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# RAPID COMMUNICATION

## Low-Temperature Reaction of Aurivillius Phases with Halides

U. Sitharaman and A. W. Sleight[1]

*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003*

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**Kijima *et al.* [T. Kijima, S. Kimura, Y. Kawahara, K. Ohe, M. Yada, and M. Machida, *J. Solid State Chem.* 146, 60 (1999)] recently reported a reaction between $Bi_4Ti_3O_{12}$ and LiI in the presence of iodine at 350°C. Their product was never obtained free of $Bi_4Ti_3O_{12}$, but their claim was that their product was $Bi_4Ti_3O_{12}$ intercalated with I and Li. We have repeated this reaction and found conditions under which the reaction goes to completion, i.e., $Bi_4Ti_3O_{12}$ is completely consumed. The dominant crystalline product is apparently identical to the product reported by Kijima *et al.* However, we conclude that no intercalation of $Bi_4Ti_3O_{12}$ has occurred. This dominant crystalline phase is in fact BiOI. The remainder of the product is poorly crystalline. Analogous reactions occur at low temperature using other halides such as NaCl and other Aurivillius phases such as $Bi_2WO_6$.**


Reactions were conducted in evacuated sealed Pyrex tubes heated at 300 to 550°C for 3 to 5 days. Reactants were $Bi_2O_3$ (Alfa 99.975%), $TiO_2$ (Baker 99.99%), $WO_3$ (Cerac 99.99%), and LiI (Alfa 98+%). To prepare $Bi_4Ti_3O_{12}$ and $Bi_2WO_6$, appropriate amounts of $Bi_2O_3$ were mixed by grinding together with $TiO_2$ or $WO_3$. These were heated at 825°C for 2 to 3 days with intermediate grinding. The X-ray diffraction patterns of these products showed only $Bi_4Ti_3O_{12}$ and $Bi_2WO_6$ to be present.

Initial reactions of $Bi_4Ti_3O_{12}$ and $Bi_2WO_6$ with LiI were conducted with and without addition of iodine. The products obtained were identical with or without iodine; thus, iodine was excluded in subsequent experiments. One mole of $Bi_4Ti_3O_{12}$ was reacted with 4 to 8 mol of LiI at 300, 350, 400, 440, and 550°C for 3 to 5 days. The products were washed with water and dried at room temperature. In all cases, the X-ray diffraction spectra of the products were dominated by the highly crystalline pattern of BiOI. For reaction temperatures of 400 and 440°C, weak peaks of $Li_2TiO_3$ became apparent. When the reaction temperature was 550°C, the peaks of $Li_2TiO_3$ became more pronounced. The data presented by Kijima *et al.* (1) in their Fig. 3 and Table 1 are also consistent with a dominant product of BiOI.

Analogous reactions between $Bi_2WO_6$ and LiI were conducted at 350, 400, and 550°C. Again, the X-ray powder diffraction spectra were always dominated by the pattern of highly crystalline BiOI. However, peaks of $Li_6W_2O_9$ were also generally observed. Reactions under similar conditions of $Bi_4Ti_3O_{12}$ and $Bi_2WO_6$ with other $AX$ halides ($A$ = Li, Na, or Ag; $X$ = Cl, Br, or I) also gave Bi$OX$ as the dominant crystalline product. Other Aurivillius phases such as $Bi_2CaNb_2O_9$, $Bi_3NbTiO_9$, and $Bi_4V_2O_{11}$ reacted with LiI at low temperatures to give BiOI as the dominant crystalline product.

We conclude that Aurivillius phases are generally highly reactive with many halides at low temperature to produce a highly crystalline Bi$OX$ phase. The other reaction products are generally noncrystalline or poorly crystalline. No indication of an intercalation reaction with Aurivillius phases was observed in any case.

### ACKNOWLEDGMENT

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### REFERENCES

1. T. Kijima, S. Kimura, Y. Kawahara, K. Ohe, M. Yada, and M. Machida, *J. Solid State Chem.* **146,** 60 (1999).

[1] To whom correspondence should be addressed. E-mail: sleighta@chem.orst.edu.



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