LETTER TO THE EDITOR

New Topotactic Derivatives of the Open-Framework Semiconductor KBi_3S_5 via a Low-Temperature Solid-State Ion-Exchange Route

Konstantinos Chondroudis and Mercouri G. Kanatzidis[1]

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824
E-mail: kanatzid@argus.cem.msu.edu

A new low-temperature solid-state ion-exchange route has been used to ion-exchange KBi_3S_5. The new method allows the solid–solid ion-exchange of the K^+ ions for the smaller cations Li^+ and Na^+, as well as for the NH_4^+ at the remarkably low temperature regime of 110–130°C. The topotactically ion-exchanged series $A_xK_{1-x}Bi_3S_5$ (A = Li, Na, and NH_4) was prepared and characterized by powder X-ray diffraction, differential scanning calorimetry, differential thermal analysis, thermal gravimetric analysis, semiquantitative microprobe analyses, solid-state UV/vis/near-IR spectroscopy, and variable-temperature solid-state ^7Li NMR spectroscopy. © 1998 Academic Press

INTRODUCTION

The prospect of constructing accessible, metal chalcogenide, framework structures is intriguing. Such nonoxidic compounds could combine the shape-selective functions of microporous oxides with the useful electronic properties of metal chalcogenides. The concept has been discussed in a few publications (1–4) and a review has appeared which describes potentially interesting nonzeolitic open-framework solids (3). In this context, the recently reported three-dimensional open-framework semiconductor KBi_3S_5 (5) is particularly relevant. Its structure, shown in Fig. 1, is composed of edge-sharing BiS_6 octahedra forming a three-dimensional $[Bi_3S_5]^-$ framework with the presence of large parallel tunnels running along the b-axis. The tunnels are independent and do not communicate. They have a rectangular cross-section with dimensions of 9.0×9.3 Å. The K^+ ions reside in these tunnels and are fractionally distributed over two crystallographic sites. The tunnels are obviously larger than what is necessary for accommodating all the K^+ ions, and this gives rise to a unit-cell volume of KBi_3S_5

(1204 Å^3), which is 20% larger than that of the related but not isostructural $CsBi_3S_5$ (1036 Å^3) and α-$RbBi_3S_5$ (991 Å^3), despite the fact that it contains the smaller K^+ ion. Therefore, KBi_3S_5 has the potential to act as a host for ion-exchange or to be converted into a microporous material. Earlier, we attempted to ion-exchange the K^+ ions by reacting the material with various aqueous Li^+ and Na^+ halide salts unsuccessfully (5). The reason for this was the high effective ionic radius of Li^+ and Na^+ due to their hydration sphere. Solid-state ion-exchange was only achieved via reaction with RbCl at ~350°C which yielded the isostructural β-$RbBi_3S_5$. However, the same conditions using other alkali halide salts were unsuccessful, leading primarily to decomposition.

To fully explore the potential of KBi_3S_5 as a host material, we have now developed a new low-temperature solid-state ion-exchange route. The new method allows the solid–solid ion-exchange of the K^+ ions for the smaller cations Li^+ and Na^+ at the remarkably low temperature regime of 110–130°C. In addition, we observe complete exchange with NH_4^+ at 115°C. We report here the topotactically ion-exchanged series $A_xK_{1-x}Bi_3S_5$ (A = Li, Na, and NH_4) using the iodide salts as ion-exchange agents. While these salts have been used for the ion-exchange of the TlM_5Q_8 (M = Ti, V; Q = S, Se, Te) compounds at temperatures of 300–600°C (6–9) to the best of our knowledge this is the first time they are reported to act at such low temperatures.

In our first attempts we prepared mixtures of the parent compound with LiI in a 1 : 50 stoichiometry. Great excess of the iodide was used to favor the ion-exchange reaction

$$KBi_3S_5 + LiI \rightarrow LiBi_3S_5 + KI. \qquad [1]$$
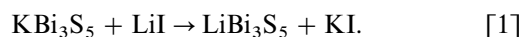
A mixture of reactants was ground together sealed in a pyrex tube in vacuum and then heated at ~200°C for
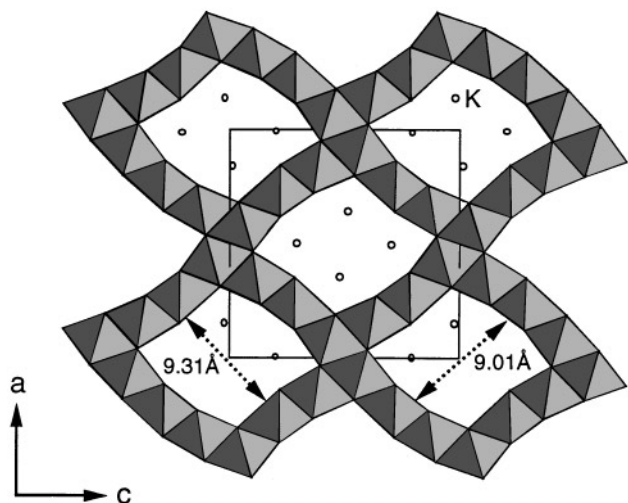
FIG. 1. Polyhedral representation of KBi_3S_5 viewed down the b-axis. The positions of the K ions are shown as small open circles and they are only half occupied.

