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A study of crystals in the cadmium oxide-tellurium dioxide system

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A partial phase diagram of the cadmium oxide—tellurium dioxide system is presented. The results of attempts to prepare substantial single crystals of congruently and incongruently melting phases are recorded along with the properties of such crystals. It is shown that one of the two compounds obtained as single crystals, namely cadmium di-tellurite, possesses a mica-like nature with excellent insulating properties, but is not piezo-electric. The other, namely cadmium mono-tellurite, can exist in two forms, one of which is piezo-electric.

1. Introduction

One of the compounds in the cadmium oxide—tellurium dioxide system namely cadmium di-tellurite ($CdTe_2O_5$) has been studied by Redman [1]. They found the crystals to be mica-like and piezo-electric. In addition another compound in this system, cadmium mono-tellurite ($CdOTeO_2$), was claimed by Bergmann [2] to exhibit optical second harmonic generation, implying that the structure had no centre of symmetry and therefore could be piezo-electric. The work below reports additional results obtained from a further study of this system with a view to producing both compounds in the form of single crystals and studying their properties, with the object of using them for electronic applications.

2. Experimental

A phase diagram was prepared using differential thermal analysis, X-ray powder photography and attempts to produce single crystals. The differential thermal analysis unit was that described previously [3]. Melts were formed in platinum crucibles by melting together the required amounts of high purity oxides, and the pulling technique used to produce crystals. Growth was performed in a flowing atmosphere of argon at a flow rate of 100 ml per minute. Studies of the structural and optical properties of any crystals were made on specimens cut from single crystals, using a Stoe X-ray precession goniometer and a polarizing microscope.

The frequency dependence of the dielectric properties from 10 Hz to 30 kHz was determined using a General Radio GR1616 capacitance bridge and the temperature dependence at a single frequency of 1592 Hz using a Wayne Kerr B331 autobalance bridge. Evidence for pyro-electricity was sought using the charge integration method [4] and for ferroelectricity by seeking for dielectric hysteresis which implies a reversible spontaneous polarization.

3. Results

The phase diagram constructed form the differential thermal analysis and X-ray studies is shown in Fig. 1. The results indicate one congruently melting compound is present, namely cadmium di-tellurite, which is the compound examined by Redman. [1].

A complex phase situation was found to exist near the 50 mol% region of the diagram. Two phases designated B and C were found and the phase C has two forms designated Cα and Cβ. The phase B has been given the composition $8CdO.9TeO_2$ and the phase C was analysed as $CdOTeO_2$. The α to β phase change of the latter occurs at 700° C.

In the region of the diagram where the melt compositions contained greater than 50 mol%

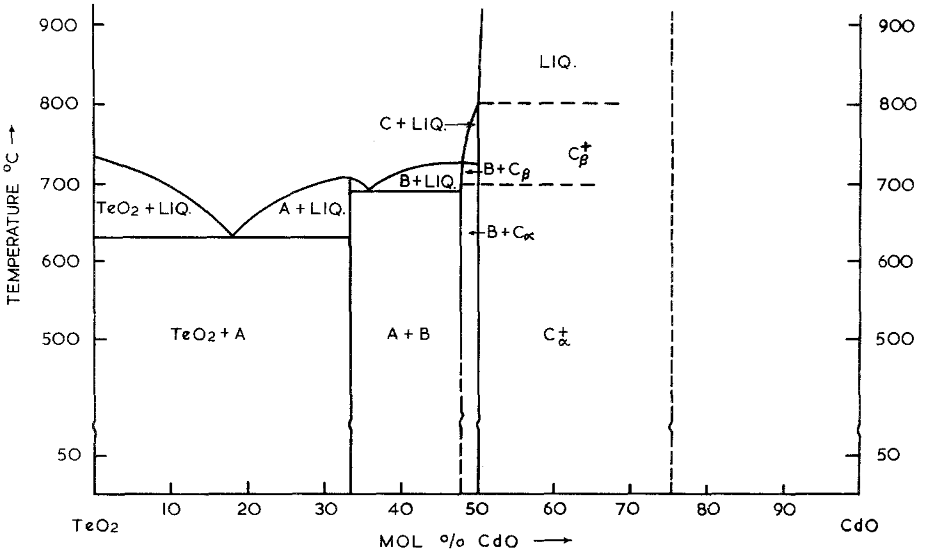

Figure 1 CdO–TeO_2 (phase diagram, major compositions and temperatures. 18 mol% CdO 630 ± 3° C eutectic; 33.3 mol% CdO 708 ± 3° C congruent point (A); 35.5 mol% CdO, eutectic 690 ± 3° C, 48 mol% CdO (approx.) 725 ± 3° C, incongruent point (B); 50 mol% CdO, 795 ± 3° C, incongruent point (C); 700 ± 3° C, phase change in (C).

