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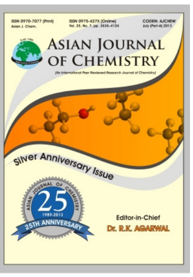

$Cd_2SeCl_2O_9$: Synthesis and Characterization of Novel Selinite-Chlorate Material

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The white crystalline material $Cd_2SeCl_2O_9$ was obtained by the solid state reaction of $CdCl_2$ with SeO_2 at 450 ºC and showed a distinct X-ray powder pattern. Elemental analysis was carried out by energy dispersive X-ray spectroscopy which confirmed the presence and ratio of the constituting elements. Decomposition temperature (527 ºC) of the product and its thermal behavior were investigated by the help of differential scanning calorimetry, whereas Fourier transform infra-red spectroscopy indicated the presence of SeO_3^{2-} and ClO_3^- groups in the structure. Magnetic analysis proved the material to be ferromagnetic in nature.

Key Words: Selenite, Chlorate, Cadmium, Solid-state, Chalcogens.

INTRODUCTION

Although a number of metal-halogen compounds in combination with chalcogens (Se^{4+}, Te^{4+}) having unshared electron pairs have been synthesized in the literature[1-7], $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ and $Cd_7Cl_8(Te_7O_{17})$[8] are the only composites found with cadmium as metal. Such compounds have possible applications as future magnetic materials. In an attempt to prepare such new materials, $Cd_2SeCl_2O_9$ was obtained which is a rare composite having selenite-chlorate system and is magnetically active. The crystals obtained were too small in size and were unsuitable for any structure determination analysis (*i.e.*, X-ray single crystal analysis).

EXPERIMENTAL

White needle shaped micro-sized crystals of the $Cd_2SeCl_2O_9$ were prepared by a solid-state reaction[9] between $CdCl_2$ and SeO_2 in a molar ratio of 3:1, respectively. The reaction mixture was thoroughly grinded to increase the reaction surface area and was heated at 450 ºC in a covered ceramic crucible for 7 days in the presence of atmospheric air. Afterwards the annealing was carried out at a rate of 5 ºC per hour. Purification of the obtained crystals was carried out by distilled water followed by acetone.

RESULTS AND DISCUSSION

Scanning electron microscopy and energy dispersive X-ray analysis: Micrograph (Fig. 1) obtained from the scanning electron microscope (SEM) revealed the crystals to be of various shapes and sizes. Most of the crystals showed a rod-like or needle shaped structure whereas plate-like and bulky particles were also present at the same time. In the same manner, difference of size (width and length) of various crystals was also observed with a range from 1.42 mm length and 17 mm width. A few particles even showed a particle size as small as 331 nm and can even be considered as nano-material of the title compound.

Energy dispersive X-ray analysis was carried out at the platform of scanning electron microscope. The analysis (Fig. 2) revealed the presence and ratio of the constituting elements of

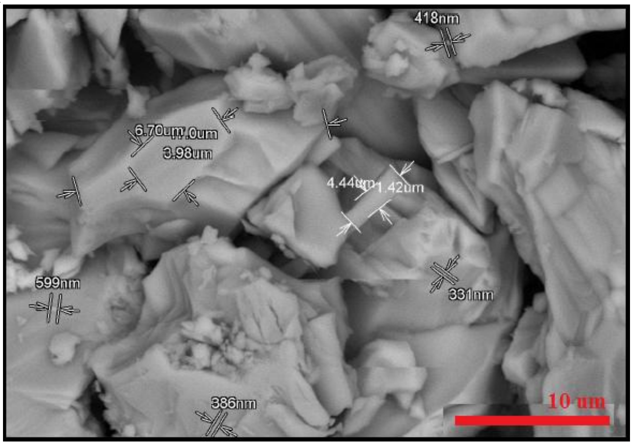

Fig. 1. Scanning electron micrograph of $Cd_2SeCl_2O_9$

the title compound which resulted in formulating of the solid as $Cd_2SeCl_2O_9$. The comparison between the observed and calculated values of $Cd_2SeCl_2O_9$ shows a good agreement (Table-1).