3 days. This led to decomposition of the parent compound to Bi_2S_3. The reaction between the metal iodides and KBi_3S_5 was probed with differential scanning calorimetry (DSC) and differential thermal analysis (DTA) techniques to determine the appropriate reaction temperatures. DSC performed on mixtures of KBi_3S_5 and the iodides displayed endothermic events occurring at 130–160°C depending on the iodide used. Control DSC experiments performed on KBi_3S_5 and on the metal iodides, separately, suggest that the thermal events are due to the metal iodides and not to an ion-exchange reaction. We then chose to perform an identical reaction at 100°C (4 days) which is well below the temperatures of the thermal events that occur in the iodides. Remarkably, substantial ion-exchange occurred producing an X-ray isomorphous product, which analyzed for $K_{0.45}Bi_3S_5$ (Li cannot be observed by our energy dispersive spectroscopy (EDS) detector). Fine tuning of the reaction conditions yielded an optimum temperature of ~115°C for Li exchange. Two more reaction cycles with fresh LiI gave $Li_{0.82}K_{0.18}Bi_3S_5$. To improve interphase contact between the reactants and shorten the reaction time we tried pressing the reactants into a pellet (see Experimental). Indeed, this resulted in the same $Li_{0.82}K_{0.18}Bi_3S_5$ phase in a fraction of the time (only one reaction cycle for maximum exchange), and with improved crystallinity. Similar results were obtained for Na^+ and NH_4^+ with the reaction from a pellet yielding materials with higher degree of exchange and better crystallinity than those coming from simple powder mixing experiments; see Table 1. The small amount of K^+ still present in the Li- and Na-exchanged material is due to the one-dimensional nature of the tunnels of $[Bi_3S_5]^-$. The residual K^+ is kinetically trapped inside because of the strictly one-dimensional diffusion in these tunnels.

The X-ray powder diffraction patterns in Fig. 2, show topotactic ion-exchange with efficiencies of 80–100%. This solid–solid reaction at the remarkably low temperatures of 110–130°C, significantly departs from the ion-exchange reactions at high temperatures and can be regarded as a true "soft" chemistry technique.

The ion-exchange process leads to materials with similar electronic structure as suggested by the optical spectra of the products. The band-gaps (E_g) of ABi_3S_5 display only a mild dependence on the nature of the cation, and they range from 0.98 to 1.20 eV; see Fig. 3. The very small shift in E_g is consistent with the topotactic nature of the exchange (no structure change) and confirms the electronic structure
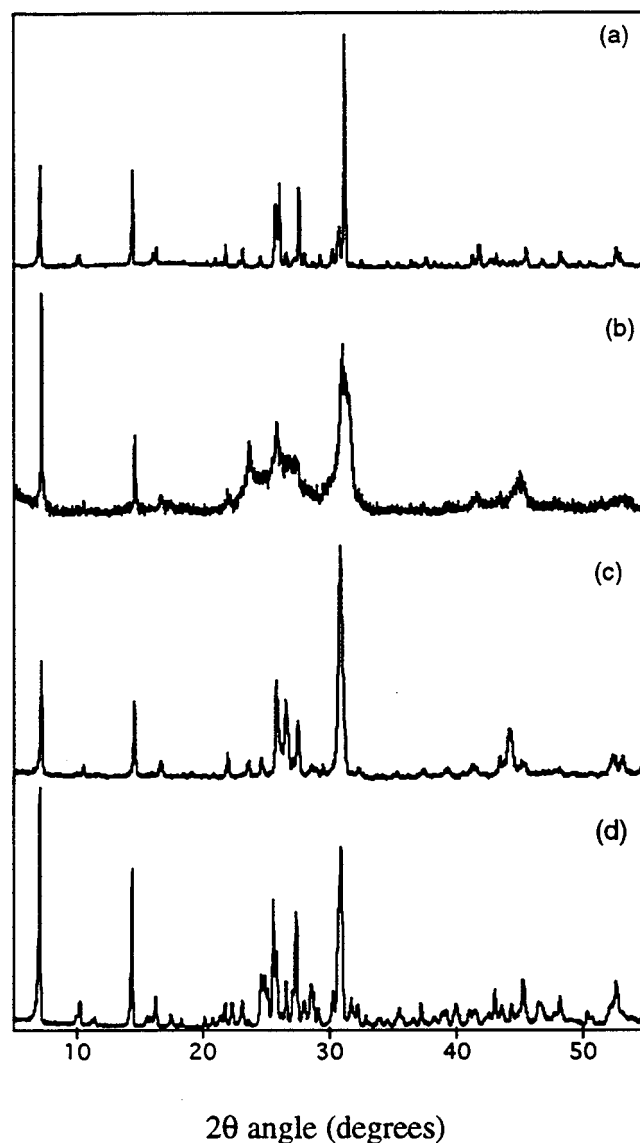

