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Note

UNUSUAL PHASE TRANSITION OF BARIUM IODATE

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Iodic acid and monovalent metal iodates, MIO_3 (M = alkali metals, NH_4^+, Tl), tend to crystallize in acentric structures and show nonlinear optical properties [1,2]. These are mostly pyroelectric and piezoelectric compounds and in a few cases ferroelectric and ferrielastic properties have been observed. The polymorphic behaviour of alkali metal iodates has been the subject of considerable interest [3—7]. During the last few years the crystallographic, magnetic and nonlinear optical properties of 3*d* and 4*f* metal iodates have been extensively studied in Bell Laboratories [8—12] in search of materials which might exhibit new interesting properties due to cross-interactions of other physical properties. To our knowledge, the alkaline earth iodates have not received any detailed consideration from such an angle. In a previous publication, we reported [13] activation energies for the conversion of $M(IO_3)_2$ to $M_5(IO_6)_2$ (M = Ca, Sr, Ba) and noted that only $Ba(IO_3)_2$ undergoes an endothermic transition prior to decomposition. As part of our interest in the dielectric behaviour and crystallographic modifications of alkaline earth and rare earth iodates we have examined the endothermic transition of $Ba(IO_3)_2$ in more detail. In what follows it will emerge that the phase transition behaviour of $Ba(IO_3)_2$ is rather uncommon.

EXPERIMENTAL

Thermal analysis was carried out with a MOM derivatograph. Throughout the study 1 g sample size and 200 mesh particle size were maintained. The heating rate was 4°C min^{-1} under flowing dry air. X-Ray powder patterns were obtained using an 11.48 cm diameter Debye—Scherrer camera with nickel filtered CuK_α radiation. The heat of transition was measured by a Shimadzu DSC-30 differential scanning calorimeter under the measuring conditions of ±50 mJ sec^{-1} range and 20 mm min^{-1} chart speed. The melting peak area of In (6.79 mcal mg^{-1}) was chosen as the standard. $Ba(IO_3)_2 \cdot H_2O$ was prepared as reported earlier [13].

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RESULTS AND DISCUSSION

$Ba(IO_3)_2 \cdot H_2O$ loses the water molecule between 80 and 180° C and the anhydrous product is stable up to 550° C. At 422° C (Fig. 1) an endothermic transition is obtained which in the cooling run from 460 to 30° C does not show any exothermic transition in DTA, indicating that the phase transition is irreversible. However, when the sample is cooled from 460° C to room temperature, and is stored over P_2O_5 for a few hours, an endotherm is observed on reheating. In this case the transition temperature is 378° C (Fig. 1) and the shape of the DTA profile is quite different from that previously observed at 422° C. Here also no exotherm can be detected in the cooling run. The sample cooled to room temperature and stored over P_2O_5 for a few hours, again in the heating cycle shows the endotherm precisely at 378° C. In several heating cycles the transition temperature at 378° C has remained invariant. It has also become apparent during experiments that the area of the endotherm at 378° C increase with time over which the sample has been stored. Figure 1 shows three such cases where samples have been kept for 4, 8 and 16 h. A time interval variation study has revealed that beyond 16 h no further increase in the area of the endotherm occurs. However, at least 2 h is needed to obtain a detectable endotherm. If instead of storing the material over P_2O_5, it is kept exposed to air for a few hours, then moisture is absorbed and on heating the endotherm is observed at a temperature slightly above 378° C. The endotherm has a sharper feature and the area is also

