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DIELECTRIC DIFFERENTIAL THERMAL ANALYSIS. VIII. Dithionates

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Dithionates ($CaS_2O_6 \cdot 4H_2O$, $SrS_2O_6 \cdot 4H_2O$, $BaS_2O_6 \cdot 2H_2O$, $MnS_2O_6 \cdot 4H_2O$, $MgS_2O_6 \cdot 6H_2O$, $CoS_2O_6 \cdot 6H_2O$, $NiS_2O_6 \cdot 6H_2O$, $ZnS_2O_6 \cdot 6H_2O$ and $CuS_2O_6 \cdot 4H_2O$) were subjected to thermodielectric analysis. The thermoanalytical curves show low temperature effects from 60 to 350°. These are related with the dehydration and decomposition of the dithionates, which could be fully correlated with the knowledge of the thermal behavior of these compouds obtained with other thermal methods.

The chemistry of dithionates started in the early years of last century when Gay–Lussac synthesized manganese dithionate by the oxidation of an aqueous solution of SO_2 with MnO_2 [1].

Table 1 Crystalline structures of the studied dithionates

Dithionates	Lattice	Space group	Reference
$BaS_2O_6 \cdot 2H_2O$	monoclinic	$C_{2h}^5 - B2_1/9$	5
$SrS_2O_6 \cdot 4H_2O$	trigonal	$P6_2$	6
$MgS_2O_6 \cdot 6H_2O$	triclinic	$P\bar{1}$	7
$NiS_2O_6 \cdot 6H_2O$	triclinic	$P\bar{1}$	7
$ZnS_2O_6 \cdot 6H_2O$	triclinic	$P\bar{1}$	8
$CoS_2O_6 \cdot 6H_2O$	triclinic	$P\bar{1}$	9
$CaS_2O_6 \cdot 4H_2O$	trigonal	$P6_1$	9
$CuS_2O_6 \cdot 4H_2O$	monoclinic		9
$MnS_2O_6 \cdot 4H_2O$	monoclinic		9

The literature describes different methods of synthesis [2–4], the crystalline structures of the dithionates selected for the present thermal study [5–

The present paper reports the application of thermodielectric analysis to dithionates as an example of the possibilities of the method for the study of dehydration and decomposition processes in inorganic materials.

Experimental

For the present thermal study we chose the following dithionates: $CaS_2O_6\cdot4H_2O$, $BaS_2O_6\cdot2H_2O$, $MnS_2O_6\cdot4H_2O$, $MgS_2O_6\cdot6H_2O$, $CoS_2O_6\cdot6H_2O$, $NiS_2O_6\cdot6H_2O$, $ZnS_2O_6\cdot6H_2O$, $SrS_2O_6\cdot4H_2O$ and $CuS_2O_6\cdot4H_2O$. The synthesis procedure is described elsewhere [2]. It consists in the oxidation of an aqueous solution of SO_2 in the presence of MnO_2 and the successive addition of $Ba(OH)_2$ to obtain $BaS_2O_6\cdot2H_2O$; the others were synthesized by adding the carbonate or sulphate of the corresponding metal to a solution of barium dithionate.

All the obtained dithionates were carefully characterized by XRD, IR spectrometry, TDA, TG and Crom–mass spectrometry [20]. Table 2 provides a resumé of the information obtained in connection with the thermal behaviour of the studied dithionates [19], which will be very useful in the interpretation of the thermodielectric curves of the dithionates, obtained as usual in the equipment described in the first part of the present series [21].

Table 2 Thermal behavior of the studied dithionates [19]