2θ angle (degrees)

FIG. 2. X-ray powder diffraction patterns of (a) KBi_3S_5, (b) $Li_{0.82}K_{0.18}Bi_3S_5$, (c) $Na_{0.66}K_{0.32}Bi_3S_5$, and (d) $NH_4Bi_3S_5$.

Exchange agent	Ratio	T (°C)	Days	Product	Alkali atom radius (Å)	Cond. (S/cm)	Bandgap (eV)
none (KBi_3S_5)	—	—	—	—	1.37	3.2×10^{-6}	1.21
LiI	1:30	115	7	$Li_{0.82}K_{0.18}Bi_3S_5$	0.59	7.1×10^{-5}	0.98
NaI	1:50	130	9	$Na_{0.66}K_{0.32}Bi_3S_5$	0.99	1.9×10^{-5}	1.14
NH_4I	1:50	115	8	$NH_4Bi_3S_5$	2.1	2.1×10^{-5}	1.20

of the material is nearly intact. This suggests that the cations are essentially noninteracting with the framework, functioning only as charge-balancing entities. The largest shift in E_g is observed with Li, suggesting that in this case there could be a more substantial interaction with the framework via considerably degree of Li–S bonding. This is expected because Li^0 is the smallest and hardest of all the alkali ions. The observed E_g values lie in the optimum range for solar energy absorption and point to possible photoconductivity response with visible light irradiation. The electrical conductivity of the exchanged materials is higher particularly for the Li compound, consistent with its smaller band-gap; see Table 1.

In order to probe the environment of the lithium ions in the tunnels, variable-temperature ^{7}Li static solid-state NMR measurements were performed for $Li_{0.82}K_{0.18}Bi_3S_5$. The uniform lineshapes even at -80°C suggest a well defined coordination environment for the Li ion; see
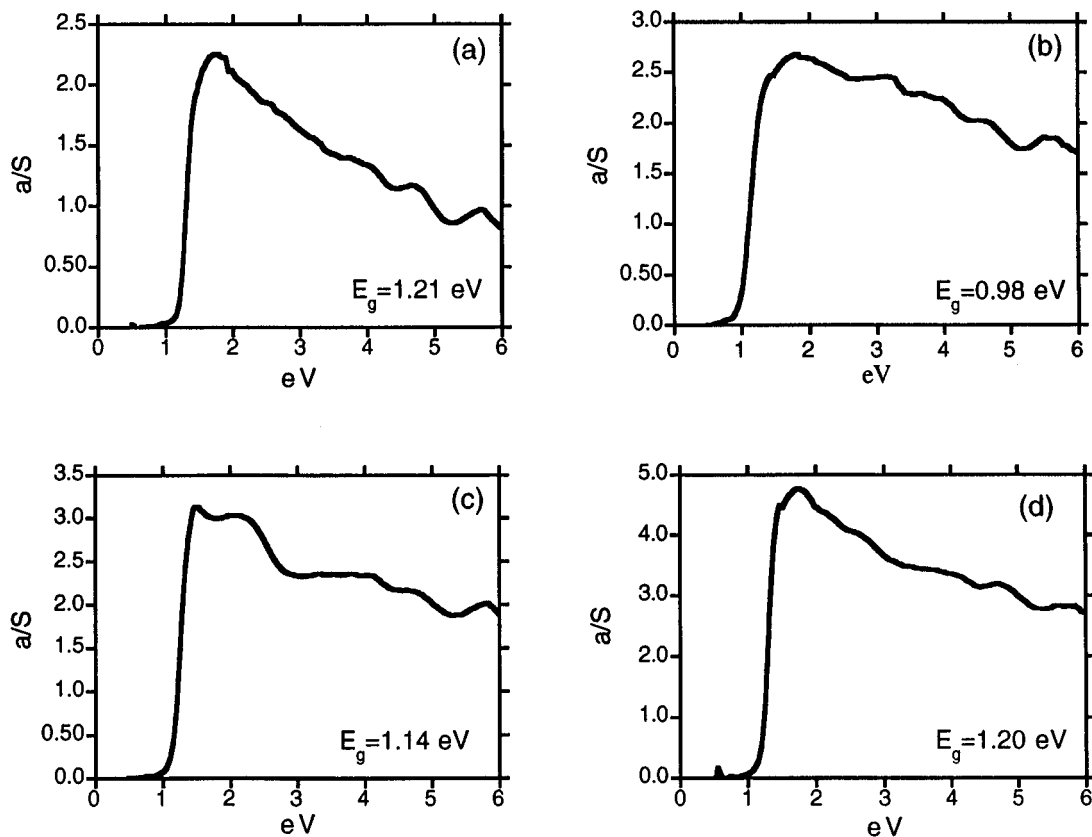