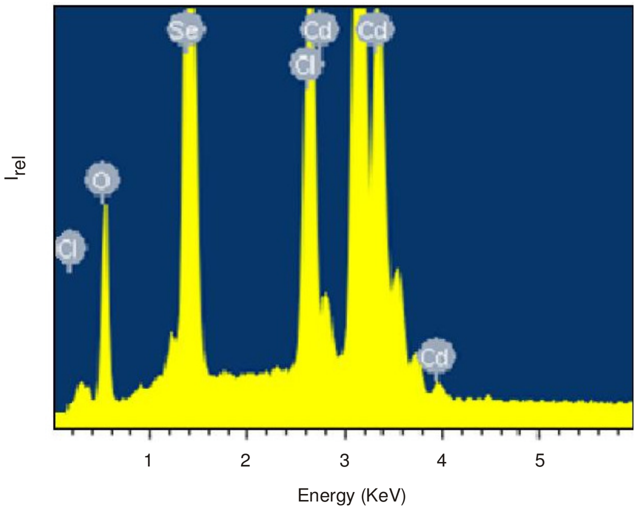

Fig. 2. Energy dispersive X-ray analysis of $Cd_2SeCl_2O_9$ showing the presence of the constituting elements (Cd, Se, Cl and O)

TABLE-1
COMPARISON BETWEEN THE OBSERVED ATOMIC PERCENTAGE (OBTAINED BY EDX ANALYSIS) AND THE CALCULATED ONES

Elements	Observed atomic (%)	Calculated atomic (%)	Deviance (%)
Cd	15.1	14.3	+6
Se	8.0	7.2	+10
Cl	13.8	14.3	-4
O	63.1	64.2	-2

X-ray powder diffraction analysis: The title compound was grinded and its X-ray powder diffraction analysis was performed at X-ray powder diffractometer (D_8-discoverer, Bruker) with a range from 2θ/º = 15 to 90, for a period of 0.5 h approximately. The analysis resulted in a distinct X-ray powder pattern (Fig. 3) of $Cd_2SeCl_2O_9$ with some peaks apparently (at 2θ/º = 33.638, 39.947, 43.004, 53.129 and 58.242) correlating with elemental selenium (confirmed by search/match procedures)[10]. But at a close examination of the pattern reveals that either the correlating peaks have dissimilar intensities or they are not exactly correlating with the corresponding peaks (shown with a star in Fig. 3) of selenium (at 2θ/º = 53.129 and 58.242).

The graphical representation of various X-ray powder diffraction parameters *versus* 2θ/º values are shown in figure. Using the following calculations, the grain size, dislocation line density and strain of the sample were calculated (Table-2).

$$\text{Grain size (D)} = 0.9\lambda/\beta\cos\theta \quad (1)$$

[11]

where λ = wavelength of the X-rays used, θ = Bragg's angle and β = value of full wave at half maximum).

$$\text{Dissociation line density } (\delta) = 1/D^2 \quad (2)$$

[12]

where D = grain size.

$$\text{Strain (S)} = 0.9\lambda/4D \quad (3)$$

[13]

The chart based on these calculations (Fig. 4a) indicates the grain size to be in a range between 42.96 nm (at 2θ/º = 25.14) to 502.53 nm (at 2θ/º = 66.89) which was also indicated by scanning electron microscopy analysis. Variation in the grain size might be as a result of re-arrangement of the particles during the growth of the material (nucleation of smaller particles) at a higher temperature of 450 ºC (thermal stress). The chart also shows variation in the intensities of the diffracted beam which could be as a result of crystal imperfections, non uniform strain, diffraction, thermal stresses, lattice vibrations of atoms and texture effects[11].

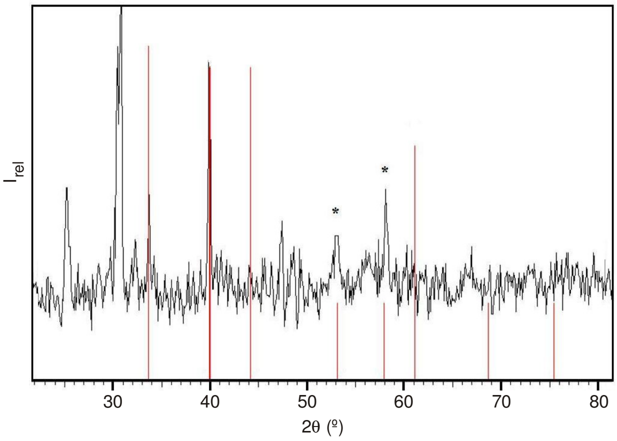

Fig. 3. X-ray powder diffractogram of $Cd_2SeCl_2O_9$ in comparison with that of selenium (red lines)

TABLE-2
MATERIAL PARAMETERS (GRAIN SIZE, DISLOCATION DENSITY AND STRAIN) CALCULATED ON THE BASIS OF INTENSITY AND 2θ/º (OBTAINED BY THE X-RAY POWDER DIFFRACTION ANALYSIS)