cadmium oxide, differential thermal analysis became uncertain, a very steep rise in melting point was encountered in this region and loss of volatile cadmium oxide and later tellurium dioxide from the melt made melt composition control difficult. Beyond 75 mol% cadmium oxide no peaks either exothermic or endothermic appeared during heating or cooling cycles of the DTA unit. These results are consistent with the fact that cadmium oxide does not melt at atmospheric

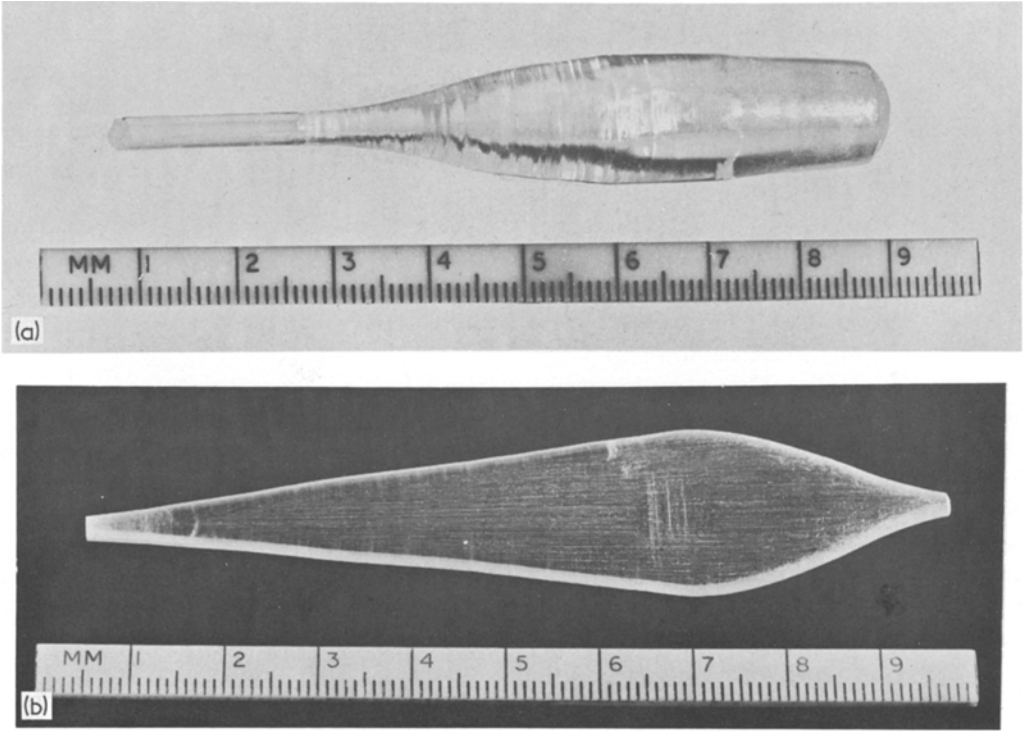

Figure 2 (a) Pulled crystal $CdTe_2O_5$. (b) Pulled crystal $CdTeO_3$.

pressure but undergoes decomposition at about 900° C and commences to sublime about the same temperature.

The results of attempts to produce crystals of compounds found to exist were that high quality crystals of cadmium di- and mono-tellurites could be obtained from melts provided the lift rate did not exceed 1 mm per hour and the rotation rate did not exceed 4 r.p.m. The Figs. 2a and b show examples of cadmium di- and mono-tellurite crystals.