FIG. 3. Optical absorption spectra of (a) KBi_3S_5, (b) $Li_{0.82}K_{0.18}Bi_3S_5$, (c) $Na_{0.66}K_{0.32}Bi_3S_5$, and (d) $NH_4Bi_3S_5$.
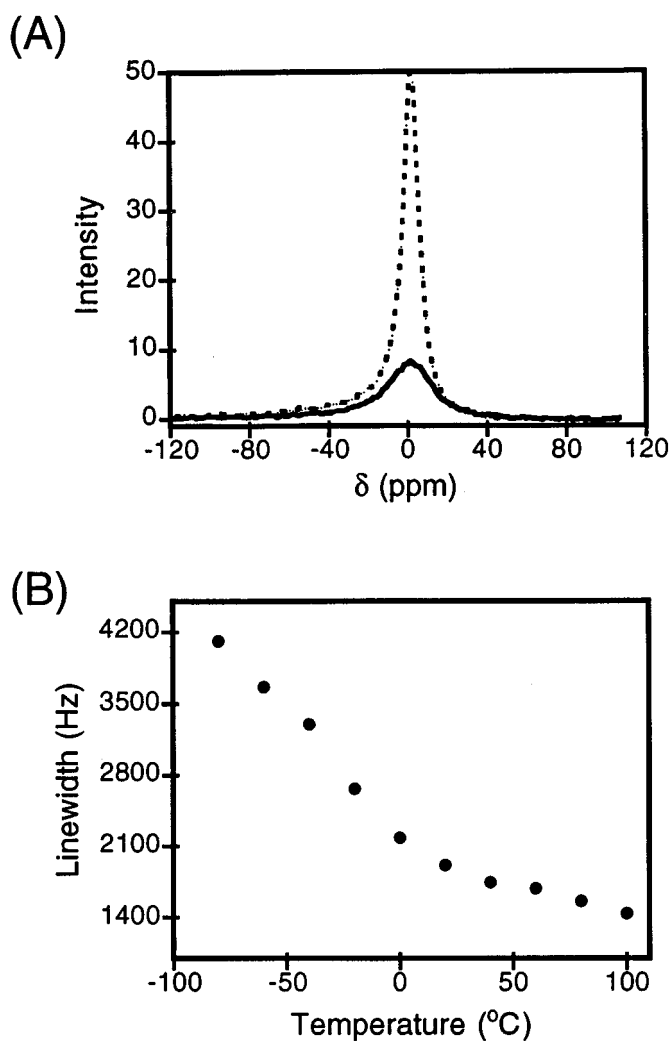
FIG. 4. (A) Static ^{7}Li NMR spectra of $Li_{0.82}K_{0.18}Bi_3S_5$ at $-80°C$ (solid line) and at $100°C$ (dashed line). (B) Temperature dependence of the linewidth of the resonance peak in the solid-state ^{7}Li NMR spectrum of $Li_{0.82}K_{0.18}Bi_3S_5$.

Fig. 4A. The resonance peak narrows dramatically as the temperature is increased from -80 to $100°C$, see Fig. 4B, suggesting rapid motion of Li ions inside the tunnels.