Dithionate	Dehydration (temperature interval, °C)	Decomposition (temperature interval, °C)
$CaS_2O_6\cdot4H_2O$	80–125 ($4H_2O$)	260–320 (SO_2)
$BaS_2O_6\cdot2H_2O$	75–110 ($2H_2O$)	160–220 (SO_2)
$MnS_2O_6\cdot4H_2O$	80–135 ($2H_2O$)	140–200 (SO_2+2H_2O)
$CoS_2O_6\cdot6H_2O$	50–140 ($4H_2O$)	150–170 (SO_2+H_2O)
		235–275 (H_2O)
$NiS_2O_6\cdot6H_2O$	85–125 ($4H_2O$)	130–135 (SO_2+3H_2O)
		290–330 (H_2O)
$MgS_2O_6\cdot6H_2O$	70–135 ($4H_2O$)	200–320 (SO_2+2H_2O)
$SrS_2O_6\cdot4H_2O$	80–115 ($3H_2O$)	150–230 (SO_2+H_2O)
$CuS_2O_6\cdot4H_2O$		120–155 (SO_2+3H_2O)
		190–220 (H_2O)
$ZnS_2O_6\cdot4H_2O$		60–140 (SO_2+5H_2O)
		200–235 (H_2O)

Results and discussion

The thermodielectric curves of the dithionates are reported in Fig. 1. The curves for $CaS_2O_6 \cdot 4H_2O$ and $BaS_2O_6 \cdot 2H_2O$ exhibit two peaks, as must be expected from the data reported in Table 2, i.e. a first peak related with dehydration and a second peak related with decomposition.

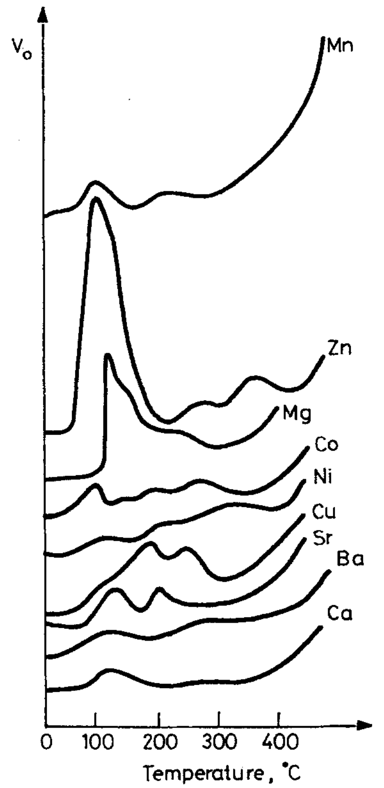

Fig. 1 Thermodielectrical curves of dithionates

The $SrS_2O_6 \cdot 4H_2O$ curve is composed of two well-defined peaks which could be fully correlated with the corresponding effects of dehydration and decomposition plus dehydration which compose the thermal behaviour of this dithionate.

$CuS_2O_6 \cdot 4H_2O$ also yields two peaks and both can be related with the corresponding effects detected in the TDA and TG curves and reported in Table 2.

The $NiS_2O_6 \cdot 6H_2O$ and $CoS_2O_6 \cdot 6H_2O$ curves exhibit three peaks and a shoulder, which describe the consecutive processes of dehydration, dehydration plus decomposition and dehydration described in Table 2.

The $MnS_2O_6 \cdot 4H_2O$ curve exhibits a complex peak involving dehydration and dehydration plus decomposition.

The curve of $ZnS_2O_6 \cdot 6H_2O$ includes a very intense peak for dehydration plus decomposition, one peak related with dehydration and another with no explanation at present.

The two peaks in the curve of $MnS_2O_6 \cdot 4H_2O$ are clearly explained in Table 2, the first being related with dehydration and the second with dehydration plus decomposition.

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Zusammenfassung — Die Dithionate $CaS_2O_6 \cdot 4H_2O$, $SrS_2O_6 \cdot 4H_2O$, $BaS_2O_6 \cdot 2H_2O$, $MnS_2O_6 \cdot 4H_2O$, $MgS_2O_6 \cdot 6H_2O$, $CoS_2O_6 \cdot 6H_2O$, $NiS_2O_6 \cdot 6H_2O$, $ZnS_2O_6 \cdot 6H_2O$ und $CuS_2O_6 \cdot 4H_2O$ wurden einer thermodielektrischen Analyse unterzogen. Die thermoanalytischen Kurven zeigen Low–temperature–Effekte zwischen 60 und 350°C. Diese rühren von der Dehydratation und der Zersetzung der Dithionate her, was vollkommen mit den Ergebnissen übereinstimmt, die über das thermische Verhalten dieser Verbindungen in anderen Verfahren erzielt wurden.