The crystals of the former were very pale yellow in colour in thick samples and were soft. They cleaved into fine sheets very readily, in agreement with the observations of Redman [1]. They are not readily attacked by concentrated alkalis but are attacked by dilute and concentrated mineral acids. Both concentrated nitric acid and concentrated hydrochloric acid when diluted 1:1 with water produced etch pits on freshly cleaved surfaces immersed for 15 sec. These crystals did not give a positive response from the Giebe–Shiebe test for piezo-electricity.

The pronounced tendency of the di-tellurite to cleave and readily bend even in very small samples presented problems in space group identification and measurement of optical properties, which were splitting of reflections on upper level precession photographs and preventing the determination of refractive index against wavelength.

The symmetry of this compound was confirmed as monoclinic [1] and the unit cell parameters calculated from zero level precession photographs were: $a = 34.35$ Å, $b = 26.74$ Å, $c = 19.72$ Å, $\beta = 115.3 \pm 0.1°$, $v = 16375$ Å^3. The calculated "*d*" values based on the above parameters are compared with the observed values in Table I. For the reason stated above the space group could not be assigned. The crystals were determined to be optically biaxial with $2V = 35°$ measured at 5461 Å (Hg). The obtuse bisectrix is collinear with the monoclinic diad axis and the cleavage plane is perpendicular to the acute bisectrix and is designated the *c*-axis.

With respect to the phases existing near the 50 mol% region of the phase diagram other workers [5] identified two forms of mono tellurite but did not indicate the existence of phase B ($8CdO.9TeO_2$). Small single crystal fragments of this latter phase were isolated from the appropriate melt and although too small for chemical analysis, when examined by precession camera the results indicated a triclinic symmetry and the likely unit cell parameters as $a = 14.73$ Å, $b = 25.04$ Å, $c = 8.07$ Å, $\alpha = 87.8°$, $\beta = 103.1°$, $\gamma = 104.2°$. Crystals of the other phase existing in this region, namely mono-tellurite, were water clear without any pronounced tendency to cleave. These crystals were designated β-$CdTeO_3$. They were attacked by mineral acids, but no etch pits were observed, and they did not give a positive response to the Giebe–Schiebe test for piezo-electricity. They were analysed as $CdOTeO_2$. Precession photographs showed these crystals to have a monoclinic symmetry. The measured parameters

TABLE I

$CdTeO_3$ pulled			$CdTe_2O_5$ pulled		
h k l	d_{obs}	d_{calc}	*h k l*	d_{obs}	d_{calc}
0 0 1	7.16	7.12	0 0 2	9.48	8.91
1 1 0	5.83	5.81	0 0 4	4.46	4.46
1 1 1	5.52	5.58	$\overline{10}$ 0 4	3.32	3.29
0 2 1	4.43	4.41	$\bar{5}$ 7 2		3.30
1 2 $\bar{1}$	4.23	4.23	5 0 6	3.27	3.28
1 1 1	3.90	3.88	10 0 0	3.10	3.11
1 0 $\bar{2}$		3.89	$\bar{5}$ 7 4	2.97	2.96
1 1 $\bar{2}$	3.66	3.67	0 0 6		2.97
2 1 $\bar{1}$	3.51	3.53	5 7 2	2.87	2.86
0 1 2	3.41	3.40	10 0 6	2.83	2.84
2 0 0		3.39	5 7 4	2.39	2.39
2 1 0	3.26	3.25	$\overline{10}$ 0 8	2.37	2.35
1 2 $\bar{2}$	3.18	3.20	15 0 $\bar{2}$	2.23	2.24
2 1 $\bar{2}$	3.08	3.09	0 0 8		2.23
2 2 $\bar{1}$		3.10	15 0 0	2.07	2.07
0 2 2	3.02	3.01	$\bar{5}$ 7 8		2.07
2 2 0	2.91	2.91	$\overline{15}$ 7 4	1.96	1.96
0 4 0	2.81	2.81	0 7 8	1.92	1.92
1 3 $\bar{2}$	2.68	2.70	10 0 6	1.79	1.80
0 4 1	2.62	2.62	$\overline{10}$ 7 10	1.73	1.74
2 3 0	2.53	2.52	$\overline{20}$ 0 4	1.70	1.71
1 1 $\bar{3}$		2.54	$\overline{20}$ 0 6		1.71
3 0 $\bar{1}$	2.47	2.47	$\overline{10}$ 14 2	1.67	1.67
2 2 1	2.41	2.41	$\overline{10}$ 14 0	1.63	1.63
3 1 $\bar{1}$		2.42	0 14 0	1.61	1.61
1 4 1	2.33	2.32			
0 1 $\bar{3}$		2.32			
3 2 1	2.26	2.26			
3 0 0		2.26			
3 1 0	2.22	2.22			
3 2 $\bar{2}$		2.22			
0 2 3	2.18	2.19			
1 5 0	2.13	2.14			
1 3 $\bar{3}$		2.14			
3 2 0	2.10	2.10			
3 1 $\bar{3}$					
2 0 2	2.08	2.07			
3 3 $\bar{1}$	2.06	2.06			
1 0 3	2.00	2.00			
3 2 $\bar{3}$					