Intensity (counts)	2θ/º	Grain size (nm)	Dislocation density (lines/cm^2)	Strain (lines^{-2} cm^{-4})
73	19.709	170.2447	0.002936948	0.002035
105	25.143	42.96238	0.01163809	0.008065
180	30.38	173.7904	0.002877029	0.001994
209	30.8	86.99436	0.005747499	0.003983
76	32.4	124.7565	0.004007807	0.002777
101	33.638	87.61237	0.005706957	0.003955
236	39.947	81.11362	0.006164193	0.004272
89	47.383	65.41643	0.007643339	0.005297
79	53.129	49.3495	0.010131816	0.007021
102	58.242	87.27956	0.005728718	0.00397
72	66.891	502.5321	0.000994961	0.00069
68	79.705	218.4774	0.002288566	0.001586
103	81.57	276.8838	0.001805812	0.001251
77	84.009	112.855	0.004430463	0.00307
82	86.026	143.3646	0.003487611	0.002417

On the other hand, due to a long heating time (450 ºC for 1 week), crystal planes show small values of strains and dislocation density (Fig. 4b) which might be due to the polygonization at a high temperature[14].

Vibrational spectroscopy (Fourier transform infrared analysis): IR spectrum of the title compound was obtained at Fourier transform infra-red spectrophotometer (Perkin Elmer) for a range of 4000-350 cm^{-1} but the absorption peaks were observed in between two ranges, *i.e.*, 500-400 cm^{-1} and 960-800 cm^{-1} (Fig. 5) whereas no absorption peak was observed in between. Absorption band 953 cm^{-1} could be assigned[15] to $(ClO_3)^-$, whereas bands at 848 cm^{-1} and 821 cm^{-1} to SeO_3^- as reported for $Sr_2Cu(SeO_3)_2Cl_2$ and $SrCu_2(SeO_3)_2Cl_2$[16]. Other absorption bands at 504, 494, 471, 438, 418 and 405 cm^{-1} are also comparable to those reported for $Sr_2M(SeO_3)_2Cl_2$ (M = Co, Ni)[17] and literature[18].

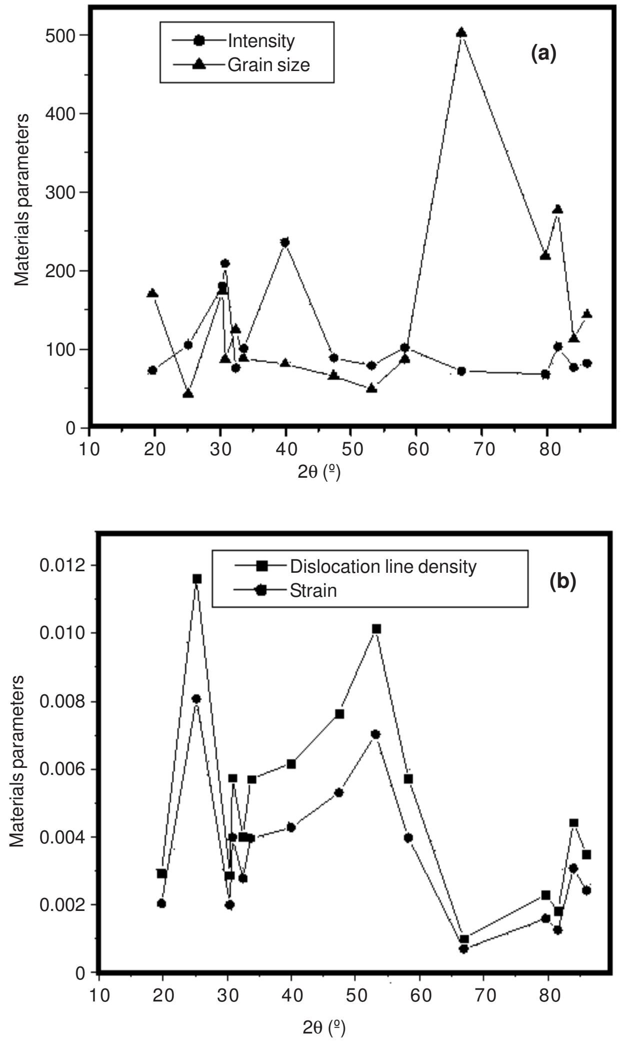

Fig. 4. Graphical representation of material parameters [intensity and grain size (a) and dislocation line density and strain (b)] *versus* 2θ/º (obtained from the X-ray powder diffraction analysis)

