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## Note

# THERMAL STABILITY AND PHASE TRANSITION STUDIES OF DIAMMONIUM ZINC AND CADMIUM HALIDES

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ABSTRACT

Diammonium zinc and cadmium tetrahalides have been investigated by thermoanalytical techniques. The results on the thermal stability and phase transition characteristics of these compounds are presented.

## INTRODUCTION

Considerable attention has been paid to the study of substances having the chemical formula $A_2BX_4$. The diammonium halide spinels, $(NH_4)_2BX_4$, where B = Zn, Cd and X = Cl, Br, I, belong to $A_2BX_4$ type ferroelectrics. Interest in these systems has been due to the successive phase transitions and 1C phases they exhibit. Whereas chloride and bromide compounds have been studied employing various techniques such as XRD [1], NQR [2], dielectric measurements [3], Raman scattering [4], DTA [3], DSC [5], etc., the iodides have not been studied at all. Data on the thermal behaviour, particularly thermal stability and decomposition, of these compounds are lacking. The present paper reports results of TG, DTA and DSC examination of the diammonium halide spinels.

## EXPERIMENTAL

Crystals of the various halide spinels were grown by slow evaporation of an aqueous solution of $NH_4X$ and $MX_2$ (M = Zn, Cd and X = Cl, Br, I) in the molar ratio 2 : 1. Wherever possible the compounds were characterized by comparison of their XRD powder patterns with those available in the literature.

X-Ray diffraction patterns were taken using nickel filtered Cu $K\alpha$ radiation at 34 kV and 18 mA.

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Thermogravimetric analysis (TG) was carried out on a Stanton thermobalance of 1 mg sensitivity. Differential thermal analysis (DTA) was carried out on a DTA unit built in this laboratory. Heating and cooling cycles were taken, wherever it was found necessary, to establish reversibility of transitions. Differential scanning calorimetry (DSC) measurements were done on a ULVAC DSC unit. Thermal cycling was carried out to establish the reversibility of transitions.

## RESULTS AND DISCUSSION

The Cd compounds, $(NH_4)_2CdX_4$ are stable only up to ca. 200 °C (Fig. 1) and the Zn compounds, $(NH_4)_2ZnX_4$ up to ca. 230 °C (Fig. 2). TG and DTA showed that $(NH_4)_2CdCl_4$ and $(NH_4)_2CdBr_4$ decompose losing the ammonium halide in two distinct steps, i.e. via an intermediate step (stable

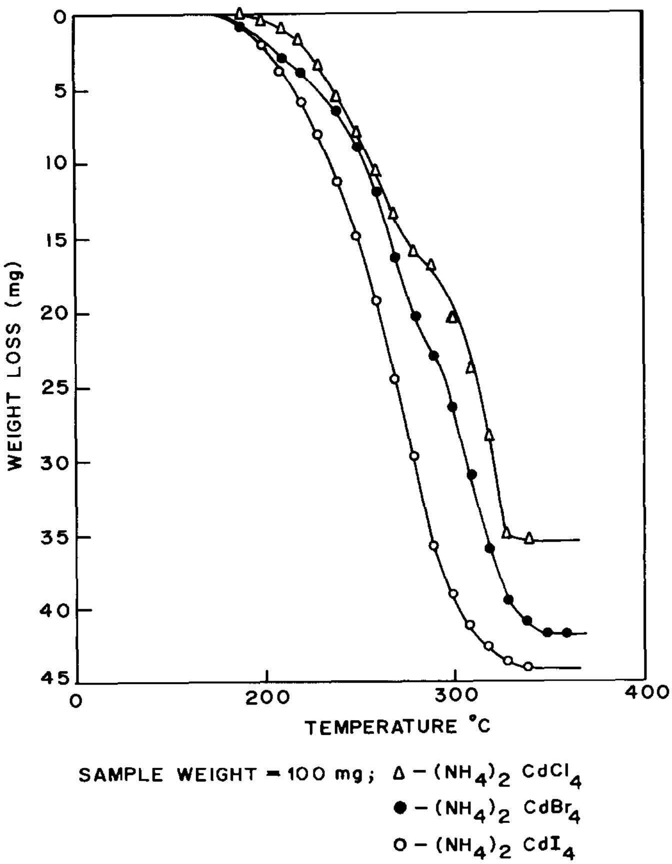


Fig. 1. TG curves of diammonium cadmium tetrahalides.