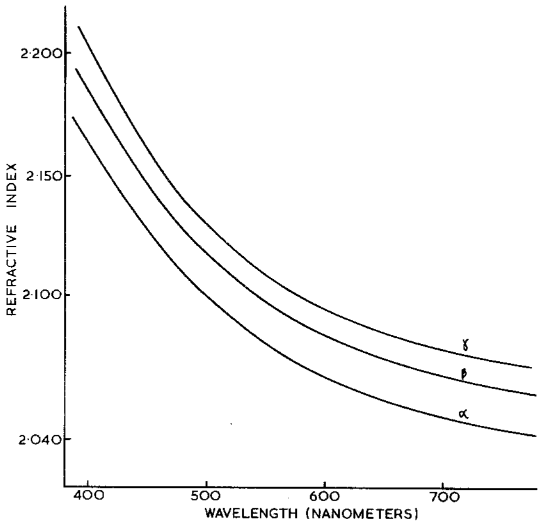

Figure 3 Refractive index versus wavelength for $CdTeO_3$.

being $a = 7.468$, $b = 11.258$, $c = 7.853$, $\beta = 114.15°$. The systematic absences were consistent with a space group $P2_1/C$. The material is optically biaxial with $2V \approx 90°$ and the variation of refractive index with wavelength is given in Fig. 3. The monoclinic diad axis is again coincident with the obtuse bisectrix.

The second form of mono-tellurite designated α-$CdTeO_3$ can be obtained as small crystals by rapid quenching of a melt of the appropriate composition. This phase gave a positive response to the Giebe–Schiebe test for piezo-electricity and was identified as having a monoclinic symmetry with the following parameters: $a = 7.19$ Å, $b = 5.64$ Å, $c = 8.29$ Å, $\beta = 113.0 \pm 0.1°$. The systematic absences on the precession photographs are consistant with a space group of $P2_1$ or $P2_1/m$ and the positive response to the Glebe–Schiebe test makes the probable space group $P2_1$.

The above work confirms the observations of Markovskii [5] that two phases of mono-tellurite exist but unlike these workers who gave α-$CdTeO_3$ a cubic symmetry and β-$CdTeO_3$ a hexagonal symmetry from X-ray powder photographs, this work assigns monoclinic symmetry to both forms. The DTA observations and Debye–Scherrer powder photographs of the α to β phase change shows it to be irreversible.

For electrical measurements polished samples with different crystallographic orientations were prepared from both di- and mono-tellurites. To overcome the natural tendency for disintegration of slices cut from the mica-like di-tellurite a section of crystal, selected to be reasonably twin free, was cast in transparent epoxy resin. The "*c*" axis samples were obtained by cleaving and were not encapsulated. These surfaces did not require polishing. Sample thicknesses ranged from 100 μm to 700 μm for samples of the di-tellurite and from 100 μm to 200 μm for the mono-tellurite. On all samples electrodes of nichrome were vacuum deposited and flying leads attached with a flexible conducting adhesive.

A pyroelectric effect was not observed in either of the compounds even after applying poling fields of 40 kV cm^{-1} both at ambient temperature and an elevated temperature, which was about 100° C for the encapsulated samples, a limit set by softening of the epoxy and 200° C for the others, a limit set by the apparatus. The pyroelectric coefficient, if it exists, is less than 2×10^{-11} C cm^{-2} ° C^{-1} at room temperature in either of the materials. At a sufficiently high temperature at about 150° C irreversible currents flowing from the samples become appreciable, irrespective of orientation, and render the charge integration method unsuitable for detecting very weak pyro-electricity above these temperatures.