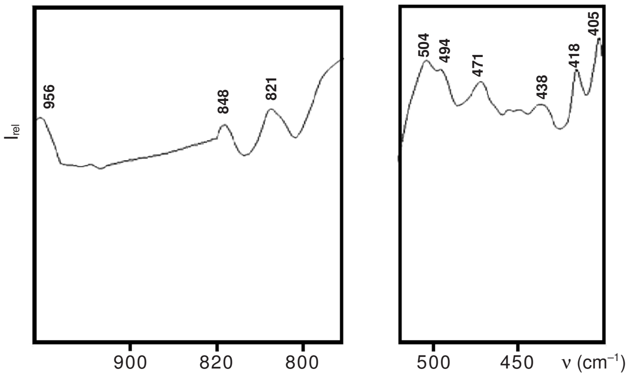

Fig. 5. Infra-red spectrum of $Cd_2SeCl_2O_9$

Thermal analysis (differential scanning calorimetry): Crystals of $Cd_2SeCl_2O_9$ were grinded and were sealed in a quartz glass tube of 2 mm diameter for differential scanning calorimetry. The measurement (Fig. 6) was carried out at the device SDT-Q600 (TA Instruments) in a temperature range from ambient conditions to 600 ºC with a heating rate of 5 ºC/min. The decomposition point of the title compound was found to be 527 ºC (± 2 ºC). The X-ray powder diffraction pattern of the differential scanning calorimetry sample indicates a total decomposition of the compound and absence of the crystalline product.

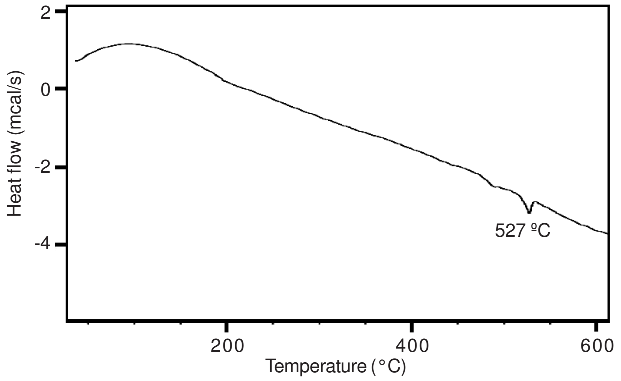

Fig. 6. Differential scanning calorimetry graph of $Cd_2SeCl_2O_9$

Magnetic measurement: Vibrating sample magnetometer (VSM 740H) was used to measure the magnetic properties of the title compound. The magnetic moment *versus* magnetic field for the clean product was measured at ambient temperature (Fig. 7) where the sample showed a clear ferromagnetic behaviour. The intrinsic coercivity (Hci) and magnetic retentivity (Mr) of the sample were determined by the measurement of magnetization curve or hysterisis which came out to be 58.920 G and 542.88 × 10^{-6} emu/cm^3 respectively. In the same way, values of saturation of the magnetization (98.1988 × 10^{-3} emu/cm^3), squareness of the curve (66.214 × 10^{-3}) and the total area corresponding to energy loss (1.2830 erg) were calculated from the measurement.

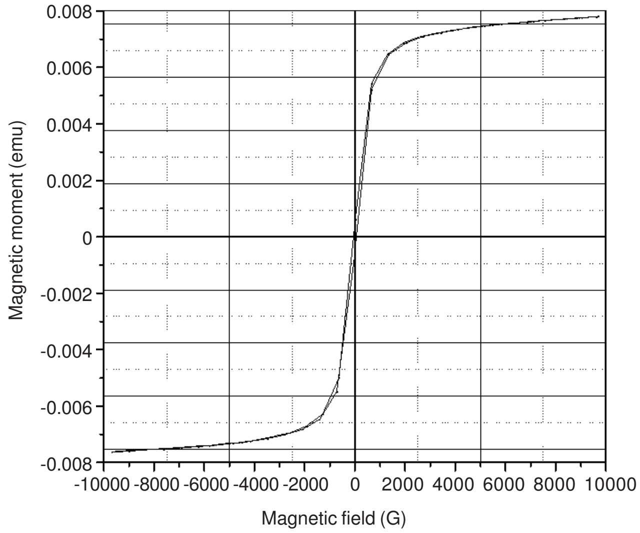

Fig. 7. Magnetic measurement of $Cd_2SeCl_2O_9$ (graphic representation of the change in magnetic moment with the change in the applied magnetic field)

Conclusion

The vibrational analysis showed the presence of both selenite and chlorate groups in the new material $Cd_2SeCl_2O_9$

which fits well with its proposed chemical composition as $(Cd_2)^{4+}$ $(SeO_3)^{2-}$ $(ClO_3)_2^{2-}$.

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