Since all materials were isolated in water, the latter was expected to be present inside the tunnels especially in the case of Li^+. We therefore performed thermogravimetric analysis (TGA) on both $Li_{0.82}K_{0.18}Bi_3S_5$ and $NH_4Bi_3S_5$. The former displayed a 2.36% weight loss starting at 120°C, which can be attributed to water loss (theoretical 2.2% assuming one molecule of H_2O per Li). The X-ray diffraction pattern of the residue showed decomposition to Bi_2S_3, which suggests instability of the framework with respect to dehydration. The thermal behavior of $NH_4Bi_3S_5$ was also studied in the hope of observing NH_3 evolution which

would leave a proton-exchanged material HBi_3S_5 behind. The TGA displayed a 4.76% weight loss starting at 180°C (theoretical 2.2%), suggesting the loss of H_2S as well. The X-ray diffraction pattern of the residue also showed decomposition.

The ion-exchanged compounds obtained in this work are metastable because none of them could be prepared by the polysulfide flux method (used for KBi_3S_5) (5) or by high-temperature techniques. The most intriguing aspect of this ion-exchange process is the fact that it proceeds at the contact interface between crystals of KBi_3S_5 and of AI ($A = $ Li, Na, and NH_4) at such low temperature. The mild conditions under which the method operates on the metastable KBi_3S_5 imply a broad scope because it should allow its application to metastable inorganic chalcogenides (10). Consequently, a great number of open-framework nonoxidic phases now become candidates for ion-exchange. Preliminary experiments suggest that the method can be extended to transition metal iodides (e.g., Cu,Ag) which dramatically alter the host's electronic structure and reduce the band-gap by 0.4–0.7 eV.

EXPERIMENTAL

DSC experiments were performed under a nitrogen atmosphere as described elsewhere (5). The samples were heated to the desired temperature at 3°C/min. Variable-temperature solid-state ^{7}Li NMR measurements were performed on a 400-MHz Varian NMR instrument.

Ion Exchange Reactions

KBi_3S_5 (5) was mixed with the desired iodide at various ratios (1 : 30 for LiI; 1 : 50 for NaI and NH_4I) inside a nitrogen-filled glovebox. The mixture was ground into a fine powder and loaded into a dye of ~ 1.3 cm diameter. The sample was pressed into a pellet outside the glovebox at a pressure of 9 metric tons (20,000 pounds). The resulting pellet was placed inside a small glass vial (20 ml size) equipped with a screw cap and heated at the desired temperature (115°C for LiI, and NH_4I; 130°C for NaI) for 8–9 days. After reaction the excess LiI, NaI, and NH_4I was dissolved in distilled water. The product was washed with water, acetone, and ether. X-ray powder diffraction and microprobe analysis did not reveal the presence of residual metal iodide.

ACKNOWLEDGMENT

REFERENCES

1. (a) R. L. Bedard, S. T. Wilson, L. D. Vail, E. M. Bennet, and E. M. Flanigen, *in* "Zeolites: Facts, Figures, Future" (P. A. Jacobs and R. A. van Santen, Eds.), p. 387. Elsevier, Amsterdam, 1989. (b) R. L. Bedard, L. D. Vail, S. T. Wilson, and E. M. Flanigen, U.S. Patent 4,880,761 (1989).
2. S. Dhingra and M. G. Kanatzidis, *Science* **258,** 1769 (1992).
3. C. L. Boews and G. A. Ozin, *Adv. Mater.* **8,** 13 (1996).
4. J. B. Parise, *Science* **251,** 293 (1991).
5. T. J. McCarthy, T. A. Tanzer, and M. G. Kanatzidis, *J. Am. Chem. Soc.* **117,** 1294 (1995).
6. J. M. Tarascon, G. W. Hull, and F. J. DiSalvo, *Mater. Res. Bull.* **19,** 915 (1984).
7. (a) G. Huan and M. Greenblatt, *Mater. Res. Bull.* **22,** 505 (1987). (b) G. Huan and M. Greenblatt, *Mater. Res. Bull.* **22,** 943 (1987).
8. T. Ohtani, Y. Sano, K. Kodama, S. Onoue, and H. Nishihara, *Mater. Res. Bull.* **28,** 501 (1993).
9. T. Novet, M. Wagner, M. Jiang, and D. C. Johnson, *Mater. Res. Bull.* **30,** 65 (1995).
10. (a) K. Chondroudis and M. G. Kanatzidis, *J. Am. Chem. Soc.* **119,** 2574 (1997). (b) E. A. Axtell, Y. Park, K. Chondroudis, and M. G. Kanatzidis, *J. Am. Chem. Soc.*, in press. (c) J. A. Hanko and M. G. Kanatzidis, *Angew. Chem. Int. Ed. Engl.*, in press.