When a 50 Hz alternating field was applied to samples of either material connected in a Sawyer–Tower Circuit [6] modified to compensate for saturation values of sample capacitance, ferroelectric hysteresis was not observed with field amplitudes up to 40 kV cm^{-1} in either of the materials. An increase in temperature, which would reduce the coercive field of a ferroelectric and thereby permit easier switching was limited to about 80° C. Again up to this temperature there was no hysteresis.

The permittivity and its variation with frequency were measured. The results given in Table II, along with values for loss tangent, are for fresh samples and at a frequency sufficiently high as to avoid space charge effects but without reducing the measurement accuracy. The value of 12.6 for ϵ_{33} cadmium di-tellurite is somewhat larger than the 10.22 quoted by Redman but may be more realistic since Redman's samples were quite thin (5 to 100 μm) and hence more sensitive to the effects of small air gaps between the micaceous layers of the material.

Thin samples (<100 μm) of di-tellurite did show considerable variation in permittivity between samples. This variation being reflected in the values of the a.c. resistivity for this material,

TABLE II

Parameter	$CdTe_2O_5$	$CdTeO_3$	Frequency of measurement	Temperature of measurement
$\epsilon_y (\epsilon_{11})$	42.3	11.6	5 kHz	20° C
$\epsilon_z (\epsilon_{22})$	31.7	13.7	5 kHz	20° C
$\epsilon_x (\epsilon_{33})$	12.6	22.9	5 kHz	20° C
$\rho_y (\rho_{11})$	2.0×10^9 Ω cm	1.2×10^{10} Ω cm	5 kHz	20° C
$\rho_z (\rho_{22})$	6.4×10^9 Ω cm	5.6×10^{10} Ω cm	5 kHz	20° C
$\rho_x (\rho_{33})$	$>5.0 \times 10^{12}$ Ω cm	3.3×10^{10} Ω cm	5 kHz	20° C
$\tan \delta_{11}$	4.2×10^{-3}	3.0×10^{-3}	5 kHz	20° C
$\tan \delta_{22}$	1.8×10^{-3}	4.5×10^{-4}	5 kHz	20° C
$\tan \delta_{33}$	6×10^{-6}	5.2×10^{-4}	5 kHz	20° C
α_{11}	5.6×10^{-4}	2.0×10^{-4}	1592 Hz	0–60° C ($CdTe_2O_5$), 0–120° C ($CdTeO_3$)
α_{22}	3.5×10^{-4}	1.6×10^{-4}	1592 Hz	0–55° C ($CdTe_2O_5$), 0–130° C ($CdTeO_3$)
α_{33}	6.5×10^{-5}	2.8×10^{-4}	1592 Hz	0–55° C ($CdTe_2O_5$), 0–95° C ($CdTeO_3$)

low permittivities were accompanied by high resistivities. These results are consistent with the presence of air gaps. The a.c. resistivity values for both compounds quoted in Table II are from measurements made prior to any treatment which would disturb the equilibrium of the material. It should be noted that the exceptionally good value for cadmium di-tellurite in the "*c*" direction can very easily be degraded by more than an order of magnitude simply by heating the material to such a temperature that large irreversible currents flow.

The temperature coefficients α of the permittivities, and the ranges of linearity are also given in Table II.

4. Discussion

This work shows that two compounds in the cadmium oxide–tellurium dioxide phase diagram can be obtained in single crystal form. The results concerning the properties of one, cadmium di-tellurite, confirm some of the results previously published but the compound is not piezo-electric. The properties of the second compound, cadmium mono-tellurite, show that the material which can be obtained in substantial crystal form is also not piezo- or pyro-electric. Bergmann and co-workers reported that in this region of the above phase diagram a compound exists which gives a positive result when tested for second harmonic generation, although the output was weak (less than quartz on the scale used). From the above results it appears possible that the compound involved was the lower temperature form of the cadmium mono-tellurite, namely α-$CdTeO_3$.

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