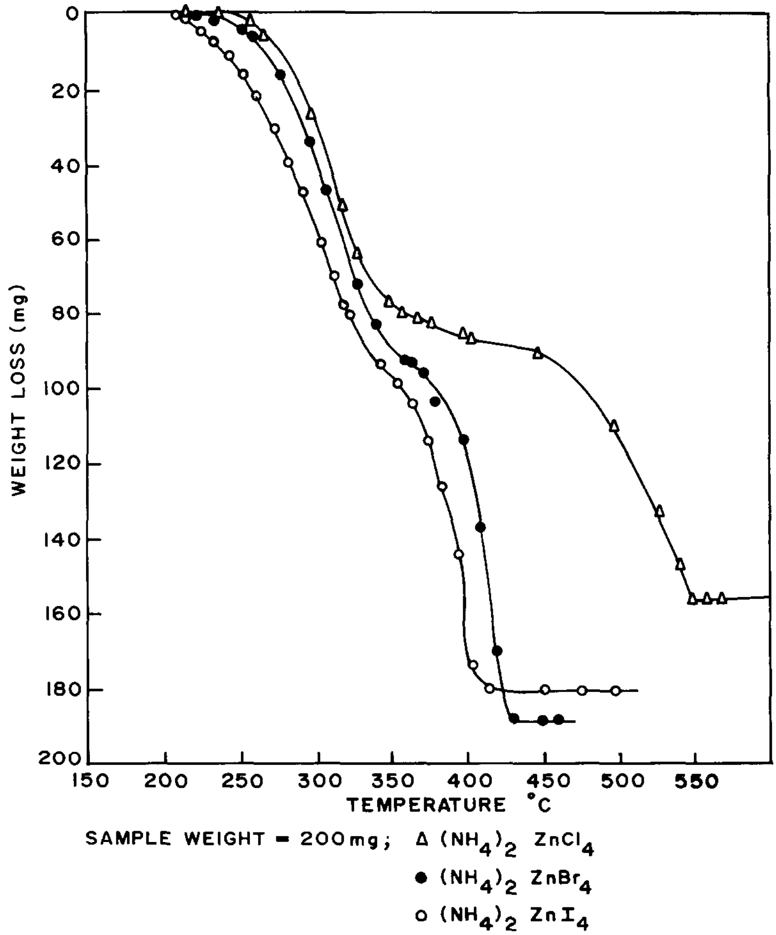


Fig. 2. TG curves of diammonium zinc tetrahalides.

phase) corresponding to the trihalide, $(NH_4)CdX_3$. The intermediates, trichlorides and tribromides of Cd, decompose at 270 °C and 280 °C respectively leading to only Cd halides. On the other hand, the loss of ammonium halide in $(NH_4)_2CdI_4$ and $(NH_4)_2ZnX_4$ takes place in one continuous step without manifestation of any intermediate trihalide. The respective Cd and Zn halide residues melt and volatilize in the normal way. However, the Zn halides undergo partial oxidation as well, leaving some Zn as oxide residue (Fig. 2).

DTA and DSC studies on $(NH_4)_2ZnCl_4$ showed an endothermic peak at 137 °C corresponding to a reversible phase transition and another endothermic peak at 283 °C attributed to melting of $ZnCl_2$. The DTA and DSC curves for $(NH_4)_2$ $ZnBr_4$, on the other hand showed four endothermic peaks at 102, 120, 166 and 393 °C, the first three endothermic effects in agreement with the reported transitions [5] and the last one corresponded to the melting of $ZnBr_2$. In the case of $(NH_4)_2ZnI_4$ only one endothermic peak was observed at 170 °C. All the above transitions have been seen to be reversible.

$(NH_4)_2CdBr_4$ and $(NH_4)_2CdI_4$ showed one endothermic peak each while heating at 285 °C and 200 °C respectively, attributed to the melting of the tribromide and tetraiodide respectively. On the other hand $(NH_4)_2CdCl_4$ is seen to decompose to $CdCl_2$ without melting of the intermediate trichloride.

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