of the known orthorhombic modification(Fig. 2(B)). In the cooling process, the transformation of the orthorhombic- into the new modification was not observed. In view of the fact that the transformation is irreversible from DTA and X-ray analysis, the new modification must be metastable.

Figure 3 shows the infra-red spectra of metastable and stable SrB_2O_4, which were obtained by quenching rapidly after heating for 30 min at 670 °C and 790 °C, respectively. The compounds were examined as a dispersion in potassium bromide, using the pressed disk technique. X-Ray determinations of the structures of the metaborate compounds have so far identified four types of borate ion with the overall formula $(BO_2)_n^{n-}$. These structures are a chain anion, made up of $(-BO_2-)^-$ units, a ring anion, made from three of the same units, a three dimensional network, in which all the boron atoms are tetrahedrally coordinated, and a double ring structure $B_5O_{10}^{5-}$, in which the two rings are joined by a tetrahedral boron atom. The four structure types exhibit

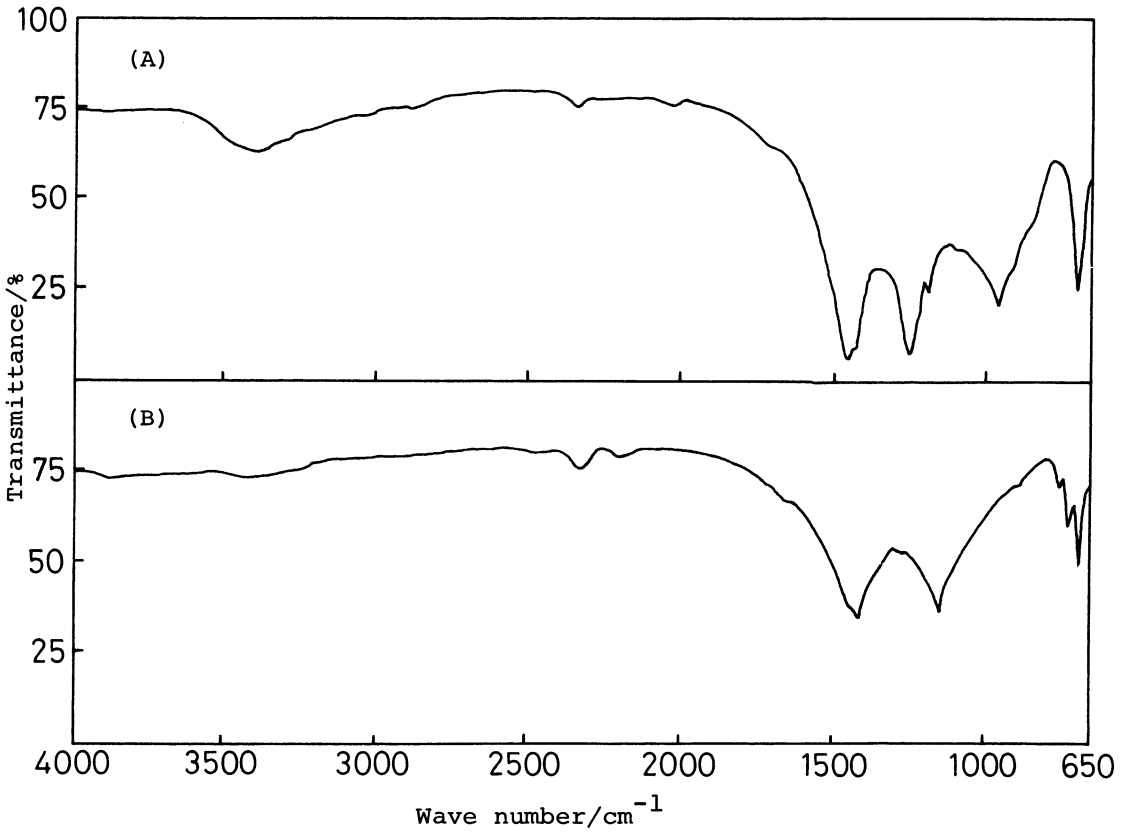

Fig. 3 Infra-red spectra of metastable SrB_2O_4(A) and stable SrB_2O_4(B).

characteristic infra-red spectra. It has been shown for the compound SrB_2O_4 to contain the chain anion reported by Hart and Smallwood.[6] The spectral pattern of the stable SrB_2O_4 obtained in the present study was consistent with the reported one. On the other hand, the spectra of metastable SrB_2O_4 were very similar to those of ZnB_2O_4,[6] although its structure has not been decided yet.

X-Ray diffraction peaks of metastable SrB_2O_4 were compared with those of ZnB_2O_4.[7] The scanning speed of 1/4°/min of the goniometer was selected to satisfy the accuracy of d-spacing. The observed d-values of metastable SrB_2O_4 were in agreement with those of ZnB_2O_4 within 0.033 Å for all peaks in 2θ=20-50°, though both compounds were disagreement with respect to relative intensities of main peaks. From the above mentioned results and the infra-red spectrum data, it can be considered that the structures of metastable SrB_2O_4 and ZnB_2O_4 resemble each other.

References

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