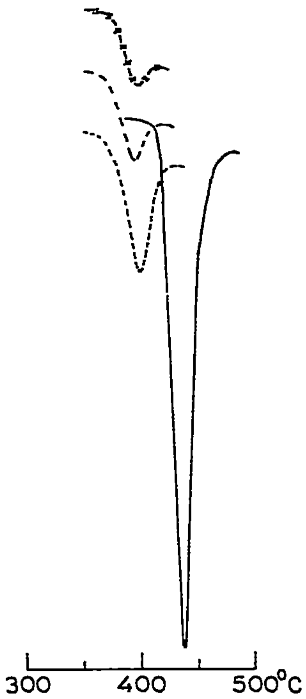
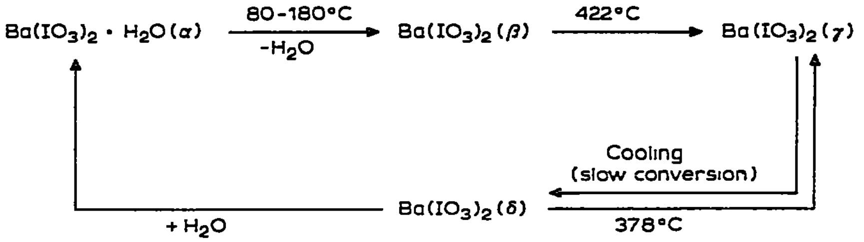


Fig. 1. DTA curve of barium iodate before standing over P_2O_5 (———) and after standing over P_2O_5 for 4 h (X———X), 8 h (· — · — ·), and 16 h (- - - - - -).

greater, compared to that stored for a similar time period in a dry atmosphere. More exposure to air causes more absorption of water with a concomitant increase in transition temperature and peak area. Eventually on keeping for several days the sample attains the composition $Ba(IO_3)_2 \cdot H_2O$ whose powder pattern and DTA is similar to that of the freshly prepared compound. The above observations can be explained by the scheme shown below



X-Ray powder data of α, β and δ phases of barium iodate are shown in Table 1. It may be noted that the powder patterns of the β and δ phases are entirely different. The β → γ transformation is irreversible but the γ → δ phase transition is quasireversible. Because the γ → δ conversion rate is slow,

TABLE 1

X-Ray powder data of α, β and γ phases of barium iodate

α	β	γ
d (obsd.)	d (obsd.)	d (obsd.)
5.9 (s)		5.07 (m)
4.45 (m)	4.33 (s)	4.35 (s)
		4.21 (s)
		4.09 (s)
	3.95 (s)	
3.95 (s)	3.57 (vw)	3.56 (w)
3.68 (s)	3.41 (w)	3.35 (m)
3.59 (s)	3.23 (s)	3.10 (vw)
3.40 (s)	3.07 (m)	
3.02 (vs)	3.03 (vw)	
2.56 (m)	2.95 (w)	2.96 (w)
2.41 (m)	2.88 (vw)	2.77 (w)
2.34 (vw)	2.54 (vw)	2.15 (m)
2.26 (s)	2.40 (vw)	
2.08 (m)	2.24 (vw)	
	2.14 (w)	
1.95 (w)	1 89 (vw)	1.97 (w)
1.90 (m)	1.85 (vw)	1.94 (m)
1.88 (m)	1.81 (vw)	1.90 (w)
1.85 (m)	1.77 (vw)	1.77 (vw)
1.83 (w)		1.71 (vw)
1.79 (vw)		1.68 (vw)
1.71 (vw)		1.57 (vw)

a corresponding exotherm is not observed. It appears that about 2 h are needed for the onset of the $\gamma \rightarrow \delta$ transformation and complete conversion requires about 16 h. The enthalpy change, ΔH, for $\beta \rightarrow \gamma$ is 2.98 kcal mole^{-1} and for $\delta \rightarrow \gamma$ it is 1.44 kcal mole^{-1}. The activation energies, E_a *, evaluated by the method of Borchardt and Daniels [14] are 110 kcal mole^{-1} ($\beta \rightarrow \gamma$) and 85 kcal mole^{-1} ($\delta \rightarrow \gamma$). The γ phase is in a highly structurally disordered form and it is likely to be a quasicrystalline state. Thus, ordering of the γ phase leads to the nucleation and growth of the δ phase. However, it is not possible to indicate at this stage which one is rate determining. A detailed study of the kinetics of phase transition and dielectric properties will be the subject matter of a future discussion.

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